NOAA Technical Memorandum NOS OMA 56

STATUS AND TRENDS IN CONCENTRATIONS OF SELECTED CONTAMINANTS IN BOSTON HARBOR SEDIMENTS AND BIOTA

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noaa NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION

National Ocean Service

Office of Oceanography and Marine Assessment
National Ocean Service
National Oceanic and Atmospheric Administration
U.S. Department of Commerce

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NOAA Technical Memorandum 56 Errata Sheet

Page 11-11	Table 11.8 and all references to Table 11.8 should read 11.7.
Page 12-12	Tenth line of last paragraph: Table 12.8 should read Table 12.7.
Page 12-13	Table 12.8 should be labelled Table 12.7.
Page 15-9	First line of last paragraph: Table 15.3 should read Table 15.4.
Page 15-12	Table 15.5 should be Table 15.6 and first line of second paragraph: Table 15.5 should read Table 15.6.

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INTRODUCTION

Under the National Status and Trends (NS&T) Program, the National Oceanic and Atmospheric Administration (NOAA) monitors the occurrence of certain contaminants and indicators of biological stress at approximately 300 sites in the United States. This program was initiated in 1984 to provide an internally consistent data base for assessing the condition of parts of the nation's coastal and estuarine environments. The program thus far has focused largely upon generating chemical contaminant data for sediments, fish, and bivalves, and analyzing certain of these data. The results of the initial analyses are summarized in progress reports (NOAA, 1987, 1988a, 1988b, and 1989).

The objectives of this report are to: (1) portray geographic trends in the concentrations of contaminants in sediment and biota, (2) portray temporal trends in concentrations of contaminants in sediment and biota, and (3) compare the trends observed in available historical data to compatible recent measurements made by NOAA in Boston Harbor. These objectives will be met through evaluation of data collected by NOAA and the many others who have studied the conditions in Boston Harbor. Some of the data from the NOAA NS&T Program will be reported for the first time in this report.

The intent of this report is to document certain conditions in Boston Harbor as they were determined through surveys and research performed by many organizations, including NOAA. The intent is not to attribute the status and trends in conditions of the system to causes or sources.

The report focuses upon contaminants thought to be toxic to marine organisms. The chemical analytes for which the data are evaluated are among those that are quantified in the NS&T Program and known to be potentially toxic to marine and estuarine organisms. Specifically, they include selected trace metals (mercury [Hg], cadmium [Cd], lead [Pb], copper [Cu], chromium [Cr], silver [Ag], nickel [Ni], and zinc [Zn]), polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroehtane (DDT) and its breakdown products (DDD, DDE), and total polynuclear aromatic hydrocarbons (PAHs). The report summarizes the results of analyses of surficial sediments and biota (specifically, bivalves, crustaceans, and fish). One chapter of the report is devoted to each of the chemicals.

The report addresses the Boston Harbor system (referred to hereafter as "the Harbor"), the largest seaport in New England and the eleventh largest in the United States. It is a relatively shallow complex of bays and tidal estuaries covering approximately 47 square miles and includes the inner harbor; Winthrop, Dorchester, Quincy, Hingham and Hull bays; President Roads and Nantasket Roads channels; and the lower reaches of the Mystic, Chelsea, Charles Neponset, Weymouth Fore, Weymouth Back, and Weir rivers (Figure 1.1). The Harbor is generally divided into the inner harbor, which includes the lower reaches of the Mystic, Chelsea, and Charles rivers east to a line drawn between the southeast tip of Logan International Airport and Castle Island and the outer harbor, which includes all the area between the mouth of the inner harbor and the seaward boundary, a line connecting the southern tip of Deer Island, Lovell Island, and Point Allerton. For discussion purposes the outer harbor was further divided into three divisions based loosely on the geographic configuration of the Harbor (Figure 1.2). The northwest harbor division consists of the area east of the mouth of the inner harbor and northwest of the line connecting Squantum, Moon Head, and Long Island and extends to the seaward boundary. It includes Winthrop and Dorchester bays, President Roads, and the lower reaches of the Neponset River. The northwest harbor division is further divided into the Winthrop Bay area, the area north of President Roads, and the Dorchester Bay area, the area south of President Roads. The central harbor division consists of the area southeast of the line connecting Squantum, Moon Head, and Long Island and northwest of the line connecting Nut Island, Peddocks Island, Windmill Point, and Point Allerton. It includes Quincy Bay and Nantasket Roads. The southeast harbor division consists of all the area southeast of the line connecting Nut Island,

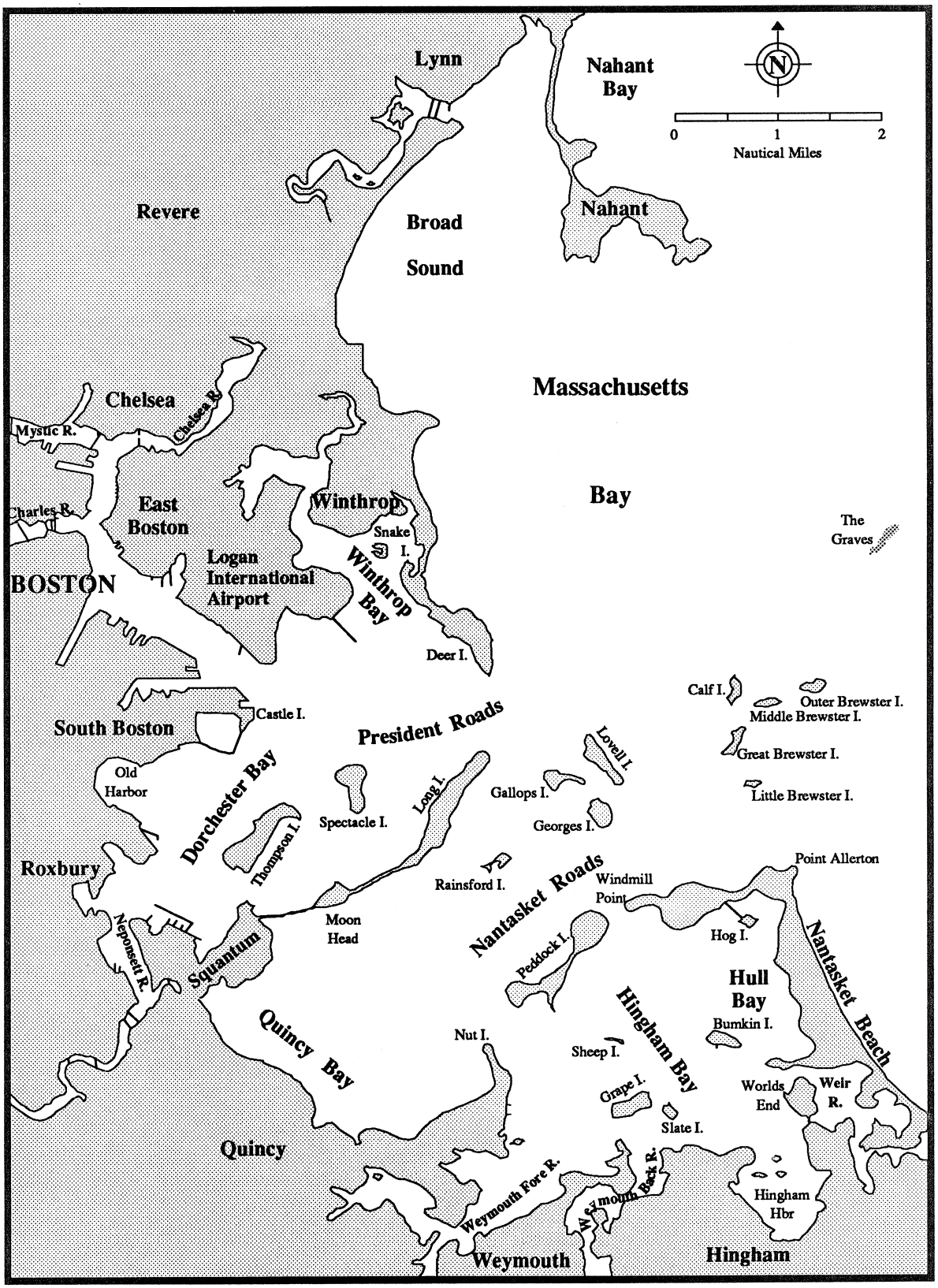


Figure 1.1. Boston Harbor and environs.

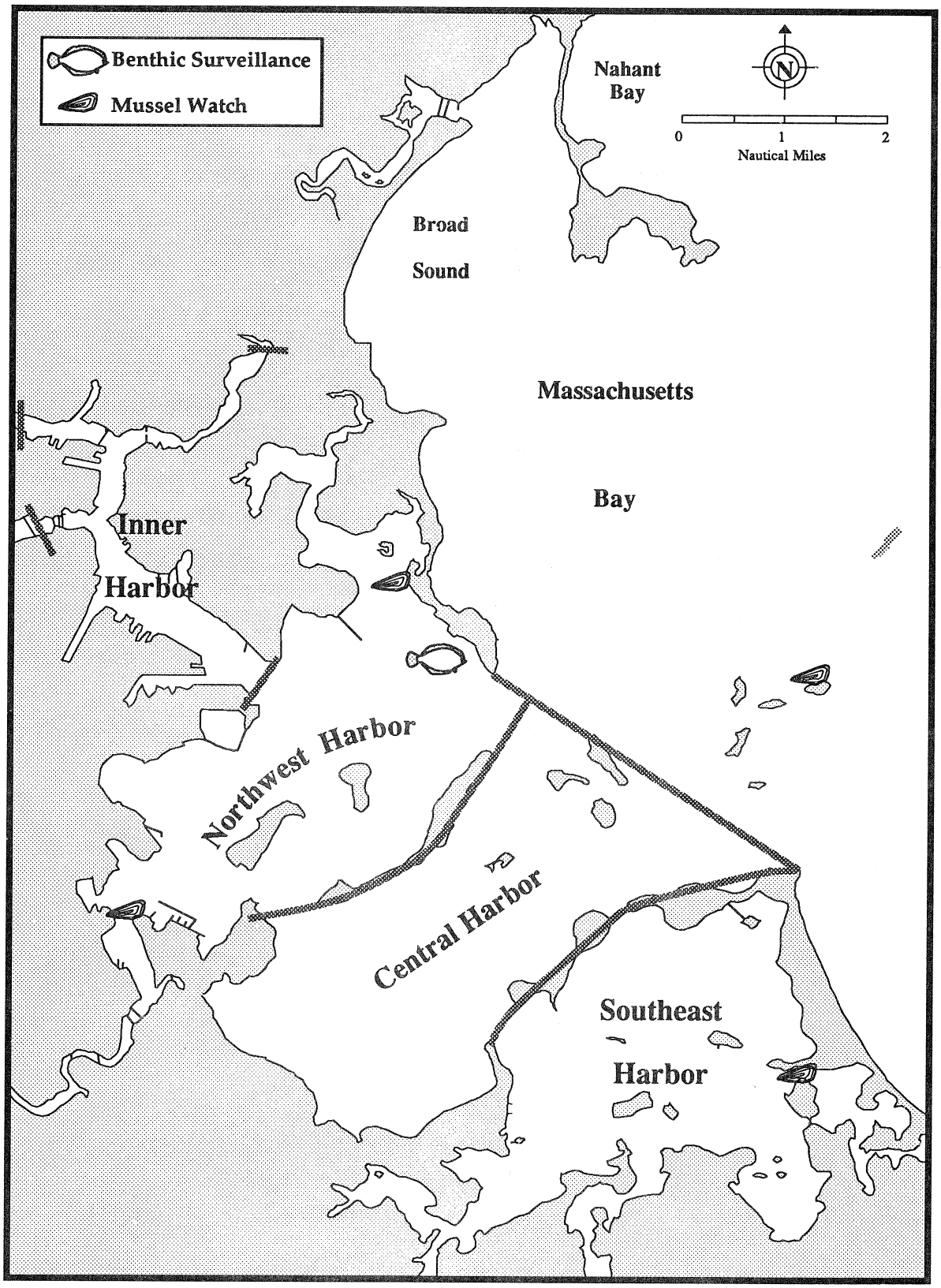


Figure 1.2. Boston Harbor divisions and NOAA's NS&T Program Benthic Surveillance and Mussel Watch sites. Gray lines (▒) indicate division boundaries.

Peddocks Island, Windmill Point, and Point Allerton. It includes Hingham and Hull bays and the lower reaches of the Weymouth Fore, Weymouth Back, and Weir rivers. Data from Massachusetts and Cape Cod bays and the New England coastline were included, when available, to help place the Harbor data into a regional perspective.

Data were acquired from many helpful colleagues in state, local, and federal agencies; universities; and consulting firms. Their helpfulness and interest in the report is greatly appreciated. Data from refereed journal articles, technical reports, contractor reports, and progress reports were used. The data in these reports were of varying quality and detail; however, they were accompanied by sufficient information on sampling and analytical methods to warrant inclusion of the data in this synthesis report. Reports in which the data were presented only in summarized form (*i.e.*, individual data points were not available) were generally not used.

As a part of the nationwide grid of sampling sites, 22 sites along the outer New England coast are being sampled annually. The outer New England coast includes Rhode Island, Massachusetts, New Hampshire, and Maine. The Benthic Surveillance Project of the NS&T Program, a project conducted by NOAA's National Marine Fisheries Service (NMFS), has sampled one site (just west of the southern end of Deer Island) in the Harbor and eight sites along the outer New England coast. (Figures 1.2 and 1.3). Data were produced annually for contaminant concentrations in bottomfish and sediments and for prevalence of certain histopathological conditions in the fish. Beginning in 1986, the Mussel Watch Project of the NS&T Program annually performed chemical analyses of resident mussels (*Mytilus edulis*) samples from three sites (northwestern Deer Island, southeastern Dorchester Bay, and off Worlds End in Hingham Bay) in the Harbor, one site (Outer Brewster Island) just outside the Harbor, and seven sites along the outer New England coast (Figures 1.2 and 1.4). In 1987, two sites were added (Cape Ann and Block Island) (Figure 1.4) and in 1988, one site (Conanicut Island) was dropped. In 1986 and 1987, sediments were also analyzed from all the sites, except Outer Brewster Island. This report presents some of the results from those sites and compares them with data collected by others in the region.

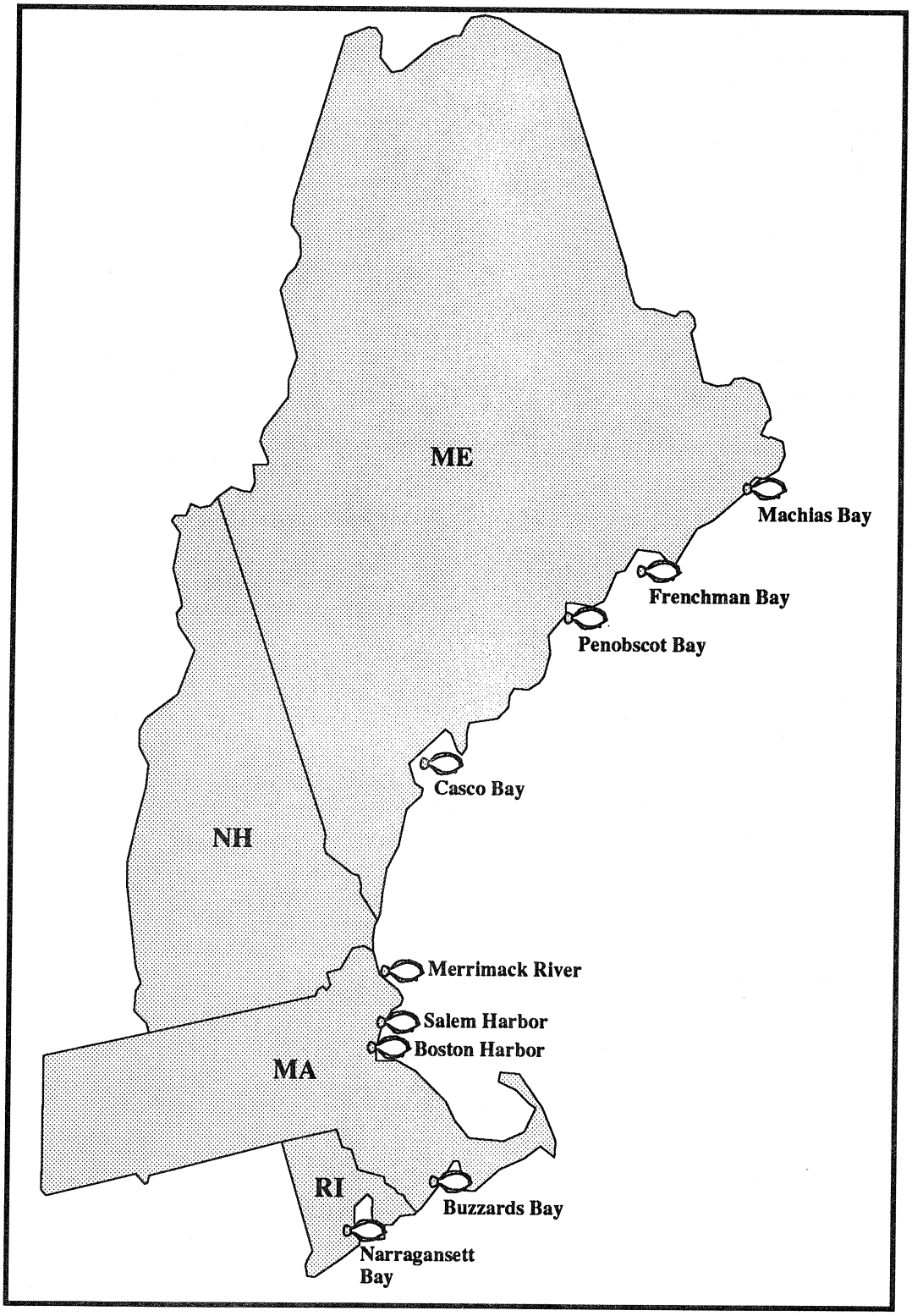


Figure 1.3. NOAA's NS&T Program Benthic Surveillance sites along the outer New England coast.

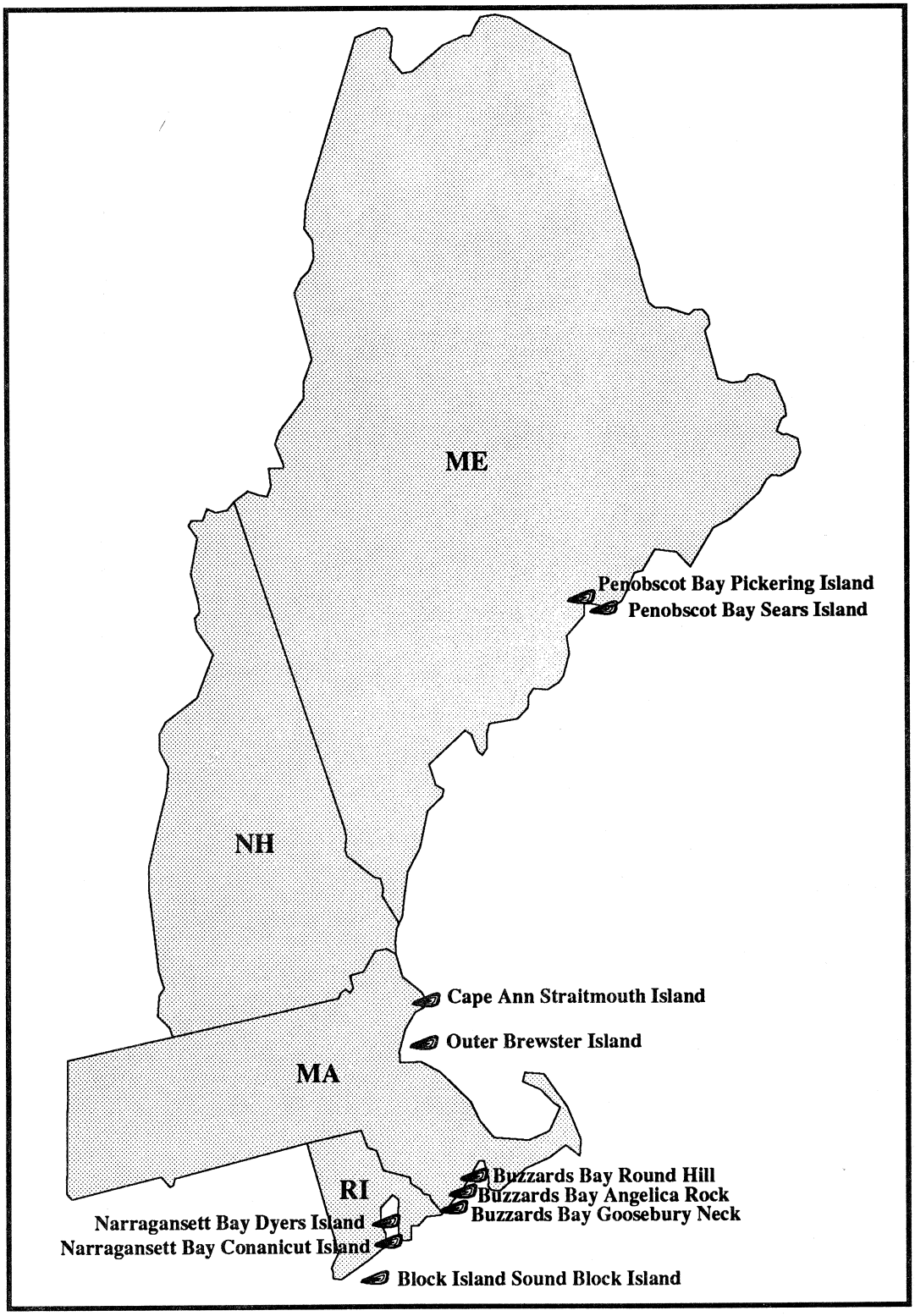


Figure 1.4. NOAA's NS&T Program Mussel Watch sites along the outer New England coast.

METHODS

Approach

The data compiled for this report were obtained from a number of investigators, each of whom had their own goals to satisfy. These various goals led to differences in sampling methodologies that, coupled with changing laboratory methods over the years, added to the variability in the resulting data due to natural environmental factors. No standardized analytical protocols have been adopted for use in Boston Harbor; thus, any attempt to summarize and merge data from various studies is severely handicapped. The use of different methods by various investigators may have resulted in incomparable data that, when merged, may indicate spatial or geographic trends that do not actually exist. Harbor-wide surveys or monitoring of contaminants have not been conducted recently in the Harbor with state-of-the-art methods. A survey of trace metals in sediments conducted about 1970 (White, 1972), is the only study that approached being a synoptic assessment on a harbor-wide scale. The methods used then are now considered to be semiquantitative.

The overall approach taken in this report was to use a preponderance of evidence from individual investigations to determine geographic and temporal trends in contamination of sediments and biota. Then, the trends would be corroborated (or refuted) with pooled (merged) data.

To determine geographic trends in contaminant concentrations in sediments and biota (Objective 1), data available from the various parts of the Harbor were compared. Where sampling protocols and replication in individual studies allowed, the data from sampling sites or areas were transformed to base 10 logarithms and were compared using analyses of variance (ANOVA), followed by Scheffé's F-test. When only two sites were compared, a t-test was performed on the transformed data. All statistical tests were conducted on a Macintosh II ™ computer, using Statview 512+, version 1.0 (Abacus Concepts, Inc.) software. Where no replication was used by the investigators, statistical tests were not performed and the analytical results were simply compared arithmetically. In those cases, no conclusions regarding between-site differences could be reached. No statistical analyses were performed with data from different studies because of the variability in methods between studies. Data from individual sites and studies were pooled for major geographic areas and harbor divisions of Boston Harbor. This data pooling step was undertaken to provide an overview of broadscale geographic trends, if any, using as much data as possible. Means, ranges, and standard deviations were usually calculated for the major harbor divisions and areas. These values must be used with caution, however, since different methods may have been used by the various investigators. All means, whether for individual sites, studies, or for combined data sets, were based on individual sample concentrations; no means of means were calculated. Laboratory replicates were averaged and the average treated as the sample concentration.

To give perspective to the levels of contamination in Boston Harbor, the NS&T Program data for the Harbor was compared to NS&T Program data for other sites along the New England coast, and, in the case of the biota data, to other NS&T Program sites around the country. In addition, the sediment data was compared to comparable sediment data from San Francisco Bay, another major United States port.

Data have been collected sporadically in an inconsistent manner in the Harbor. Most studies have focused upon only selected portions of the system. Therefore, the pooled mean values for the overall harbor and the major harbor divisions are to be treated very cautiously. The location of individual sampling sites within each division provided varying representation of conditions within the respective division. The proportion of samples within the Harbor that were from clean sites and contaminated sites was not consistent. The number of samples taken over the years in each division differed. Therefore, the degree of contamination of one division may be exaggerated or underestimated, depending upon the location of sites within the division.

To determine temporal trends in contamination of sediments and biota (Objective 2), data from investigations by individual agencies or investigators that used apparently consistent methods were sought and used when available. Strongest evidence of temporal trends would likely be attainable by using internally consistent methods applied to samples taken with the same methods from the same sites on succeeding sampling dates. These data, which are not available for all analytes, were supplemented by examination of merged data sets, but the latter approach is clearly much weaker and susceptible to error. Since very little monitoring is conducted in Boston Harbor expressly to determine temporal trends in contamination, little reliable, internally consistent data exist.

The comparability of site-specific trends observed in available historical data with those from recent measurements made by the NS&T Program (Objective 3) was tested by simply extending historical trend analyses with the more recent measures from the same sites and determining if the direction of historical patterns continued with the new data. Furthermore, the NS&T Program data were compared to the means and ranges in historical data from respective basins to determine if the NS&T Program sites were representative of conditions within the basin. If the means of the NS&T Program values were within an arbitrarily selected factor of 2 or less of the historical mean for the respective basin, the NS&T Program site was considered to be representative.

Contaminant concentrations in this document are reported in dry weight (dw) units, since most of the available data were given in those units. Where data (usually those for biota) were reported only in wet weight (ww), the values were converted to dw by using the moisture data provided. Where no moisture data were provided to facilitate this conversion, the average moisture content from other surveys of the same species was used.

For those data that were reported as less than the detection limits, a value of half the reported detection limit was used in the calculation of means. The detection limits varied considerably for some analytes within and between data sets.

The general format of the report includes individual chapters for each of the analytes or classes of analytes. With the exception of the methods discussed in this chapter, each analyte chapter contains all the available information for the particular analyte being discussed and was meant to stand alone. The Discussion and Conclusions chapter gives an overview of all the analyte chapters.

Sources of Data

A varying number of chemicals have been measured by various investigators who have studied the Harbor. The sources of data and the analytes quantified are summarized in Table 2.1. The largest single source of the contaminant data for sediments is from dredging studies conducted by the U.S. Army Corps of Engineers (USACOE). They were obtained for Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, DDT, and PCB in the "Environmental Assessment for Boston Harbor, Boston Massachusetts" (USACOE, 1981) supplemented by unpublished dredging data sheets for 1972, 1976, and 1983 through 1988 (USACOE 1972-88). In most of these studies, only the trace metals were measured. Other data from dredging studies included those from the draft and final "Feasibility Report and Environmental Assessment for Deep-Draft Navigation Improvements to Boston Harbor including Mystic River, Chelsea River, and Reserved Channel" (USACOE, 1988).

The most comprehensive sediment data set, about the area covered was from the master's thesis of R. J. White, Jr., "The Distribution and Concentrations of Selected Metals in Boston Harbor Sediments" (White, 1972). Other early studies that contained sediment data used in this report were the New England Aquarium (NEA)-sponsored study of trace metals in the Harbor (Gilbert *et al.*, 1972), and part of the statewide toxic element survey conducted jointly by the Massachusetts Division of Water Pollution Control (DWPC) and Division of Environmental Health (DEH) (Isaac and Delaney, 1975). While these early studies generally were restricted to metals analyses, DDT data were obtained from the Massachusetts Department of Natural Resources (DNR) Division of Marine Fisheries (DMF) study of Hingham Bay (Iwanowicz *et al.*, 1973). This report also included data on DDT levels in flounder.

Table 2.1. Sources of sediment and biota contamination data for Boston Harbor used in the preparation of this report.

Study	Agency	# of Sites	Matrix	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	DDT	PCB	PAH
White, 1972		133	sediment			x	x	x	x	x	x	x			
Gilbert *et al.*, 1972	NEA	56	sediment			x	x	x	x	x	x	x			
Isaac & Delaney, 1975	DWPC/ DEH	24	sediment		x	x	x	x	x	x	x	x			
USACOE, 1981	USACOE	12	sediment		x	x	x	x	x	x	x	x	x	x	
USACOE dredging studies, 1972-88	USACOE	101	sediment		x	x	x	x	x	x	x	x	x	x	
Hubbard, 1987	USACOE	21	sediment	x	x	x	x	x	x	x	x	x			
MA DEQE, 1986	DEQE	19	sediment	x	x	x	x	x	x	x	x	x		x	x
MA DEQE, 1987	DEQE	11	sediment	x		x	x	x	x	x	x	x		x	x
Shiaris and Jambard-Sweet, 1986	EPA	23	sediment												x
EPA, 1988	EPA	27	sediment			x	x	x	x		x		x	x	x
		8	lobster			x	x	x	x		x		x	x	x
		1	clams			x	x	x	x		x		x	x	x
		4	oysters			x	x	x	x		x		x	x	x
		4	flounder			x	x	x	x		x		x	x	x
NS&T Program Benthic Surveillance, 1984-86	NOAA	2	sediment	x	x	x	x	x	x	x	x	x	x	x	x
		2	flounder	x	x	x	x	x	x	x	x	x	x	x	x
NS&T Program Mussel Watch, 1986-88	NOAA	3	sediment	x	x	x	x	x	x	x	x	x	x	x	x
		3	mussel	x	x	x	x	x	x	x	x	x	x	x	x
Boehm *et al.*, 1984	NOAA	5	sediment											x	x
		3	crab											x	x
		4	flounder											x	x
Iwanowicz *et al.*, 1973	DMF	3	sediment										x		
		3	clams										x		
Jerome *et al.*, 1966	DMF	3	clams										x		
Chesmore *et al.*, 1971	DMF	3	clams										x		
		4	flounder										x		
Goldberg *et al.*, 1978; Farrington *et al.*, 1982	EPA	1	mussels	x		x		x		x	x	x	x	x	x
Metcalf & Eddy, 1984	MDC	4	lobster	x		x		x	x		x			x	
		4	flounder		x		x		x	x		x		x	
Schwartz, 1987	DMF	8	flounder											x	
Wallace *et al.*, 1988	EPA	1	lobster			x	x	x	x	x	x	x		x	
		1	clams				x	x	x	x	x	x	x	x	
Robinson *et al.*, 1990	NEA	2	mussels	x		x	x	x		x		x			

More recently the Massachusetts Department of Environmental Quality Engineering (DEQE) in annual reports on water quality and waste discharge in Boston Harbor has included sediment contaminant data (MA DEQE, 1986, 1987). In 1982 the U. S. Environmental Protection Agency (EPA) sponsored a study of PAHs in Boston Harbor sediments (Shiaris and Jambard-Sweet, 1986). In 1987 they sponsored an intensive study of Quincy Bay (EPA, 1988) which included both sediment and biota contamination data that has been used to prepare this report. In addition to the ongoing Benthic Surveillance and Mussel Watch projects that include both sediment and biota contamination data; NOAA sponsored a study in 1983 of organic contaminants in Boston Harbor and Massachusetts and Cape Cod bays (Boehm *et al.*, 1984). This latter report also included both sediment and biota data that have been used in this report.

Besides the previously mentioned studies that included both sediment and biota contamination data, several studies that included just biota data were available. The earliest available organic contamination data were from a series of reports on Massachusetts' bays prepared by the DMF. These reports included data on DDT levels in clams and flounders (Chesmore *et al.*, 1971; Jerome *et al.*, 1966). As NOAA is currently doing, the EPA in the mid to late 1970s conducted a nationwide mussel watch program that analyzed resident mussels for levels of metal and organic contamination and included one site in Boston Harbor (Goldberg *et al.*, 1978; Farrington *et al.*, 1982). Other early data used were 1979 data for metals and PCBs in lobster and flounder which were reported in the Metropolitan District Commission's secondary treatment waiver request (Metcalf and Eddy, 1984).

More recent biota contamination data used in this report included two state-sponsored projects concerned with contamination of marine biological resources. The DMF sponsored a study of PCBs in coastal water biota between 1983 and 1986 (Schwartz, 1987). The DEQE sponsored a biota study in Boston and Salem harbors in 1987 (Wallace *et al.*, 1988). The only ongoing study in the Harbor from which data were obtained was the NEA Mussel Watch Project. This project has been sampling resident mussels at two sites in the Harbor and two sites outside the Harbor since 1987. Since the NEA uses the protocols established by NOAA's Mussel Watch Project, the two projects compliment each other and will eventually supply a substantial data base from which temporal trends can be analyzed.

A considerable number of place names are used in the report. The locations of many are shown in Figure 1.1. The names are those assigned by the original investigators and their reports should be checked for exact locations.

Sources of Variability in Data

All the data summarized in this report are subject to different sources of variability. All were collected with the hope that they would be representative of conditions in the particular part of the Harbor that was sampled. But, each data point can be affected by sampling protocols, analytical methods, and natural factors.

Sampling protocols for sediments differed among the various investigations performed in the Bay. Though only data for surficial sediments were used in this document, a variety of definitions of "surficial" has been used. Surficial sediment samples have been collected with a variety of thicknesses from 1 to 2 cm to 9-feet. Some have been collected to the bottom of the oxidized layer, whatever its thickness. In this report, data from the upper 1-cm to 2.5-ft were used. Sampling equipment varied from piston corers to grab samplers; the data were used regardless of the type of sampling device.

Analytical methods used in chemical analyses have changed remarkably since contaminant analyses began in the Harbor 25 years ago. Trace metal analyses performed with samples collected in the early 1970s are now considered to be semiquantitative. Analyses for DDT were performed as early as the mid 1960s. However, few analyses for a broad suite of organic compounds such as aromatic hydrocarbons and pesticides were performed until the late 1970s and mid 1980s. Methods used in organic chemical analyses have changed and evolved in the past 10 to 15 years. The data summarized in this document are from many investigators and laboratories and are subject to interlaboratory differences in analytical methods. The data are also subject to changes in methods with time at any particular laboratory as personnel changed and procedures and equipment evolved. As a result, apparent trends in concentrations of contaminants may merely reflect differences or changes in methods. Therefore, the approach taken in this report initially was to examine data from each study individually where it was hoped that the methods were internally consistent. Then, the data were gradually pooled from many studies to substantiate the trends seen in each study with the larger pooled data set. A preponderance of evidence from individual studies was expected to indicate possible trends in contamination.

No consistent analytical protocols have been developed for use in Boston Harbor by all investigators. It is difficult to determine which of the methods is "correct," and, therefore, which provides the best data that represent conditions in the Harbor. This document uses data from most of the studies that have been performed in the Harbor. Few data sets have been excluded. Data from studies in which the methods were not described, inadequately described, or clearly very poor, were excluded.

A wide variety of natural or environmental factors can affect the concentration of contaminants in sediments and biota. In sediments these factors include texture (grain size), mineralogy, organic carbon content, salinity, oxidation-reduction potential, presence and activity of burrowing animals, depth, and scouring/erosion processes. The bioavailability of sediment-associated contaminants can vary remarkably with many of these factors, but is obscured in chemical analyses by use of strong acids or solvents to extract the contaminants for quantification. Fine-grained sediments with high surface area-to-volume ratios often attract the highest contaminant levels. Because fine-grained sediments have a very low specific gravity, they tend to accumulate only in areas with low water currents and no scouring of the bottom. Therefore, high contaminant levels are usually found in the protected low-energy areas with high percent fine-grained sediments. However, this generality may be violated in places where local sources of contaminants may exist nearby. Most chemical analyses of sediments in the Harbor were not accompanied by analyses of these "normalizing" factors that may affect contaminant concentrations. Therefore, there is no way to account for differences in contaminant concentrations in those data sets. Some surveys, however, did include tests for texture and/or organic carbon. The relationship observed in the data from the Harbor between contaminant concentrations in sediments and sediment texture is illustrated and discussed in Chapter 15.

GEOGRAPHIC AND TEMPORAL TRENDS IN MERCURY CONTAMINATION

Mercury is one of the most toxic heavy metals. Its salts have been shown, in short term bioassays, to be more toxic to marine organisms than the salts of other heavy metals (Eisler, 1981). While inorganic mercury compounds have relatively low levels of toxicity, they can be readily converted to highly toxic organic compounds by biological and other processes (Eisler, 1981). In a review of the literature, Long and Morgan (1990) found data suggesting that chronic effects have been associated with sediments having mercury concentrations as low as 0.032 ppm; and, in most cases, toxic effects were observed whenever mercury concentrations in the sediment exceeded 1.0 ppm. Concentrations as high as 2.2 ppm have been reported for the soft parts of the mussel *M. edulis*. Concentrations in the edible portion of crustaceans, on a worldwide basis, were well below the U. S. Food and Drug Administration (FDA) guideline of 1.0 ppm fresh weight except in areas impacted by anthropogenic wastes, such as Minamata Bay, Japan where concentrations as high as 100 ppm have been reported (Eisler, 1981).

Sediments

Since the late 1960s, over 400 surficial sediment samples from Boston Harbor have been analyzed for mercury content. Based on this data, the overall mean concentration of mercury in the surficial sediments of the Harbor was 1.33 ppm, with a standard deviation of 1.34, and a range of from 0.006 to 9.40 ppm (Table 3.1). The median concentration was 0.92 ppm. The large standard deviation and the difference between the mean and the median values were because approximately 10 percent of the samples analyzed had concentrations greater than 3.00 ppm. Over 50 percent of the samples had values of less than 1.00 ppm.

Table 3.1. Means, standard deviations, medians, ranges, and number of samples (count) for mercury concentrations (ppm) in surficial sediments for all of Boston Harbor and the four regions of the Harbor, based on all the available data sets.

	Mean	Standard Deviation	Median	Range	Count
OVERALL	1.33	1.34	0.92	0.006-9.40	433
INNER HARBOR	1.62	1.60	1.12	0.009-9.40	113
NORTHWEST HARBOR	1.56	1.39	1.15	0.026-8.00	167
CENTRAL HARBOR	0.96	1.08	0.69	0.006-5.40	90
SOUTHEAST HARBOR	0.71	0.49	0.70	0.040-1.90	63

Geographic Trends

When the combined data set was broken down into the four harbor divisions, both the means and medians suggested that there was no significant difference between mercury concentrations in the surficial sediments from the inner and northwestern harbor (means, 1.62 versus 1.56 ppm; medians 1.14 versus 1.10 ppm, respectively) and from the central and southeastern harbor (means, 0.96 versus 0.71 ppm; medians, 0.64 versus 0.70 ppm, respectively) (Table 3.1). However, the data did suggest that the surficial sediments in the central and southeast portions of the Harbor were slightly less contaminated with mercury than were the surficial sediments from the inner and northwestern harbor. The northwest harbor division is subdivided into two areas by President Roads. The area north of President Roads, that includes Winthrop Bay, had a mean mercury concentration of 0.91 ppm and a median of 0.70 ppm. The area south of President Roads, that includes Dorchester Bay,

had a mean of 2.15 ppm and a median of 1.90 ppm. This data suggests that the Dorchester Bay area sediments have the highest levels of mercury in Boston Harbor.

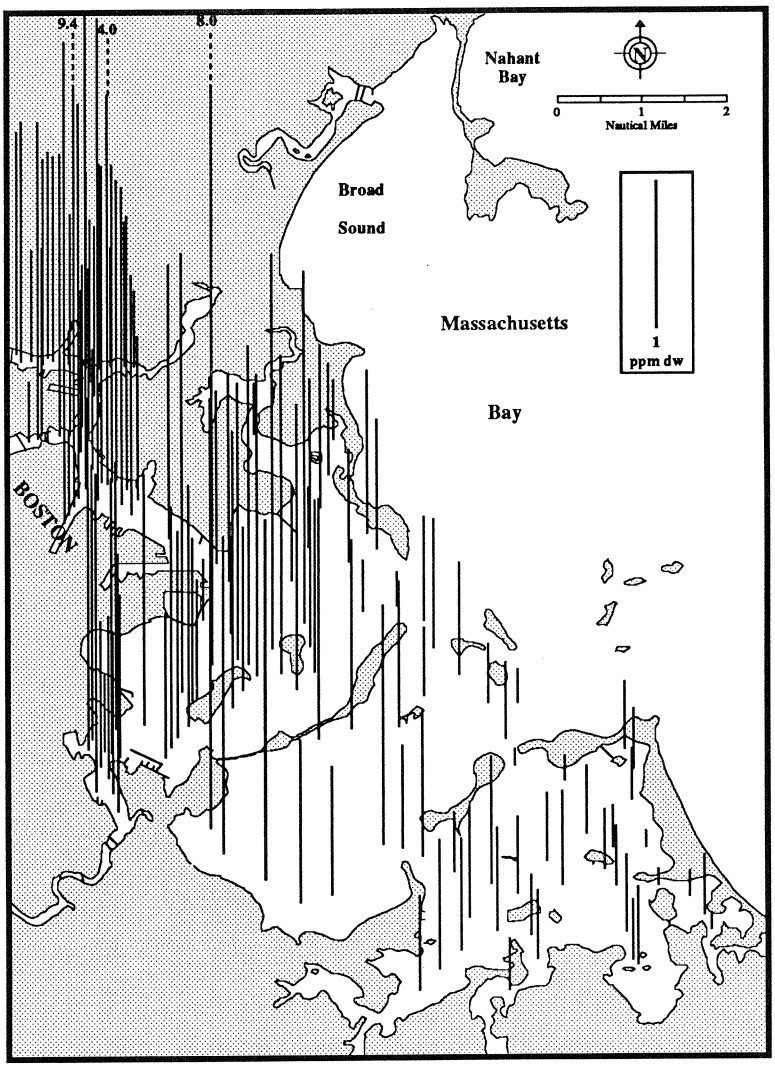


Figure 3.1 Mercury concentrations (ppm dw) in the surficial sediments of Boston Harbor from around 1970 (White, 1972).

Around 1970, White (1972) collected and analyzed 135 sediment samples from Boston Harbor for a variety of metals, including mercury. He found mercury concentrations ranging from a low of 0.2 ppm in several samples, to 9.4 ppm in a sample from the Fort Point Channel of the inner harbor (Figure 3.1). From this figure it appears that mercury concentrations decreased from northwest to southeast. The highest concentrations were in the inner harbor and Dorchester Bay. The lowest concentrations were at the mouth of the Harbor and in the southeastern harbor. Relatively high concentrations also occurred in the inner reaches of Quincy Bay. When the data were log transformed and the four harbor divisions statistically compared, the southeast harbor was found to be significantly different from the other three harbor divisions at p=0.05 (Table 3.2). When the northwest harbor division was subdivided, the Winthrop Bay area had a mean of 1.62±0.98 ppm; while the Dorchester Bay area had a mean of 3.05±1.45 ppm. When the data for the five divisions/areas were log transformed and statistically analyzed, the southeast harbor was still significantly different than the other harbor divisions/areas at p=0.05. Also, the inner harbor division and the Dorchester Bay area were found to be significantly different from the northwest and central harbor divisions (p=0.05). The statistical analysis supports the assumption that mercury levels in the sediments tend to decrease in a seaward direction. A further breakdown of the data suggested that the Chelsea and Mystic rivers section of the inner harbor had lower concentrations of mercury (1.97±0.88 ppm) in their surficial sediments than the rest of the inner harbor (3.48±1.90 ppm). However, statistical analysis of the log transformed data did not indicate any significant difference between the rivers and the rest of the inner harbor at p=0.05.

In 1971 the NEA collected 55 cores of Boston Harbor sediments and analyzed various sections of the cores for heavy metal content (Gilbert *et al.*, 1972). Based on 53 samples of

Table 3.2. Overall mean and the means of the four Boston Harbor divisions (ppm dw) for Hg in the surficial sediments based on the data of White (1972), Gilbert *et al.* (1972), Isaac and Delaney (1975), and NOAA's NS&T Program (NOAA, unpublished). The numbers in parentheses are the number of data points used to calculate the means.

YEAR(S) SAMPLED	White 1970?	Gilbert *et al.* 1971	Isaac & Delaney 1972	NOAA NS&T 1984-87
OVERALL	2.27 (132)	1.82 (54)	1.53 (18)	0.79 (31)
INNER HARBOR	3.08 (38)	2.61 (4)	0.87 (2)	NA
NORTHWEST HARBOR	2.60 (47)	2.13 (30)	2.23 (6)	0.87 (22)
CENTRAL HARBOR	2.13 (16)	1.45 (13)	1.60 (4)	1.38 (3)
SOUTHEAST HARBOR	0.86 (31)	0.70 (6)	1.00 (6)	0.21 (6)

the upper surface of the cores which were analyzed for mercury, they found mercury concentrations ranging from lows of 0.04 and 0.07 ppm in the samples from the Weymouth Back River and west of Worlds End, respectively, to a high of 6.7 ppm in a sample from southwestern Dorchester Bay. The vast majority of the sample concentrations (80%) were between 0.1 and 3.0 ppm. As with the White data, a graphic representation (Figure 3.2) suggests higher levels of mercury contamination in the northwestern and inner harbor regions. Somewhat lower levels of contamination are evident in the central and southeastern regions of the Harbor. However, it should be noted that some of the lowest levels of mercury in the surficial sediments were recorded for individual sites in Dorchester Bay and north of President Roads. The fifth and eighth highest levels of mercury were recorded from sites in Quincy Bay. These levels indicated that mercury was heterogeneously distributed through the sediments. When the data were grouped by the four harbor divisions (Table 3.2) and the log transformed data compared statistically, only the southeast and

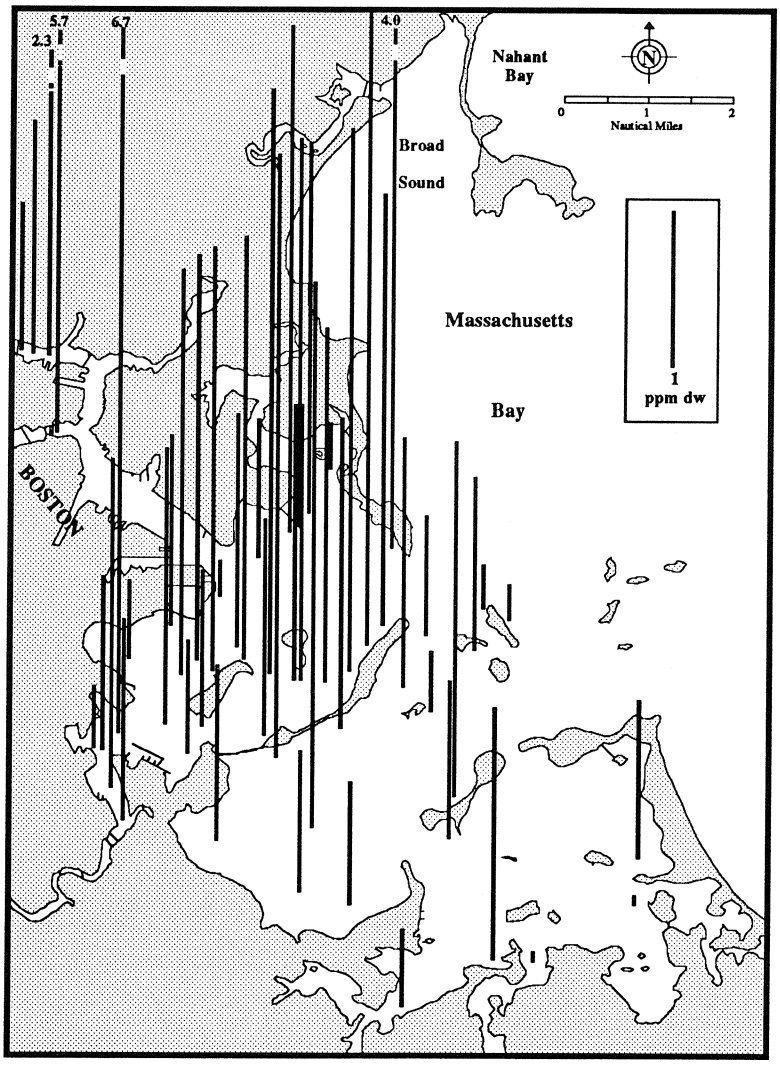


Figure 3.2 Mercury concentrations in the surficial sediments of Boston Harbor in 1971 (Gilbert *et al.*, 1972).

northwest harbor divisions were found to be significantly different at p=0.05. When the northwest harbor division was subdivided, the Winthrop Bay area had a mean of 2.23±1.40 ppm while the Dorchester Bay area had a mean of 2.11 ppm. Statistical analysis of the log transformed data indicated that only the southeast harbor division and the Dorchester Bay area were significantly different at p=0.05. A possible explanation for the lack of a statistically significant difference between the southeast harbor and the inner harbor and Winthrop Bay area was the relatively small sample sizes for these divisions and area (6, 4 and 6, respectively). The Dorchester Bay area had a sample size of 24.

Between 1971 and 1974, the State conducted a toxic element survey throughout the waters of Massachusetts (Isaac and Delaney, 1975). The survey included the analysis of sediment samples for volatile solids and a variety of heavy metals, including mercury. The combined mean mercury concentration based on 18 samples from around Boston Harbor was 1.53±0.87 ppm with a range of from 0.14 ppm to 3.20 ppm (Figure 3.3). When the data were grouped by harbor division and the log transformed data compared statistically, there was no significant difference between any of the divisions at p=0.05 even though the mean for the northwest harbor (2.13 ppm) was more than twice the mean for the southeast (1.00 ppm) and inner (0.87 ppm) harbor divisions (Table 3.2). When the northwest harbor data were subdivided the single sample from the Winthrop Bay area had a mercury concentration of 2.20 ppm, while the mean of the five samples from the Dorchester Bay area was 2.24 ppm. Statistical analysis of the log transformed data still indicated no significant difference between any of the divisions/areas. The relatively low mean for the inner harbor given in Table 3.2 was based on the average of only two samples. One sample had the low mercury concentration of 0.14 ppm, and the other sample had a concentration of 1.60 ppm, even though both samples were taken in the vicinity of the mouth of the inner harbor. Excluding the inner harbor data and although the statistical analysis indicated no significant difference, the division means suggest a trend of decreasing mercury concentrations in a northwest to southeast direction.

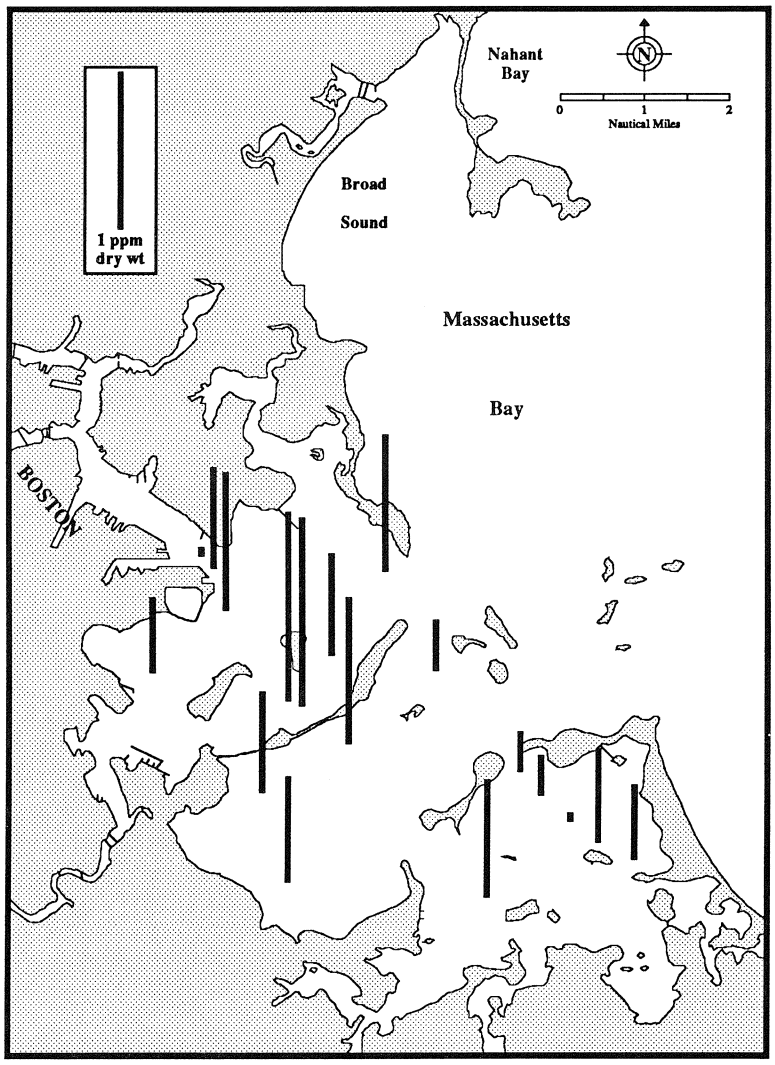


Figure 3.3 Mercury concentrations (ppm dw) in the surficial sediments of Boston Harbor from 1971-74 (Isaac & Delaney, 1975).

Data were obtained from the New England Division of the USACOE for dredging studies

conducted in and around Boston Harbor from 1972 through 1988 (USACOE, 1972-1988; 1981; USACOE, 1988). The USACOE analyzed 141 samples during this period for mercury content. The overall mean mercury concentration for the Harbor based on this data was 0.65±0.60 ppm, with a range of from 0.009 to 3.90 ppm. The majority of the samples (67%) had mercury concentrations between 0.1 and 1.0 ppm inclusive, while 12 percent of the samples had less than 0.1 ppm, and only 3 percent of the samples had concentrations in excess of 2.0 ppm. When the data was grouped by harbor divisions, the means ranged between 0.30±0.35 ppm in the central harbor, and 0.78±0.50 ppm in the inner harbor, with 0.61±0.75 ppm in the northwest harbor, and 0.45±0.35 ppm in the southeast harbor. Statistical analysis of the log transformed data indicated a significant difference only between the inner and central harbor (p=0.05). While neither the northwest nor the central harbor divisions were found to be significantly different from any of the other divisions, the data still suggest that the highest levels of mercury are in the inner and northwest harbor sediments with lower levels in the central and southeast harbor sediments. When the northwest harbor data were subdivided, the Dorchester Bay area mean was 1.21±1.18 ppm; while the Winthrop Bay area mean was 0.38±0.31 ppm. Statistical analysis indicated that the central harbor division was significantly different from both the inner harbor division and the Dorchester Bay area (p=0.05). The USACOE data suggest that the highest mercury levels are in the sediments of the inner harbor and the Dorchester Bay area of the northwest harbor.

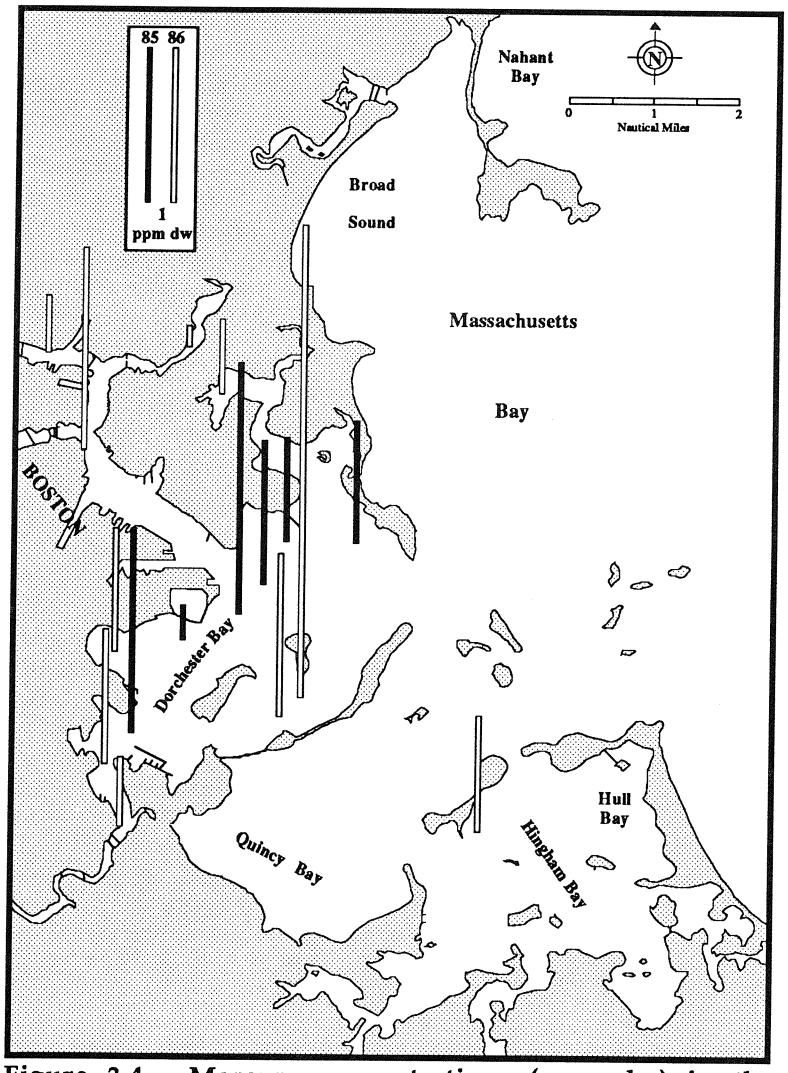


Figure 3.4. Mercury concentrations (ppm dw) in the surficial sediments of Boston Harbor for 1985 and 1986, based on data from Massachusetts DEQE (1986, 1987).

Other studies of Boston Harbor sediments which included analysis for mercury content were the Annual Water Quality and Wastewater Discharge surveys for 1985 and 1986, conducted by the Massachusetts DEQE (1986 and 1987) and the 1987 Quincy Bay Study conducted under the auspices of the U. S. EPA (EPA, 1988). The DEQE analyzed samples principally from the northwestern harbor with three samples from the inner harbor and one from the southeastern harbor (Figure 3.4). The overall mean for the Harbor was 0.93±0.67 ppm with a range of from 0.13 to 3.01 ppm. One point of interest concerning this data was that the two inner harbor sites located in the Chelsea and Mystic rivers appear to be significantly lower in mercury concentration than the inner harbor site in the Main Channel (Figure 3.4). This supports the supposition, based on White's data, that the

Mystic and Chelsea rivers generally have lower concentrations of mercury in the sediments than does the Main Channel area of the Harbor.

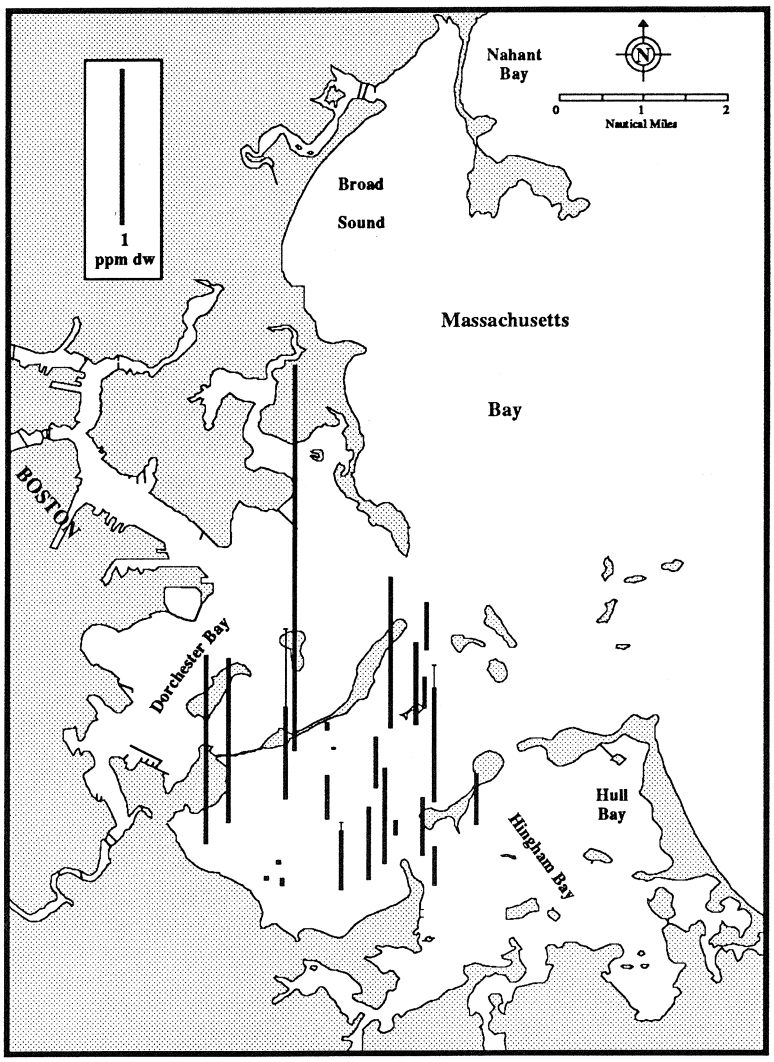
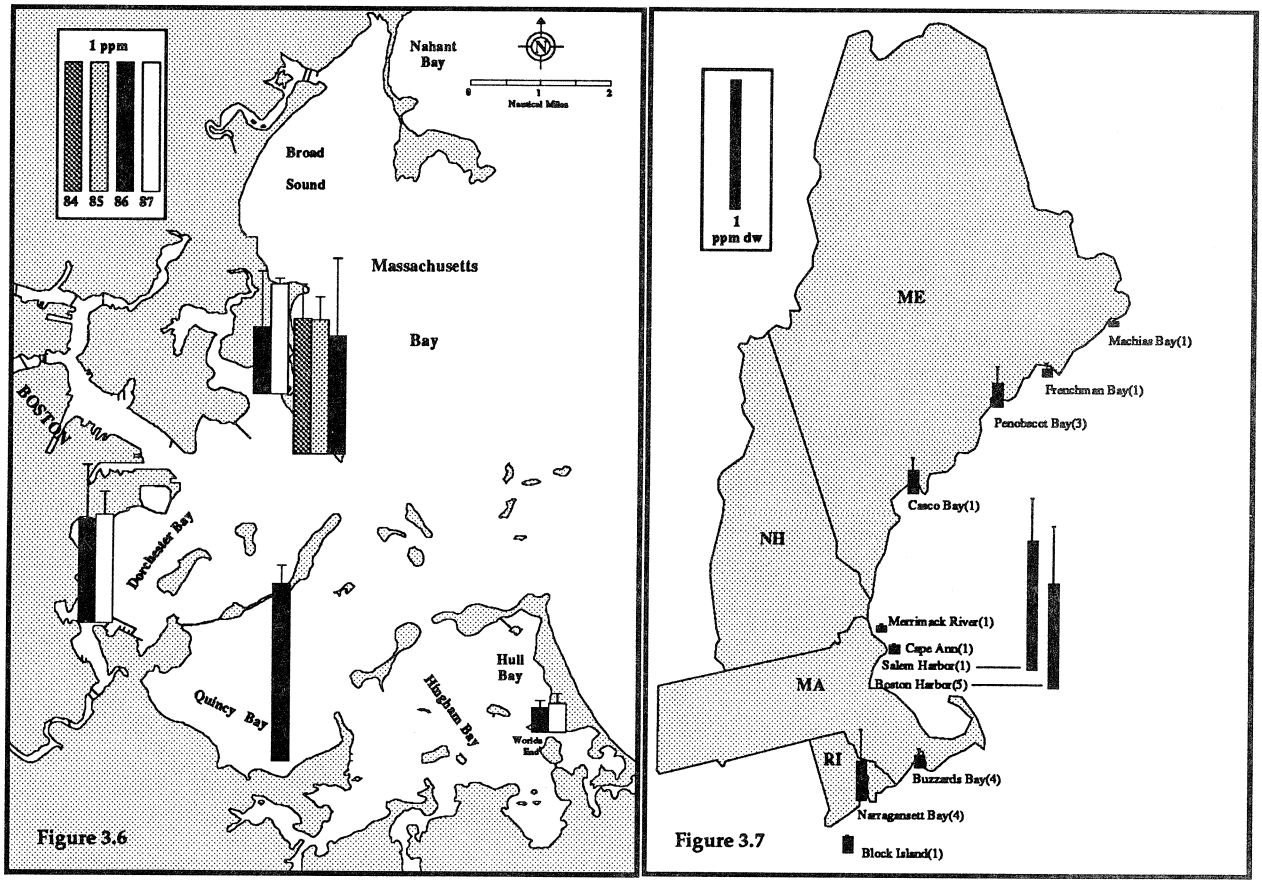


Figure 3.5. Mean mercury concentrations (ppm dw) in the surficial sediments of Quincy Bay and environs in 1987 (US EPA, 1988) (bars represent one standard deviation).

The EPA's Quincy Bay Study (U.S. EPA, 1988), using both core and grab samples, reported mercury concentrations principally in the sediments of the central harbor area and in the southeastern harbor, with the exception of five sites located between Peddocks and Nut islands. Figure 3.5 graphically displays the results of the grab sample analysis. The overall mean mercury concentration in the surficial sediments for the study was 0.46±0.47 ppm with a range of 0.006 to 2.48 ppm.

NOAA's NS&T Program has sampled and analyzed surficial sediments from several sites around Boston Harbor since 1984 for several analytes, including mercury (NOAA, unpublished). Figure 3.6 portrays this data graphically by year and site. Individual sample values ranged from 0.03 to 1.49 ppm. Site means, based on all 4 years of available data, ranged from 0.21 ppm at the site off the northern tip of Worlds End to 1.38 ppm at the site in southeastern Quincy Bay. Statistical comparison of the log transformed data indicated that the Worlds End site was significantly different from all but the site off the northwestern end of Deer Island ($p=0.05$). When the data were grouped by harbor divisions (Table 3.2) and log transformed, the southeast harbor was found to be significantly different from both the northwest and central harbors at $p=0.05$. When the northwest harbor data were subdivided, the southeast harbor was significantly different from both the Winthrop Bay and Dorchester Bay areas as well as the central harbor division ($p=0.05$). The NOAA data supports the assumption that mercury concentrations are lower towards the southeast of Boston Harbor but fails to indicate any trends throughout the rest of the harbor.

On a broader scale, the NOAA NS&T Program has analyzed surficial sediment samples at 23 sites from 11 areas along the outer New England coast between 1984 and 1987. Figure 3.7 displays the means with standard deviations for the 11 coastal areas. The figure clearly shows that the mean concentration of mercury at the NS&T Program sites in Boston



Figures 3.6 & 3.7. Mercury concentrations (ppm dw) in the surficial sediments of Boston Harbor by site and year (Fig. 3.6) and along the outer New England coast by area (Fig. 3.7) for 1984-87 (NOAA, unpublished) (bars represent one standard deviation).

Harbor was higher than the means for all other areas sampled in New England, except Salem Harbor. It should be noted that the Salem Harbor value was based on only one site and may not be representative of Salem Harbor in general. The Boston Harbor value was based on five sites including one, Worlds End, which had a relatively low mean concentration (0.21 ppm) and two sites, southwestern Deer Island and southeastern Quincy Bay, which had means greater than 1.00 ppm. Statistical analysis of the log transformed data indicated that Boston Harbor was significantly different (p=0.05) from all the other areas of New England sampled except Salem Harbor and Block Island. A possible reason for

When the means of the individual New England NS&T Program sites were compared, three of the five sites with the highest mean concentrations of mercury in the surficial sediments were located in Boston Harbor (Table 3.3). The five sites with the highest levels of mercury contamination all had means more than an order of magnitude higher than any of the five sites with the lowest levels of mercury contamination. The mean for the site with the highest mean mercury concentration, Quincy Bay, was 38 times the mean for the site with the lowest mean mercury concentration, Machias Bay (Table 3.3). In an attempt to determine a value for background mercury levels, the overall mean was calculated for the five NS&T Program sites with the lowest mercury concentrations in their surficial sediments. This mean was 0.050±0.023 ppm which compared favorably with worldwide background mercury levels which have been reported as ranging from 0.004 to 0.08 ppm (GESAMP, 1986a). The overall NS&T Program mean for Boston Harbor (0.792 ppm) was more than 15 times higher than the calculated background value.

Table 3.3. The five outer New England coast NOAA NS&T Program sites with the highest and lowest mean mercury concentrations based on data from 1984 through 1987.

Site	Mean	Standard Deviation	Count
MACHIAS BAY, MAINE	0.036	0.006	7
MERRIMAC RIVER	0.045	0.010	5
GOOSEBURY NECK, BUZZARDS BAY	0.051	0.015	6
FRENCHMAN ISLAND, MAINE	0.061	0.042	6
STRAITSMOUTH ISLAND, CAPE ANN	0.066	0.008	3
MOUNT HOPE BAY, RHODE ISLAND	0.81	0.04	3
DORCHESTER BAY	0.83	0.29	6
SALEM HARBOR	0.98	0.32	9
SOUTHWESTERN DEER ISLAND	1.01	0.34	10
QUINCY BAY	1.38	0.14	3

Temporal Trends

Figure 3.8 compares the yearly mean mercury concentrations in the surficial sediments of Boston Harbor, based on all the available data sets. It appears that mercury underwent an approximate twofold reduction during the time span covered by these data sets. However, conclusions must be drawn with caution because of a possible variability between data sets due to factors other than mercury contamination levels.

Data was available from the USACOE on dredging studies for most of the years from 1972 through 1988. When the yearly means based on this data were calculated and the log transformed data compared, there was no significant difference between any of the years despite means ranging from 0.18 ppm (1972) to 1.37 ppm (1975) at $p=0.05$. One factor contributing to the lack of any statistically significant difference was the variation in the number of sites sampled each year, from 1 in 1975 and 1988 to 59 in 1986 (Table 3.4). In addition to the variability in the number of sites sampled each year, the sites themselves varied from year to year. Therefore, while the data sets would be expected to be internally consistent with regards to methodology, any conclusions concerning temporal trends based on the data must be viewed with extreme caution.

The only other available data which spanned more than 2 years was that from NOAA's NS&T Program Benthic Surveillance (1984-86) and Mussel Watch (1986-87) projects (NOAA, unpublished). The yearly mean mercury concentrations in the surficial sediments of Boston Harbor based on this data ranged from a high of 1.05 ppm in 1984, remained about the same, 1.04 ppm in 1985, decreased to 0.764 ppm in 1986, and fell to a low of 0.642 ppm in 1987. While it appears that mercury levels are decreasing based on these means, statistical comparison of the log transformed data indicated no significant difference among years at $p=0.05$. The differences in the yearly overall mean mercury concentrations can be explained by the difference in the sites sampled each year (Figure 3.4). In 1984 and 1985 only the southwestern Deer Island site was sampled and the means for each year were virtually identical. In 1986, four additional sites were sampled, including the Worlds End site which had relatively low levels of mercury. For 1987, no data were available for the southwestern Deer Island and Quincy Bay sites. Each of these sites have had relatively high levels of mercury in the past.

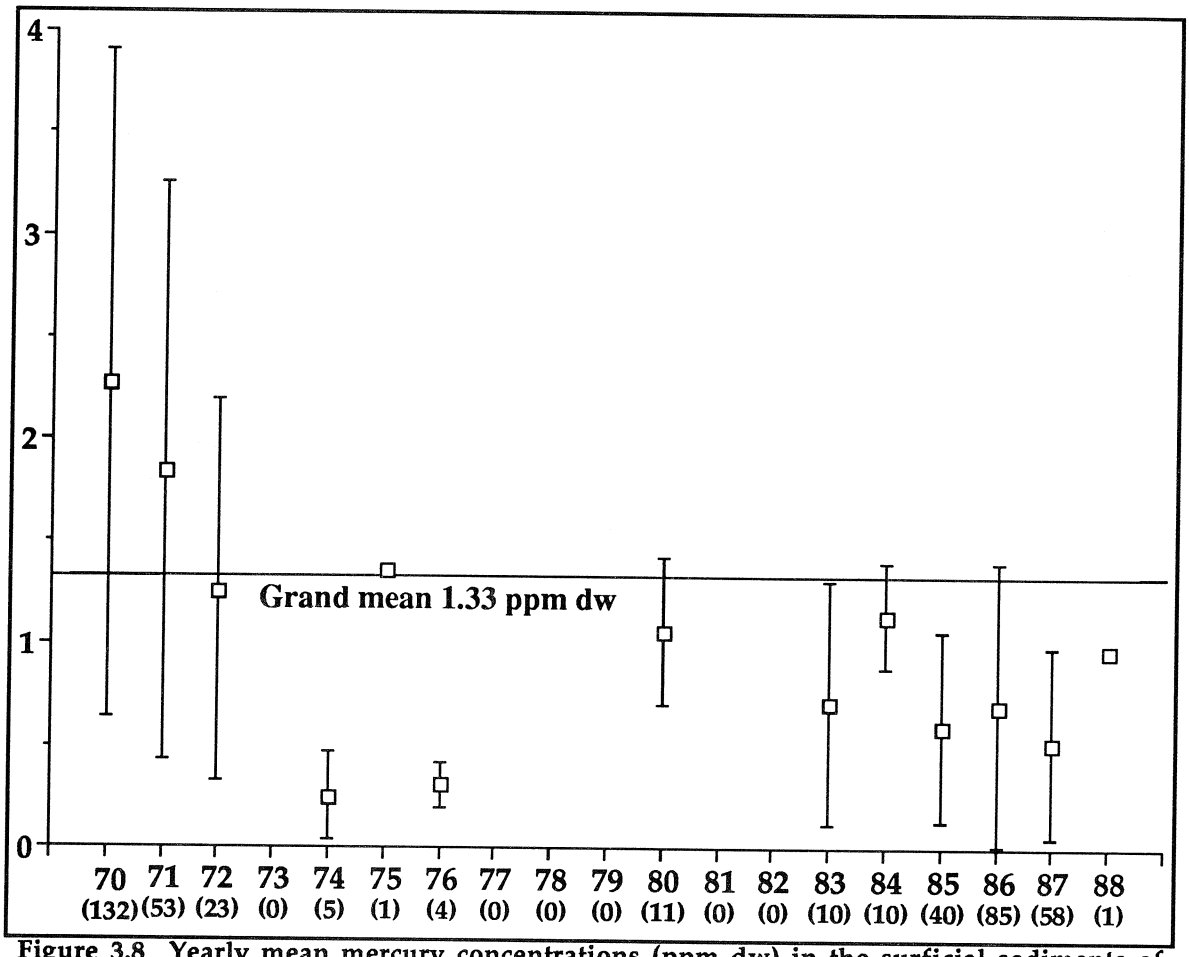


Figure 3.8 Yearly mean mercury concentrations (ppm dw) in the surficial sediments of Boston Harbor based on all the available data sets. The bars represent one standard deviation and the numbers in parentheses are number of samples.

Table 3.4. Yearly mean mercury concentrations in Boston Harbor surficial sediments based on dredging study data from the USACOE.

Year	Mean	Standard Deviation	Count
1972	0.175	0.099	4
1974	0.253	0.214	5
1975	1.370	N/A	1
1976	0.307	0.108	4
1980	1.064	0.359	11
1983	0.717	0.594	10
1984	1.189	0.262	7
1985	0.385	0.423	21
1986	0.647	0.719	59
1987	0.668	0.581	9
1988	0.980	N/A	1

Biota

Since 1979 over 200 tissue samples from a variety of organisms in Boston Harbor have been analyzed for levels of mercury contamination. Mercury concentrations ranged from a low of 0.011 ppm in the muscle of a lobster (*H. americanus*) to a high of 1.704 ppm in the liver of a winter flounder (*P. americanus*). Table 3.5 gives the statistics on mercury contamination of biota by organism and tissue. The U. S. FDA action level for mercury in the edible portion of an organism is 1.00 ppm ww. All the medians and means were well below this level even though the data were all in dry weight which resulted in higher values than if it had been reported as wet weight. A 1978 NMFS report (cited in GESAMP, 1986a) listed mean mercury concentrations in seafood sampled in the United States. Northern lobster had means of 0.509 and 0.339 ppm, depending on average weight (1,423 and 704 grams, respectively), however, it was not stated whether these values were for just the muscle tissue or the muscle and hepatopancreas combined. Flounder (unspecified) had a mean of 0.096 ppm suggesting that Boston Harbor lobster and flounder have above average levels of mercury contamination. It was unclear whether the same species of flounder was sampled for the NMFS report as was sampled in Boston Harbor.

Table 3.5. Harborwide means, standard deviations, medians, ranges, and sample sizes (count) for mercury concentrations (ppm) in biota by organism and tissues based on all the available data sets (* transplants).

	Mean	SD	Median	Range	Count
Pseudopleuronectes americanus					
liver	0.415	0.474	0.144	0.028-1.704	36
muscle	0.148	0.104	0.120	0.027-0.453	28
Homarus americanus					
hepatopancreas	0.090	0.027	0.097	0.051-0.123	8
muscle	0.581	0.342	0.511	0.011-1.388	48
Mya arenaria					
soft parts	0.285	0.081	0.286	0.012-0.444	34
Mytilus edulis					
soft parts	0.252	0.084	0.220	0.140-0.450	27
*Crassostrea virginica**					
soft parts	0.018	0.005	0.018	0.013-0.024	4

Geographic Trends

Based on an overview of all the available data concerning mercury in biota, broken down by division, there were no clear geographic trends in the mercury content of biota within Boston Harbor (Table 3.6). The winter flounder liver and lobster muscle data suggested that the inner harbor biota had lower levels of mercury than did the biota from the northwest harbor. The winter flounder liver data further suggested that the inner harbor biota had a lower level of mercury than did the central harbor biota. This central harbor biota had the highest levels of mercury among the four divisions. The lobster muscle data suggested that the northwest harbor biota had the highest levels of mercury. The winter flounder muscle data suggested there was no difference in mercury levels between the northwest and central harbor areas. The winter flounder liver data suggested that the northwest harbor biota had lower levels of mercury than did the central harbor biota. The lobster muscle data suggested the reverse. Part of this difference may be due to the fact that, at least in finfish, inorganic mercury tends to accumulate in the liver, while organic mercury tends to accumulate in the muscle tissue (GESAMP, 1986a). Therefore the difference between the pattern of

contamination suggested by the winter flounder liver and muscle data might have been due to different distribution patterns for inorganic and organic mercury.

Table 3.6. Mean mercury concentrations (ppm dw)for the entire Harbor and the four divisions in various organisms and tissues (the number in parentheses is the sample size).

	Pseudopleuronectes americanus		*Homarus americanus*	*Mytilus edulis*
	liver	muscle	muscle	soft parts
OVERALL	0.42 (36)	0.15 (28)	0.58 (48)	0.25 (27)
INNER HARBOR	0.21 (4)	N/A	0.45 (2)	N/A
NORTHWEST HARBOR	0.37 (28)	0.14 (3)	0.73 (28)	0.28 (18)
CENTRAL HARBOR	0.93 (4)	0.15 (25)	0.36 (18)	N/A
SOUTHEAST HARBOR	N/A	N/A	N/A	0.20 (9)

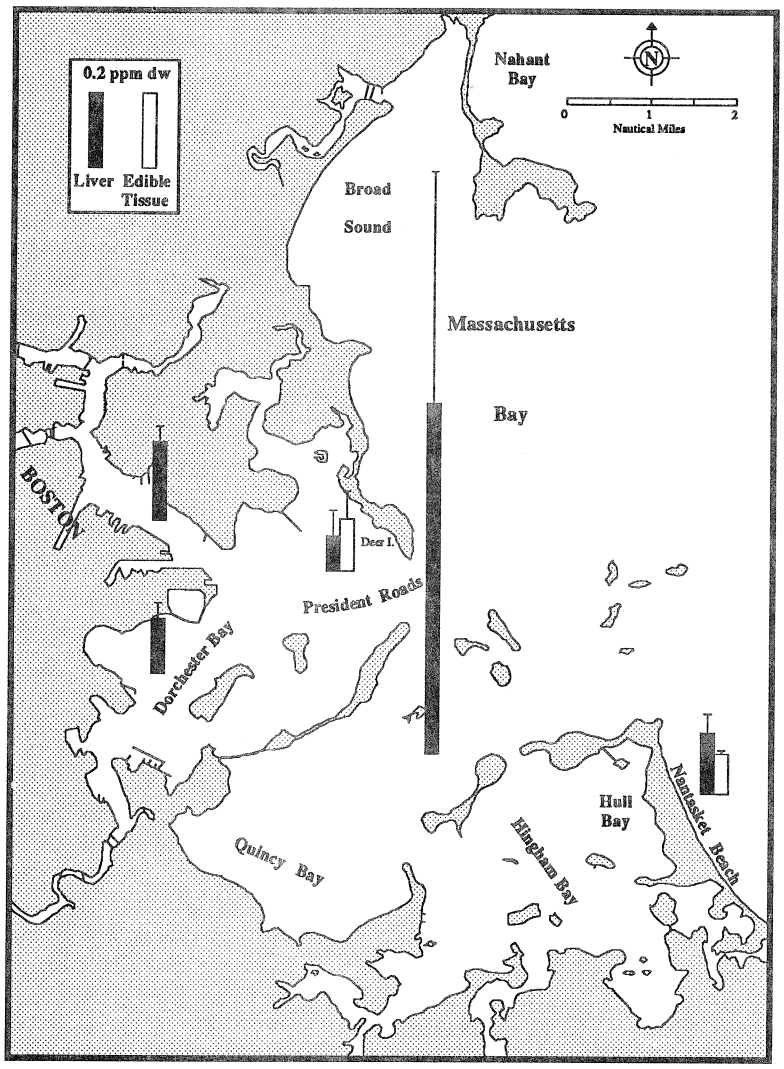


Figure 3.9. Mercury concentrations (ppm dw) in *P. americanus* liver and edible tissue from in and around Boston Harbor, based on data for 1979 (Metcalf & Eddy, 1984) (bars represent one standard deviation).

In 1979, as a part of the 301h waiver application for the Deer Island and Nut Island sewage treatment plants, winter flounder (*P. americanus*) and lobster (*H. americanus*) tissue samples from five sites in and around Boston Harbor were analyzed for levels of several analytes, including mercury (Metcalf and Eddy, 1984). The livers of four winter flounder from each of four different sites in Boston Harbor and one site outside the Harbor (Nantasket Beach) were analyzed for mercury content. The concentrations reported for the individual samples ranged from 0.028 ppm, in a sample from the President Roads site, to 1.70 ppm in a sample from the Nut Island Discharge site. The mean mercury concentrations in livers for the five sites ranged from 0.090±0.069 ppm at the President Roads site, to 0.932±0.621 ppm at the Nut Island Discharge site (Figure 3.9). When the data were log transformed and analyzed, the Nut Island Discharge site was found to be significantly different from the President Roads, Dorchester Bay, and

Nantasket Beach sites at p=0.05. When the data were looked at with regard to the harbor divisions, they suggested that the central harbor had the highest levels of mercury in winter flounder liver, followed by the inner harbor, and then the northwestern harbor. It also suggested that winter flounder liver from the Nantasket Beach had higher concentrations of mercury than did winter flounder liver from the northwestern harbor (Figure 3.9). Unfortunately, edible tissue samples from only two sites (President Roads and Nantasket Beach) were analyzed for mercury levels. Three samples from President Roads had a mean concentration of 0.140±0.073 ppm. Two samples from Nantasket Beach had a mean concentration of 0.105 ppm.

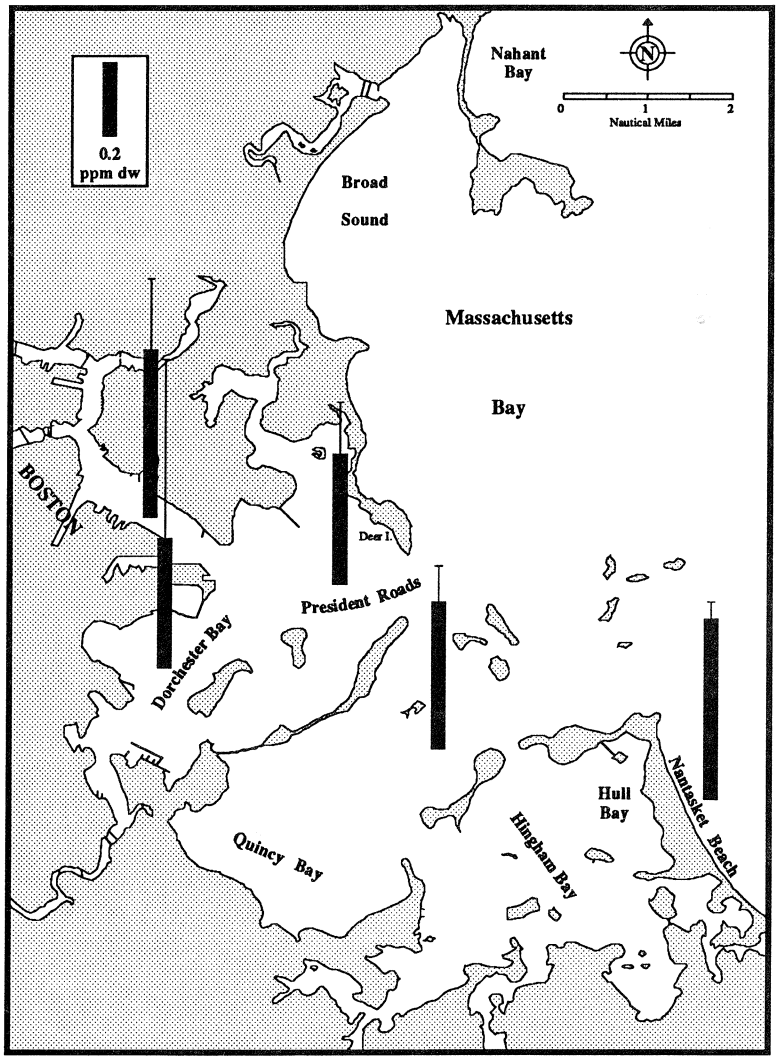


Figure 3.10. Mercury concentrations (ppm dw) in *H. americanus* muscle tissue from in and around Boston Harbor, based on data for 1979 (Metcalf & Eddy, 1984) (bars represent one standard deviation).

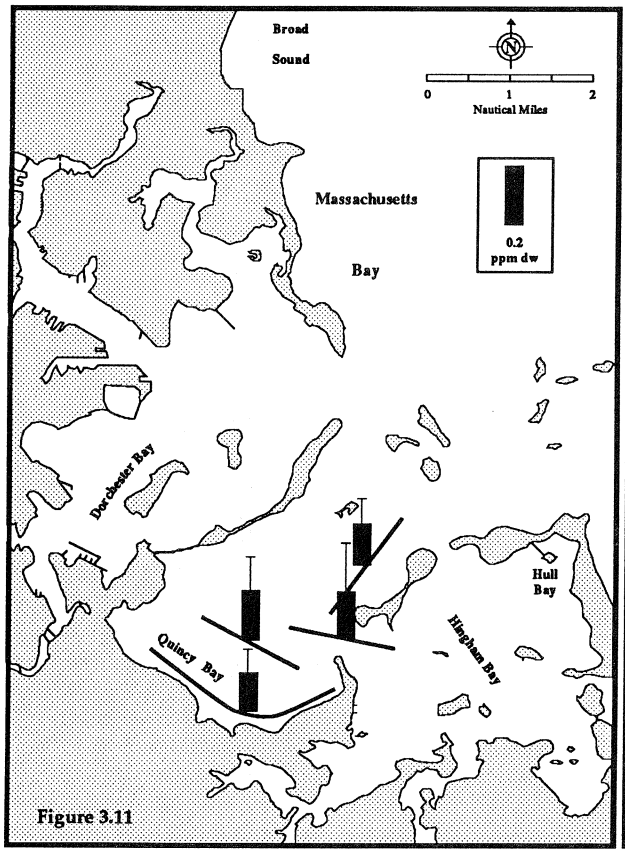
Two lobsters were collected from each of the same five sites, and claw and tail muscle tissue was analyzed for mercury content. Mercury concentrations in the individual specimens ranged from 0.011 to 0.686 ppm. The means for the five sites ranged from lows of 0.348 and 0.351 ppm at the Dorchester Bay and President Roads sites, respectively, to a high of 0.478 ppm at the Nantasket Beach site. The inner harbor site had a mean of 0.449 ppm, while the Nut Island Discharge site had a mean of 0.391 ppm (Figure 3.10). Unlike the flounder data, statistical analysis of the log transformed lobster data did not indicate any significant difference among the five sites (p=0.05).

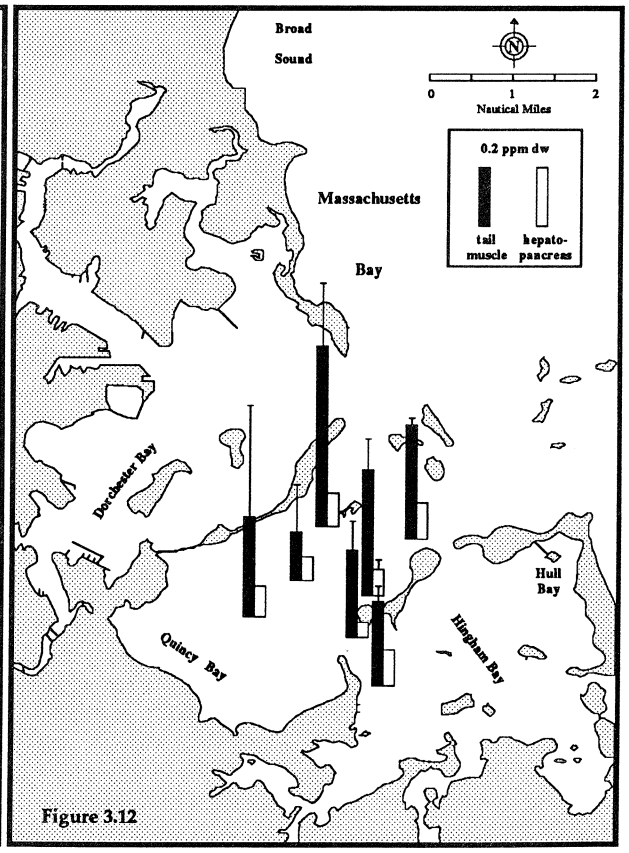
In 1985 and 1986, lobster (*H. americanus*) and soft-shelled clams (*M. arenaria*) were collected from Boston and Salem harbors and analyzed for contaminant levels of various analytes, including mercury, as part of a study of contaminants in marine resources (Wallace *et al.*, 1988). The mean mercury concentration in the combined claw and tail muscle tissue of 24 lobsters collected from around Deer Island was 0.794±0.332 ppm, with a range of from 0.255 to 1.388 ppm. Lobsters were collected from two sites in Salem Harbor, the treatment plant outfall and Willows Pier. The mean mercury concentrations in combined claw and tail muscle tissue based on the analysis of 25 lobsters per site were 0.730±0.264 and 0.857±0.563 ppm, respectively. Statistical analysis of the log transformed data indicated no significant difference among the three sites at p=0.05. The mean mercury concentration for 33 soft-

shelled clams from Wollaston Beach in Quincy Bay was 0.294±0.66 ppm, with a range of 0.192 to 0.444 ppm.

An intensive study of Quincy Bay was conducted in 1987 which included the analysis for levels of mercury contamination in the tissues of native winter flounder (*P. americanus*), lobsters (*H. americanus*), and soft-shelled clams (*M. arenaria*), as well as transplanted oysters (*C. virginica*) (EPA, 1988). The muscle tissue of from five to seven winter flounder from each of four different trawl transects was analyzed for levels of mercury contamination. The mercury concentration of individual samples ranged from 0.027 ppm to 0.453 ppm, while the mean mercury concentrations for each of the four trawl transects ranged from 0.130±0.078 ppm to 0.165±0.111 ppm (Figure 3.11). Statistical analysis of the log transformed data indicated no significant differences among the different trawl sites at p=0.05.

Both the tail muscle and the hepatopancreas tissue of lobsters from seven sites were analyzed for levels of mercury content. The tail muscles from 16 lobsters, 1 to 3 from each of the seven sites were analyzed. The mercury concentrations in the individual samples ranged from less than 0.088 to 0.746 ppm. The mean tail muscle concentrations for the seven sites ranged from 0.160±0.164 ppm to 0.415±0.100 ppm (Figure 3.12). There was no significant difference in tail muscle mercury levels among sites based on the statistical analysis of the log transformed data (p=0.05). The hepatopancreas tissue of 16 lobsters was also analyzed for mercury; mercury concentrations ranged from less than 0.102 to 0.123 ppm. Because only one lobster was analyzed from six of the seven sites, no statistical analysis could be performed on the data. However, when the mean level of mercury contamination in the hepatopancreas samples was compared to the mean of the tail muscle samples from the





Figures 3.11 & 3.12. Mercury concentrations (ppm dw) in *P. americanus* muscle tissue (Figure 3.11) (lines represent trawl transects) and *H. americanus* muscle and hepatopancreas tissue (Figure 3.12) from Quincy Bay, based on 1987 data (US EPA, 1988) (bars represent one standard deviation).

same specimens, the hepatopancreas mean was significantly lower than the tail muscle mean based on a one-tailed t-test at p=0.01. As previously mentioned, finfish predominantly accumulate organic mercury in their muscle tissue while inorganic mercury is predominantly accumulated in the liver. If this is also true for lobster, the higher levels of mercury in the muscle tissue as opposed to the hepatopancreas may have been due to organic mercury being the predominant form of mercury accumulated.

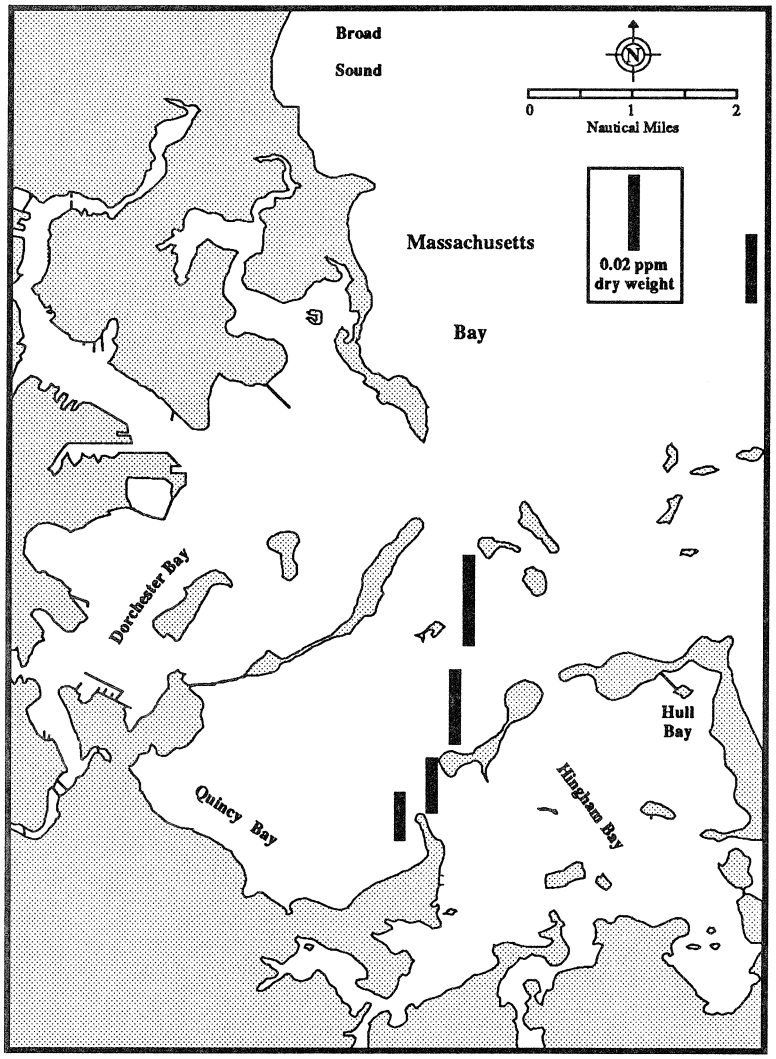


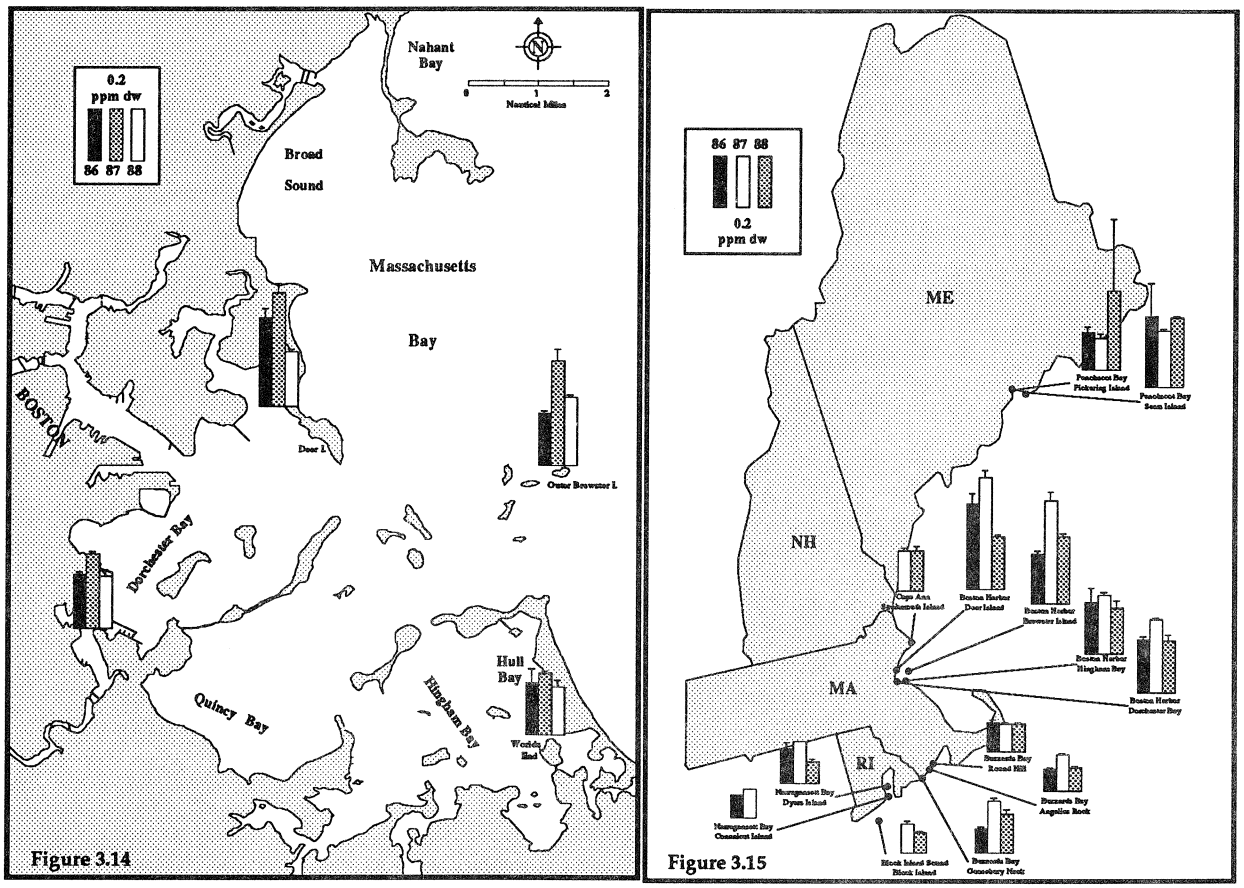
Figure 3.13. Mercury concentrations (ppm dw) in whole transplanted *C. virginica* at four sites in Boston Harbor and at The Graves, based on 1987 data (US EPA, 1988).

Oysters (*C. virginica*) were collected from a commercial bed located in Cotuit Bay, Cotuit, Massachusetts. They were deployed at four sites in Quincy Bay and one site located at The Graves in Massachusetts Bay from June 5 through July 16, 1987. The mercury concentrations in the oysters at the four sites ranged from 0.013 to 0.024 ppm. The oysters from The Graves had 0.018 ppm mercury. Those from the source bed in Cotuit Bay had a mercury concentration of 0.024 ppm (Figure 3.13). One sample of the soft-shelled clam from around Moon Island, Quincy Bay was also analyzed for mercury and was found to have a concentration of 0.012 ppm.

NOAA's Mussel Watch Project, a part of the NS&T Program, has sampled mussels (*M. edulis*) since 1986 from four sites in and around Boston Harbor on an annual basis. Three whole-body composite samples from each site were analyzed for a variety of analytes, including mercury. The overall mean concentration of mercury in the mussels for the three sites in Boston Harbor from 1986 through 1988 was 0.252±0.084 ppm, with a range of from 0.140 to 0.450 ppm. The means for the individual sites were 0.202±0.038 ppm in Hingham Bay off Worlds End, 0.229±0.043 ppm in southwestern Dorchester Bay, and 0.324±0.101 ppm northwest of Deer Island. Mussels from the site outside the Harbor, Outer Brewster Island, had a mean mercury concentration of 0.286±0.092 ppm (Figure 3.14). Statistical analysis of the log transformed data for the four sites indicated that only the Deer Island and Hingham Bay sites were significantly different (p=0.05) from each other.

On a broader scale, when the Boston Harbor NS&T sites were compared to the other outer New England coast NS&T Mussel Watch sites (Table 3.7 and Figure 3.15), the Deer

Island site was found to be significantly different from the Pickering Island site in Penobscot Bay and from all the sites south of Cape Cod. The Dorchester Bay site was significantly different from all the sites south of Cape Cod except the site at Goosebury Neck in southwestern Buzzards Bay (p=0.05). The Hingham Bay site was significantly different from only two sites, Round Hill in Buzzards Bay and Block Island (p=0.05). It should be noted that the site just outside Boston Harbor (Outer Brewster Island) was significantly different from all the sites south of Cape Cod except the site at Goosebury Neck (p=0.05). It appeared that generally, mercury levels in the soft parts of mussels north of Cape Cod were higher than those south of Cape Cod. When a reference value was calculated based on the five sites with the lowest levels of mercury contamination in mussels, a value of 0.105±0.025 ppm was obtained. The Boston Harbor sites had mean mercury concentrations of from 2 to 3 times higher than this reference value.



Figures 3.14 & 3.15. Mean mercury concentrations (ppm dw) in the soft-parts of *M. edulis* from Boston Harbor (Fig. 3.14) and the outer New England coast (Fig. 3.15) for 1986-88 (NOAA, unpublished) (bars represent one standard deviation).

NOAA's Benthic Surveillance Project (a part of the NS&T Program) has sampled winter flounder (*P. americanus*) since 1986 from an area just west of Deer Island on an annual basis. The mean mercury concentration in the liver of the fish sampled in 1984 and 1985 was 0.479±0.495 ppm with a range of 0.055 to 1.46 ppm. The mean concentration of mercury in flounder livers for all of the New England Benthic Surveillance sites, except Boston Harbor, ranged from a low of 0.152±0.113 ppm at the Salem Harbor site to a high of 0.315±0.148 ppm at the Casco Bay site (Figure 3.16). Statistical analysis of the log transformed data indicated that only the Boston Harbor and Salem Harbor sites were significantly different at p=0.05. No comparison could be made between Boston Harbor and the three northern-Maine sites; because a different species, longhorn sculpin (*Myoxcephalus octodecemspinosus*),

Table 3.7. The mean mercury concentrations (ppm) in *M. edulis* at the 13 New England NS&T Program Mussel Watch sites. The outlined means are for Boston Harbor sites.

Site	Mean	Standard Deviation	Count
DEER ISLAND, BOSTON HARBOR	0.324	0.101	9
OUTER BREWSTER ISLAND	0.286	0.092	9
SEARS ISLAND, PENOBSCOT BAY	0.251	0.070	9
DORCHESTER BAY, BOSTON HARBOR	0.229	0.043	9
HINGHAM BAY, BOSTON HARBOR	0.202	0.038	9
PICKERING ISLAND, PENOBSCOT BAY	0.189	0.167	9
CAPE ANN, STRAITSMOUTH ISLAND	0.157	0.012	9
GOOSEBURY NECK, BUZZARDS BAY	0.155	0.045	8
DYERS ISLAND, NARRAGANSETT BAY	0.125	0.036	9
ROUND HILL, BUZZARDS BAY	0.107	0.007	9
CONANICUT ISLAND NARRAGANSETT BAY	0.100	0.011	6
ANGELICA ROCK, BUZZARDS BAY	0.097	0.027	11
BLOCK ISLAND, RHODE ISLAND	0.095	0.018	6

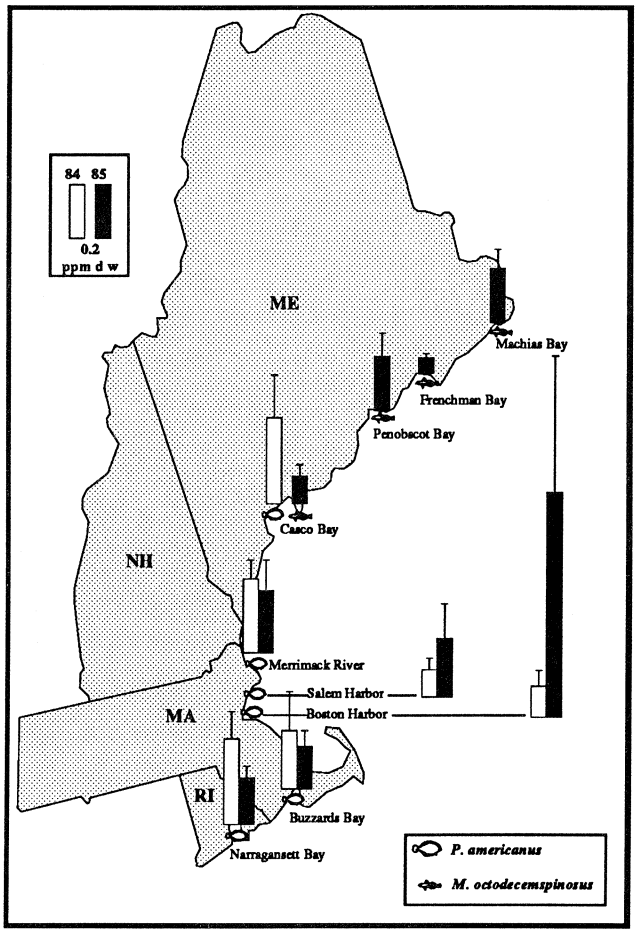


Figure 3.16. Mean mercury concentrations (ppm dw) in liver tissue of *P. americanus* and *M. octodecemspinosus* for 1984-85 from the outer New England coast (NOAA, unpublished) (bars represent one standard deviation).

was sampled at these sites. The Benthic Surveillance Project sampled winter flounder at four other sites during the same time frame: two in Long Island Sound and one each in Raritan and Great bays in New Jersey. Only the Raritan Bay site had a mean mercury concentration (0.733±0.505) greater than Boston Harbor.

Temporal Trends

Based on the available data, no temporal trends in the mercury content of Boston Harbor biota could be determined. The reason for this being, the only internally consistent data sets sampling the same organism from the same locations over a number of years were the NS&T Program's Benthic Surveillance and Mussel Watch projects. Data for these projects were only available for 2 and 3 years, respectively. Between 1984 and 1985 there was approximately a sevenfold increase in the level of mercury in winter flounder livers (0.118±0.053 to 0.825±0.487 ppm) (Figure 3.16) which was significantly different based on a one-tailed t-test of the log transformed data (p=0.01). However, whether this indicates a trend in the mercury content of Boston Harbor biota or was just due to random sampling could not be determined,

based on only 2 years of data. Likewise, the 3 years of data for *M. edulis* from the Mussel Watch Project failed to indicate any trend with mercury levels increasing between 1986 and 1987 and then decreasing in 1988 (Figure 3.15). The yearly means were 0.246±0.074, 0.316±0.093, and 0.194±0.022 ppm, respectively.

Summary

Boston Harbor sediments were found to be contaminated with mercury at levels which exceeded regional background levels by more than an order of magnitude. When the overall mean value of mercury in Boston Harbor (1.33±1.34 ppm) was compared to the overall mean of San Francisco Bay (0.50±0.67 ppm) (Long *et al.*, 1988) it was found to be more than 2 1/2 times higher than the San Francisco Bay mean. When just the NS&T Program data for the two ports were compared, the Boston Harbor mean (0.792±0.434 ppm) was again more than 2 1/2 times higher than the San Francisco Bay mean (0.292±0.408 ppm) (Long *et al.*, 1988) (Table 3.8). The available data suggested that mercury in Boston Harbor surficial sediments showed a trend of decreasing concentration from the inner harbor towards the southeastern harbor and towards the mouth. The data also suggested that the inner reaches of the Harbor, specifically the Mystic and Chelsea rivers, had lower levels of mercury than did the main channel. No clear temporal trends were apparent with regards to sediment contamination.

Table 3.8. Comparison of mercury conentrations in the sediment for Boston Harbor, NS&T Program Reference (mean of five outer New England coast NS&T Program sites with the lowest mercury concentrations), and San Francisco Bay in ppm dw. Statistics for San Francisco Bay derived from Long *et al.*, 1988.

Area	Mean	Standard Deviation	Median	Range	Count
Boston	1.330	1.344	0.915	0.006-9.400	433
NS&T Boston	0.792	0.434	0.900	0.030-1.490	31
NS&T Reference	0.055	0.024	0.050	0.021-0.125	28
San Francisco Bay	0.500	0.670	0.380	0.010-6.800	1097
NS&T San Francisco Bay	0.292	0.408	0.195	0.010-2.170	40

Based on mussel, flounder, and lobster data, Boston Harbor biota had above average concentrations of mercury in their tissues. Boston Harbor mussels (*M. edulis*) and winter flounder (*P. americanus*) liver tissue had the highest mean mercury concentrations of all the New England NS&T Program areas sampled. A reference value for mercury contamination in mussels was calculated based on the five least contaminated New England NS&T Program sites. This value showed that the Boston Harbor mean (0.252±0.084 ppm) was approximately 2 1/2 times greater than the reference mean (0.105±0.025 ppm). The winter flounder and lobster (*H. americanus*) muscle tissue in Boston Harbor had mean concentrations of mercury higher than the average mean concentrations in flounder and lobster based on a NMFS seafood study (cited in GESAMP, 1986a). There were no obvious geographic or temporal trends in biota contamination within Boston Harbor based on the available data. This is because relative concentrations among different areas of the Harbor varied with the organism and tissue sampled. With the exception of the NS&T Program, none of the studies sampled the same organism from the same sites over a period of years.

CADMIUM

Cadmium is a naturally occurring element that has no known biological function, on the contrary, it is known to be teratogenic and mutagenic (Eisler, 1985). Cadmium levels in uncontaminated marine sediments range from 0.030 to 1.000 ppm (Eisler, 1985). In a review of the literature, Long and Morgan (1990) found data suggesting that cadmium levels in sediment below about 5.0 ppm have little or no effect on biota while levels of 9.0 ppm or greater generally have either a chronic or acute effect on the organisms tested. Cadmium concentrations as high as 10.5 ppm have been reported for the soft parts of the mussel *M. edulis* (Goldberg *et al.*, 1978).

Sediments

Since the late 1960s, over 400 surficial sediment samples from Boston Harbor have been analyzed for cadmium concentrations. Based on this data, the overall mean concentration of cadmium in the surficial sediments of the harbor was 2.73 ppm with a standard deviation of 3.45 and a range of from 0.05 to 35.06 ppm (Table 4.1). The median concentration was 2.00 ppm. The large standard deviation and the difference between the mean and the median values are because approximately 13 percent of the samples analyzed had concentrations greater than 5.00 ppm. Approximately 63 percent of the samples had values between 1.00 and 5.00 ppm inclusive. The remaining 24 percent of the samples contained less than 1.00 ppm cadmium.

Table 4.1. Means, standard deviations, medians, ranges, and number of samples (count) for cadmium concentrations (ppm) in surficial sediments of all of Boston Harbor and for the four regions of the harbor, based on all the available data sets.

	Mean	Standard Deviation	Median	Range	Count
OVERALL	2.75	3.46	2.00	0.05-35.06	406
INNER HARBOR	4.32	5.45	2.50	0.10-35.06	109
NORTHWEST HARBOR	2.91	2.32	2.50	0.05-14.90	149
CENTRAL HARBOR	1.48	1.63	1.00	0.10-11.20	84
SOUTHEAST HARBOR	1.28	1.12	1.00	0.16- 5.52	64

Geographic Trends

When the combined data set was broken down into the four harbor divisions, the means suggested that the surficial sediments of the inner harbor had the highest levels of cadmium (4.32 ppm). Those of the northwest harbor had the second highest (2.91 ppm). There was no significant difference in cadmium levels between the southeast and central harbor surficial sediments (Table 4.1). However, the medians, while supporting the lower levels of cadmium in the surficial sediments of the southeast and central harbor divisions (both 1.00 ppm) and the lack of significant difference in cadmium concentrations between these divisions, also suggested that there was no significant difference between cadmium levels in the surficial sediments of the inner and northwest harbor (both 2.50 ppm) (Table 4.1). When the northwest harbor was subdivided, the Dorchester Bay area sediments had a mean concentration of 3.31±2.20 ppm with a median concentration of 2.85 ppm, while the Winthrop bay area sediments had a mean concentration of 2.61±2.40 ppm with a median concentration of 2.22 ppm.

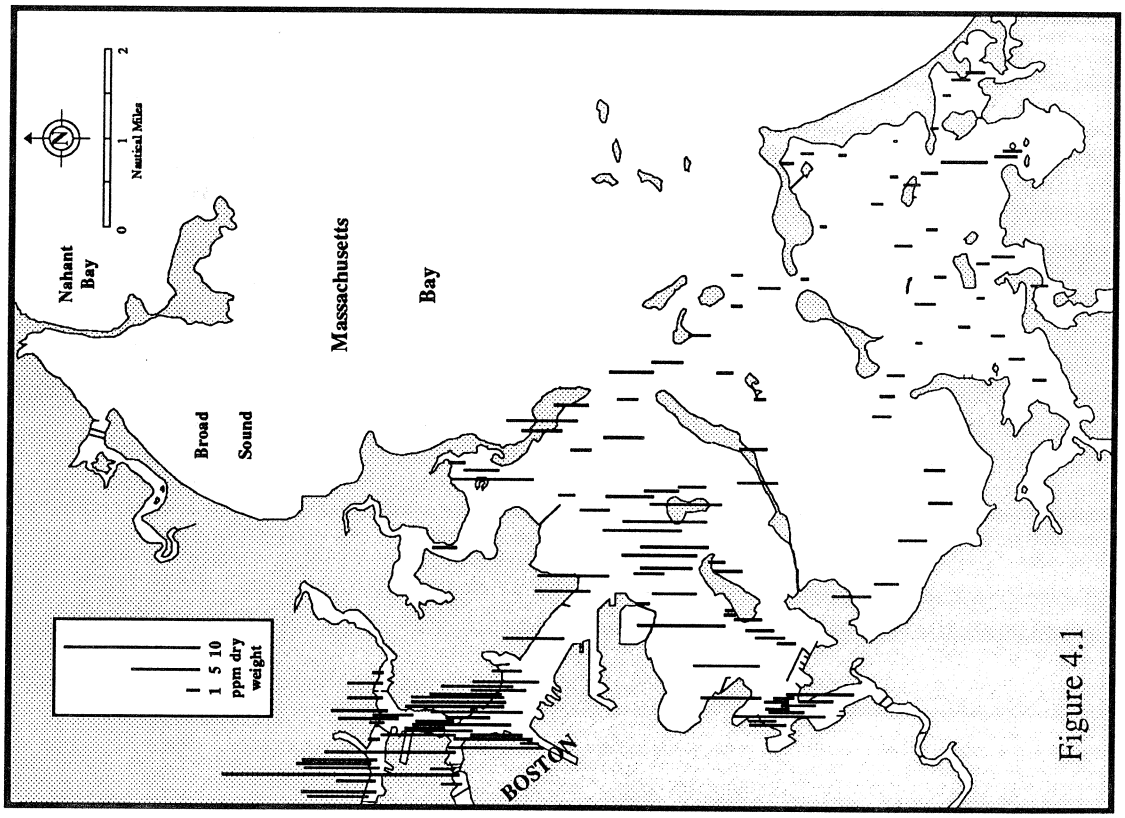
Around 1970, White (1972) collected and analyzed over 130 surficial sediment samples from Boston for a variety of metals, including cadmium. He found cadmium concentrations

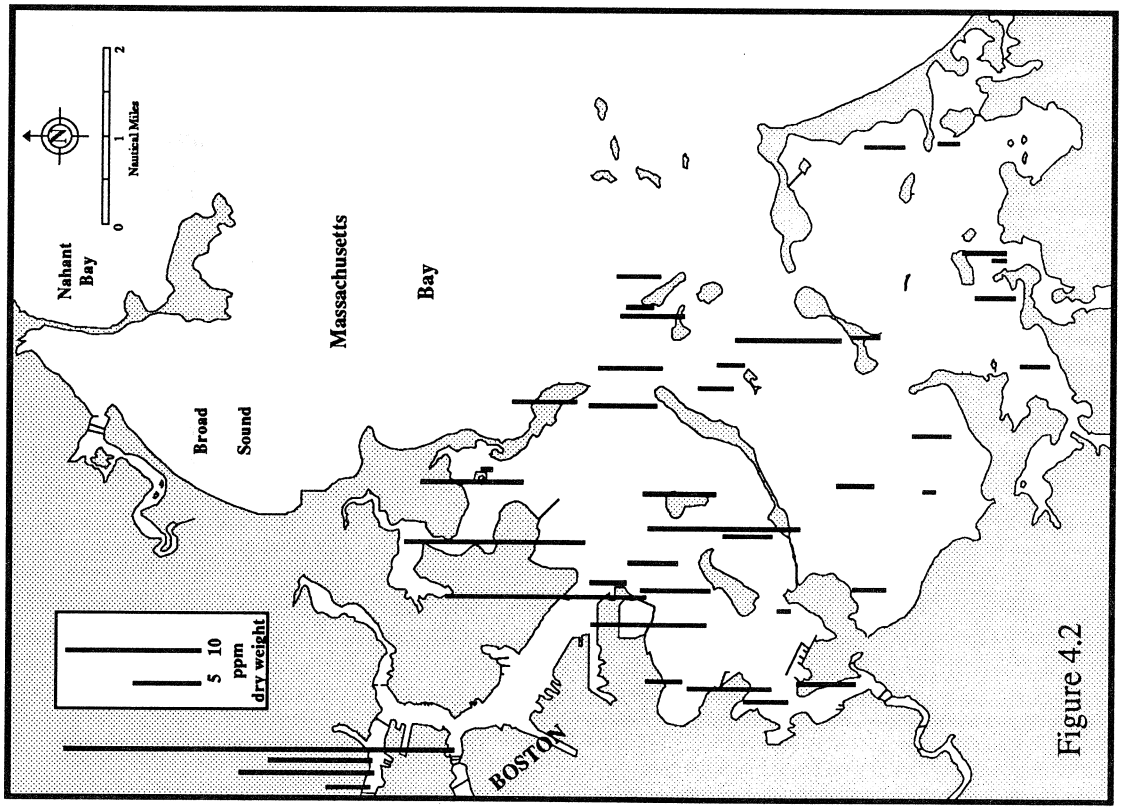
ranging from a low of 0.1 ppm, in two samples from Dorchester Bay, to a high of 17.5 ppm, in a sample from the lower Charles River. From this study, it appears that cadmium concentrations in the surficial sediments decreased from northwest to southeast. The highest concentrations occurred in the inner harbor and Dorchester Bay. The lowest concentrations occurred at the mouth of the Harbor and in the southeastern harbor (Figure 4.1). This trend of decreasing cadmium in the surficial sediments from northwest to southeast was supported by statistical analysis of the log transformed data for the four harbor divisions. These data indicated that all four harbor divisions were significantly different from each other at p=0.05 (Table 4.2). When the northwest harbor was subdivided, the Dorchester Bay area sediments had a mean concentration of 3.11±1.82 ppm, while the Winthrop Bay area sediments had a mean concentration of 2.93±1.53 ppm. Statistical analysis of the log transformed data indicated no significant difference between the two subdivisions or among the two subdivisions and the other three harbor divisions at p=0.05.

Table 4.2. Mean cadmium concentrations in the surficial sediments of Boston Harbor and the four divisions of the harbor, in ppm, based on the data of White (1972), Gilbert *et al.* (1972), Isaac and Delaney (1975), MA DEQE, 1986 and 1987), and NOAA NS&T Program (unpublished). The numbers in parentheses are the number of data points used to calculate the means.

	White 1970?	Gilbert *et al.* 1971	Isaac and Delaney 1972	MA DEQE 1985-86	NOAA NS&T 1984-87
OVERALL	2.87 (133)	5.17 (41)	2.07 (6)	2.44 (30)	1.25 (31)
INNER HARBOR	4.66 (38)	12.52 (4)	0.70 (1)	3.73 (8)	NA
NORTHWEST HARBOR	3.05 (48)	5.49 (17)	6.10 (1)	2.31 (14)	1.56 (22)
CENTRAL HARBOR	1.69 (16)	3.98 (12)	1.80 (2)	1.44 (5)	0.90 (3)
SOUTHEAST HARBOR	1.03 (31)	2.61 (8)	1.00 (2)	1.20 (3)	0.27 (6)

In 1971, the NEA collected 55 cores of Boston Harbor sediments and analyzed various sections of the cores for heavy metal content (Gilbert *et al.*, 1972). Based on 41 samples of the upper surface of the cores that were analyzed for cadmium, they found cadmium concentrations ranging from a low of 0.80 ppm in a sample taken from just south of Snake Island (Winthrop Bay), to a high of 29 ppm in a sample taken from the lower reaches of the Charles River (Inner Harbor). The majority of the sample concentrations (71%) were less than or equal to 5.0 ppm. As with the White data, a graphic representation (Figure 4.2) suggests higher levels of cadmium in the surficial sediments of the northwestern and inner harbor divisions. Somewhat lower levels are shown for the central and southeastern divisions of the harbor. However, it should be noted that some of the lowest levels of cadmium in the surficial sediments were recorded for individual sites in Dorchester Bay and north of President Roads. The fourth and seventh highest levels of cadmium were recorded from sites in Quincy Bay; indicating that cadmium was heterogeneously distributed throughout the sediments. When the data were grouped by the four harbor divisions and the log transformed data compared statistically, only the inner and southeast harbor divisions were found to be significantly different at p=0.05. When the northwest harbor was subdivided, the Dorchester Bay area sediments had a mean concentration of 5.13±5.30 ppm, while the Winthrop bay area sediments had a mean concentration of 6.65±5.30 ppm. Statistical analysis of the log transformed data indicated that the two subdivisions were significantly different from only the southeast harbor division at p=0.05.





Figures 4.1 & 4.2. Cadmium concentrations (ppm dw) in the surficial sediments of Boston Harbor for around 1970 based on data from White, 1972 (Fig. 4.1) and for 1971 based on data from Gilbert *et al.*, 1972 (Fig. 4.2).

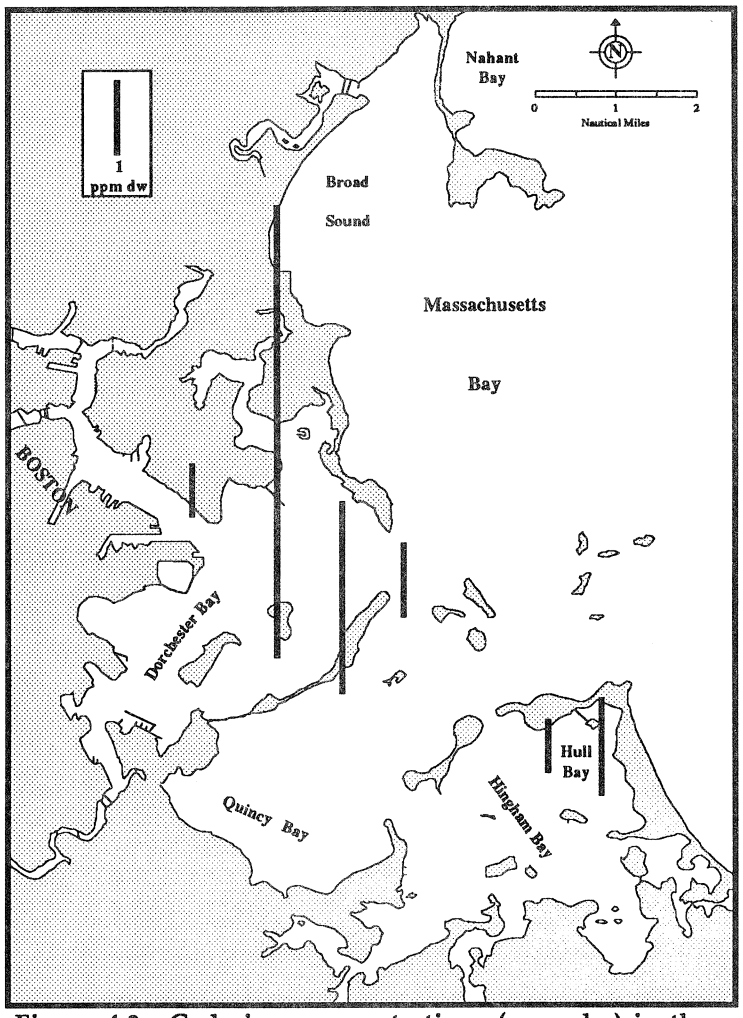


Figure 4.3. Cadmium concentrations (ppm dw) in the surficial sediments of Boston Harbor in the early 1970's, based on data from Isaac & Delaney, 1975.

Between 1971 and 1974, Massachusetts conducted a toxic element survey of the waters of the State (Isaac and Delaney, 1975). The survey included the analysis of sediment samplesfor volatile solids and a variety of heavy metals including cadmium. Six surficial sediment samples from around Boston Harbor had a combined mean cadmium concentration of 2.07±2.10 ppm with a range of from 0.70 to 6.10 ppm (Figure 4.3). Because so few samples were analyzed, no statistical comparison between harbor divisions could be made. The data suggested a trend of decreasing cadmium concentrations from northwest to southeast although the lowest level of cadmium contamination was found in the single sample from the inner harbor (Table 4.2). This sample, located near the mouth of the inner harbor, also had relatively low concentrations of the other metals for which it was analyzed, as well as the lowest concentration of volatile solids in the Harbor.

Data were obtained from the New England Division of the USACOE for dredging studies conducted in and around Boston Harbor from 1972 through 1988 (USACOE, 1972-1988; 1981; 1988). The USACOE analyzed 125 samples for cadmium content during this period. The overall mean cadmium concentration for the Harbor based on this data was 2.96±4.47 ppm with a range of from 0.05 to 35.06 ppm. The vast majority of the samples (70%) had cadmium concentrations between 1.0 and 5.0 ppm inclusive. While 22 percent of the samples had less than 1.0 ppm, only 8 percent had concentrations in excess of 5.0 ppm. When the data was grouped by harbor divisions, the means ranged between 1.14±1.42 ppm in the central harbor to 3.68±6.12 ppm in the inner harbor with 2.73±2.18 ppm in the northwest harbor, and 1.59±1.68 ppm in the southeast harbor. Statistical analysis of the log transformed data indicated a significant difference only between the inner and central harbor at $p=0.05$. As with the other data sets, there was the suggestion of decreasing cadmium concentrations going from the inner to the southeast harbor. However, it should be noted that the vast majority of the samples analyzed were from the inner and northwest harbor (58 and 47 respectively). Only 6 samples were from the central harbor and 14 from the southeast harbor. When the northwest harbor was subdivided, the Dorchester Bay area sediments (14 samples) had a mean concentration of 3.03±0.97 ppm, while the Winthrop Bay area sediments (33 samples) had a mean concentration of 2.60±2.53 ppm. Statistical analysis of the log transformed data indicated no significant difference between the two subdivisions or among the two subdivisions and the other three harbor divisions at $p=0.05$.

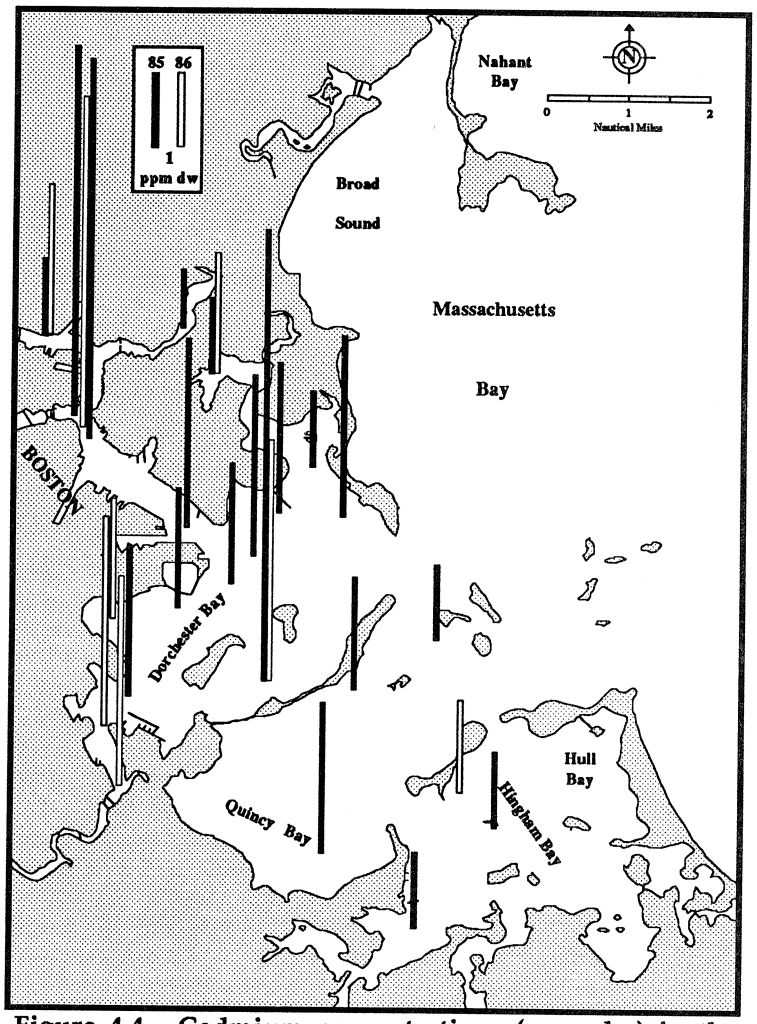


Figure 4.4. Cadmium concentrations (ppm dw) in the surficial sediments of Boston Harbor in 1985 and 1986, based on data from Massachusetts DEQE, 1986 & 1987.

In 1985 and 1986, the Massachusetts DEQE, as part of their annual Boston Harbor Water Quality and Wastewater Discharge Survey, analyzed 30 surficial sediment samples for cadmium content (MA DEQE, 1986; 1987). They found an overall mean cadmium concentration of 2.44±1.77 ppm with a range of 0.80 to 8.00 ppm. Both the low and high values were from sites in the inner harbor (Chelsea River, and off Commerce Street). While the means for the harbor divisions (Table 4.2) suggested a trend of decreasing cadmium levels from the inner harbor to the southeast harbor, statistical analysis of the log transformed data indicated no significant difference between any of the divisions at p=0.05. This trend can also be seen in Figure 4.4 that graphically displays the data by site and year. When the northwest harbor was subdivided, the Dorchester Bay area sediments had a mean concentration of 2.75±1.44 ppm, while the Winthrop Bay area sediments had a mean concentration of 1.73±0.64 ppm. Statistical analysis of the log transformed data indicated no significant difference between the two subdivisions or among the two subdivisions and the other three harbor divisions at p=0.05.

In 1987 a study of Quincy Bay was conducted under the auspices of the U. S. EPA (EPA, 1988), which was essentially restricted to the central harbor area. Figure 4.5 graphically displays the results of the grab sample analysis. The overall mean cadmium concentration in the surficial sediments for the study was 0.72±0.42 ppm with a range of 0.10 to 1.87 ppm.

Since 1984, NOAA's NS&T Program has sampled and analyzed surficial sediments from several sites around Boston Harbor for several analytes, including cadmium. Figure 4.6 portrays this data graphically by year and site. The overall mean cadmium concentration in surficial sediments of the harbor was 1.25±0.83 ppm. Individual sample values ranged from 0.15 to 3.08 ppm. Site means, based on all 4 years of available data, ranged from 0.27 ppm, at the site off the northern tip of Worlds End, to 1.91 ppm, at the site southwest of Deer Island. Statistical comparison of the log transformed data indicated that the Worlds End site was significantly different from all but the site in Quincy Bay at p=0.05. When the data were grouped by harbor divisions (Table 4.2), the means suggested a trend of decreasing cadmium concentration from the northwest harbor to the southeast harbor. The log transformed data indicated that the southeast harbor was significantly different from both the northwest and central harbors at p=0.05. When the northwest harbor was subdivided,

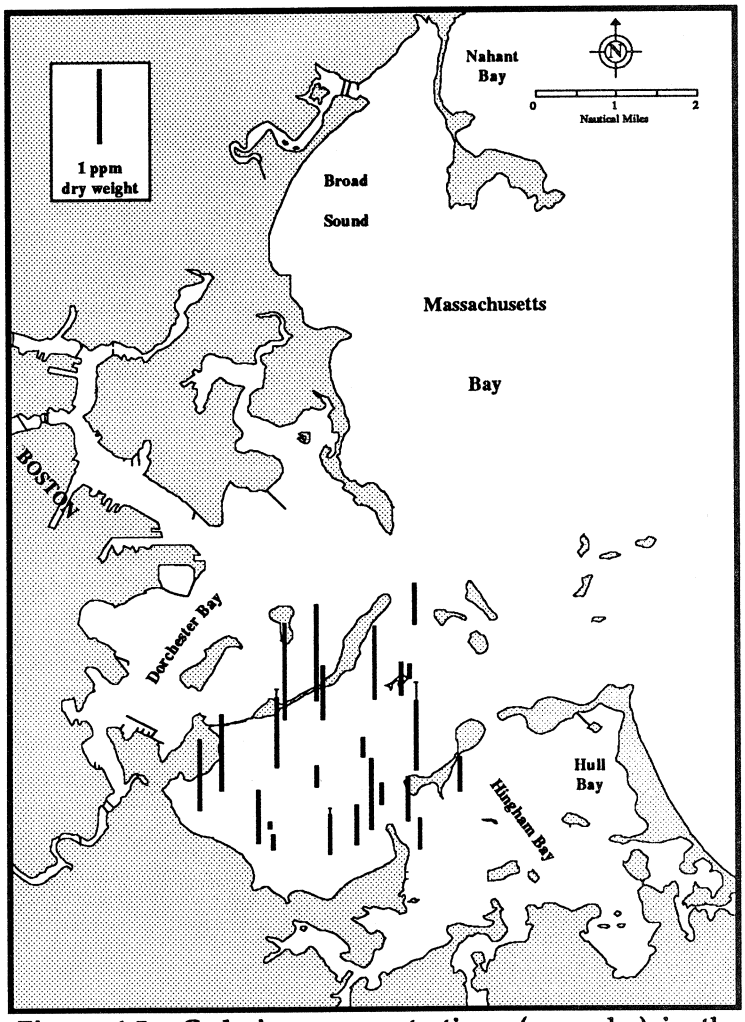
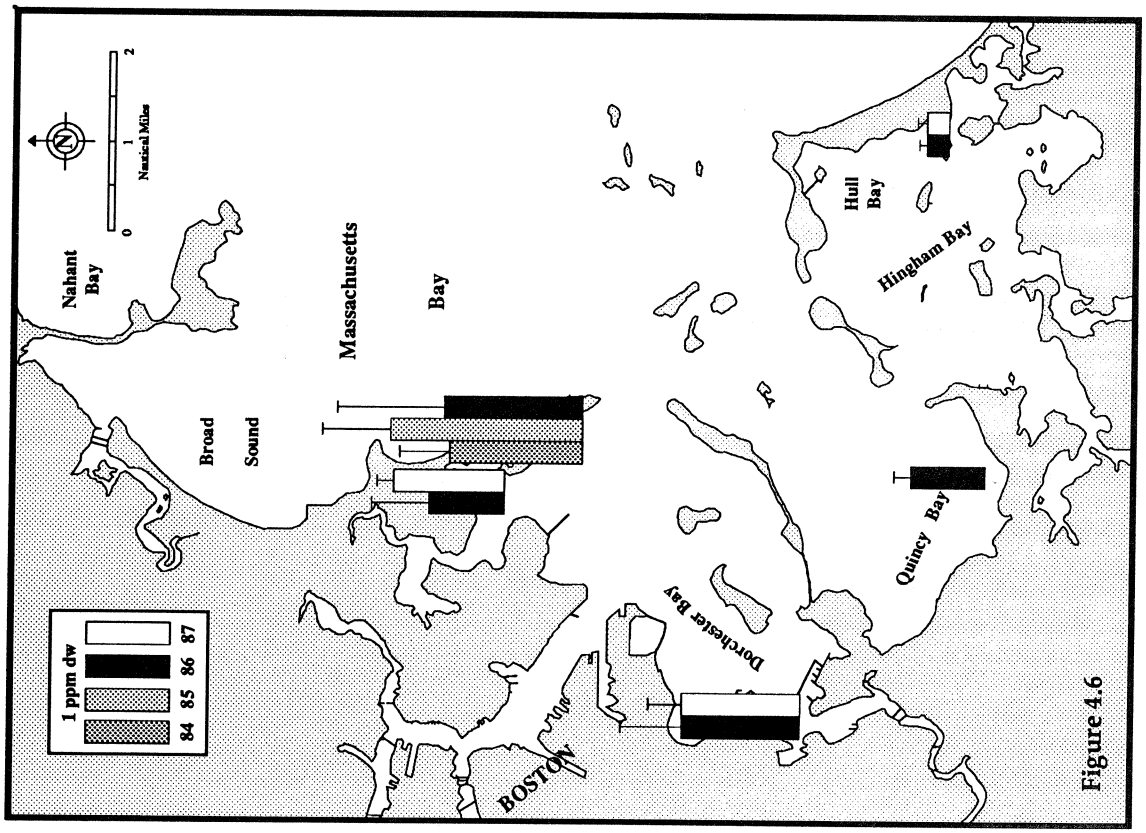


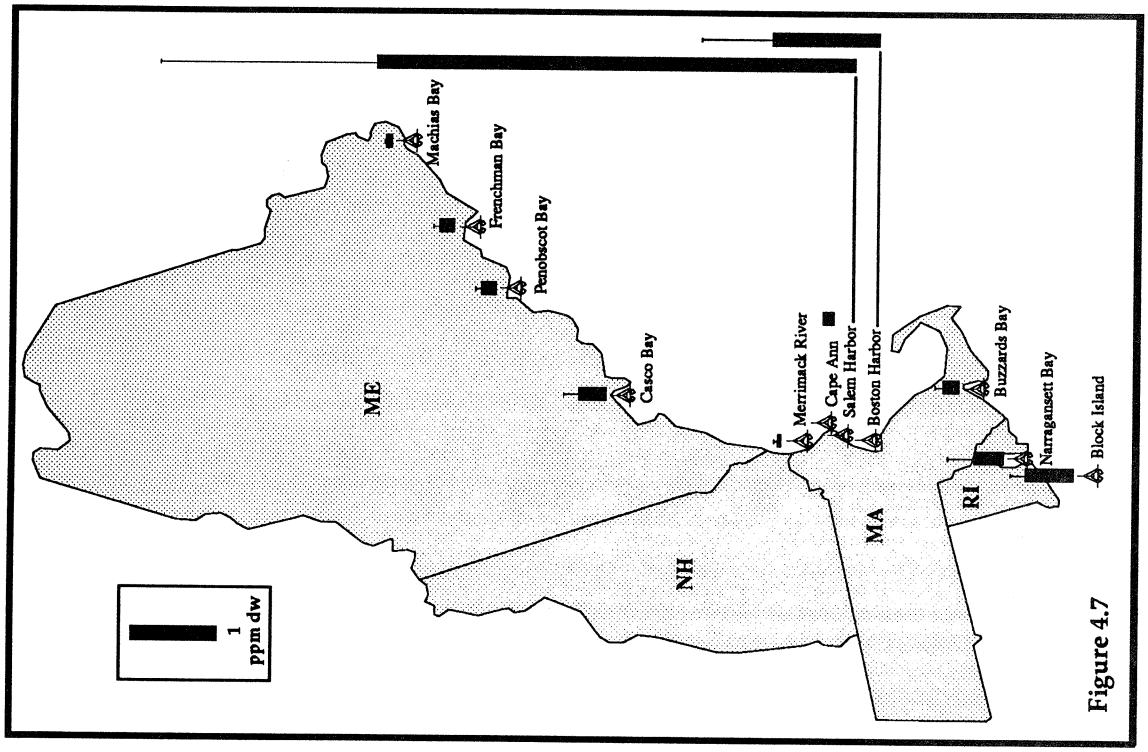
Figure 4.5. Cadmium concentrations (ppm dw) in the surficial sediments of Quincy Bay and environs, based on 1987 grab sample data from US EPA, 1988 (bars represent one standard deviation).

the Dorchester Bay area sediments had a mean concentration of 1.43±0.52 ppm, while the Winthrop Bay area sediments had a mean concentration of 1.61±0.85 ppm. Statistical analysis of the log transformed data indicated no significant difference between the two subdivisions, but they were both significantly different from the southeast harbor division at p=0.05.

On a broader scale, between 1984 and 1987, the NOAA NS&T Program analyzed surficial sediment samples from 23 sites from 11 areas, along the outer New England coast. Figure 4.7, which displays the means and standard deviations for the 11 coastal areas, clearly shows that the mean concentration of cadmium at the NS&T Program sites in Boston Harbor was higher than the means for all other areas sampled in New England, except Salem Harbor. It should be noted that the Salem Harbor value was based on only one site and may not be representative of Salem Harbor in general. The Boston Harbor value was based on five sites including one (Worlds End) whose surficial sediments had a relatively low mean cadmium concentration (0.27 ppm) and three sites that had mean cadmium concentrations greater than 1.00 ppm (northwestern and southwestern Deer Island and Dorchester Bay). Statistical analysis of the log transformed data indicated that Boston Harbor was significantly different (p=0.05) from all the other areas of New England sampled except Salem Harbor and Block Island. A possible reason for the lack of a significant difference between Boston Harbor, with a mean cadmium concentration of 1.25±0.83 ppm and Block Island, with a mean cadmium concentration of 0.56±0.17 ppm, was the small sample size (three) for Block Island.

When the mean cadmium concentrations in the surficial sediments of the individual New England NS&T Program sites were compared, four of the five sites with the highest mean cadmium concentrations were located in Boston Harbor (Table 4.3). In an attempt to determine a value for background cadmium levels, the overall mean was calculated for the five NS&T Program sites with the lowest cadmium concentrations in their surficial sediments (Table 4.3). This mean was 0.092±0.042 ppm. The overall mean cadmium concentration in the surficial sediments of Boston Harbor, based on the NS&T Program data, was more than an order of magnitude greater than this reference mean. The four Boston Harbor sites with the highest cadmium concentrations all had means an order of magnitude





Figures 4.6 & 4.7. Cadmium concentrations (ppm dw) in the surficial sediments of Boston Harbor by site and year (Fig. 4.6), and the 11 areas sampled along the outer New England Coast for 1984- 1987, based on NOAA's NS&T Program data (NOAA, unpublished) (bars represent one standard deviation).

or higher than this reference mean. The Boston Harbor site with the lowest mean cadmium concentration (Worlds End) was three times higher than the reference mean.

Table 4.3. The five NOAA NS&T Program sites from the outer New England coast with the lowest and highest mean cadmium concentrations (ppm) based on data from 1984 through 1987.

Site	Mean	Standard Deviation	Count
MERRIMAC RIVER	0.041	0.039	5
MACHIAS BAY, MAINE	0.069	0.017	7
GOOSEBURY NECK, BUZZARDS BAY	0.107	0.024	6
PENOBSCOT BAY, MAINE	0.124	0.032	6
STRAITSMOUTH ISLAND, CAPE ANN	0.133	0.006	3
QUINCY BAY	0.90	0.20	3
NORTHWESTERN DEER ISLAND	1.12	0.51	6
DORCHESTER BAY	1.43	0.52	6
SOUTHWESTERN DEER ISLAND	1.91	0.90	10
SALEM HARBOR	5.62	2.53	9

Temporal Trends

Figure 4.8 compares the yearly mean cadmium concentrations in the surficial sediments of Boston Harbor, based on all the available data sets. There is no overall temporal trend apparent from Figure 4.8 and the yearly fluctuations were more likely due to differences in sites sampled than any overall change in cadmium concentrations. The high mean for 1984 was due to the inclusion of three of the four highest cadmium values reported (35, 29.6, and 18.7 ppm) for the 18-year period covered by this report and were all from the same site in the inner harbor. The mean for 1984 excluding these three samples was 0.99 ppm.

Data was available from the USACOE on dredging studies for most of the years from 1975 through 1988. When the yearly mean cadmium concentrations in the surficial sediments based on this data were calculated and the log transformed data compared, there was no significant difference between any of the years despite means ranging from 1.51±1.47 ppm (1987) to 12.22±15.35 ppm (1984) at $p=0.05$. One factor contributing to the lack of any statistically significant difference was the variation in the number of sites sampled each year, from 1 in 1975 and 1988 to 59 in 1986 (Table 4.4). In addition to the variability in the number of sites sampled each year, the sites themselves varied from year to year. Therefore, while the data sets would be expected to be internally consistent concerning methodology, any conclusions concerning temporal trends based on the data must be viewed with extreme caution.

The only other available data that spanned more than 2 years was that from NOAA's NS&T Program Benthic Surveillance (1984-86) and Mussel Watch (1986-87) projects. The yearly mean cadmium concentrations in the surficial sediments of Boston Harbor based on this data ranged from a high of 2.32±0.82 ppm in 1985 to a low of 1.01±0.60 ppm in 1987. The yearly means for 1984 and 1986 were 1.61±0.60 ppm and 1.04±0.80 ppm, respectively. There was no indication of any temporal trends in cadmium contamination. The difference in the yearly mean cadmium concentrations can be explained by the difference in the sites sampled each year (Figure 4.6).

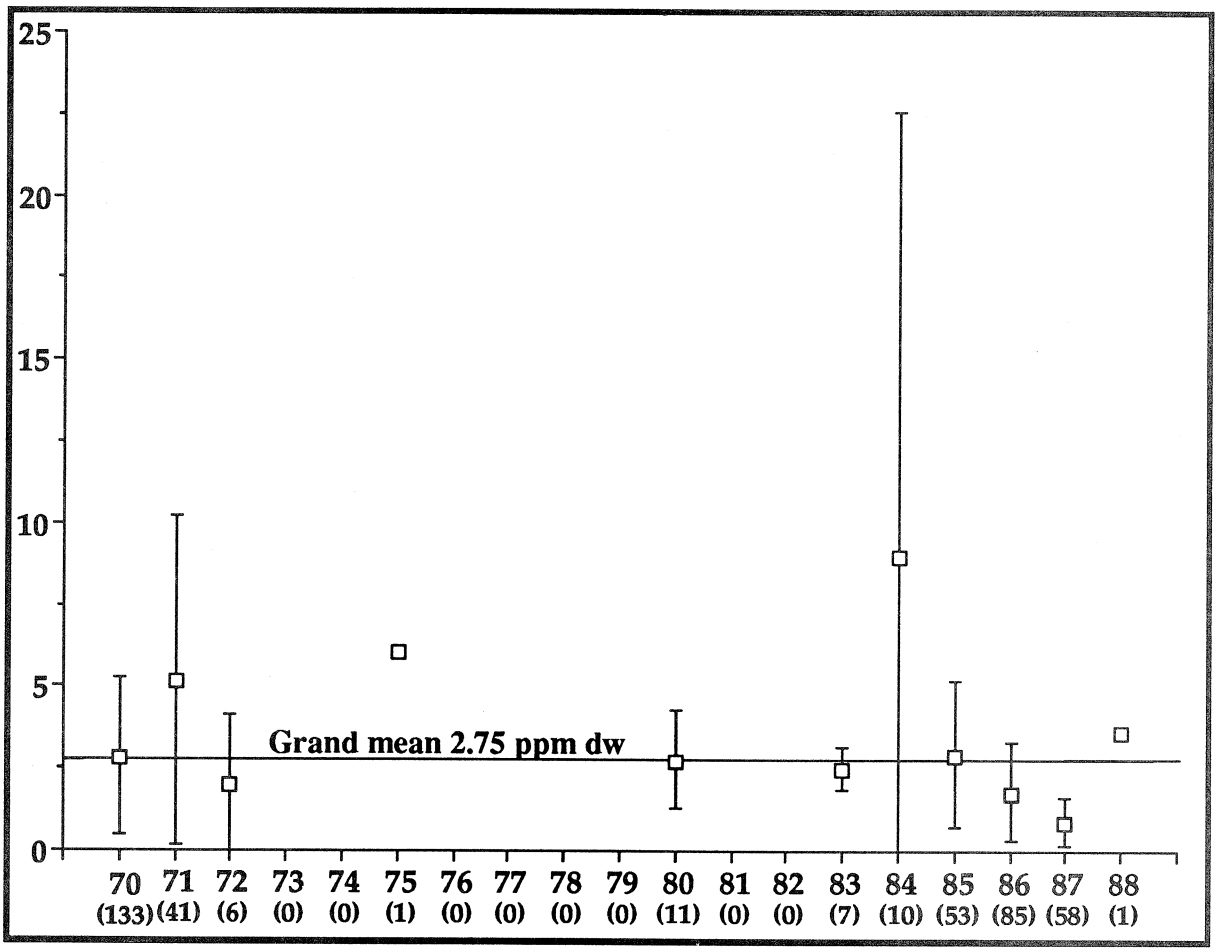


Figure 4.8. Yearly mean cadmium concentrations (ppm dw) in the surficial sediments of Boston Harbor, based on White (1972), Gilbert *et al.* (1972), Isaac & Delaney (1975), USACOE (1972-1988, 1981, 1988), MA DEQE (1986, 1987), U.S. EPA (1988), and NOAA (unpublished). The bars represent one standard deviation, and the numbers in parentheses are the number of samples analyzed each year.

Table 4.4. Yearly mean cadmium concentrations (ppm) in Boston Harbor surficial sediments based on dredging study data from the USACOE.

Year	Mean	Standard Deviation	Count
1975	6.10	N/A	1
1980	2.77	1.51	11
1983	2.55	0.65	7
1984	12.22	15.35	7
1985	3.40	2.38	30
1986	1.88	1.62	59
1987	1.51	1.47	9
1988	3.68	N/A	1

Biota

Since 1976 over 250 tissue samples from a variety of organisms in Boston Harbor have been analyzed for cadmium content. Cadmium concentrations ranged from a low of 0.001 ppm in the muscle of a winter flounder (*P. americanus*) to a high of 39.02 ppm in the liver of a winter flounder. When this extraordinarily high value for cadmium in flounder liver (the second highest cadmium concentration in flounder liver was 1.330 ppm) was excluded from the calculations, the overall mean cadmium concentration in winter flounder liver was 0.392±0.365 ppm. The highest cadmium concentration in any tissue became 5.92 ppm in the hepatopancreas of a lobster (*H. americanus*). Table 4.5 gives the statistics on cadmium contamination of biota by organism and tissue. The data in Table 4.5 suggest that cadmium tends to accumulate more in the liver or liver-like tissue than in muscle tissue. It should be noted that the vast majority of the cadmium levels in muscle were below the detection limits.

Table 4.5. Harborwide means, standard deviations, medians, ranges, and sample sizes (count) for cadmium concentrations (ppm) in biota by organism and tissues based on all the available data sets (* transplants).

		Mean	Standard Deviation	Median	Range	Count
P. americanus						
	liver	1.465	6.448	0.258	0.028-39.02	36
	muscle	0.010	0.017	0.001	0.001-0.056	28
H. americanus						
	hepatopancreas	2.819	1.446	2.402	1.380-6.630	8
	muscle	0.027	0.036	0.016	0.003-0.232	48
M. arenaria						
	soft parts	0.326	0.023	0.310	0.103-0.740	36
M. edulis						
	soft parts	1.629	0.743	1.430	0.620-4.550	86
*C. virginica**						
	soft parts	0.361	0.092	0.348	0.267-0.479	4

Geographic Trends

There were no clear geographic trends in the cadmium content of biota within Boston Harbor based on an overview of all the biota data broken down by division (Table 4.6). The mussel data suggested that the inner harbor biota contained higher levels of cadmium than did the biota from the northwest and central harbors. The flounder liver data suggested the northwest harbor biota contained more cadmium than the inner and central harbor biota, even when the 39.02 ppm was excluded from the calculations reducing the northwest harbor mean to 0.450 ppm. The mussel data also suggested that there was little, if any, difference in cadmium content of the biota among the southeast harbor and the northwest and central harbor divisions. Little could be concluded from the winter flounder and lobster muscle data because so many of the values were below the detection limits. Caution is needed in comparing data from different species. Mussels are sedentary and can be assumed to represent cadmium levels in the area where they are collected. Lobster and flounder, however, are motile organisms and therefore may not be representative of environmental cadmium levels in the area of collection.

In 1976 the U. S. EPA sampled mussels and other bivalves from 107 sites nationwide and analyzed the samples for a variety of metals and organic analytes, including cadmium (Goldberg *et al.*, 1978). A composite sample of *M. edulis* from a site on the northwest side of Deer Island was found to have a cadmium concentration in the soft parts of 1.7 ppm. Between Block Island and the Canadian Border, 11 other New England sites were sampled and had cadmium concentrations in the soft parts of *M. edulis* ranging from 0.9 ppm at two

sites in Maine (Bailey Island and Portland) to 2.2 ppm at Sakonnet Point, Rhode Island. Boston and Cape Ann mussels had the third highest concentration of cadmium.

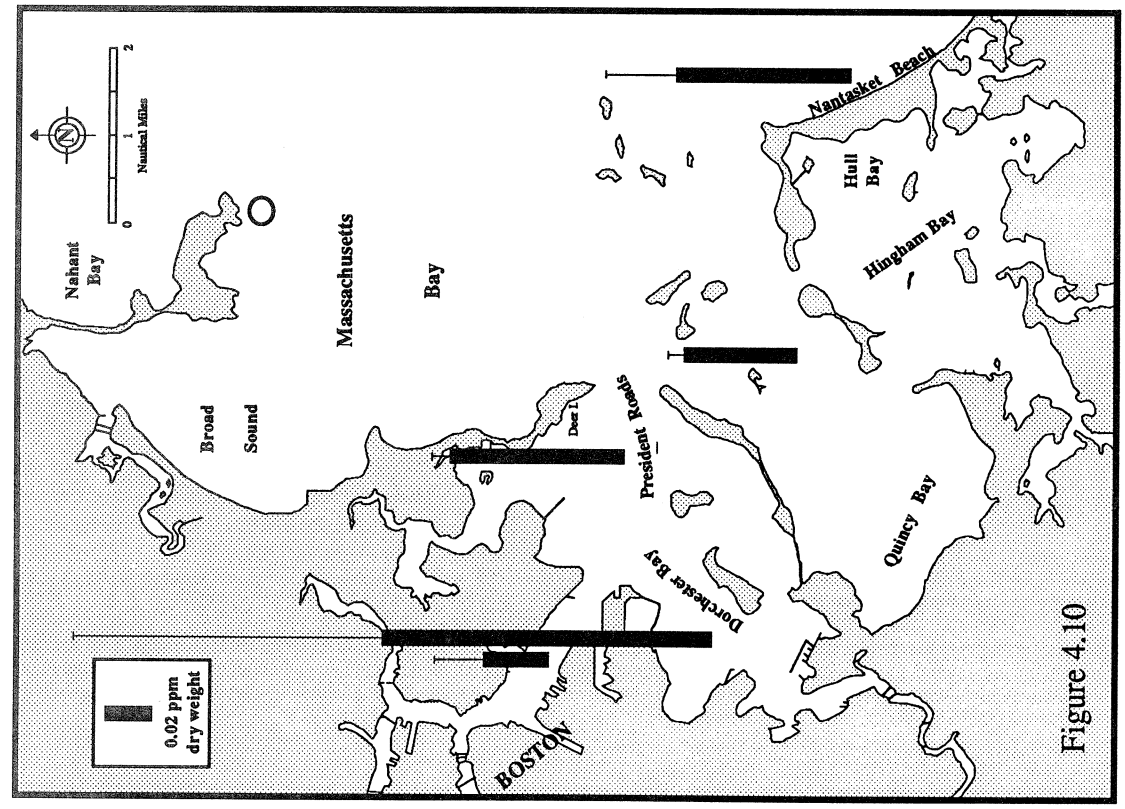
Table 4.6. Mean cadmium concentrations (ppm) of the entire harbor and the four divisions in various organisms and tissues (the number in parentheses is the sample size).

	P. americanus		*H. americanus*	*M. edulis*
	liver	**muscle**	**muscle**	**soft parts**
OVERALL	1.465 (36)	0.010 (28)	0.027 (48)	1.629 (86)
INNER HARBOR	0.249 (4)	N/A	0.028 (2)	2.246 (29)
NORTHWEST HARBOR	1.828 (28)	0.051 (3)	0.037 (28)	1.551 (19)
CENTRAL HARBOR	0.145 (4)	0.005 (25)	0.012 (18)	1.230 (29)
SOUTHEAST HARBOR	N/A	N/A	N/A	1.094 (9)

In 1979, as a part of the 301h waiver application for the Deer Island and Nut Island sewage treatment plants, winter flounder (*P. americanus*) and lobster (*H. americanus*) tissue samples from five sites in and around Boston Harbor were analyzed for levels of several analytes, including cadmium (Metcalf and Eddy, 1984). The livers of four winter flounder from each of four different sites in Boston Harbor and one site outside the Harbor (Nantasket Beach) were analyzed for cadmium levels. The values for the individual samples ranged from less than 0.055 ppm to 39.02 ppm with both specimens coming from the President Roads site. The second highest cadmium concentration was 1.093 ppm in a sample from Dorchester Bay. The mean cadmium concentrations in livers for the five sites ranged from 0.145±0.063 ppm at the Nut Island Discharge site to 9.862±19.44 ppm at the President Roads site (Figure 4.9). However, if the 39.02 ppm value is excluded from the calculations, the mean for the President Roads site becomes 0.142±0.166 ppm (the low mean cadmium concentration) and the Dorchester Bay site at 0.560±0.356 ppm becomes the high mean. When the data were log transformed and analyzed, none of the sites were significantly different at p=0.05; when the 39.02 ppm was excluded from the calculations there still was no significant difference between sites at p=0.05. When the data were looked at with regard to the harbor divisions, they suggested that, with or without the high value (39.02 ppm), the northwestern harbor had the highest level of cadmium contamination in winter flounder livers followed by the inner harbor and then the central harbor. It also suggested that the Nantasket Beach site biota had cadmium levels as high as the inner harbor biota (Figure 4.9). However, statistical analysis of the log transformed data found no significant difference between any of the harbor divisions nor between any of the divisions and the Nantasket Bay site. Unfortunately only five edible tissue samples (three samples from President Roads and two samples from Nantasket Beach) were analyzed for cadmium. All samples had cadmium levels below the detection limit (0.01 ppm).

Two lobsters each were collected from the same five sites and claw and tail muscle tissue was analyzed for levels of cadmium content. Cadmium concentrations in the individual specimens ranged from less than 0.026 to 0.232 ppm. The means for the five sites ranged from lows of 0.028 ppm, at the Inner Harbor site, to a high of 0.140 ppm at the Dorchester Bay site. The President Roads and Nantasket Beach sites had means of 0.074 ppm and the Nut Island Discharge site had a mean of 0.047 ppm (Figure 4.10). None of the sites were significantly different based on analysis of the log transformed data (p=0.05). As with the winter flounder liver data, when the lobster muscle data was grouped by division, the northwestern harbor had the highest mean cadmium concentration (0.107 ppm). Statistical analysis of the log transformed data indicated no significant difference between any of the divisions nor between any of the divisions and the Nantasket Beach site at p=0.05.

In 1985 and 1986, lobster (*H. americanus*) and soft-shelled clams (*M. arenaria*) were collected from Boston and Salem Harbors and analyzed for various analytes, including cadmium, as part of a study of contaminants in marine resources (Wallace *et al.*, 1988). The mean cadmium concentration in the combined claw and muscle tissue of 24 lobsters collected from around Deer Island was 0.025±0.017 ppm with a range of from 0.010 to 0.081 ppm.



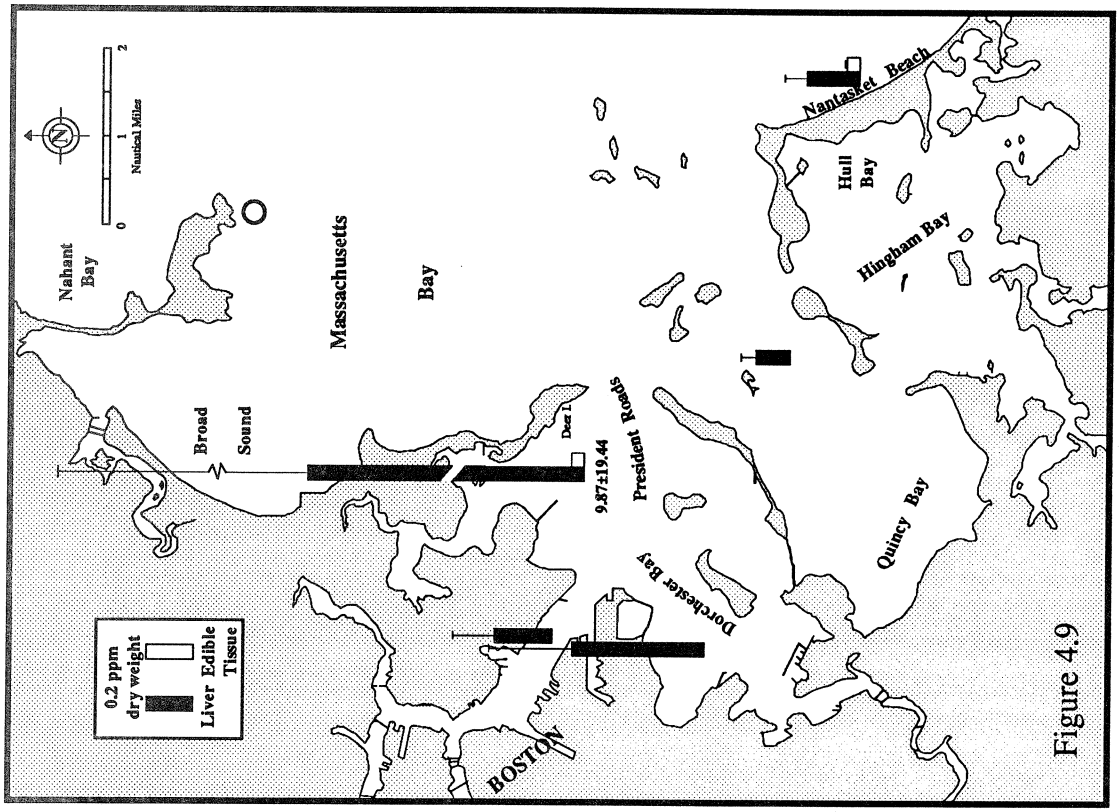
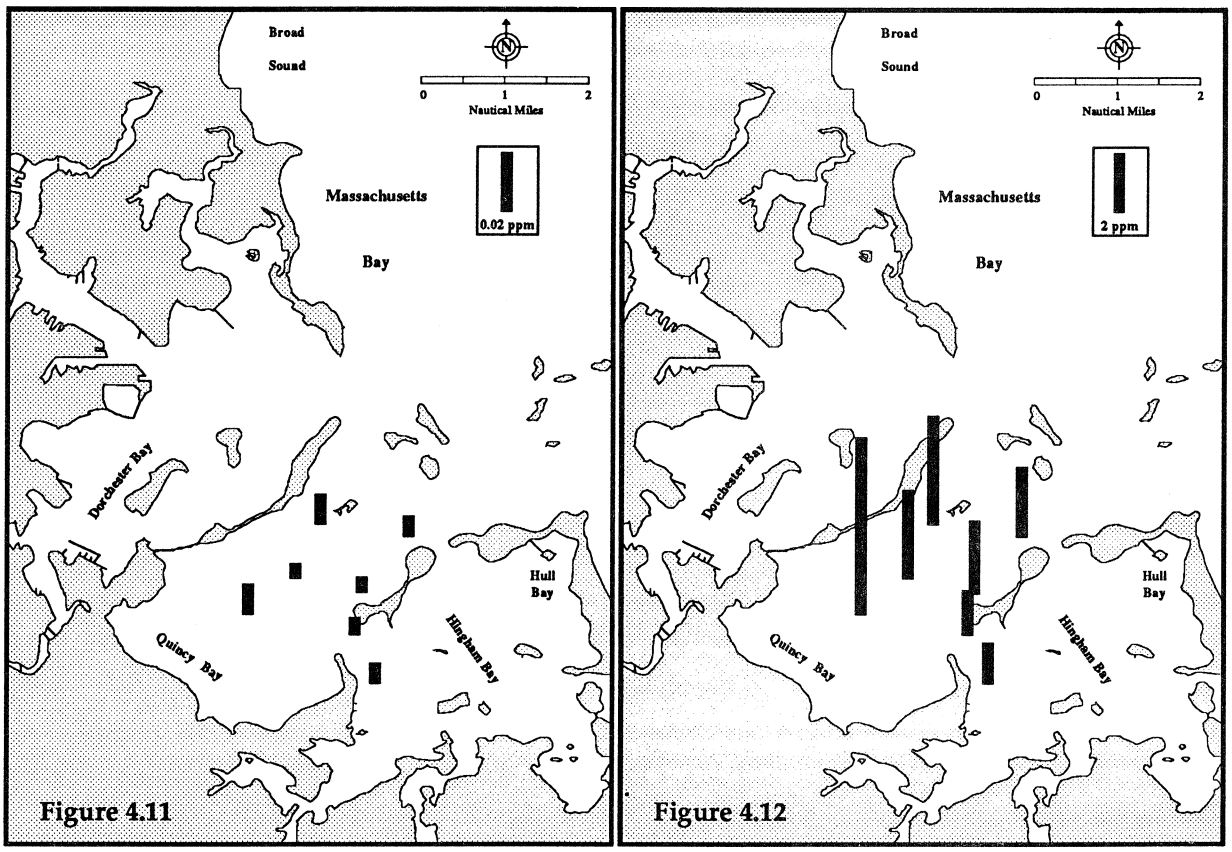


Figure 4.9 & 4.10. Mean cadmium concentrations (ppm dw) in the liver and edible tissue of *P. americanus* (Fig. 4.9) and muscle tissue of *H. americanus* (Fig. 4.10) from Boston Harbor, based on 1979 data from Metcalf & Eddy, 1984 (bars represent one standard deviation). Note the difference in scale between the two figures.

Lobsters were collected from two sites in Salem Harbor, the treatment plant outfall and Willows Pier. The mean cadmium concentrations in combined claw and tail muscle tissue based on the analyses of 25 lobsters per site were 0.026±0.019 and 0.020±0.013 ppm, respectively. Statistical analysis of the log transformed data indicated no significant difference among the three sites at p=0.05. The mean cadmium concentration for 33 soft-shelled clams from Wollaston Beach in Quincy Bay was 0.336±0.135 ppm with a range of 0.103 to 0.740 ppm.

An intensive study of Quincy Bay was conducted in 1987 that included the analysis for cadmium levels in the tissues of native winter flounder (*P. americanus*), lobsters (*H. americanus*), soft-shelled clams (*M. arenaria*), and transplanted oysters (*C. virginica*) (U.S. EPA, 1988). The muscle tissue of from five to seven winter flounder from each of four different trawl transects was analyzed for cadmium levels. The cadmium concentration in all but one of the samples was below the limit of detection that ranged, for the individual samples, from 0.003 to 0.024 ppm. The one sample that was above detection had a cadmium concentration of 0.044 ppm.

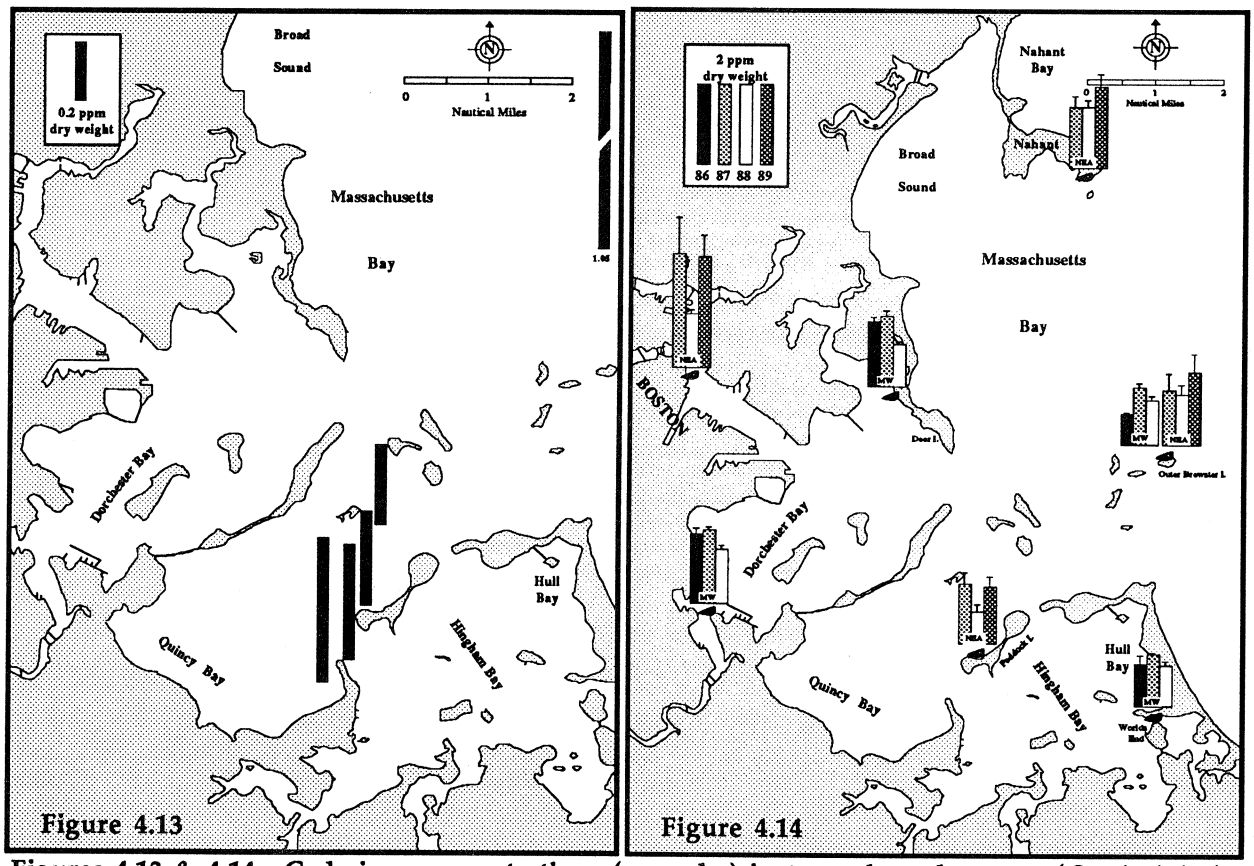
Both the tail muscle and the hepatopancreas of lobsters from seven sites were analyzed for levels of cadmium content. Two replicate samples from the tail muscles of a total of 16 lobsters; 1 to 3 from each of the seven sites were analyzed. The cadmium concentrations in the individual samples ranged from 0.003 to 0.029 ppm. The mean tail muscle concentrations for the seven sites ranged from 0.005 ppm to 0.011±0.012 ppm (Figure 4.11). There was no significant difference in tail muscle cadmium levels among sites based on statistical analysis of the log transformed data (p=0.05). Two replicate samples of the hepatopancreas of 8 of the 16 lobsters were also analyzed for cadmium. Cadmium concentrations for the eight hepatopancreases ranged from less than 1.380 to 5.915 ppm (Figure 4.12).



Figures 4.11 & 4.12. Cadmium concentrations (ppm dw) in lobster (*H. americanus*) tail muscle (Fig. 4.11) and hepatopancreas (Fig. 4.12) tissue sampled in 1987, based on data from US EPA, 1988. Note the 100-fold difference in scale.

Oysters (*C. virginica*) were collected from a commercial bed located in Cotuit Bay (Cotuit, Massachusetts) and deployed at four sites in Quincy Bay and one site at The Graves in Massachusetts Bay from June 5 through July 16, 1987. The cadmium concentrations in the oysters at the four sites ranged from 0.267 to 0.479 ppm. The oysters from The Graves had 1.050 ppm cadmium, while those from the source bed in Cotuit Bay had a cadmium concentration of 0.702 ppm (Figure 4.13). Two samples of the soft-shelled clam from around Moon Island, Quincy Bay also were analyzed for cadmium and had concentrations of 0.120 and 0.185 ppm.

Since 1986, NOAA's Mussel Watch Project, a part of the NS&T Program, has sampled mussels (*M. edulis*) on an annual basis from four sites in and around Boston Harbor. Three whole-body composite samples from each site were analyzed for a variety of analytes, including cadmium. The overall mean concentration of cadmium in the mussels for the three sites in Boston Harbor from 1986 through 1988 was 1.393±0.341 ppm with a range of from 0.760 to 1.900 ppm. The means for the individual sites were 1.094±0.182 ppm in Hingham Bay off Worlds End, 1.633±0.245 ppm northwest of Deer Island, and 1.451±0.339 ppm in southwestern Dorchester Bay. Mussels from the site outside the Harbor, Outer Brewster Island, had a mean cadmium concentration of 1.086±0.289 ppm (Figure 4.14). Statistical analysis of the log transformed data for the four sites indicated that only the Dorchester Bay site was significantly different from the Hingham Bay and Brewster Island sites (p=0.05).



Figures 4.13 & 4.14. Cadmium concentrations (ppm dw) in transplanted oysters (*C. virginica*) for 1987 (Fig. 4.13), based on data from U.S. EPA, 1988 and in native mussels for 1986-1989 (Fig. 4.14), based on data from NOAA's (MW) and NEA's (NEA) mussel watch projects (NOAA, unpublished; Robinson *et al.*, 1990) (bars represent one standard deviation). Note the difference in scale.

Since 1987, the NEA has conducted their own Mussel Watch Program, sampling mussels from two sites within Boston Harbor and two sites in Massachusetts Bay (Robinson *et al.*, 1990). They also sample the same site on Outer Brewster Island that NOAA's Mussel Watch samples. The mean cadmium concentration in Boston Harbor, based on data from the two sites for the 3 years from 1987 through 1989, was 1.738±0.855 ppm with a range of from 0.620 to 4.550 ppm. The means for the two sites were 1.230±0.379 ppm at the Peddocks Island site and 2.246±0.900 ppm at the Central Wharf, Boston Harbor site. The two sites from Massachusetts Bay had means of 1.688±0.355 ppm at the Pumphouse Beach, Nahant site and 1.466±0.439 ppm at the Outer Brewster Island site. When the data for the four sites were log transformed and the sites statistically compared, the Central Wharf site was found to be significantly different from the Peddocks and Outer Brewster islands sites (p=0.05). The Peddocks Island site was also significantly different from the Pumphouse Beach site (p=0.05). Figure 4.14 plots the NEA data alongside the NOAA Mussel Watch data.

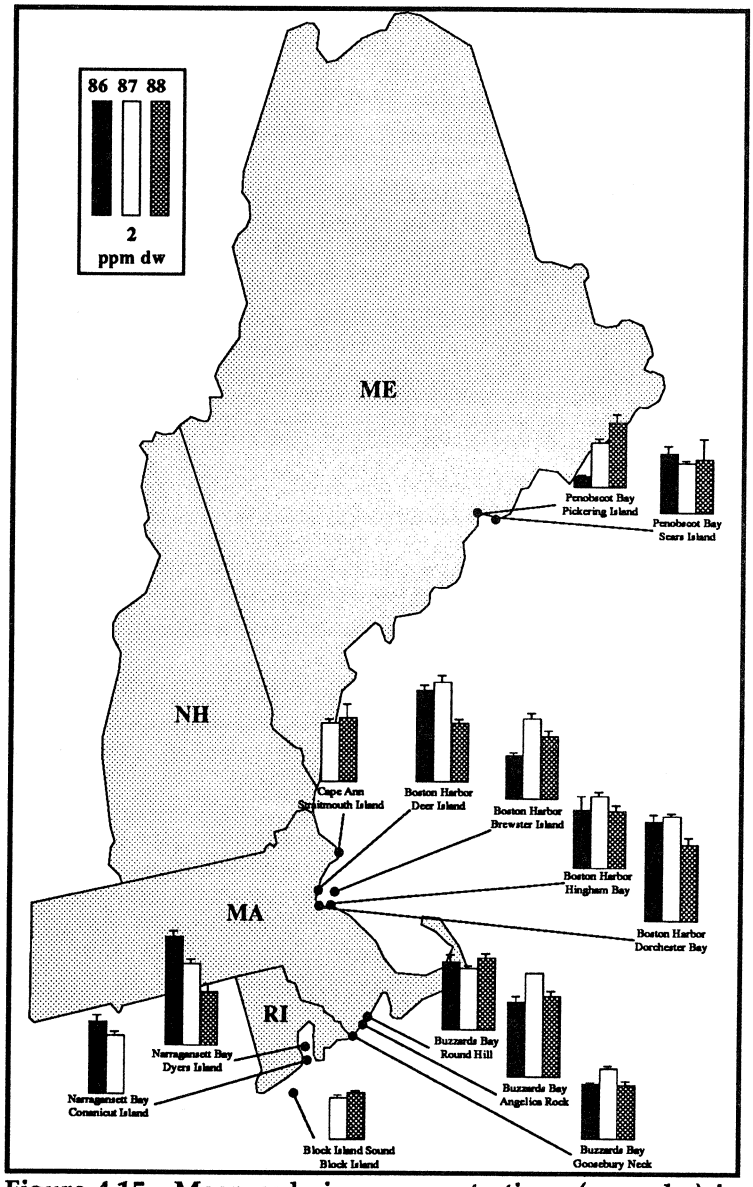


Figure 4.15. Mean cadmium concentrations (ppm dw) in the soft-parts of *M. edulis* for 1986-88 from the outer New England NS&T Program Mussel Watch sites (NOAA, unpublished) (bars represent one standard deviation).

On a broader scale, when the Boston Harbor sites were compared to the other outer New England coast Mussel Watch sites (Table 4.7 and Figure 4.15), the Deer Island and Dorchester Bay sites were found to be significantly different from the Pickering Island site in Penobscot Bay (p=0.05). The only significant difference between any of the 13 New England Mussel Watch sites was between the Pickering Island site, which had the lowest mean cadmium concentration in mussels, and the five sites with the highest mean cadmium concentrations (Table 4.7) at p=0.05. From this data it appears that cadmium levels in mussels vary little throughout New England. The range of means are just over a factor of 2. When a reference value is calculated, based on the five sites with the lowest mean cadmium concentrations in mussels, a value of 0.911±0.279 ppm is obtained. The Boston Harbor sites have mean cadmium values of from just over 1 to less than 2 times higher than this reference value. On a national scale, the Mussel Watch sites where *M. edulis* was sampled had

mean cadmium concentrations ranging from 0.707 to 10.833 ppm with an overall mean for all the sites of 2.862±2.006 ppm; 65 percent of the sites had means greater than 2.00 ppm while only 15 percent had concentrations less than 1.00 ppm. When the sites where *M. californianus* was sampled were included in the calculations, the overall mean became 3.126±2.146 ppm, with 69 percent of the sites having means greater than 2.00 ppm and only 12 percent having means less than 1.00 ppm. Based on this, data Boston Harbor mussels appeared to be only moderately contaminated with cadmium since all the Harbor sites had means between 1.00 and 2.00 ppm.

Table 4.7. The mean cadmium concentrations (ppm) in *M. edulis* at the 13 outer New England coast NS&T Program Mussel Watch sites. The outlined means are for Boston Harbor sites.

Site	Mean	Standard Deviation	Count
DORCHESTER BAY, BOSTON HARBOR	1.633	0.245	9
ANGELICA ROCK, BUZZARDS BAY	1.482	0.218	11
DEER ISLAND, BOSTON HARBOR	1.451	0.339	9
DYERS ISLAND, NARRAGANSETT BAY	1.422	0.429	9
ROUND HILL, BUZZARDS BAY	1.178	0.109	9
CONANICUT ISLAND NARRAGANSETT BAY	1.150	0.152	6
HINGHAM BAY, BOSTON HARBOR	1.094	0.182	9
OUTER BREWSTER ISLAND	1.086	0.289	9
CAPE ANN, STRAITSMOUTH ISLAND	1.072	0.168	6
GOOSEBURY NECK, BUZZARDS BAY	1.064	0.151	8
SEARS ISLAND, PENOBSCOT BAY	0.956	0.203	9
BLOCK ISLAND, RHODE ISLAND	0.785	0.059	6
PICKERING ISLAND, PENOBSCOT BAY	0.707	0.417	9

Since 1984, NOAA's Benthic Surveillance Project, a part of the NS&T Program, has sampled winter flounder (*P. americanus*) from an area just west of Deer Island on an annual basis. The mean cadmium concentration in the liver of the fish sampled in 1984 and 1985 was 0.475±0.413 ppm with a range of 0.056 to 1.33 ppm. The mean concentration of cadmium in flounder livers for all the New England Benthic Surveillance sites, including Boston Harbor, ranged from a low of 0.223±0.214 ppm at the Salem Harbor site to a high of 1.136±0.418 ppm at the Casco Bay site (Figure 4.16). Boston Harbor winter flounder had the second lowest mean cadmium concentration in their livers. Statistical analysis of the log transformed data indicated that the Boston Harbor site was significantly different only from the Casco Bay site. The Salem Harbor site was significantly different from all but the Boston Harbor site at $p=0.05$. No comparison could be made between Boston Harbor and the three northern-Maine sites; because a different species, longhorn sculpin (*M. octodecemspinosus*), was sampled at these sites. The Benthic Surveillance Project sampled winter flounder at four other sites during the same period: two in Long Island Sound and one each in Raritan and Great bays in New Jersey. Both of the Long Island Sound sites had mean cadmium concentrations in winter flounder liver greater than 1.00 ppm. Only the Great Bay site had a mean cadmium concentration (0.174±0.067) lower than Boston Harbor.

Temporal Trends

No temporal trends in the cadmium levels of Boston Harbor biota could be determined based on the available data. The reason for this being that the only internally consistent data sets sampling the same organism from the same locations over a number of years were the NS&T Program's Benthic Surveillance and Mussel Watch projects and the NEA Mussel Watch program. Data for these projects were only available for 2, 3, and 3 years, respectively. Between 1984 and 1985, there was more than a fivefold increase in the level of cadmium in winter flounder livers (0.145±0.090 to 0.803±0.333 ppm) (Figure 4.16) which was significantly different at $p=0.01$. However, whether this indicates a trend in levels of

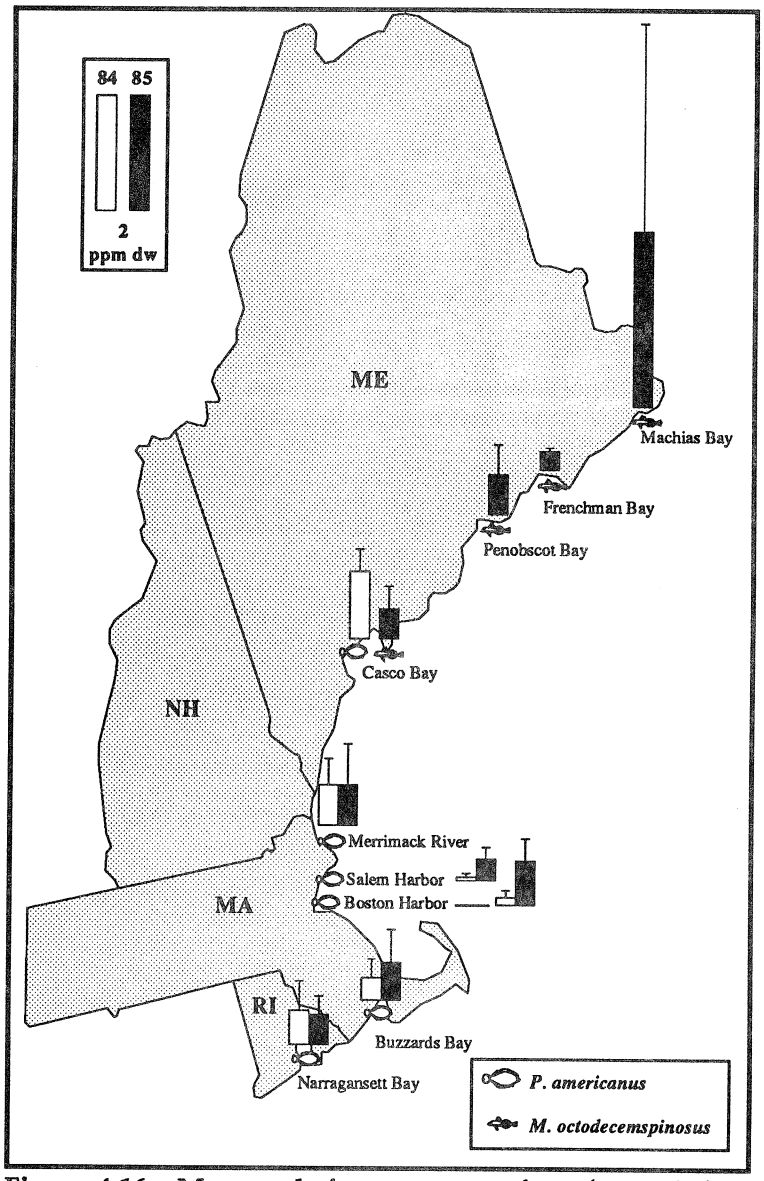


Figure 4.16. Mean cadmium concentrations (ppm dw) in the liver tissue of *P. americanus* and *M. octodecemspinosus* for 1984 and 1985 from the outer New England NS&T Program Benthic Surveillance sites (NOAA, unpublished) (bars represent one standard deviation).

cadmium contamination in Boston Harbor biota or is just due to random sampling could not be determined based on only 2 years. Likewise, the 3 years of data for *M. edulis* from the NS&T Program Mussel Watch Project failed to indicate any trend with cadmium levels very slightly increasing between 1986 and 1987 and then decreasing in 1988 (Figure 3.15). The yearly means were 1.451±0.356, 1.611±0.271, and 1.117±0.182 ppm, respectively. The yearly means for the NEA Mussel Watch Program showed no apparent trend, decreasing from 2.13±0.93 ppm (1987) to 1.06±0.29 ppm (1988) and then increasing to 2.06±0.76 ppm (1989). In addition, when the EPA Deer Island site, that had a cadmium concentration in the soft parts of mussels of 1.7 ppm in 1976, was compared to the NS&T Program Deer Island site (which is about 0.5 miles northwest of the EPA site) with yearly means of 1.60, 1.73, and 1.02 ppm (1986, 1987, and 1988, respectively) there was no change in cadmium concentrations in the 11 years between 1976 and 1987 although there appeared to be a decrease in cadmium levels between 1987 and 1988.

SUMMARY

Boston Harbor sediments were found to contain cadmium at levels that exceeded regional background levels by more than an order of magnitude. When the overall mean value of cadmium in Boston Harbor (2.753±3.463 ppm) was compared to the overall mean of San Francisco Bay (1.060±1.160 ppm) (Long *et al.*, 1988) it was found to be more than 2 1/2 times higher than the San Francisco Bay mean. When just the NS&T Program data for the two ports were compared, the Boston Harbor mean, 1.249±0.833 ppm, was more than 3 1/2 half times higher than the San Francisco Bay mean, 0.350±0.203 ppm (Long *et al.*, 1988) (Table 4.8). The available data suggested that cadmium in Boston Harbor surficial sediments showed a trend of decreasing concentration from the inner harbor towards the southeastern

harbor and towards the mouth. No clear temporal trends were apparent concerning cadmium concentrations in the surficial sediment.

Table 4.8. Comparison of cadmium sediment statistics among Boston Harbor, NS&T Program Reference (mean of five sites with lowest cadmium levels), and San Francisco Bay in ppm. Statistics for San Francisco Bay derived from Long *et al.*, 1988.

Area	Mean	Standard Deviation	Median	Range	Count
Boston	2.753	3.463	2.000	0.050-35.06	406
NS&T Program Boston	1.249	0.833	1.130	0.150-3.080	31
NS&T Program Reference	0.120	0.049	0.113	0.043-0.258	28
San Francisco Bay	1.060	1.160	0.710	0.020-17.30	999
NS&T San Francisco Bay	0.350	0.203	0.320	0.020-1.000	40

Based on the available data, Boston Harbor biota appears to be only moderately contaminated with cadmium. Boston Harbor mussels (*M. edulis*) had some of the highest mean cadmium concentrations of all the New England NS&T Program sites sampled, but, when compared to all NS&T Program mussel sites sampled in the country, the Boston Harbor sites fall into the lower 30 percent. The winter flounder (*P. americanus*) liver data suggested that Boston Harbor had only low levels of cadmium since among the NS&T Program sites the Boston site had the second lowest mean cadmium concentration in New England and the third lowest among all the winter flounder sites. The winter flounder and lobster (*H. americanus*) muscle tissue data suggested that cadmium tends not to accumulate in muscle tissue. There were no obvious geographic or temporal trends in cadmium content of biota within Boston Harbor based on the available data because relative concentrations between different areas of the Harbor varied with the organism and tissue sampled. And, with the exception of the NS&T Program and the NEA Mussel Watch Program, none of the studies sampled the same organism from the same sites over a period of years.

LEAD

Lead is a naturally occurring element that has no known biological function. On the contrary, it is an accumulative metabolic poison that can affect the hematopoietic, vascular, nervous, renal, and reproductive systems; and it is known to be teratogenic and mutagenic (Eisler, 1988b). Lead levels in uncontaminated marine sediments have been reported to range from 8.4 to 60 ppm (GESAMP, 1985b). In a review of the literature, Long and Morgan (1990) found data suggesting that lead concentrations in sediment as low as 27 ppm had a toxic effect on sensitive organisms while bioeffects were usually observed at concentrations of 110 ppm or greater and always observed at lead concentrations greater than 300 ppm.

The analysis of lead content in biological tissue presents special problems due to the relatively low levels being measured (0.001 ppm in albacore tuna, *Thunnus alalunga*, muscle) and the likelihood of sample contamination during handling and analysis (Patterson and Settle, 1976, 1977; Burnett and Patterson, 1980; Burnett, 1980). Industrial lead is ubiquitous in the environment. Hirao and Patterson (1974) found industrial lead being deposited in a remote canyon in the High Sierras at the rate of approximately $1 kg/km^2/yr$. This ubiquitousness of lead means that when a fish is removed from the water, the slime coating of the epidermis is still capable of adsorbing lead from the atmosphere, from the exhaust fumes of the fishing vessel, from anything it comes into contact with, including human hands and laboratory bench tops before dissection. If the proper precautions are not taken during dissection, the muscle or other tissue of the specimen being analyzed can become contaminated with lead by contacting the slime layer (Patterson and Settle, 1977). Contamination is also derived from the reagents used during analysis. And, because of the relatively low levels of lead that may actually exist in the tissue being analyzed, these two sources of contamination may significantly increase the amount of lead actually measured. Burnett and Patterson (1980) reported that from 60 to 90 percent of lead levels in the whole soft parts of bivalves were derived from the stomach contents and the lead was not actually incorporated into the tissues of the organism. Because of these problems, Patterson and his colleagues, as cited above, feel that most data for lead content of biological tissues is invalid. To analyze biota for lead properly, ultra-clean capture and laboratory procedures along with increased sensitivity of analysis methodologies would have to be instituted. This problem does not exist for sediment analysis because the higher levels of lead involved are not significantly altered by handling and laboratory contamination.

Sediments

Since the late 1960s over 400 surficial sediment samples from Boston Harbor have been analyzed for lead content. Based on this data, the overall mean concentration of lead in the surficial sediments of the Harbor was 131 ppm with a standard deviation of 128 ppm and a range of from 1.6 to 1180 ppm (Table 5.1). The median lead concentration was 100 ppm. The large standard deviation and the difference between the mean and the median values are because approximately 8 percent of the samples analyzed had concentrations greater than 300 ppm. Approximately 89 percent of the samples had values between 10 and 300 ppm inclusive. The remaining 3 percent of the samples contained less than 10 ppm lead.

Geographic Trends

When the combined data set was broken down into the four harbor divisions, both the means and medians suggested that the surficial sediments of the inner harbor had the highest lead content (192 and 175 ppm). The surficial sediments of the northwest harbor had the second highest lead content (127 and 108 ppm) (Table 5.1). The sediments with the third highest lead content were in the southeast harbor (101 and 82 ppm), closely followed by those of the central harbor (83 and 70 ppm). The difference between the central and southeast harbor means was almost entirely the result of one high outlier sample of 840 ppm

from the southeast harbor. This sample was more than twice as high as the second highest value from the southeast harbor. When the 840 ppm sample was excluded from the calculations, the mean lead concentration for the southeast harbor became 89±73 ppm. When the northwest harbor was subdivided, the Dorchester Bay area sediments had a mean concentration of 166±157 ppm with a median concentration of 139 ppm, while the Winthrop bay area sediments had a mean concentration of 88±74 ppm with a median concentration of 80 ppm.

Table 5.1. Means, standard deviations, medians, ranges, and number of samples (count) for lead concentrations in surficial sediments for all of Boston Harbor and the four regions of the harbor, based on all the available data sets.

	Mean	Standard Deviation	Median	Range	Count
OVERALL	131	128	100	1.6-1180	407
INNER HARBOR	192	148	175	1.6-700	109
NORTHWEST HARBOR	127	128	108	10-1180	149
CENTRAL HARBOR	83	58	70	6.6-314	85
SOUTHEAST HARBOR	101	118	82	2.5-840	64

Around 1970, White (1972) collected and analyzed over 130 sediment samples from Boston Harbor for a variety of metals including lead. He found lead concentrations ranging from a low of 20 ppm in a sample from north of Worlds End in Hingham Bay, to a high of 700 ppm in a sample from the lower Charles River (Figure 5.1). From this figure it appears that lead concentrations were highest in the inner harbor, decreasing significantly in the northwest harbor, and showing a further slight decrease in the central and southeastern harbor divisions. Statistical analysis of the log transformed data for the four harbor divisions indicated that the inner harbor was significantly different from the other three harbor divisions. The other three harbor divisions were not significantly different from each other at p=0.05 (Table 5.2). When the northwest harbor was subdivided, the Dorchester Bay area sediments had a mean concentration of 143±67 ppm, while the Winthrop bay area sediments had a mean concentration of 104±46 ppm. Statistical analysis of the log transformed data indicated that the two subdivisions were significantly different from only the inner harbor division at p=0.05.

In 1971, the NEA collected 55 cores of Boston Harbor sediments and analyzed various sections of the cores for heavy metal content (Gilbert *et al.*, 1972). Based on 42 samples of the upper surface of the cores that were analyzed for lead, they found concentrations ranging from a low of 13 ppm from a site in southeastern Dorchester Bay, to a high of 675 ppm in a sample from the lower reaches of the Mystic River, with an overall mean concentration of 137±142 ppm. The vast majority of the sample concentrations were less than 200 ppm, with 48 percent less than 100 ppm and 38 percent between 100 and 200 ppm, inclusive. As with the White data, a graphic representation (Figure 5.2) suggests higher levels of lead contamination in the inner harbor regions. The northwestern harbor is only very slightly more contaminated than the central and southeastern harbor divisions. However, it should be noted that the fourth highest lead concentration was recorded for a site in the southeastern harbor, suggesting that lead was heterogeneously distributed throughout the harbor sediments. When the data were grouped by the four harbor divisions and the log transformed data compared statistically, the inner harbor was significantly different from the other three harbor divisions. The other three harbor divisions were not significantly different from each other at p=0.05 (Table 5.2). When the northwest harbor was subdivided, the Dorchester Bay area sediments had a mean concentration of 113±60 ppm, while the Winthrop Bay area sediments had a mean concentration of 97±44 ppm. Statistical analysis of the log transformed data indicated that the two subdivisions were not significantly different from each other or the other three harbor divisions at p=0.05.

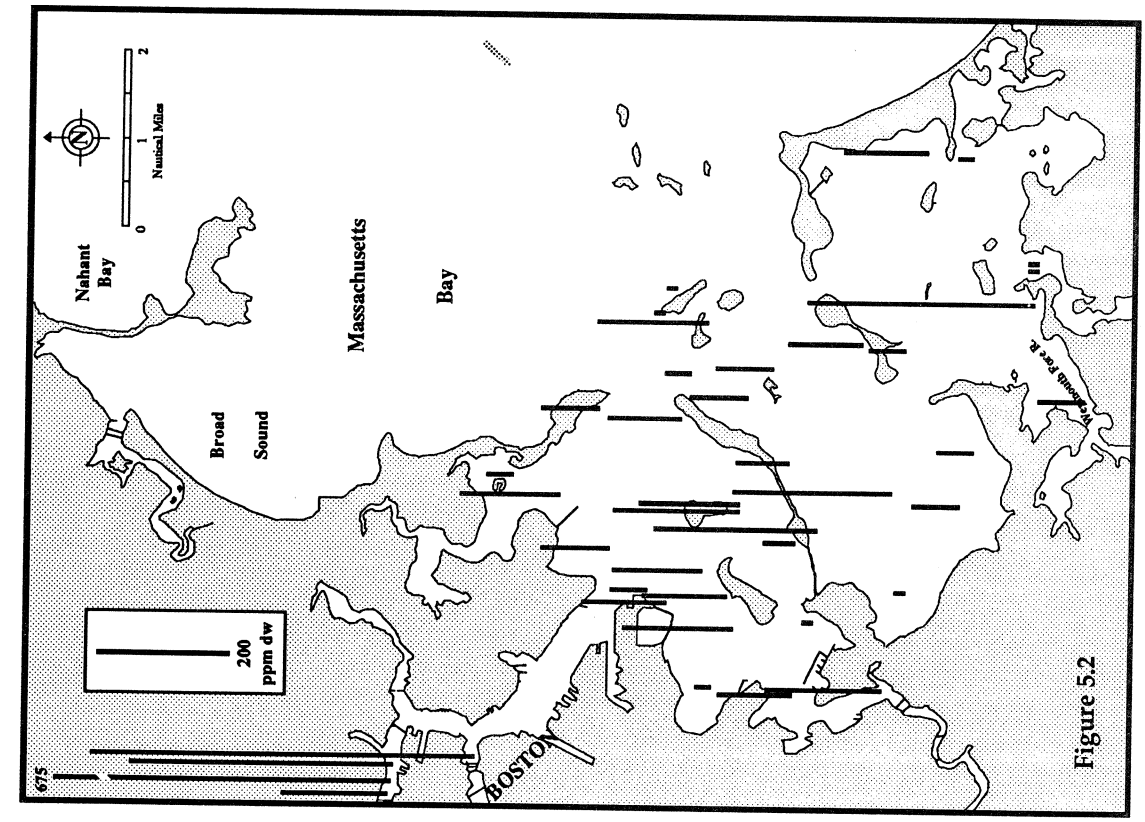


Figure 5.2

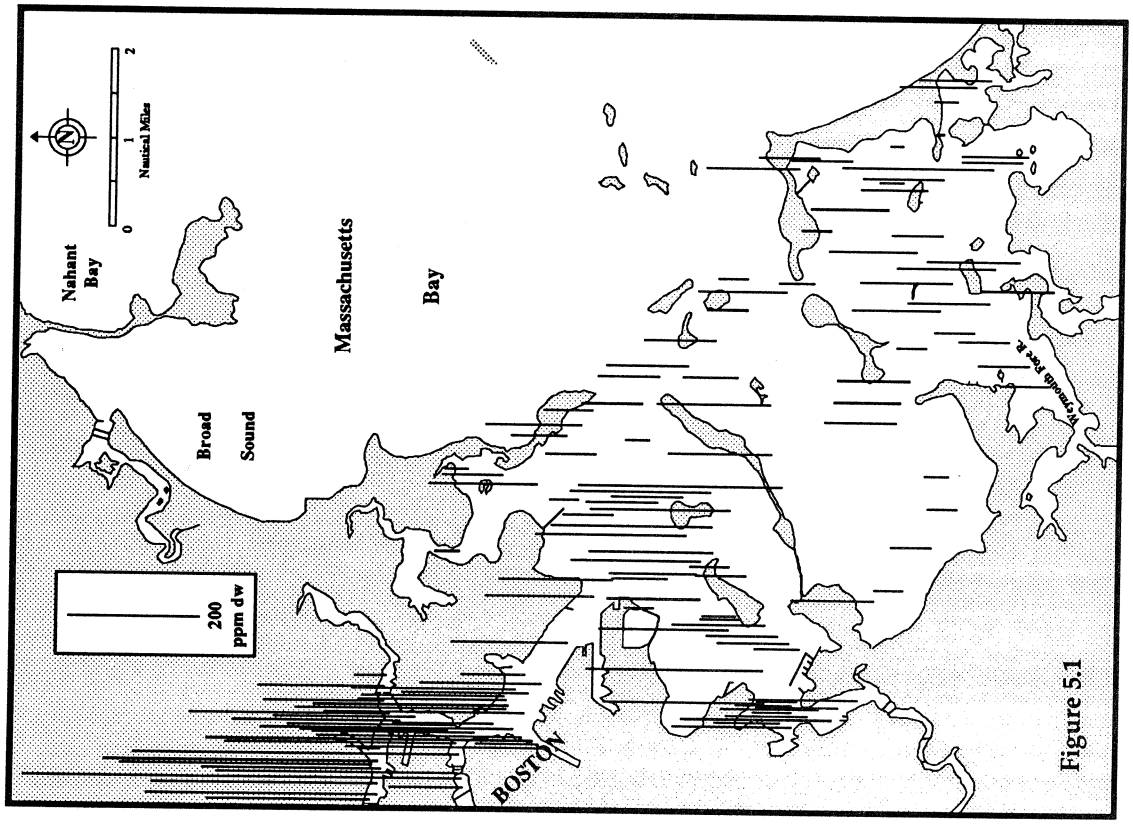


Figure 5.1

Figures 5.1 & 5.2. Lead concentrations (ppm dw) in the surficial sediments of Boston Harbor for around 1970 based on data from White, 1972 (Fig. 5.1) and for 1971 based on data from Gilbert et al., 1972 (Fig. 5.2).

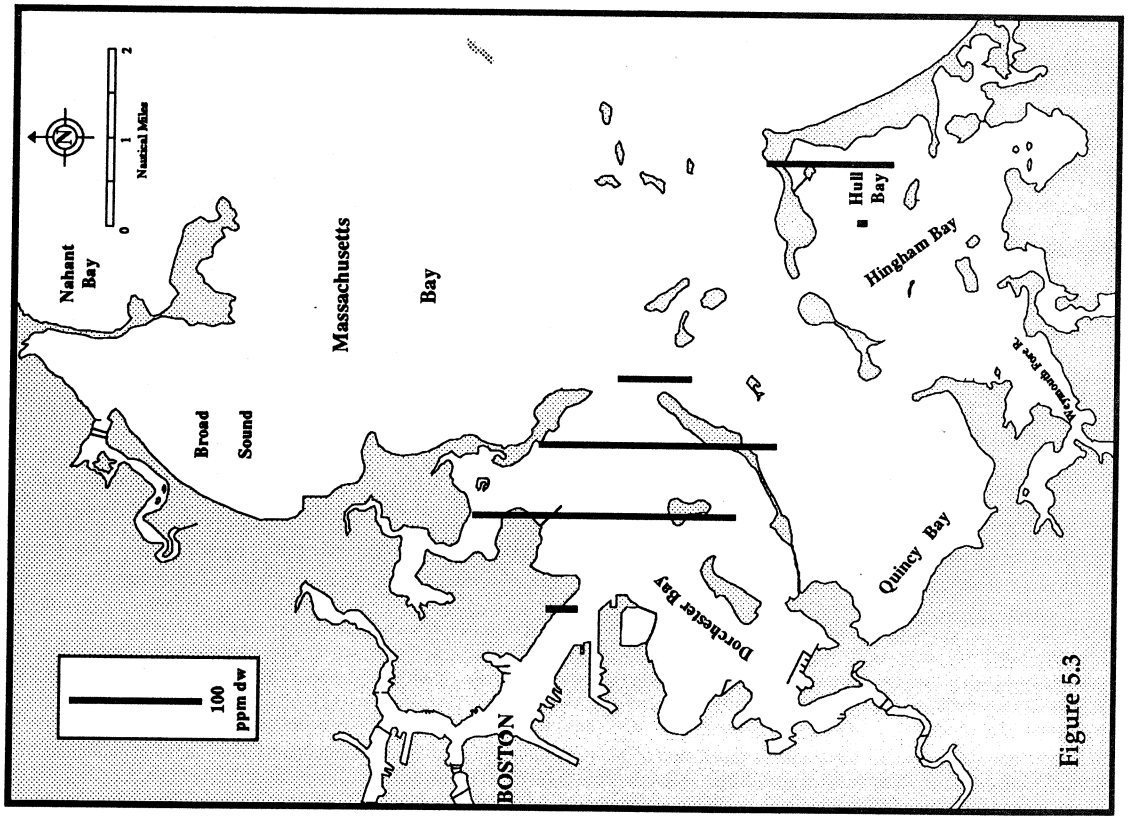
Table 5.2. Mean lead concentrations in the surficial sediments of Boston Harbor and the four divisions of the harbor, in ppm, based on the data of White (1972), Gilbert *et al.* (1972), Isaac and Delaney (1975), MA DEQE, (1986 and 1987), and NOAA's NS&T Program (unpublished). The numbers in parentheses are the number of data points used to calculate the means.

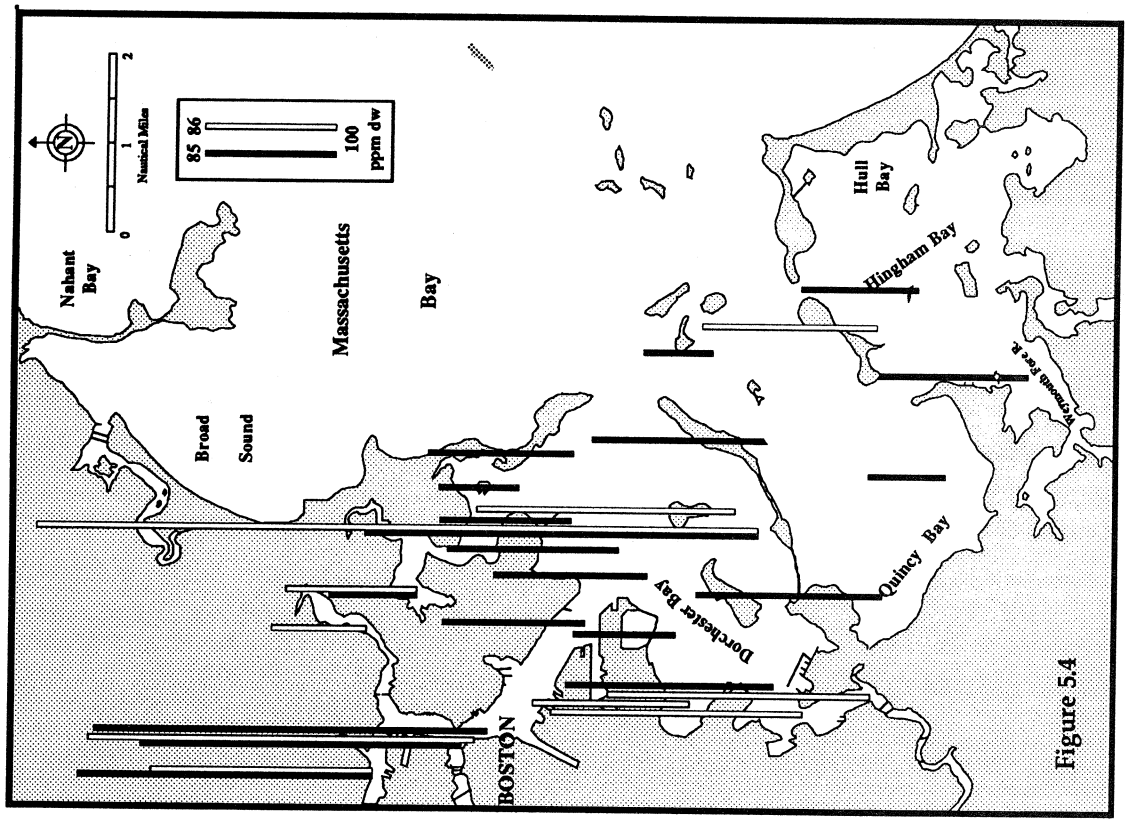
	White 1970?	Gilbert 1971	Isaac and Delaney 1972	MA DEQE 1985-86	NOAA NS&T 1984-87
OVERALL	160 (133)	137 (42)	94(6)	171(30)	99(31)
INNER HARBOR	268 (38)	460 (4)	23(1)	235 (8)	N/A
NORTHWEST HARBOR	130 (48)	110 (17)	200(1)	172(14)	117(22)
CENTRAL HARBOR	106 (16)	97(13)	118(2)	106 (5)	96 (3)
SOUTHEAST HARBOR	100 (31)	99 (8)	52(2)	103 (3)	36 (6)

Between 1971 and 1974, Massachusetts conducted a toxic element survey of its waters (Isaac and Delaney, 1975). The survey included the analysis of sediment samples for volatile solids and a variety of heavy metals, including lead. Six surficial sediment samples from around Boston Harbor had a combined mean lead concentration of 94±81 ppm with a range of from 7.2 to 200 ppm (Figure 5.3). Because so few samples were analyzed, no statistical comparison between harbor divisions could be made (Table 5.2). The second lowest concentration of lead was reported for the single sediment sample taken from the inner harbor. This sample, located near the mouth of the inner harbor, also had relatively low concentrations of the other metals for which it was analyzed, as well as the lowest concentration of volatile solids in the Harbor.

Data were obtained from the New England Division of the USACOE for dredging studies conducted in and around Boston Harbor from 1972 through 1988 (USACOE, 1972-1988; 1981; 1987). The USACOE analyzed 125 sediment samples during this period for levels of lead content. The overall mean lead concentration in the surficial sediments of Boston Harbor based on this data was 117±162 ppm with a range of from 1.6 to 1180 ppm. The vast majority of the samples (74%) had lead concentrations between 10 and 200 ppm inclusive, while 8 percent of the samples had less than 10 ppm, and only 6 percent of the samples had concentrations in excess of 300 ppm. When the data were grouped by harbor divisions, the means ranged between 90±227 ppm (13 samples) for the central harbor to 125±141 ppm (7 samples) for the southeastern harbor. The inner harbor had a mean lead concentration of 118±104 ppm (59 samples), while the northwestern harbor had a mean of 119±202 ppm (47 samples). While statistical analysis of the log transformed data indicated no significant difference between any of the Harbor divisions at $p=0.05$, the data did suggest that lead content of the sediments decreased from the inner to the central harbor. The high mean for the southeastern harbor was the result of two samples from the Fore River (267 and 357 ppm) without which the mean for the southeastern harbor would have been 51±68 ppm. When the northwest harbor was subdivided, the Dorchester Bay area sediments had a mean concentration of 244±313 ppm, while the Winthrop Bay area sediments had a mean concentration of 66±96 ppm. The high mean and standard deviation for the Dorchester Bay area were due to a single sample with 1180 ppm; when this one sample was excluded from the calculations the mean became 172±166 ppm. Statistical analysis of the log transformed data indicated that the only significant difference was between the Dorchester Bay area subdivision and the central harbor division, with or without the 1180 ppm sample, at $p=0.05$.

In 1985 and 1986, the Massachusetts DEQE, as part of their annual Boston Harbor Water Quality and Wastewater Discharge Survey, analyzed 30 surficial sediment samples for levels of lead contamination (MA DEQE, 1986; 1987). They found an overall mean lead concentration of 171±116 ppm ranging from a low of 55 ppm, from a site southwest of Gallops Island (central harbor), to a high of 560 ppm, from a site north of Moon Head (northwestern harbor) (Figure 5.4). While the means for the harbor divisions (Table 5.2) suggested a trend





Figures 5.3 & 5.4. Lead concentrations (ppm) in surficial sediments of Boston Harbor in the early 1970's (Isaac & Delaney, 1975) (Fig. 5.3) and in 1985 and 1986 (Massachusetts DEQE, 1986, 1987) (Fig. 5.4).

of decreasing lead levels from the inner harbor to the southeast harbor, statistical analysis of the log transformed data indicated no significant difference between any of the divisions at p=0.05. This trend can also be seen in Figure 5.4 that graphically displays the data by site and year. When the northwest harbor was subdivided, the Dorchester Bay area sediments had a mean concentration of 228±150 ppm, while the Winthrop Bay area sediments had a mean concentration of 98±30 ppm. Statistical analysis of the log transformed data indicated no significant difference between the two subdivisions or between the two subdivisions and the other three harbor divisions at p=0.05.

In 1987, a study of Quincy Bay was conducted under the auspices of the EPA (U.S. EPA, 1988), which was essentially restricted to the central harbor area (Figure 5.5). The overall mean lead concentration in the surficial sediments for the study was 72±41 ppm with a range of 6.6 to 164 ppm.

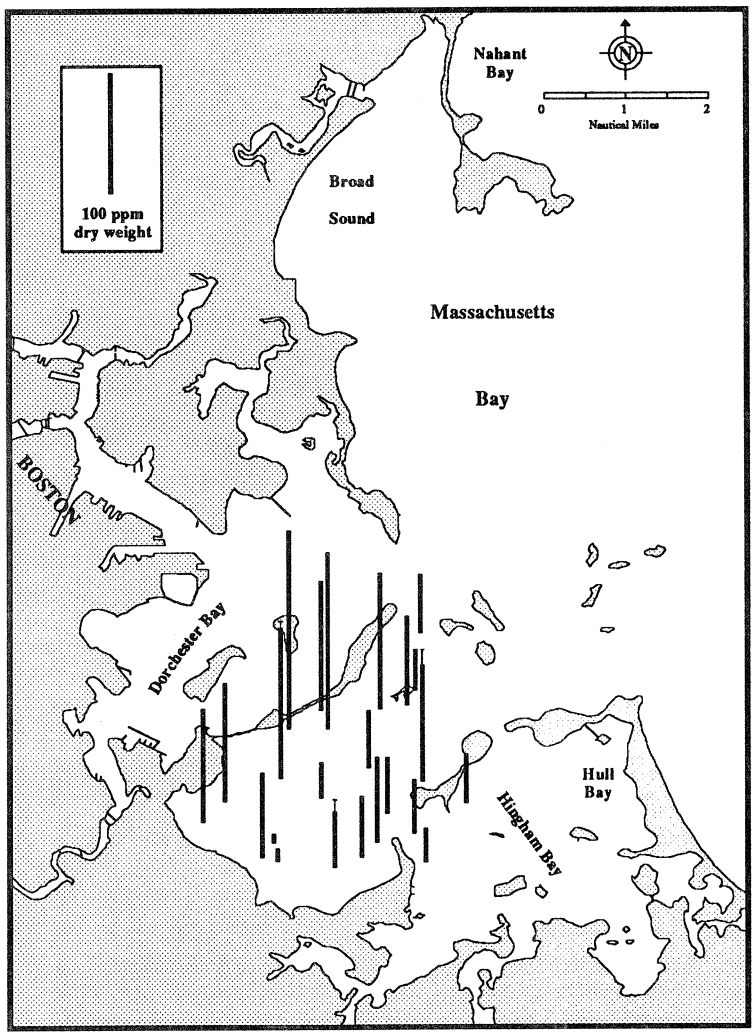
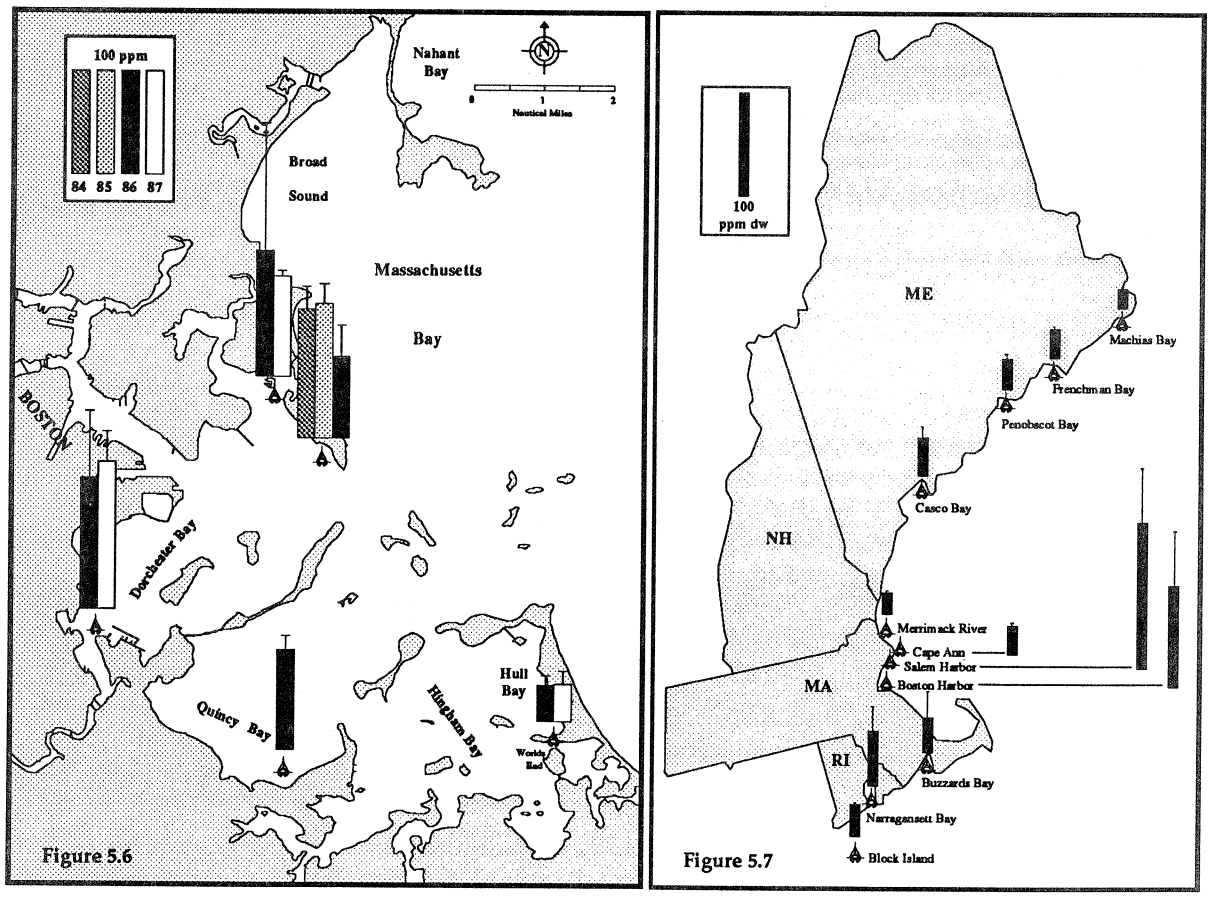


Figure 5.5. Lead concentrations (ppm dw) in the surficial sediments of Quincy Bay and environs, based on data for 1987 from U.S. EPA, 1988.

Since 1984, NOAA's NS&T Program has sampled and analyzed surficial sediments from a number of sites around Boston Harbor for several analytes, including lead (Figure 5.6). The overall mean lead concentration in the surficial sediments of the harbor was 99±53 ppm. Individual sample values ranged from 20 to 260 ppm. Site means, based on all 4 years of available data, ranged from 36 ppm, at the site off the northern tip of Worlds End, to 132 ppm, at the site in southeastern Dorchester Bay. Statistical comparison of the log transformed data indicated that the Worlds End site was significantly different from all but the site in Quincy Bay at p=0.05. When the data were grouped by harbor divisions (Table 5.2), the means suggested a trend of decreasing lead concentration from the northwest harbor to the southeast harbor. The log transformed data indicated that the southeast harbor was significantly different from the northwest and central harbors at p=0.05. When the northwest harbor was subdivided, the Dorchester Bay area sediments had a mean concentration of 132±46 ppm, while the Winthrop Bay area sediments had a mean concentration of 111±52 ppm. Statistical analysis of the log transformed data indicated no significant difference between the two subdivisions, but they were both significantly different from the southeast harbor division, at p=0.05.

On a broader scale, the NOAA NS&T Program has analyzed surficial sediment samples from 23 sites in 11 areas along the outer New England coast between 1984 and 1987. Figure 5.7 displays the means with standard deviations for the 11 coastal areas. The figure clearly indicates that the mean concentration of lead at the NS&T Program sites in Boston Harbor was higher than the means for all other areas sampled in New England except for Salem Harbor. It should be noted that the Salem Harbor value was based on only one site and may not be representative of Salem Harbor in general. The Boston Harbor value was based on five sites including one (Worlds End) which had a relatively low mean concentration (35 ppm) and three sites that had means greater than 100 ppm (northwestern and southwestern Deer Island and Dorchester Bay). Statistical analysis of the log transformed data indicated that Boston Harbor was significantly different (p=0.05) from all the other areas of New England sampled except Salem Harbor, Cape Ann, and Block Island. A possible reason for the lack of a significant difference among Boston Harbor, with a mean lead concentration of 99±53 ppm and Cape Ann and Block Island, with mean lead concentrations of 2.9 and 2.0 ppm, respectively, was the small number of samples (three each) from Cape Ann and Block Island.

When the means of the individual New England NS&T Program sites were compared, four of the five sites with the highest mean concentrations of lead in their surficial sediments were located in Boston Harbor (Table 5.3). In an attempt to determine a value for background lead levels, the overall mean was calculated for the five NS&T Program sites in New England with the lowest lead concentrations in their surficial sediments (Table 5.3).



Figures 5.6 & 5.7. Mean lead concentrations (ppm dw) in the surficial sediments of Boston Harbor by site and year (Fig. 5.6) and the 11 areas sampled along the outer New England coast for 1984-87, based on NOAA's NS&T Program data (NOAA, unpublished) (bars represent one standard deviation).

This reference mean was 23±5.8 ppm. The overall mean lead concentration in the surficial sediments of Boston Harbor (99±53 ppm), based on the NS&T Program data, was more than 4 times greater than this reference mean. The four Boston Harbor sites with the highest levels of lead contamination all had means from 4 to almost 6 times higher than this reference mean. The Boston Harbor site with the lowest mean concentration of lead (Worlds End, 36±9.8 ppm) was 1 1/2 times higher than the reference mean.

Table 5.3. The five outer New England coast NOAA NS&T Program sites with the lowest and highest mean lead concentrations (ppm) in the surficial sediments based on data from 1984 through 1987.

Site	Mean	Standard Deviation	Count
GOOSEBURY NECK, BUZZARDS BAY	17	4.3	6
MACHIAS BAY, MAINE	20	2.0	7
PICKERING ISLAND, PENOBSCOT BAY, MAINE	26	6.5	3
FRENCHMAN BAY, MAINE	28	2.8	6
STRAITSMOUTH ISLAND, CAPE ANN	28	2.9	3
QUINCY BAY	96	15	3
NORTHWESTERN DEER ISLAND	110	80	6
SOUTHWESTERN DEER ISLAND	112	32	10
DORCHESTER BAY	132	46	6
SALEM HARBOR	143	52	9

Temporal Trends

Figure 5.8 compares the yearly mean lead concentrations in the surficial sediments of Boston Harbor based on all the available data sets (White, 1972: Gilbert *et al.*, 1972: Isaac & Delaney, 1975: USACOE, 1972-1988; 1981, 1988: MA DEQE, 1986; 1987: U.S. EPA, 1988: NOAA, unpublished). There is no overall temporal trend apparent from Figure 5.8. The yearly fluctuations were more likely due to differences in sites sampled than any overall change in lead concentrations.

Data was available from the USACOE on dredging studies for most of the years from 1975 through 1988. When the yearly mean lead concentrations in the surficial sediments based on this data were calculated and the log transformed data compared, only the year with the lowest mean lead concentration (1983, 24 ppm) and the year with the second highest mean lead concentration (1986, 164 ppm) were significantly different at p=0.05 (Table 5.4). The variability in yearly means was probably representative of geographic differences in lead concentrations rather than temporal differences, because different sites were sampled in different years.

The only other available sediment data that spanned more than 2 years was data from NOAA's NS&T Program Benthic Surveillance (1984-86) and Mussel Watch (1986-87) projects. The yearly mean lead concentrations in the surficial sediments of Boston Harbor based on this data ranged from a high of 129±20 ppm in 1985 to a low of 91 ppm in 1986 and 1987 with a standard deviation of ±64 and ±48, respectively. The yearly mean for 1984 was 124±22 ppm. There was no indication of any temporal trends in lead contamination. The difference in the yearly mean lead concentrations can be explained by the difference in the sites sampled each year (Figure 5.6). When the inner harbor data was excluded from the 1970 (White, 1972) and 1971 (Gilbert *et al.*, 1972) data sets, the overall means became 116 and 103 ppm (1970 and 1971, respectively). When these early yearly means were compared to the NS&T Program yearly means for 1984 through 1987 (1984, 124; 1985, 129; 1986, 91; and 1987, 91 ppm), there appeared to be little if any change in lead concentrations in the surficial sediments of outer Boston Harbor.

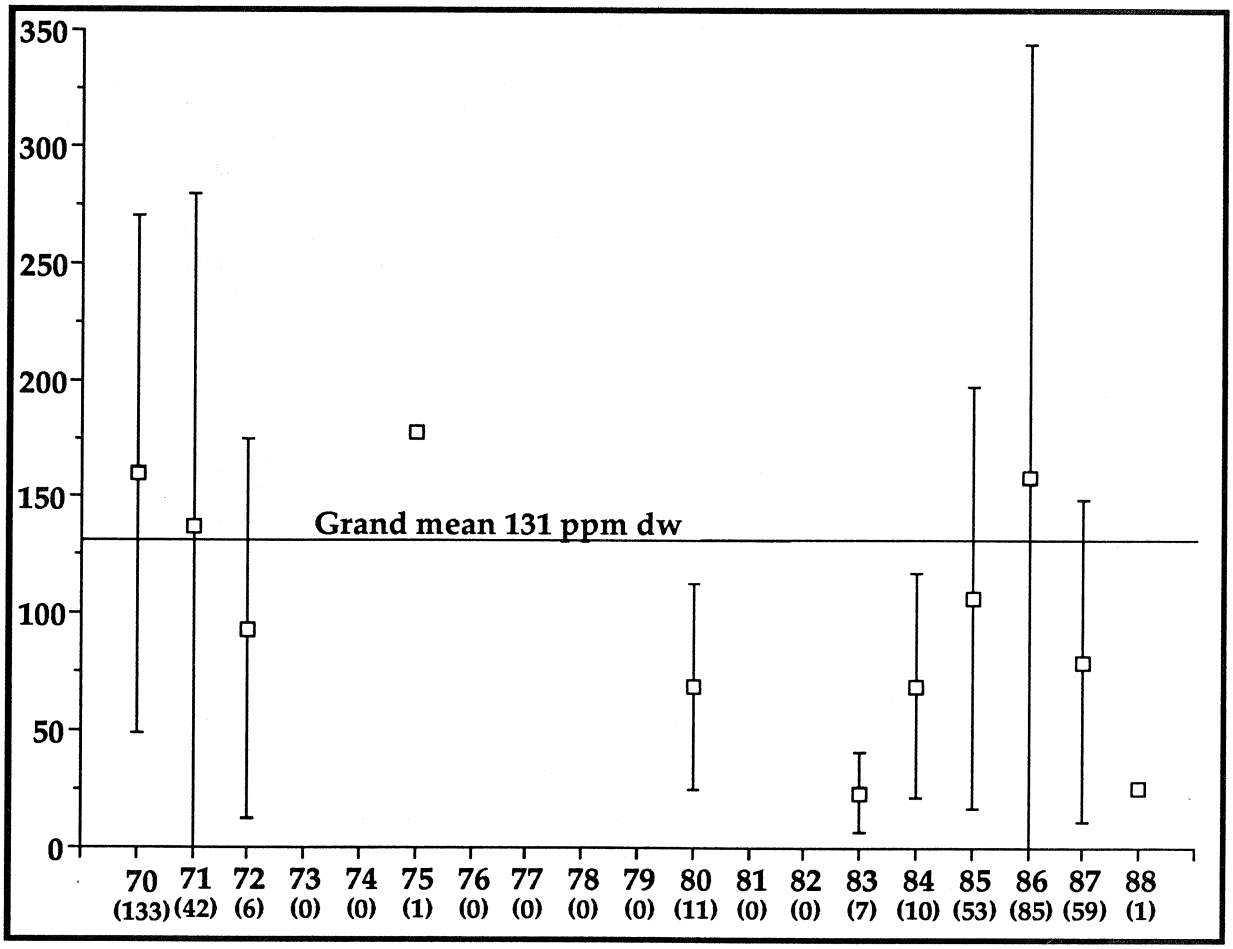


Figure 5.8. Yearly mean lead concentrations (ppm) in the surficial sediments of Boston Harbor based on White (1972), Gilbert *et al.* (1972), Isaac & Delaney (1975), USACOE (1972-1988, 1981, 1988), MA DEQE (1986, 1987), U.S. EPA (1988), and NOAA (unpublished). The bars represent one standard deviation and the numbers in parenthesis are the number of samples analyzed each year.

Table 5.4. Yearly mean lead concentrations (ppm) in Boston Harbor surficial sediments based on dredging study data from the USACOE.

Year	Mean	Standard Deviation	Count
1975	178	N/A	1
1980	69	43	11
1983	24	17	7
1984	45	33	7
1985	84	97	30
1986	164	207	59
1987	110	147	9
1988	26	N/A	1

Biota

Since 1976, over 190 tissue samples from a variety of organisms in Boston Harbor have been analyzed for levels of lead contamination. Lead concentrations ranged from a low of 0.01 ppm in the muscle of a winter flounder (*P. americanus*) to a high of 19.00 ppm in the soft parts of the mussel *M. edulis*. Table 5.5 gives the statistics on lead contamination of biota by organism and tissue. These numbers must be viewed with caution based on the previously cited work of Patterson and colleagues. It should be noted that 70 percent of the winter flounder muscle samples and 8 percent of the lobster (*H. americanus*) muscle samples had lead levels that were below the detection limits, which ranged from 0.03 to 0.21 ppm for winter flounder and was 0.033 ppm for lobster (half these detection limits were used in the calculations of the means). No lobster hepatopancreas data is presented in the table because all but one of the eight pairs of replicate samples were below the detection limits (0.24 to 2.26 ppm). The single sample with a measurable value had a lead concentration of 0.41 ppm. Since the majority of the bivalves analyzed in the various studies were not depurated before analysis, it would be expected that the values given for lead levels in the soft parts of bivalves included lead contained in the gut contents as well as that actually contained within the tissues of the organisms (Burnett and Patterson, 1980). The values given for the lead content in the soft parts of various bivalves can be considered to represent the degree of lead contamination of the environment; since the level of lead in the gut would be expected to vary with the amount of lead in the environment.

Table 5.5. Harborwide means, standard deviations, medians, ranges, and sample sizes (count) for lead concentrations (ppm) in biota by organism and tissues based on all the available data sets (* transplants).

		Mean	Standard Deviation	Median	Range	Count
P. americanus						
	liver	1.25	0.93	0.88	0.11 - 4.20	36
	muscle	0.07	0.09	0.04	0.01 - 0.39	26
H. americanus						
	muscle	0.33	0.29	0.21	0.02 - 0.82	48
M. arenaria						
	soft parts	7.38	2.23	7.34	3.08 - 16.32	36
M. edulis						
	soft parts	10.71	4.27	10	4.90 -19.00	28
*C. virginica**						
	soft parts	1.44	0.55	1.35	0.89 - 2.18	4

Geographic Trends

Based on the combined data, no overview of geographic trends in lead levels in biota was conducted because of the possible problems with sample contamination (Patterson and Settle, 1976).

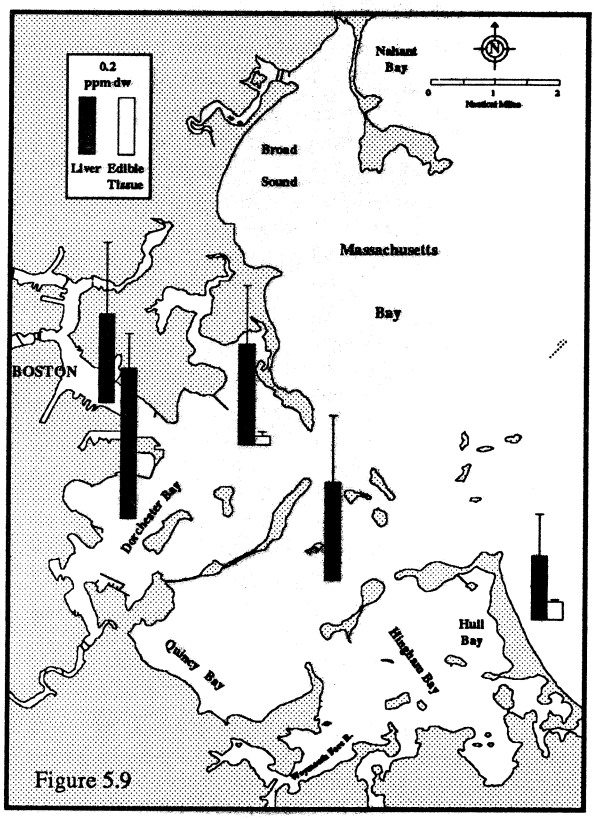
In 1976, the EPA sampled mussels and other bivalves from 107 sites nationwide and analyzed the samples for a variety of metals and organic contaminants including lead (Goldberg *et al.*, 1978). A composite sample of *M. edulis* from a site on the northwest side of Deer Island was found to have a lead concentration in the soft parts of 5.9 ppm. Between Block Island and the Canadian Border, 11 other New England sites were sampled. They had lead concentrations in the soft parts of *M. edulis* ranging from 1.1 ppm at the Blue Hill Falls, Maine site to 9.5 ppm at the Cape Newagen, Maine site. Boston mussels had the third highest concentration of lead.

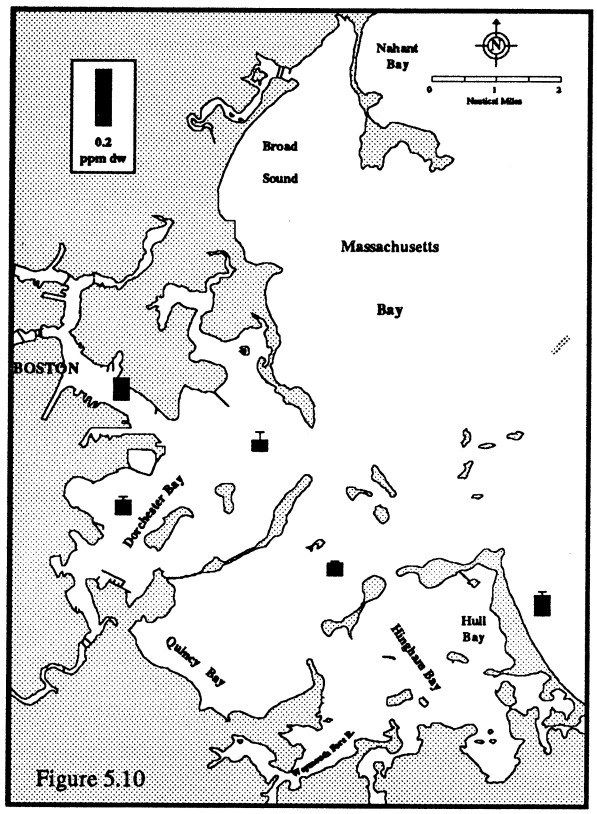
In 1979, as a part of the 301h waiver application for the Deer Island and Nut Island sewage treatment plants, winter flounder (*P. americanus*) and lobster (*H. americanus*) tissue samples from five sites in and around Boston Harbor were analyzed for levels of several analytes, including lead (Metcalf and Eddy, 1984). The livers of four winter flounder from each of four different sites in Boston Harbor and one site outside the Harbor (Nantasket Beach) were analyzed for lead levels. The values for the individual samples ranged from less than 0.11 ppm at President Roads sites to 2.76 ppm at Dorchester Bay sites. The mean lead concentrations in livers for the five sites ranged from 0.71±0.57 ppm at the President Roads site to 1.98±0.63 ppm at the Dorchester Bay site (Figure 5.9). When the data were log transformed and analyzed, none of the sites were significantly different at p=0.05. When the data were looked at with regard to the harbor divisions, they suggested that the northwestern harbor had the highest level of lead contamination (1.35 ppm) in winter flounder livers. The inner harbor and the central harbor had essentially the same level of lead contamination (0.92 and 0.96 ppm, respectively). The data also suggested that the Nantasket Beach site was nearly as contaminated (1.13 ppm) as the northwestern harbor (Figure 5.9). However, statistical analysis of the log transformed data found no significant difference between any of the harbor divisions nor between any of the divisions and the Nantasket Bay site (p=0.05). Unfortunately, only five edible tissue samples (three samples from President Roads and two samples from Nantasket Beach) were analyzed for lead. Lead concentrations in the individual samples ranged from 0.07 to 0.39 ppm, while the site means were 0.15±0.11 and 0.31±0.07 ppm at Nantasket Beach and President Roads, respectively.

Two lobsters each were collected from the same five sites and claw and tail muscle tissue was analyzed for lead content. Lead concentrations in the individual specimens ranged from less than 0.11 to 0.42 ppm. The means for the five sites ranged from a low of 0.21 ppm, at the President Roads site, to a high of 0.42 ppm at the Inner Harbor site. The Nantasket Beach site had the second highest mean of 0.37 ppm, while the Dorchester Bay and Nut Island discharge sites had means of 0.26 and 0.24 ppm, respectively (Figure 5.10). None of the sites were significantly different based on analysis of the log transformed data (p=0.05). When the lobster muscle data were grouped by division, the inner harbor had the highest mean lead concentration (0.42 ppm), with the northwestern and central harbors both having means of 0.24 ppm. Statistical analysis of the log transformed data indicated no significant difference between any of the divisions nor between any of the divisions and the Nantasket Beach site at p=0.05.

In 1985 and 1986, as part of a study of contaminants in marine resources, lobster (*H. americanus*) and soft-shelled clams (*M. arenaria*) were collected from Boston and Salem harbors and analyzed for various analytes, including lead, (Wallace *et al.*, 1988). The mean lead concentration in the combined claw and tail muscle tissue of 24 lobsters collected from around Deer Island was 0.09±0.07 ppm with a range of from less than 0.03 to 0.28 ppm. Lead concentrations were below the detection limit of 0.03 ppm in four of the samples. Lobsters were collected from two sites in Salem Harbor, the treatment plant outfall and Willows Pier. The mean lead concentrations in combined claw and tail muscle tissue based on the analysis of 25 lobsters per site were 0.12±0.07 and 0.33±0.71 ppm, respectively. The relatively high mean for the Willows Pier site was the result of two samples having lead concentrations of over 2.00 ppm. When these two samples were excluded from the calculations, the mean for Willows Pier became 0.13±0.10. Statistical analysis of the log transformed data indicated no significant difference among the three sites at p=0.05. The mean lead concentration for 34 soft-shelled clams (*M. arenaria*) from Wollaston Beach in Quincy Bay was 7.63±2.04 ppm with a range of 4.40 to 16.32 ppm. About one third of the clams were depurated before analysis but there was no significant difference found in lead concentrations between the depurated and non-depurated clams (Wallace *et al.*, 1988).

An intensive study of Quincy Bay was conducted in 1987 (U.S. EPA, 1988). The study included the analysis for lead contamination levels in the tissues of native winter flounder (*P. americanus*), lobsters (*H. americanus*), soft-shelled clams (*M. arenaria*), and transplanted



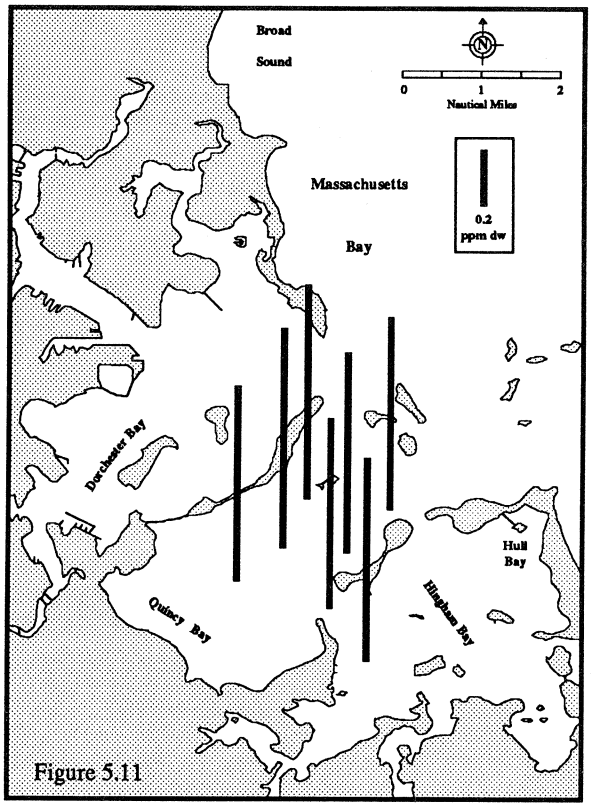


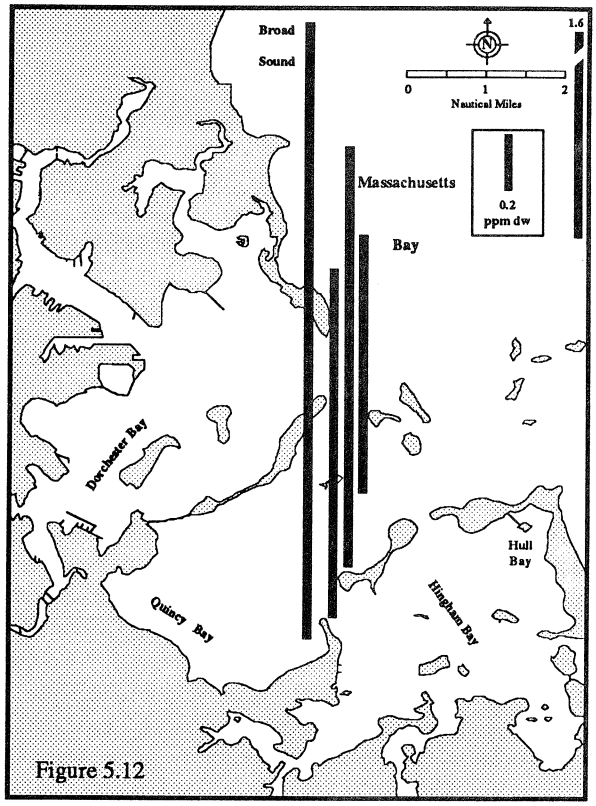
Figures 5.9 & 5.10. Mean lead concentrations (ppm dw) in the liver and edible tissue of *P. americanus* (Fig. 5.9) and muscle tissue of *H. americanus* (Fig. 5.10) from Boston Harbor, based on 1979 data from Metcalf & Eddy, 1984. The bars represent one standard deviation.

oysters (*C. virginica*) (U. S. EPA, 1988). The muscle tissue of from five to seven winter flounder from each of four different trawl transects was analyzed for lead content. The lead concentrations in all but 3 of the 35 samples were below the limits of detection that ranged, for the individual samples, from 0.03 to 0.21 ppm. The samples that were above detection had lead concentrations of 0.01 ppm dw (two samples) and 0.04 ppm (one sample).

Both the tail muscle and the hepatopancreas of lobsters from seven sites were analyzed for levels of lead content. Two replicate samples from the tail muscles of 16 lobsters; 1 to 3 from each of the seven sites were analyzed. The lead concentrations in the individual samples ranged from 0.51 to 0.85 ppm while the mean tail muscle concentrations for the seven sites ranged from 0.67±0.06 ppm to 0.79±0.04 ppm (Figure 5.11). There was no significant difference in tail muscle lead levels between sites based on statistical analysis of the log transformed data (p=0.05). Two replicate samples of hepatopancreas tissue from 8 of the 16 lobsters were also analyzed for lead. Lead concentrations in seven of the eight lobsters were below the detection limits (0.34 to 2.02 ppm). The eighth lobster had a lead concentration of 0.27 ppm based on replicate values of 0.41 and <0.24 ppm.

Oysters (*C. virginica*) were collected from a commercial bed located in Cotuit Bay, Cotuit, Massachusetts. They were deployed at four sites in Quincy Bay and one site at The Graves in Massachusetts Bay from June 5 through July 16, 1987. The lead concentrations in the oysters at the four sites ranged from 0.89 to 2.18 ppm. The oysters from The Graves had 1.63 ppm lead while those from the source bed in Cotuit Bay had a lead concentration of 1.48 ppm (Figure 5.12). Two samples of the soft-shelled clam (*M. arenaria*) from the vicinity of Moon Island, Quincy Bay also were analyzed for lead and had concentrations of





Figures 5.11 & 5.12. Lead concentrations (ppm dw) in the tail muscle of *H. americanus* (Fig. 5.11) from Boston Harbor and whole transplanted *C, virginica* (Fig. 5.12), based on 1987 data from U.S. EPA, 1988.

3.08 and 3.36 ppm. It should be noted that neither the clams nor the oysters were depurated before analysis.

NOAA's Mussel Watch Project, a part of the NS&T Program, has sampled mussels (*M. edulis*) from four sites in and around Boston Harbor on an annual basis since 1986. Shortly after sampling, the mussels were frozen and three whole-body composite samples from each site were analyzed for a variety of analytes, including lead. The overall mean concentration of lead in the mussels for the three sites in Boston Harbor from 1986 through 1988 was 10.89±4.24 ppm with a range of from 4.90 to 19.0 ppm. The means for the individual sites were 8.29±2.68 ppm northwest of Deer Island, 9.93±4.09 ppm in Hingham Bay off Worlds End, and 14.44±3.43 ppm in southwestern Dorchester Bay. Mussels from the site outside the Harbor, Outer Brewster Island, had a mean lead concentration of 6.62±2.06 ppm (Figure 5.13). Statistical analysis of the log transformed data for the four sites indicated that the Dorchester Bay site was significantly different from the Deer Island and Brewster Island sites at $p=0.05$.

On a broader scale, when the Boston Harbor NS&T sites were compared to the other outer New England coast NS&T Mussel Watch sites (Table 5.6 and Figure 5.14), the Dorchester Bay site was found to be significantly different from all the New England sites. The Deer Island and Hingham Bay sites were significantly different from all but two of the New England sites (Brewster Island and Dyers Island, Narragansett Bay) at $p=0.05$. The Brewster Island site was found to be significantly different from all but two of the New England sites outside Boston Harbor (Dyers Island and Angelica Rock, Buzzards Bay) at $p=0.05$. From this data, it appears that lead levels in mussels vary over approximately an order of magnitude throughout New England (Table 5.7). When a reference value is calculated based on the five sites with the lowest levels of lead contamination in mussels, a

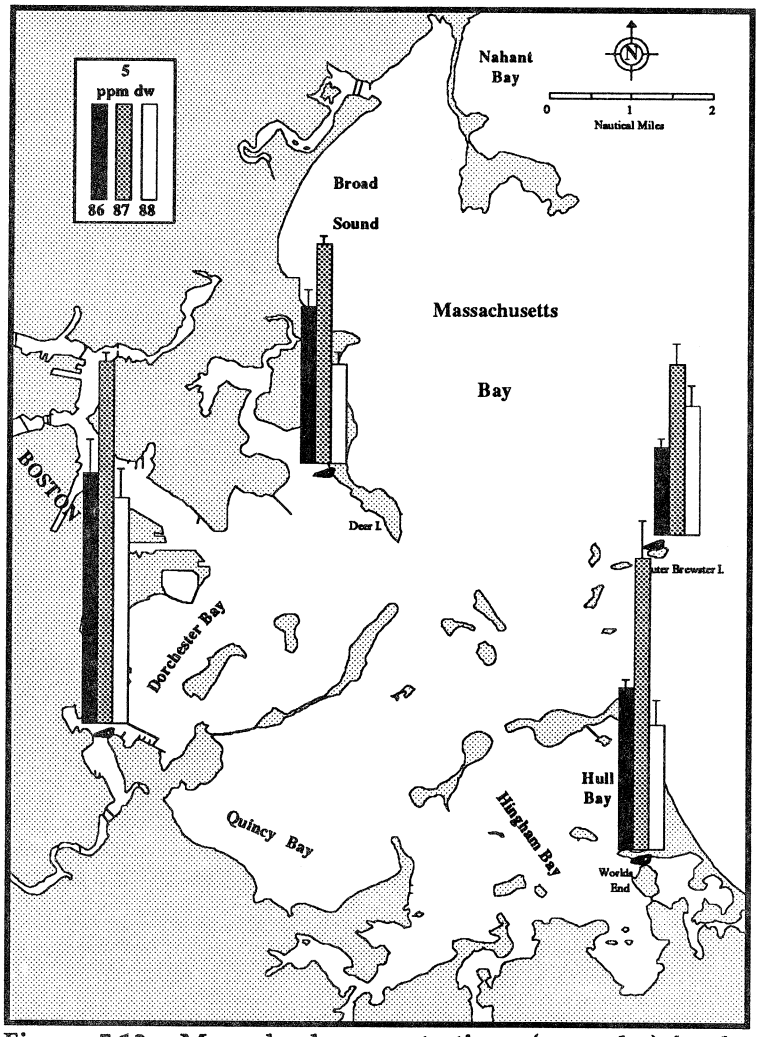


Figure 5.13. Mean lead concentrations (ppm dw) in the soft-parts of *M. edulis* from Boston Harbor for 1986-88, based on NOAA's NS&T Program Mussel Watch data (NOAA, unpublished) (bars represent one standard deviation).

value of 1.73±0.54 ppm is obtained. The Boston Harbor sites had mean lead values from approximately 4 to 7 times higher than this reference value. On a national scale, the Mussel Watch sites where *M. edulis* was sampled had mean lead concentrations ranging from 0.39 to 25.78 ppm with an overall mean for all the sites of 4.15±5.63 ppm; 73 percent of the sites had means less than 4.00 ppm, 20 percent had means of less than 1.00 ppm, while only 13 percent had mean lead concentrations greater than 8.00 ppm. When the sites where *M. californianus* was sampled were included in the calculations, the overall mean became 3.57±4.95 ppm, with 77 percent of the sites having means less than 4.00 ppm, with 25 percent less than 1.00 ppm, and 11 percent having means greater than 8.00 ppm. Based on this data, Boston Harbor mussels appeared to be highly contaminated with lead since all the Harbor sites had means greater than 8.00 ppm and included the fourth highest site mean (Dorchester Bay, 14.44 ppm) in the country.

NOAA's Benthic Surveillance Project, a part of the NS&T Program, has sampled winter flounder (*P. americanus*) from an area just west of Deer Island on an annual basis since 1984. The mean lead concentration in the liver of the fish sampled in 1984 and 1985 was 1.34±1.05 ppm with a range of 0.18 to 4.20 ppm. The mean concentration of lead in flounder livers for all the New England Benthic Surveillance sites, including Boston Harbor, ranged from a low of 1.14±2.03 ppm at the Salem Harbor site to a high of 7.48±17.3 ppm at the Casco Bay site (Figure 5.16). Boston Harbor winter flounder liver had the second highest mean lead concentration. Statistical analysis of the log transformed data indicated that only the Casco Bay and Salem Harbor sites were significantly different at p=0.05. No comparison could be made between Boston Harbor and the three northern-Maine sites; because a different species, longhorn sculpin (*Myoxcephalus octodecemspinosus*), was sampled at these sites. The Benthic Surveillance Project sampled winter flounder at four other sites during the same period: two in Long Island Sound and one each in Raritan and Great bays in New Jersey. Both the East Long Island Sound and Great Bay sites had mean lead concentrations in winter flounder liver of less than 1.00 ppm (0.71 and 0.83 ppm, respectively). Both the West Long Island Sound and Raritan Bay sites had mean lead concentrations higher than Boston Harbor's mean (2.09 and 3.75 ppm, respectively).

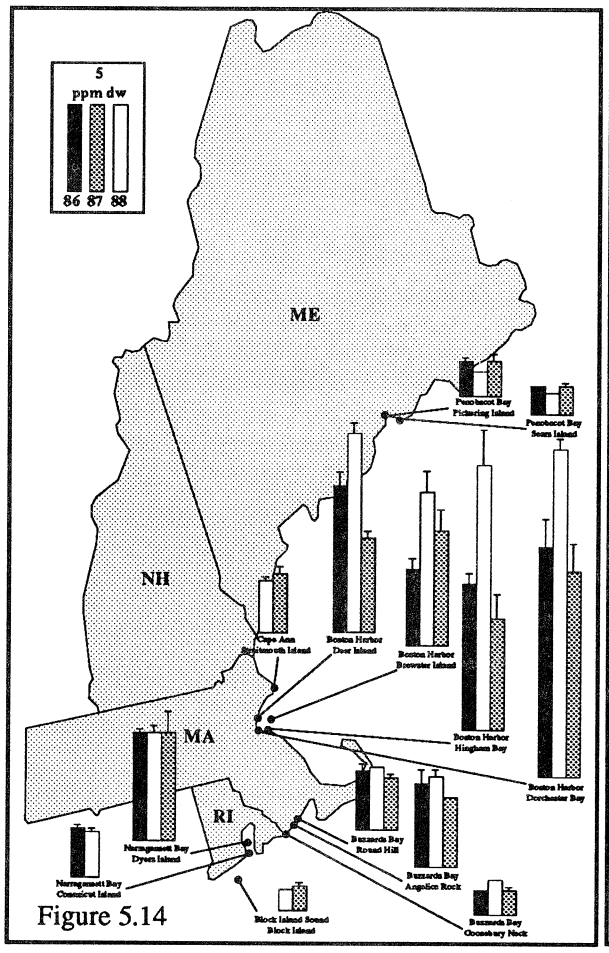


Figure 5.14

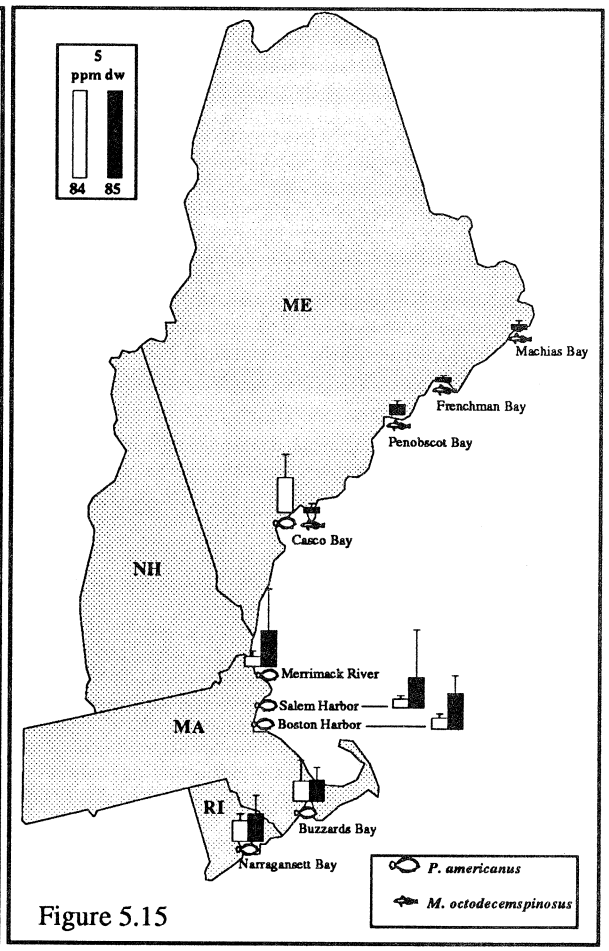


Figure 5.15

Figures 5.14 & 5.15. Mean lead concentrations (ppm dw) in the soft-parts of *M. edulis* for 1986-88 (Fig. 5.14) and liver tissues of *P. americanus* for 1984 and 1985 (Fig. 5.15) from the outer New England coast NS&T Program sites (NOAA, unpublished) (bars represent one standard deviation).

Table 5.6. The mean lead concentrations (ppm) in *M. edulis* at the 13 outer New England coast NS&T Program Mussel Watch sites. The outlined means are for Boston Harbor sites.

Site	Mean	Standard Deviation	Count
DORCHESTER BAY, BOSTON HARBOR	14.44	3.43	9
HINGHAM BAY, BOSTON HARBOR	9.93	4.09	9
DEER ISLAND, BOSTON HARBOR	8.29	2.68	9
OUTER BREWSTER ISLAND	6.62	2.06	9
DYERS ISLAND, NARRAGANSETT BAY	6.14	0.61	9
ANGELICA ROCK, BUZZARDS BAY	4.72	0.67	11
ROUND HILL, BUZZARDS BAY	3.31	0.33	9
CAPE ANN, STRAITSMOUTH ISLAND	3.22	0.38	6
CONANICUT ISLAND NARRAGANSETT BAY	2.77	0.16	6
PICKERING ISLAND, PENOBSCOT BAY	1.73	0.38	9
GOOSEBURY NECK, BUZZARDS BAY	1.60	0.29	8
SEARS ISLAND, PENOBSCOT BAY	1.43	0.22	9
BLOCK ISLAND, RHODE ISLAND	1.30	0.16	6

Temporal Trends

No temporal trends in levels of lead contamination of Boston Harbor biota could be determined based on the available data because the only internally consistent data sets sampling the same organism from the same locations over a number of years were the NS&T Program's Benthic Surveillance and Mussel Watch projects. Data for these projects were only available for 2 and 3 years, respectively. Between 1984 and 1985 there was more than a threefold increase in the level of lead in winter flounder livers (0.63±0.26 to 2.05±1.07 ppm) (Figure 5.16) which was significantly different at p=0.01. However, whether this indicated a trend in levels of lead contamination in Boston Harbor biota or was just due to random sampling could not be determined based on only 2 years. Likewise, the 3 years of data for *M. edulis* from the Mussel Watch Project failed to indicate any trend with lead levels increasing between 1986 and 1987 and then decreasing in 1988 (Figure 5.15). The yearly means were 9.89±2.53 for 1986, 15.0±3.35 for 1987, and 7.78±3.14 ppm for 1988. In addition, when the EPA Deer Island site, which had a lead concentration in the soft parts of mussels of 5.9 ppm in 1976, was compared to the NS&T Program Deer Island site (which is about 0.5 miles northwest of the EPA site) with yearly means of 8.27, 11.3, and 5.27 ppm (1986, 1987, and 1988, respectively), lead concentrations appeared to increase in the 11 years between 1976 and 1987 and then decrease back to the 1976 levels between 1987 and 1988.

Summary

Boston Harbor sediments were found to be contaminated with lead at levels that were more than 4 times higher than background levels. It should be noted that background levels in this case do not refer to levels of naturally occurring lead because of the ubiquitous nature of industrial lead in the environment (Hirao and Patterson, 1974). San Francisco Bay had a mean lead concentration in its surficial sediments of 107±727 ppm (Long *et al.*, 1988). However, this included one sample of 10,000 ppm from the vicinity of a slag heap. When this single sample was excluded from the calculations the mean became 59±221 ppm; less than half the overall mean lead concentration found in Boston Harbor (131±128 ppm). When just the NS&T Program data for the two reports were compared, the Boston Harbor mean (99±53 ppm) was approximately 3 times higher than the San Francisco Bay mean (29±37 ppm) (Long *et al.*, 1988) (Table 5.7). The available data suggest that lead in Boston Harbor surficial sediments show a trend of slightly decreasing concentration from the inner harbor towards the southeastern harbor and towards the mouth. No clear temporal trends were apparent concerning sediment contamination.

Table 5.7. Comparison of lead sediment statistics for Boston Harbor, NS&T Program Reference (based on the five New England sites with the lowest levels of lead), and San Francisco Bay in ppm. Statistics for San Francisco Bay derived from Long *et al.*, 1988 (*excludes single extraneously high sample of 10,000 ppm, see text).

Area	Mean	Standard Deviation	Median	Range	Count
Boston	131	128	100	2 -1180	407
NS&T Program Boston	99	53	100	20 - 260	31
NS&T Program Reference	23	6	30	12 - 33	25
San Francisco Bay*	59	221	30	1 -3000	1313
NS&T Program San Francisco Bay	29	37	22	3 - 223	40

Based on the available data, Boston Harbor biota appear to be moderately to highly contaminated with lead. Boston Harbor mussels (*M. edulis*) had the highest mean lead concentrations of all the New England NS&T Program sites sampled. When compared to all NS&T Program mussel sites sampled in the country, the Boston Harbor sites fell into the upper 11 percent. The winter flounder (*P. americanus*) liver data suggested that Boston Harbor had only moderate levels of lead contamination since, among the NS&T Program

sites, the Boston site had the second highest mean lead concentration in New England and the fourth highest among all the winter flounder sites; but, the Boston mean was less than one fifth that of the most contaminated site. The winter flounder and lobster (*H. americanus*) muscle tissue data suggest that lead tends not to accumulate in muscle tissue. There were no obvious geographic or temporal trends in lead contamination of biota within Boston Harbor based on the available data. This is because relative concentrations among different areas of the Harbor varied with the organism and tissue sampled, and, with the exception of the NS&T Program, none of the studies sampled the same organism from the same sites over a period of years.

COPPER

Copper is a naturally occurring element that functions both as a necessary component of the blood of many marine invertebrates and as a biocide. In a review of the literature, Long and Morgan (1990) found data suggesting that copper levels in sediment below about 70 ppm have little or no effect on biota, while levels of 310 ppm or greater generally have either a chronic or acute effect on the organisms tested.

Sediments

Since the late 1960s, over 400 surficial sediment samples from Boston Harbor have been analyzed for copper concentrations. Based on this data, the overall mean concentration of copper in the surficial sediments of the Harbor was 105 ppm with a standard deviation of 91 and a range of from 0.2 to 785 ppm (Table 6.1). The median concentration was 83 ppm. The large standard deviation and the difference between the mean and the median values are because approximately 10 percent of the samples analyzed had concentrations greater than 200 ppm. The vast majority of the samples, approximately 88 percent, had values between 10 and 200 ppm inclusive. The remaining 2 percent of the samples contained less than 10 ppm copper.

Table 6.1. Means, standard deviations, medians, ranges, and number of samples (count) for copper concentrations (ppm dw) in surficial sediments for all of Boston Harbor and the four regions of the harbor, based on all the available data sets.

	Mean	Standard Deviation	Median	Range	Count
OVERALL	105	91	83	0.2 - 785	408
INNER HARBOR	150	113	129	0.2 - 625	109
NORTHWEST HARBOR	105	86	94	11.0 - 785	150
CENTRAL HARBOR	84	66	72	6.8 - 363	85
SOUTHEAST HARBOR	57	37	53	8.0 - 210	64

Geographic Trends

When the combined data set was broken down into the four harbor divisions, both the means and medians suggested that the surficial sediments of the inner harbor had the highest levels of copper (150 and 129 ppm). The northwest harbor had the second highest level of copper (105 and 94 ppm), followed by the central harbor (84 and 72 ppm), and then the southeast harbor (57 and 53 ppm) (Table 6.1). When the northwest harbor was subdivided, the Dorchester Bay area sediments had a mean concentration of 118±109 ppm with a median concentration of 97 ppm, while the Winthrop bay area sediments had a mean concentration of 92±52 ppm with a median concentration of 76 ppm.

Around 1970, White (1972) collected and analyzed over 130 surficial sediment samples from Boston for a variety of metals, including copper. He found an overall mean copper concentration in Boston Harbor surficial sediments of 109 ppm. Individual sample concentrations ranged from a low of 8 ppm, in a sample taken off Worlds End, to a high of 625 ppm, in a sample taken from the lower reaches of the Charles River (Figure 6.1). Figure 6.1 indicates that copper concentrations in the surficial sediments decreased from northwest to southeast. The highest concentrations occurred in the inner harbor and Dorchester Bay, and the lowest concentrations occurred in the central and southeastern harbor divisions. This trend of decreasing copper in the surficial sediments from northwest to southeast was supported by the means for the individual harbor divisions. These means decreased from a high of 186 ppm in the inner harbor to a low of 58 ppm in the southeast harbor (Table 6.2). Statistical analysis of the log transformed data for the four harbor divisions indicated that the inner harbor was significantly different from the other three divisions and the northwest harbor was significantly different from the southeast harbor at $p=0.05$. When

Table 6.2. Mean copper concentrations in the surficial sediments of Boston Harbor and the four divisions of the harbor, in ppm dw, based on the data of White (1972), Gilbert *et al.* (1972), Isaac and Delaney (1975), MA DEQE (1986 and 1987), and NOAA's NS&T Program (unpublished). The numbers in parentheses are the number of data points used to calculate the means.

	White 1970?	Gilbert *et al.* 1971	Isaac and Delaney 1972	MA DEQE 1985-86	NOAA NS&T 1984-87
OVERALL	109 (133)	121 (43)	76 (6)	137 (30)	108 (31)
INNER HARBOR	186 (38)	298 (4)	32 (1)	204 (8)	N/A
NORTHWEST HARBOR	95 (48)	104 (18)	180 (1)	127 (14)	127 (22)
CENTRAL HARBOR	67 (16)	113 (13)	82 (2)	90 (5)	134 (3)
SOUTHEAST HARBOR	58 (31)	58 (8)	40 (2)	88 (3)	25 (6)

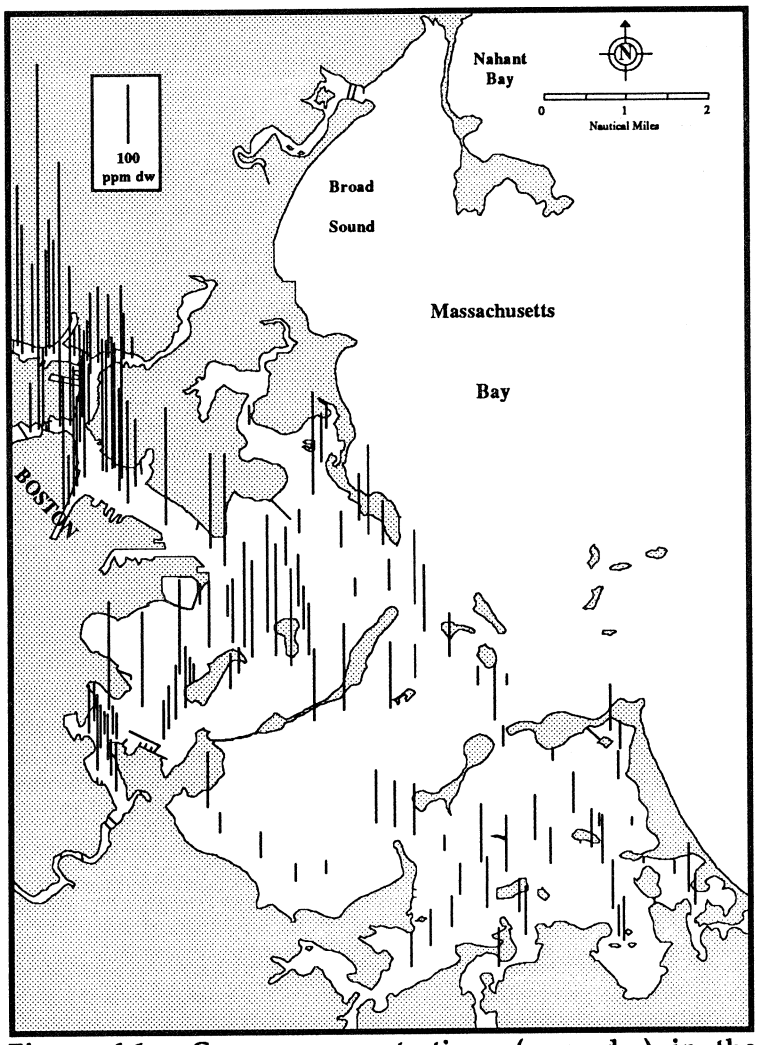


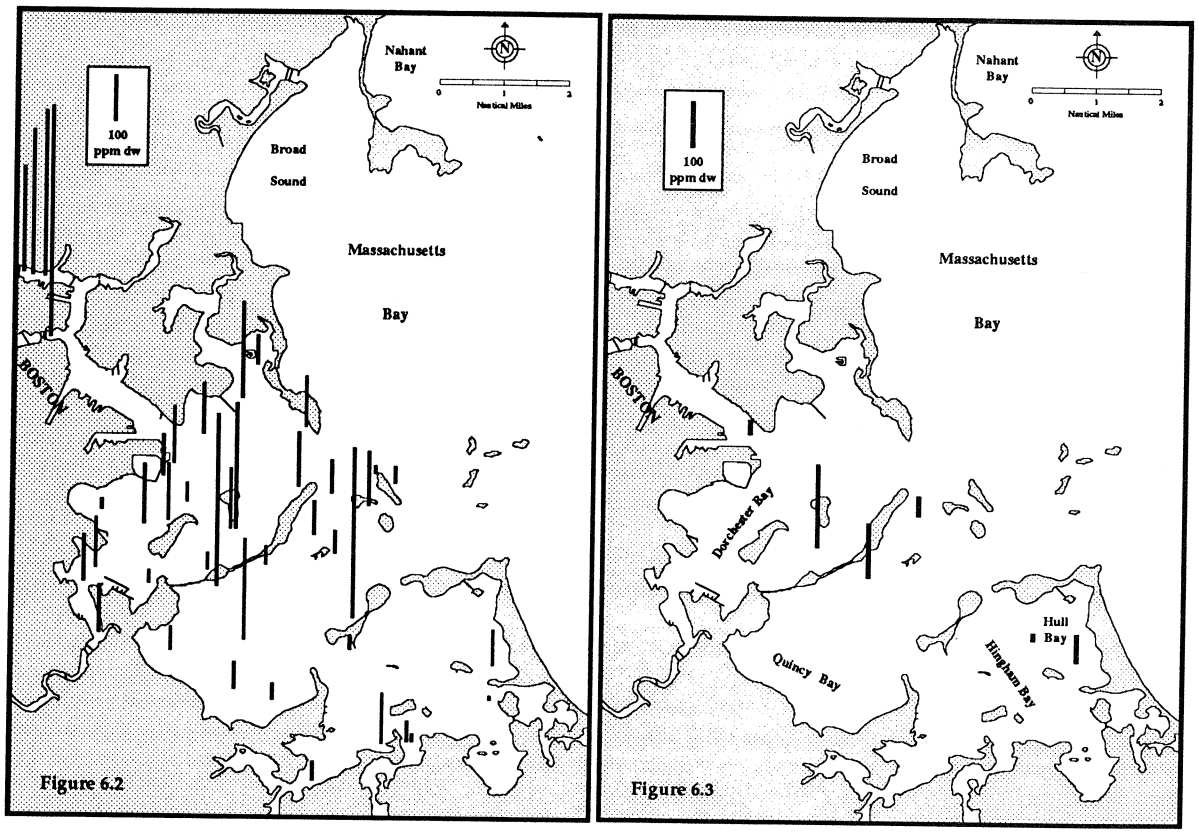
Figure 6.1. Copper concentrations (ppm dw) in the surficial sediments of Boston Harbor for around 1970 (White, 1972).

the northwest harbor was subdivided, both the Dorchester Bay area and Winthrop Bay area sediments had mean concentrations of 96 ppm, with standard deviations of 51 and 50 ppm, respectively. Statistical analysis of the log transformed data indicated that the two subdivisions were both significantly different from the inner harbor division, and the Dorchester Bay area subdivision was different from the southeast harbor at p=0.05. The difference in significance between the two subdivisions and the southeast harbor division was probably due to the difference in sample sizes, 32 for the Dorchester Bay area and 16 for the Winthrop Bay area.

In 1971 the NEA collected 55 cores of Boston Harbor sediments and analyzed various sections of the cores for heavy metal content (Gilbert *et al.*, 1972). Based on 43 samples of the upper surface of the cores that were analyzed for copper, concentrations of copper were found to range from a low of 9 ppm in a sample taken off Worlds End, to a high of 494 ppm in a sample taken from the lower reaches of the Charles River (the same general locations as the low and high samples taken by White). The overall mean copper concentration in the surficial sediments was 121±112 ppm (Table 6.2). As with the White data, a graphic representation (Figure 6.2) suggests a trend of decreasing copper

6.2) suggests a trend of decreasing copper concentrations in the surficial sediments from the inner harbor to the southeastern harbor. When the data were grouped by the four harbor divisions, the inner harbor had the highest mean copper concentration (298 ppm) and the southeast harbor had the lowest (58 ppm). The northwest and central harbor divisions had intermediate levels of copper (104 and 113 ppm). When the log transformed data for the harbor divisions were compared statistically; only the inner and southeast harbor divisions were found to be significantly different at p=0.05. When the northwest harbor was subdivided, the Dorchester Bay area sediments had a mean concentration of 100±62 ppm, while the Winthrop Bay area sediments had a mean concentration of 120±61 ppm. Statistical analysis of the log transformed data indicated that the two subdivisions were not significantly different from each other or the other three harbor divisions at p=0.05.

Between 1971 and 1974, Massachusetts conducted a toxic element survey of the waters of the State (Isaac and Delaney, 1975). The survey included the analysis of sediment samples for volatile solids and a variety of heavy metals, including copper. Six surficial sediment samples from around Boston Harbor had a combined mean copper concentration of 76±62 ppm with a range of from 16 to 180 ppm (Figure 6.3). Because so few samples were analyzed, no statistical comparison between harbor divisions could be made; but, the data did suggest a trend of decreasing copper concentrations from northwest to southeast. Although the second lowest copper concentration was found in the single sample from the inner harbor (Table 6.2), this sample, located near the mouth of the inner harbor, also had relatively low concentrations of the other metals for which it was analyzed, as well as the lowest concentration of volatile solids in the Harbor.



Figures 6.2 & 6.3 Copper concentrations (ppm dw) in the surficial sediments of Boston Harbor for 1971 (Fig. 6.2) (Gilbert *et al.*, 1972) and for the early 1970s (Fig. 6.3) (Isaac & Delaney, 1975).

Data were obtained from the New England Division of the USACOE for dredging studies conducted in and around Boston Harbor from 1972 through 1988 (USACOE, 1972-88, 1981; Hubbard, 1987). The USACOE analyzed 125 samples during this period for copper content. The overall mean copper concentration for the Harbor based on this data was 97±103 ppm with a range from 0.2 ppm in a sample taken from the lower reaches of the Mystic River, to 785 ppm in a sample from western Dorchester Bay near the John F. Kennedy Library. The main reason for the high standard deviation was that the vast majority of the samples (89%) had copper concentrations between 10 and 200 ppm, inclusive, while approximately 2 percent of the samples had less than 10 ppm, and only 9 percent of the samples had concentrations in excess of 200 ppm. When the data were grouped by harbor divisions, the means ranged between 63±62 ppm in the central harbor, 107±90 ppm in the inner harbor, 73±48 ppm in the northwest harbor, and 66±56 ppm in the southeast harbor. The division means suggested a trend of decreasing copper concentration in a northwest to southeast direction. However, statistical analysis of the log transformed data indicated no significant difference between any of the harbor divisions at p=0.05. It should be noted that the vast majority of the samples analyzed were from the inner and northwest harbor (58 and 47, respectively). Only 6 samples were analyzed from the central harbor and 14 from the southeast harbor. When the northwest harbor was subdivided, the Dorchester Bay area sediments (14 samples) had a mean concentration of 168±217 ppm, while the Winthrop Bay area sediments (33 samples) had a mean concentration of 67±47 ppm. The high mean and standard deviation for the Dorchester Bay area were due to two samples in excess of 500 ppm (523 and 785 ppm); the next highest sample was 154 ppm. When these high samples were excluded from the calculations, the mean became 87±49 ppm. Statistical analysis of the log transformed data indicated that there was no significant difference between any of the subdivisions and divisions, with or without the two samples in excess of 500 ppm, at p=0.05.

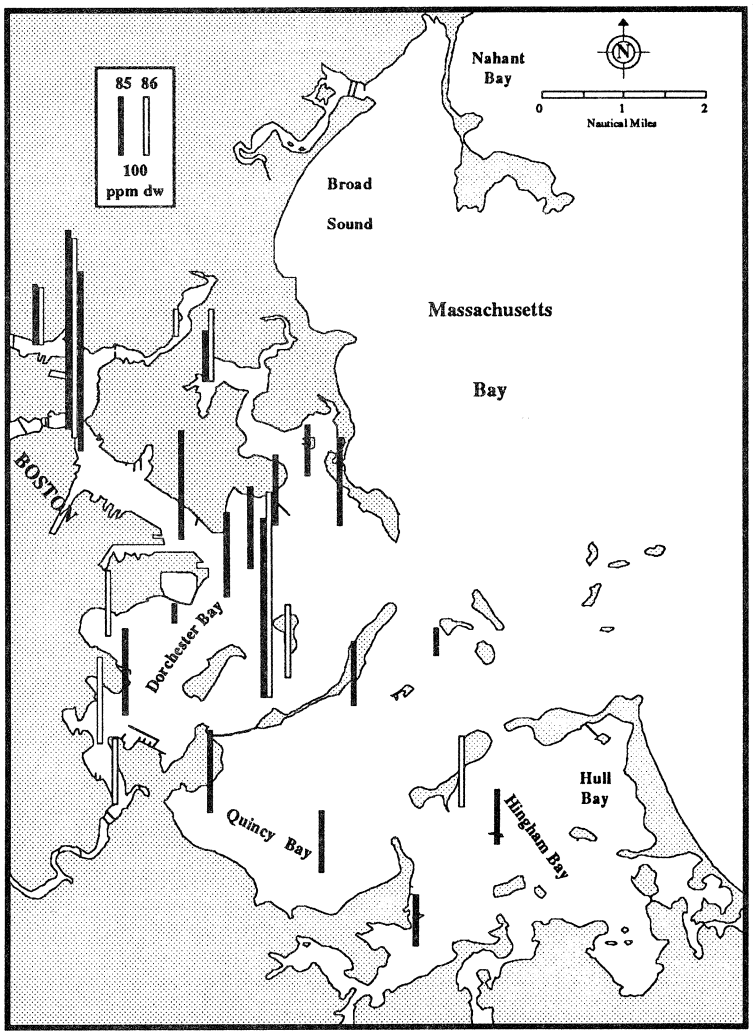


Figure 6.4. Copper concentrations (ppm dw) in the surficial sediments of Boston Harbor for 1985 and 1986 (Massachusetts DEQE, 1986; 1987).

In 1985 and 1986 the Massachusetts DEQE, as part of their annual Boston Harbor Water Quality and Wastewater Discharge Survey, analyzed 30 surficial sediment samples for copper content (Figure 6.4) (MA DEQE, 1986; 1987). They found an overall mean copper concentration of 137±92 ppm ranging from a low of 29 ppm, in a sample taken from northwestern Dorchester Bay,

to a high of 400 ppm, in a sample taken from the lower reaches of the Mystic River. The vast majority (80%) of the surficial sediment samples had copper concentrations between 10 and 200, while 20 percent of the samples had concentrations in excess of 200 ppm, and 5 percent of the samples had more than 300 ppm. While the means for the harbor divisions (Table 6.2) suggested a trend of decreasing copper levels from the inner harbor to the southeast harbor, statistical analysis of the log transformed data indicated no significant difference between any of the divisions at p=0.05. This trend can also be seen in Figure 6.4 that graphically displays the data by site and year. When the northwest harbor was subdivided, the Dorchester Bay area sediments had a mean concentration of 144±92 ppm, while the Winthrop Bay area sediments had a mean concentration of 104±24 ppm. Statistical analysis of the log transformed data indicated no significant difference between the two subdivisions or among the two subdivisions and the other three harbor divisions at p=0.05.

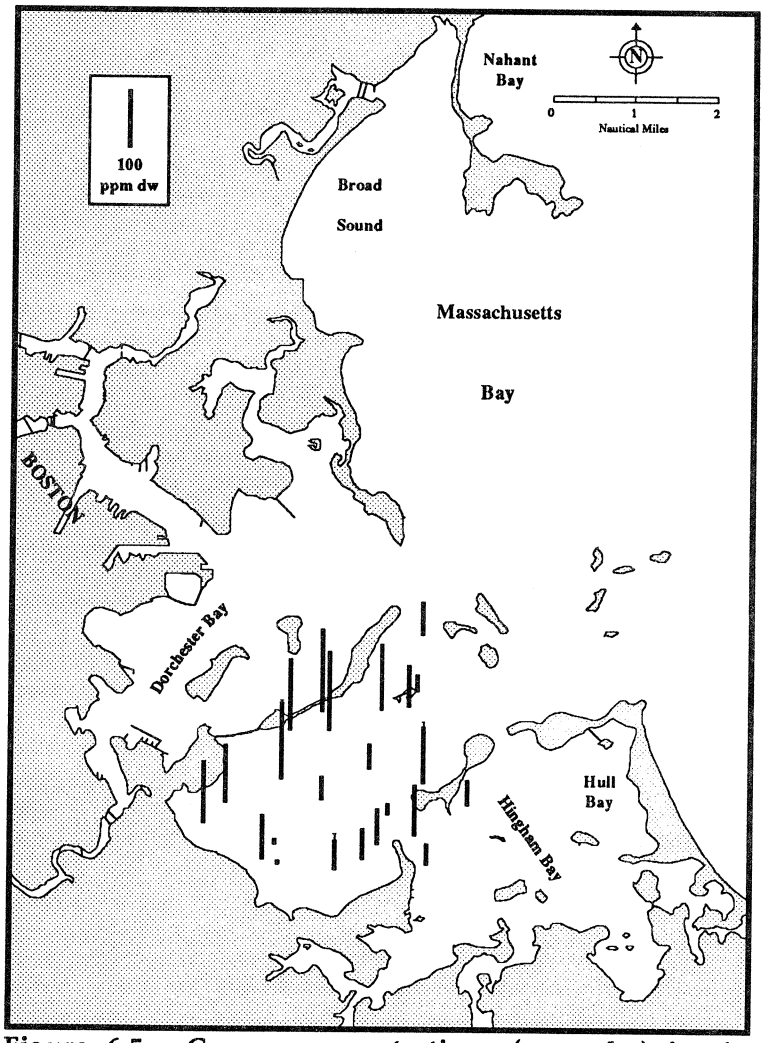


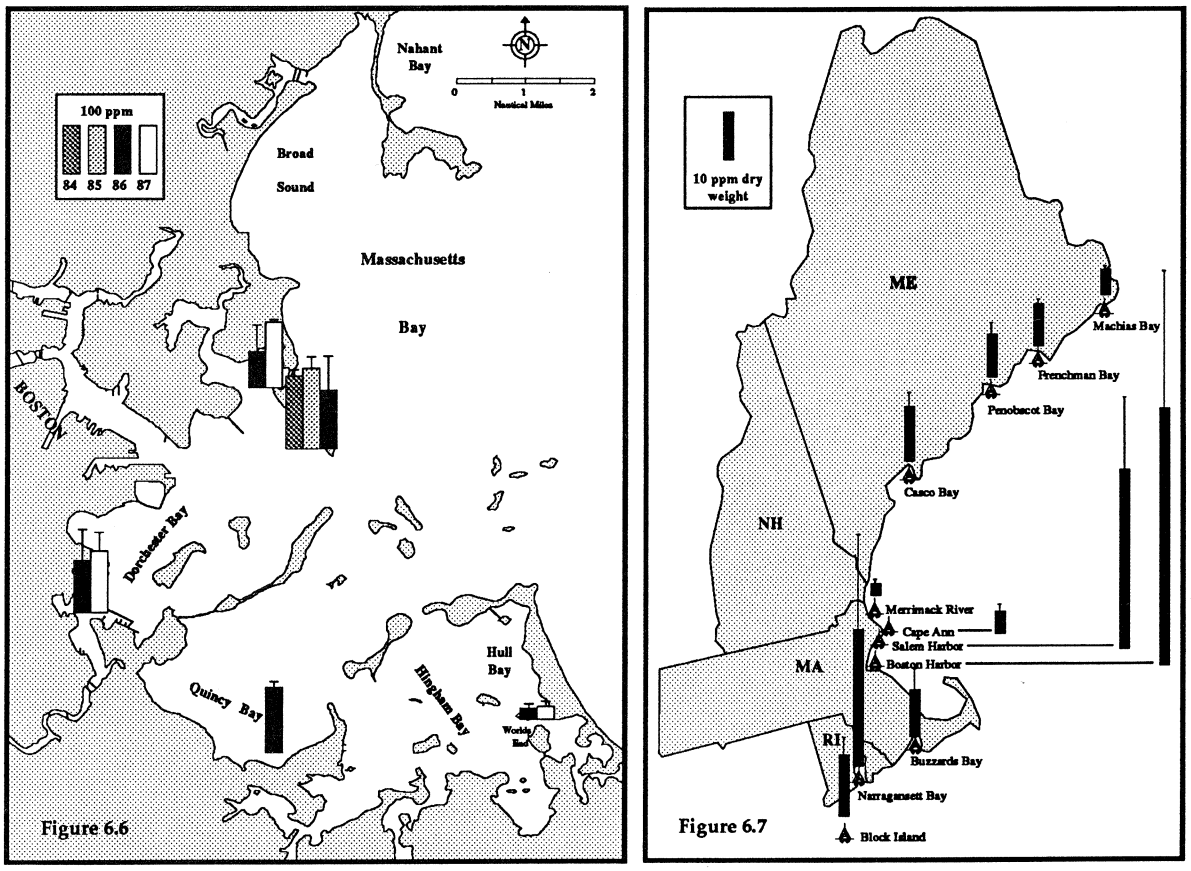
Figure 6.5. Copper concentrations (ppm dw) in the surficial sediments of Quincy Bay and environs based on 1987 grab sample data (U. S. EPA, 1988).

In 1987, a study of Quincy Bay was conducted under the auspices of the EPA (U.S. EPA, 1988) that was essentially restricted to the central harbor area. Figure 6.5 graphically displays the results of the grab sample analysis. Based on the analysis of 40 samples, the overall mean copper concentration in the surficial sediments for the study was 79±55 ppm with a range of 7 to 316 ppm.

NOAA's NS&T Program has sampled and analyzed surficial sediments from several sites around Boston Harbor for several analytes, including copper, since 1984. Figure 6.6 portrays this data graphically by year and site. The overall mean copper concentration in surficial sediments of the harbor was 108±57 ppm. Individual sample values ranged from 11 to 183 ppm. Site means, based on all 4 years of available data, ranged from 25±9 ppm at the site off the northern tip of Worlds End, to 146±41 ppm at the site southwest of Deer Island. The mean copper concentrations in the surficial sediments of the other sites were: northwest of Deer Island, 103±48 ppm; Dorchester Bay, 118±48 ppm; and Quincy Bay, 134±10 ppm. Statistical comparison of the log transformed data, indicated that the Worlds End site was significantly different from all the other sites at p=0.05. When the data were grouped by harbor divisions (Table 6.2), the means suggested that there was little difference in mean copper concentrations in the northwest and central harbor; but, the copper

concentrations were significantly lower in the southeast harbor. Statistical analysis of the log transformed data indicated that the southeast harbor was significantly different from both the northwest and central harbors at p=0.05. When the northwest harbor was subdivided, the Dorchester Bay area sediments had a mean concentration of 118±48 ppm, while the Winthrop Bay area sediments had a mean concentration of 130±47 ppm. Statistical analysis of the log transformed data indicated no significant difference between the two subdivisions, but they were both significantly different from the southeast harbor division, at p=0.05.

On a broader scale, between 1984 and 1987, the NOAA NS&T Program analyzed surficial sediment samples from 23 sites from 11 areas along the outer New England coast. Figure 6.7, which displays the means and standard deviations for the 11 coastal areas, clearly shows that the mean copper concentration of the NS&T Program sites in Boston Harbor (108±57 ppm) was higher than the means for all other areas sampled in New England. The only two areas that had mean copper concentrations approaching those of Boston Harbor were Salem Harbor (75±30 ppm) and Narragansett Bay (57±40 ppm). Statistical analysis of the log transformed data indicated that Boston Harbor was significantly different (p=0.05) from all the other areas of New England sampled except Salem Harbor and Block Island. A possible reason for the lack of a significant difference between Boston Harbor (mean copper concentration 108±57 ppm) and Block Island (mean copper concentration of 25±8 ppm) was the small sample size (three) for Block Island.



Figures 6.6 & 6.7. Mean copper concentrations (ppm dw) in the surficial sediments of Boston Harbor by site and year for 1984-87 (Fig. 6.6) and for the outer New England coast, based on combined data from NOAA's NS&T Program Benthic Surveillance and Mussel Watch projects (NOAA, unpublished) (bars represent one standard deviation). Note the order of magnitude difference in the scales.

When the mean copper concentrations in the surficial sediments of the individual New England NS&T Program sites were compared, the four sites with the highest mean copper concentrations were located in Boston Harbor (Table 6.3). In an attempt to determine a value for background copper levels, the overall mean was calculated for the five NS&T Program sites with the lowest copper concentrations in their surficial sediments (Table 6.3). This mean was 8.4±3.1 ppm. The overall mean copper concentration in the surficial sediments of Boston Harbor, based on the NS&T Program data, was more than an order of magnitude greater than this reference mean. The four Boston Harbor sites with the highest copper concentrations had means more than an order of magnitude higher than the reference mean. While the Boston Harbor site with the lowest mean copper concentration (Worlds End) was approximately 3 times higher than the reference mean.

Table 6.3. The five outer New England coast NOAA NS&T Program sites with the lowest and highest mean copper concentrations (ppm dw) based on data from 1984-1987.

Site	Mean	Standard Deviation	Count
MERRIMAC RIVER	4.7	1.9	5
GOOSEBURY NECK, BUZZARDS BAY	7.3	2.6	6
STRAITSMOUTH ISLAND, CAPE ANN	9.0	3.1	3
MACHIAS BAY, MAINE	10.8	1.2	7
PICKERING ISLAND, MAINE	10.9	2.0	3
MOUNT HOPE, NARRAGANSETT BAY	82	5	3
NORTHWESTERN DEER ISLAND	103	48	6
DORCHESTER BAY	118	48	6
QUINCY BAY	134	10	3
SOUTHWESTERN DEER ISLAND	146	41	10

Temporal Trends

Figure 6.8 compares the yearly mean copper concentrations in the surficial sediments of Boston Harbor, based on all the available data sets (White, 1972: Gilbert *et al.*, 1972: Isaac & Delaney, 1975: USACOE, 1972-88; 1981; 1988: MA DEQE, 1986; 1987: U.S. EPA, 1988: NOAA, unpublished). There is no overall temporal trend apparent from Figure 6.8, and the yearly fluctuations were more likely due to differences in sites sampled than any overall change in copper concentrations.

Data were available from the USACOE on dredging studies for most of the years from 1980 through 1988. When the yearly mean copper concentrations in the surficial sediments based on this data were calculated and the log transformed data compared, there was no significant difference between any of the years at $p=0.05$. One factor contributing to the lack of any statistically significant difference was the variation in the number of sites sampled each year, from 1 in 1975 and 1988 to 59 in 1986 (Table 6.4). In addition to the variability in the number of sites sampled each year, the sites themselves varied from year to year. Therefore, while the data sets would be expected to be internally consistent with regard to methodology, any conclusions concerning temporal trends based on the data must be viewed with extreme caution.

The only other available data that spanned more than 2 years was that from NOAA's NS&T Program Benthic Surveillance (1984-86) and Mussel Watch (1986-87) projects. The yearly mean copper concentrations in the surficial sediments of Boston Harbor based on this data, ranged from a high of 164±24 ppm in 1985 to a low of 96±56 ppm in 1987. The yearly means for 1984 and 1986 were 148±13 ppm and 92±58 ppm, respectively. There was no indication of any temporal trends in copper contamination. The difference in the yearly mean copper concentrations can be explained by the difference in the sites sampled each year (Figure 6.6).

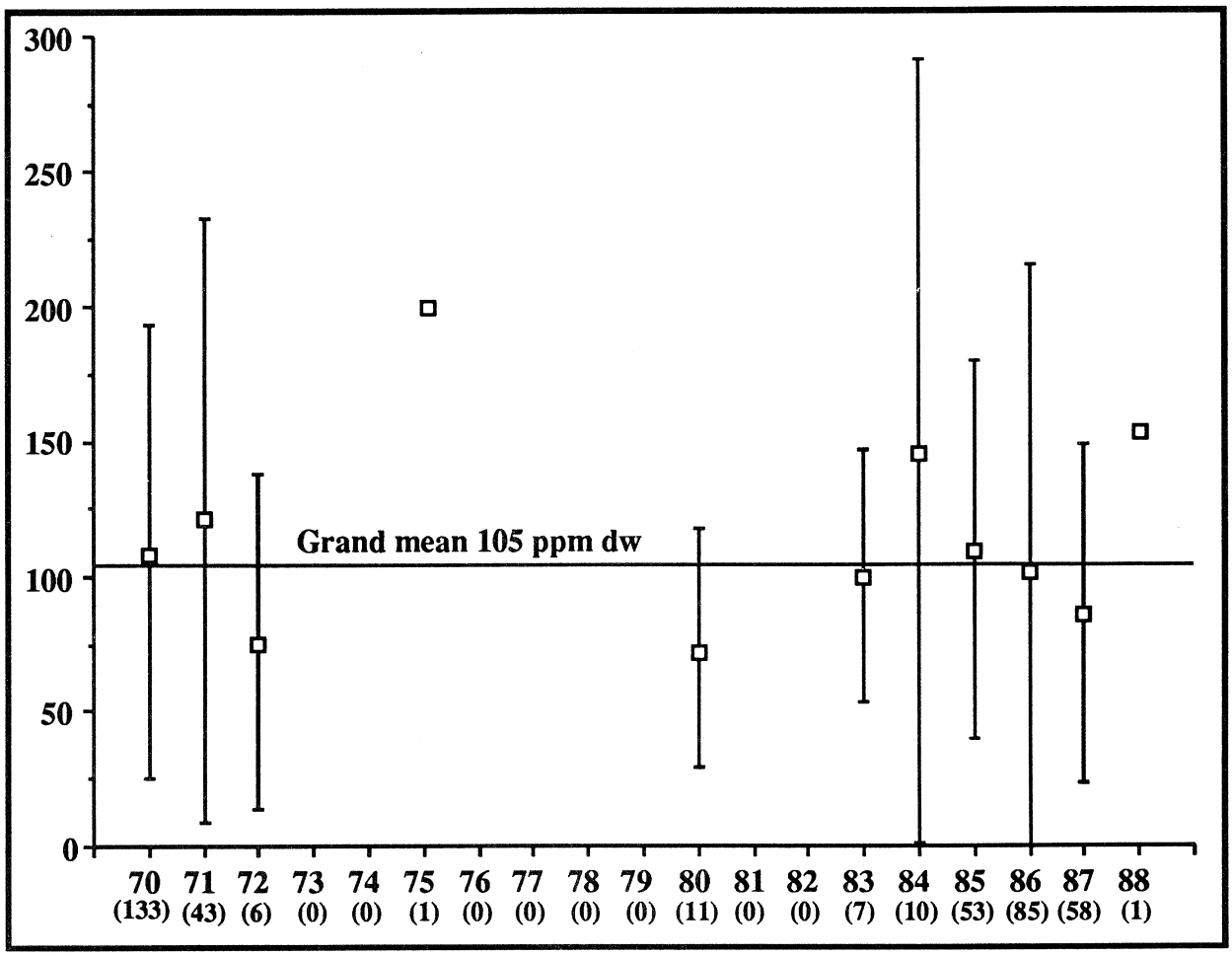


Figure 6.8. Yearly mean copper concentrations (ppm dw) in the surficial sediments of Boston Harbor, based on White (1972), Gilbert *et al.* (1972), Isaac & Delaney (1975), USACOE (1972-88, 1981, 1988), MA DEQE (1986, 1987), U.S. EPA (1988), and NOAA (unpublished). The bars represent one standard deviation and the numbers in parenthesis are the number of samples analyzed each year.

Table 6.4 Yearly mean copper concentrations (ppm dw) in Boston Harbor surficial sediments based on dredging study data from the USACOE.

Year	Mean	Standard Deviation	Count
1975	200	N/A	1
1980	73	44	11
1983	100	47	7
1984	145	177	7
1985	93	68	30
1986	93	122	59
1987	106	95	9
1988	153	N/A	1

Biota

Since 1976, over 250 tissue samples from a variety of organisms in Boston Harbor have been analyzed for copper content. Copper concentrations ranged from 0.17 ppm in the muscle of a winter flounder (*P. americanus*), to 644 ppm in the hepatopancreas of a lobster (*H. americanus*). Table 6.5 gives the statistics on copper contamination of biota by organism and tissue. The large difference between the mean and median copper concentration and the standard deviation for winter flounder muscle was due to a single sample with an extraordinarily high copper concentration, 14.6 ppm. This concentration was more than 2 1/2 times higher than the second highest reported copper concentration (5.20 ppm). If it was excluded from the calculations, the mean copper concentration in winter flounder muscle would become 0.73±0.93 ppm. The data for winter flounder and lobster in Table 6.5 suggest that copper tends to accumulate more in the liver or liver-like tissue than in muscle tissue. However, a problem arises in evaluating levels of copper contamination in lobster because copper is a component of the lobster respiratory pigment hemocyanin.

Table 6.5. Harborwide means, standard deviations, medians, ranges, and sample sizes (count) for copper concentrations (ppm dw) in biota by organism and tissues based on all the available data sets (* transplants).

		Mean	Standard Deviation	Median	Range	Count
P. americanus						
	liver	19.8	15.4	17.0	0.44-60.1	36
	muscle	1.23	2.77	0.60	0.17-14.6	28
H. americanus						
	hepatopancreas	293	221	306	39.0-621	8
	muscle	53.3	38.2	46.2	11.6-176	48
M. arenaria						
	soft parts	32.5	8.37	31.4	12.3-48.2	36
M. edulis						
	soft parts	10.6	2.85	10.0	6.37-22.2	86
*C. virginica**						
	soft parts	10.1	3.10	9.50	7.40-13.9	4

Geographic Trends

There were no clear geographic trends in the copper content of biota within Boston Harbor based on an overview of all the biota data broken down by division (Table 6.6). The mussel data suggested that the northwest and southeast harbor biota contained approximately the same levels of copper. The biota of these harbor divisions contained slightly higher levels of copper than did the biota from the inner and central harbor. While the flounder liver data suggested the central harbor biota contained slightly more copper than the inner and northwest harbor biota. Both the winter flounder and lobster muscle data suggested that the northwest harbor biota were significantly more contaminated than that of the central harbor. However, when the high value for copper in flounder muscle was excluded from the calculations, there was virtually no difference in copper levels between the northwest and central harbor biota. Caution is needed in comparing data from different species. Mussels are sedentary and can be assumed to represent copper levels in the area where they are collected. Lobster and flounder are motile organisms and, therefore, may not be representative of environmental copper levels in the area of collection.

In 1976, the EPA sampled mussels and other bivalves from 107 sites nationwide and analyzed the samples for a variety of metals and organic analytes, including copper (Goldberg *et al.*, 1978). A composite sample of *M. edulis* from a site on the northwest side of Deer Island was found to have a copper concentration in the soft parts of 6.5 ppm. Between

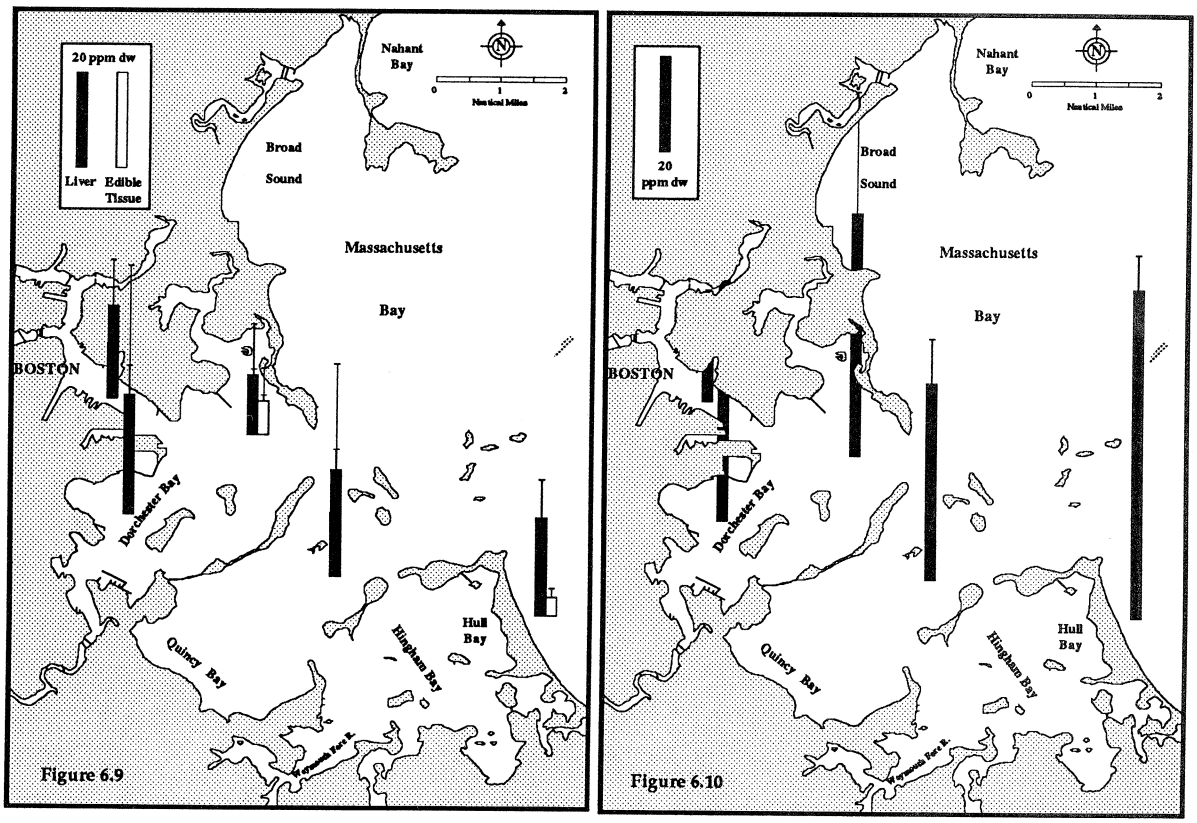
Block Island and the Canadian Border, 11 other New England sites were sampled and had copper concentrations in the soft parts of *M. edulis* ranging from 4.3 ppm from the Cape Cod Canal to 7.0 ppm at Bailey Island, Maine. Boston mussels had the second highest concentration of copper among the 11 sites.

Table 6.6. Mean copper concentrations (ppm dw) of the entire harbor and the four divisions in various organisms and tissues (the number in parentheses is the sample size).

	P. americanus		*H. americanus*	*M. edulis*
	liver	muscle	muscle	soft parts
OVERALL	19.8 (36)	1.23 (28)	53.9 (88)	10.6 (86)
INNER HARBOR	19.5 (4)	NA	20.8 (2)	9.47 (29)
NORTHWEST HARBOR	19.6 (28)	6.98 (3)	77.1 (28)	12.74 (19)
CENTRAL HARBOR	22.2 (4)	0.54 (25)	19.8 (18)	9.86 (29)
SOUTHEAST HARBOR	NA	NA	NA	12.02 (9)

In 1979, as a part of the 301h waiver application for the Deer Island and Nut Island sewage treatment plants, winter flounder (*P. americanus*) and lobster (*H. americanus*) tissue samples from five sites in and around Boston Harbor were analyzed for levels of several analytes, including copper (Metcalf and Eddy, 1984). The livers of four winter flounder from each of four different sites in Boston Harbor and one site outside the Harbor (Nantasket Beach) were analyzed for copper levels. The values for the individual samples ranged from 2.1 to 57 ppm with both specimens coming from the Dorchester Bay site. The mean copper concentrations in livers for the five sites ranged from 12.5±10.4 ppm, at the President Roads site, to 25.0±27.0 ppm, at the Dorchester Bay site (Figure 6.9). The Inner Harbor, Nantasket Beach, and Nut Island Discharge sites had means of 19.5±9.5, 20.4±7.81, and 22.2±22.3 ppm, respectively. When the data were log transformed and analyzed, none of the sites was significantly different at p=0.05. When the data were looked at concerning the harbor divisions, the means for the three divisions sampled had a range of less than 4 ppm. This suggested that while copper concentrations in the levels of individual winter flounder may show a high degree of variability; there was little difference in mean copper levels from the various harbor divisions. This was supported by statistical analysis of the log transformed data that found no significant difference between any of the harbor divisions (p = 0.05). Also, no differences were found between any of the divisions and the Nantasket Bay site (p = 0.05). Unfortunately, only five edible tissue samples (three samples from President Roads and two samples from Nantasket Beach) were analyzed for copper. The copper concentrations in individual specimens ranged from 1.2 to 14.6 ppm. Both specimens came from the President Roads site. The mean copper concentrations in winter flounder edible tissue at the two sites were 3.88 ppm at the Nantasket Beach site and 6.86 ppm at the President Road site (Figure 6.9). The President Roads site included a specimen containing 14.6 ppm copper, more than twice that of the second highest value reported for copper in edible tissue. When this value was excluded from the calculations, the mean for the President Roads site became 3.19 ppm.

From the same five sites, two lobsters each were collected and claw and tail muscle tissue was analyzed for levels of copper. Copper concentrations in the individual specimens ranged from less than 19.0 to 73.9 ppm. The means for the five sites ranged from 20.8 ppm at the Inner Harbor site to 70.4 ppm at the Dorchester Bay site. The Nantasket Beach, President Roads, and Nut Island Discharge sites had means of 68.6, 50.9, and 41.2 ppm, respectively (Figure 6.10). None of the sites were significantly different based on analysis of the log transformed data (p=0.05). When the lobster muscle data were grouped by division, the northwestern harbor had the highest mean copper concentration (60.7 ppm), followed by the central harbor (41.2 ppm), and then the inner harbor (20.8 ppm). Statistical analysis of the log transformed data indicated no significant difference between any of the divisions nor between any of the divisions and the Nantasket Beach site at p=0.05.



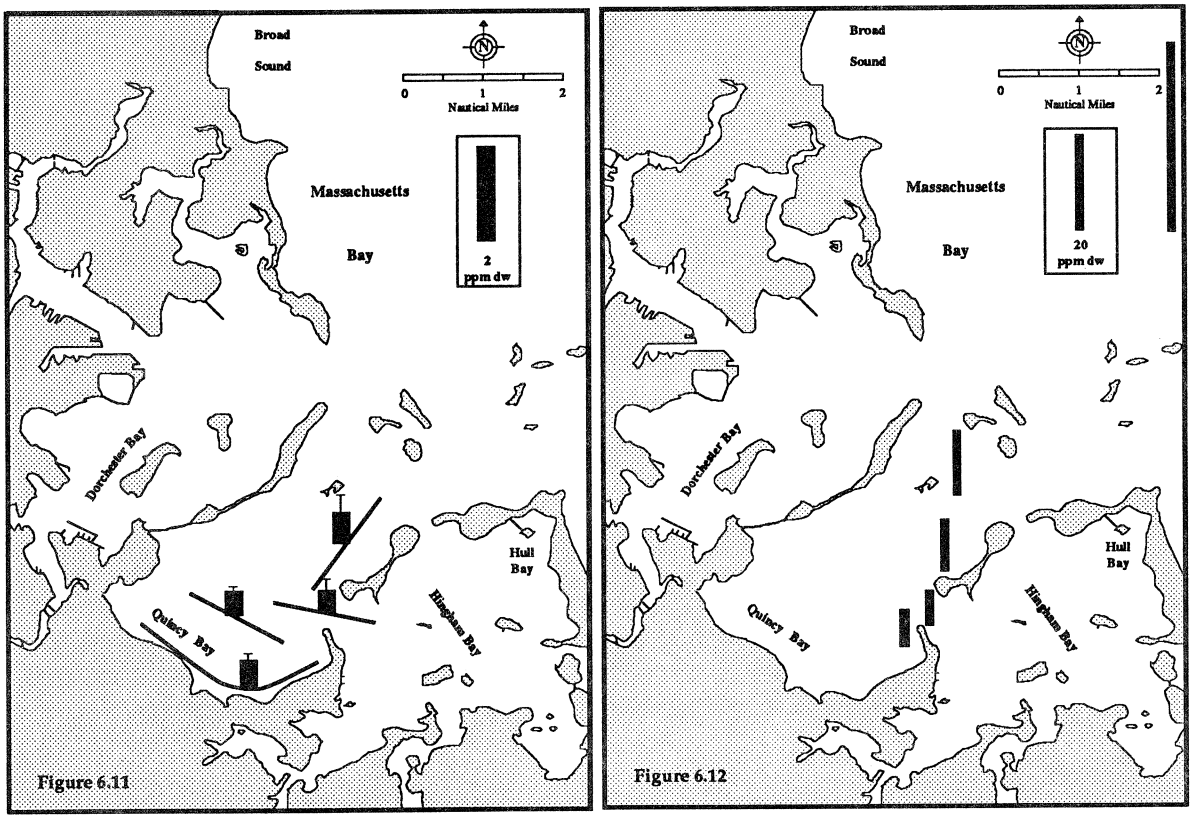
Figures 6.9 & 6.10. Mean copper concentrations (ppm dw) in the liver and edible tissue of *P. americanus* (Fig. 6.9) and muscle tissue of *H. americanus* (Fig. 6.10) sampled from Boston Harbor in 1979 (Metcalf & Eddy, 1984) (bars represent one standard deviation).

In 1985 and 1986, lobster (*H. americanus*) and soft-shelled clams (*M. arenaria*) were collected from Boston and Salem harbors and analyzed for various analytes, including copper, as part of a study of contaminants in marine resources (Wallace *et al.*, 1988). The mean copper concentration of the combined claw and muscle tissue of 24 lobsters collected around Deer Island was 79.8±33.5 ppm with a range of from 37.9 to 175 ppm. Lobsters were collected from two sites in Salem Harbor, the treatment plant outfall and Willows Pier. The mean copper concentrations in combined claw and tail muscle tissue based on the analysis of 25 lobsters per site were 48.9±15.7 and 41.6±17.2 ppm, respectively. Statistical analysis of the log transformed data indicated that copper concentration in the muscle tissue of Deer Island lobsters was significantly different from that for either of the two Salem Harbor sites at p=0.05. The mean copper concentration for 34 soft-shelled clams from Wollaston Beach in Quincy Bay was 33.7±7.1 ppm with a range of 24.1 to 48.2 ppm.

An intensive study of Quincy Bay was conducted in 1987 (U.S. EPA, 1988). The study included the analysis for copper levels in the tissues of native winter flounder (*P. americanus*), lobsters (*H. americanus*), soft-shelled clams (*M. arenaria*), and transplanted oysters (*C. virginica*) (EPA, 1988). The muscle tissue of from five to seven winter flounder from each of four different trawl transects was analyzed for copper content. The copper concentrations in individual samples ranged from a low of 0.17 ppm to a high of 1.12 ppm, while the means for the individual trawls ranged from 0.47±0.21 to 0.64±0.37 ppm (Figure 6.11). Statistical analysis of the log transformed trawl data indicated no significant difference between any of the trawls at p=0.05.

Oysters (*C. virginica*) were collected from a commercial bed located in Cotuit Bay, Cotuit, Massachusetts. They were deployed at four sites in Quincy Bay and one site at The Graves

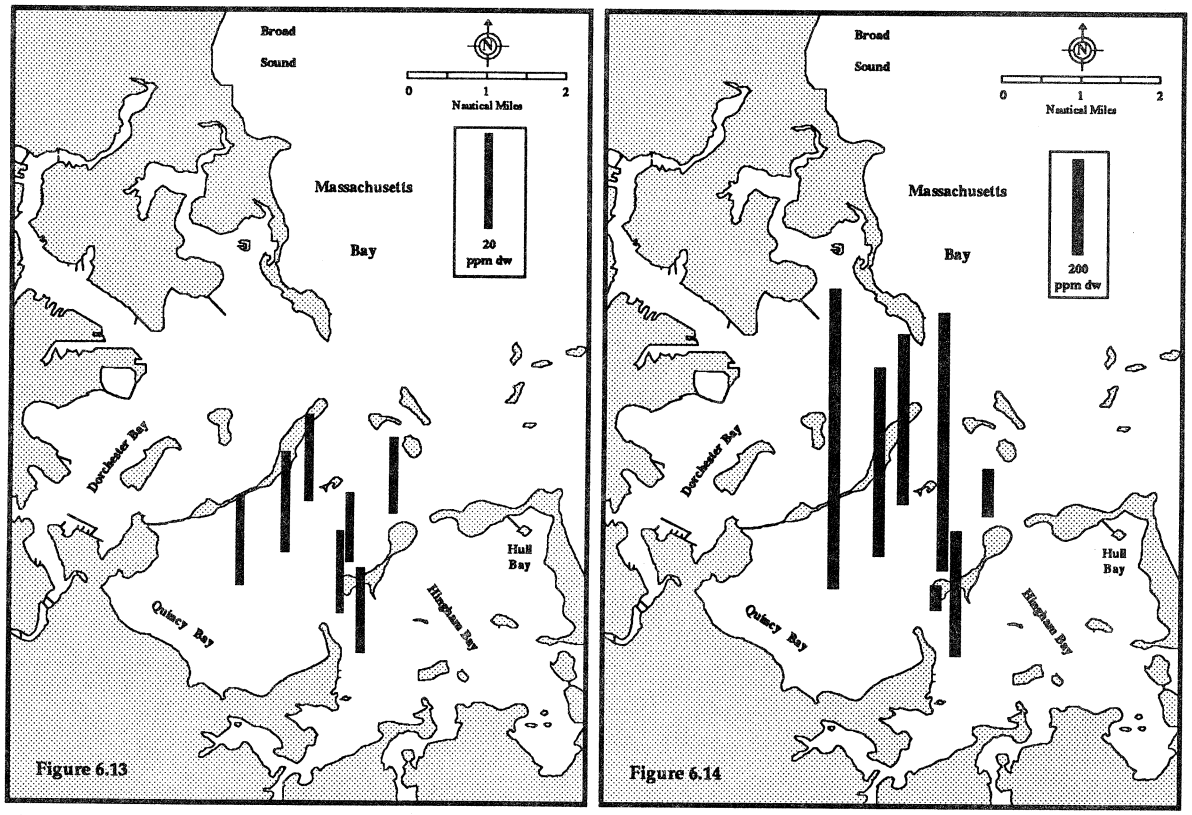
Graves in Massachusetts Bay from June 5 through July 16, 1987. The copper concentrations in the oysters at the four sites ranged from 7.4 to 13.9 ppm. The oysters from The Graves had 40.2 ppm copper; while those from the source bed in Cotuit Bay had a copper concentration of 13.4 ppm (Figure 6.12). Two samples of the soft-shelled clam from around Moon Island, Quincy Bay also were analyzed for copper and were found to have concentrations of 12.3 and 14.2 ppm.



Figures 6.11 & 6.12. Mean copper concentrations (ppm dw) in the edible tissue of *P. americanus* from Boston Harbor (Fig. 6.11) and in whole transplanted *C. virginica* (Fig. 6.12) in 1987 (U.S. EPA, 1988) (bars represent one standard deviation). Note the order of magnitude difference in the scales.

Both the tail muscle and the hepatopancreas of lobsters from seven sites were analyzed for levels of copper content. Two replicate samples from the tail muscles of a total of 16 lobsters; 2 to 3 from each of the seven sites were analyzed. The copper concentrations in the individual samples ranged from 10.1 to 24.6 ppm while the mean tail muscle concentrations for the seven sites ranged from 14.2 ppm to 20.6 ppm (Figure 6.13). There was no significant difference in tail muscle copper levels among sites based on statistical analysis of the log transformed data ($p=0.05$). Two replicate samples of hepatopancreas from 8 of the 16 lobsters (1 each from six of the sites and 2 from the remaining site) were also analyzed for copper. Copper concentrations for the individual specimens ranged from 40.0 to 621 ppm (Figure 6.14). Copper concentrations in the hepatopancreas of three of the specimens were less than 100 ppm, while five had concentrations in excess of 250 ppm.

NOAA's Mussel Watch Project, a part of the NS&T Program, has sampled mussels (*M. edulis*) on an annual basis from four sites in and around Boston Harbor since 1986. Three whole-body composite samples from each site were analyzed for a variety of analytes including copper. The overall mean concentration of copper in the mussels for the three sites in Boston Harbor from 1986 through 1988 was 12.7±2.4 ppm with a range of from 9.6 to 18.0



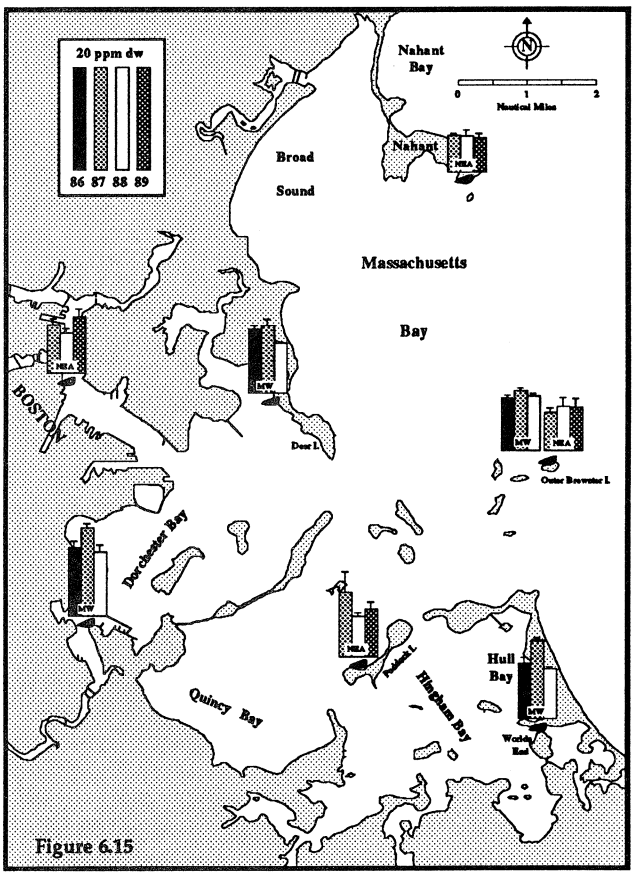
Figures 6.13 & 6.14. Mean copper concentrations (ppm dw) in the tail muscle (Fig. 6.13) and hepatopancreas tissue (Fig. 6.14) of *H. americanus* sampled in 1987 (U.S. EPA, 1988) (bars represent one standard deviation). Note the order of magnitude difference in the scales.

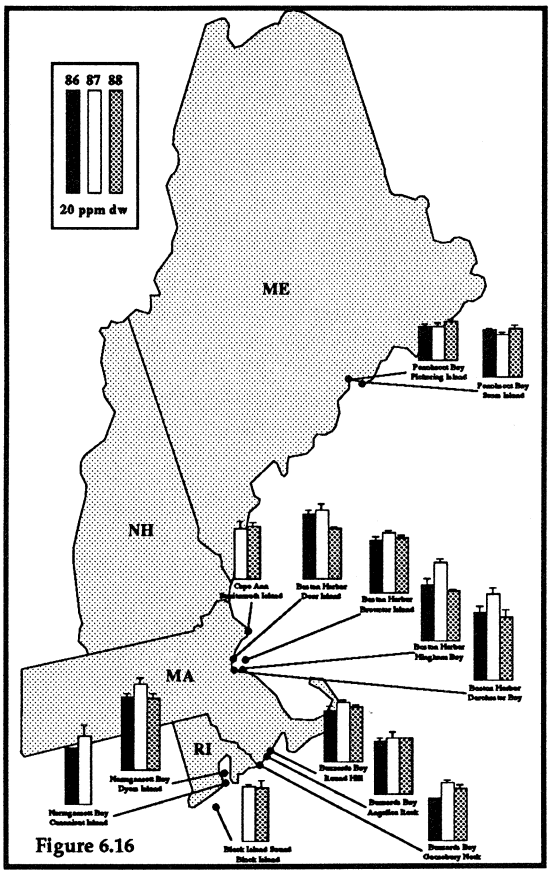
ppm. The means for the individual sites were 11.9±1.7 ppm northwest of Deer Island, 12.0±2.6 ppm in Hingham Bay off Worlds End, and 14.2±2.4 ppm in southwestern Dorchester Bay. Mussels from the site outside the Harbor, Outer Brewster Island, had a mean copper concentration of 10.9±0.8 ppm (Figure 6.15). Statistical analysis of the log transformed data for the four sites indicated that only the Dorchester Bay and Brewster Island sites were significantly different (p=0.05).

Since 1987, the NEA has conducted their own Mussel Watch Program (Robinson *et al.*, 1990. They sample mussels from two sites within Boston Harbor and two sites in Massachusetts Bay, including the same site on Outer Brewster Island which NOAA's Mussel Watch samples. The mean copper concentration in Boston Harbor, based on data from the two sites for the 3 years from 1987 through 1989, was 9.7±2.5 ppm with a range of from 6.4 to 22.2 ppm. The means for the two sites were 9.9±3.0 ppm at the Peddocks Island site and 9.5±1.8 ppm at the Central Wharf, Boston site. The two sites from Massachusetts Bay had means of 7.0±0.9 ppm at the Pumphouse Beach, Nahant site and 8.2±1.6 ppm at the Outer Brewster Island site. When the data for the four sites is log transformed and the sites statistically compared, the Pumphouse Beach site was found to be significantly different from the other three sites and the Peddocks Island and Brewster Island sites were significantly different at p=0.05. Figure 6.15 plots the NEA data alongside the NOAA Mussel Watch data.

On a broader scale, the Boston Harbor NS&T sites were compared to the other outer New England coast NS&T Mussel Watch sites (Table 6.7 and Figure 6.16) and the log transformed data were statistically analyzed. All three Boston Harbor sites were significantly different from the New England site with the lowest mean copper

concentration in mussels, Pickering Island in Penobscot Bay, (p=0.05). The Boston Harbor site with the highest mean copper concentration in mussels, Dorchester Bay, was significantly different from the five New England sites with the lowest copper concentrations in mussels (p=0.05). The only significant difference between any of the 13 New England Mussel Watch sites was between the Pickering Island site, which had the lowest mean copper concentration in mussels and all the other sites; and between the Dyers Island site, which had the highest mean copper concentration and the eight sites with the lowest copper concentrations in mussels (Table 6.7) at p=0.05. From this data it appears that copper levels in mussels vary little throughout New England with the range of means being just over a factor of 2. When a reference value is calculated, based on the five sites with the lowest mean copper concentrations in mussels, a value of 9.3±1.6 ppm is obtained. The Boston Harbor sites have mean copper values of from 1.3 to 1.5 times higher than this reference value. On a national scale, the Mussel Watch sites where *M. edulis* was sampled had mean copper concentrations ranging from 5.4 to 20.8 ppm with an overall mean for all the sites of 11.2±6.2 ppm. The means for 56 percent of the sites were less than 11.0 ppm. Only 12 percent of the sites had concentrations greater than 15.0 ppm. When the sites where *M. californianus* was sampled were included in the calculations, the overall mean became 10.2±5.4 ppm. The means for 69 percent of the sites were less than 11.0 ppm and only 8 percent had means greater than 15.0 ppm. Based on this data, Boston Harbor mussels appeared to be only moderately contaminated with copper since all the harbor sites had means between 11.00 and 15.00 ppm.





Figures 6.15 & 6.16. Mean copper concentrations (ppm dw) in the soft-parts of *M. edulis* by site and year in and around BostonHarbor for 1986-89 (Fig. 6.15) and at the outer New England coast NS&T Program Mussel Watch sites for 1986-88 (Fig. 6.16) (NOAA, unpublished; Robinson *et al.*, 1990) (bars represent one standard deviation).

Table 6.7. The mean copper concentrations (ppm) in *M. edulis* at the 13 outer New England coast NS&T Program Mussel Watch sites. The outlined means are for Boston Harbor sites.

Site	Mean	Standard Deviation	Count
DYERS ISLAND, NARRAGANSETT BAY	15.1	1.6	9
DORCHESTER BAY, BOSTON HARBOR	14.2	2.4	9
CONANICUT ISLAND NARRAGANSETT BAY	12.2	1.8	6
HINGHAM BAY, BOSTON HARBOR	12.0	2.6	9
DEER ISLAND, BOSTON HARBOR	11.9	1.7	9
OUTER BREWSTER ISLAND	10.9	0.8	9
ROUND HILL, BUZZARDS BAY	10.8	1.0	9
BLOCK ISLAND, RHODE ISLAND	10.6	0.9	6
ANGELICA ROCK, BUZZARDS BAY	10.5	0.9	11
GOOSEBURY NECK, BUZZARDS BAY	10.2	1.3	8
CAPE ANN, STRAITSMOUTH ISLAND	10.0	0.9	6
SEARS ISLAND, PENOBSCOT BAY	9.1	0.7	9
PICKERING ISLAND, PENOBSCOT BAY	7.0	0.6	9

NOAA's Benthic Surveillance Project, a part of the NS&T Program has sampled winter flounder (*P. americanus*) on an annual basis since 1984, from an area just west of Deer Island. The mean copper concentration in the liver of the fish sampled in 1984 and 1985 was 19.9±13.8 ppm with a range of 0.44 to 60.1 ppm. The mean concentration of copper in flounder livers for all the New England Benthic Surveillance sites, excluding Boston Harbor, ranged from a low of 21.7±22.3 ppm at the Salem Harbor site to a high of 69.0±35.8 ppm at the Casco Bay site (Figure 6.17). The mean copper concentration of winter flounder liver from Boston Harbor was lower than the mean for any other New England site. Statistical analysis of the log transformed data indicated that the Boston Harbor site was significantly different from the Casco Bay and Merrimac River sites; and, the Casco Bay site was significantly different from all but the Merrimac River site at p=0.05. The Merrimac River site was also significantly different from the Salem Harbor site. The lowest reported value for copper in a single sample was 0.44 ppm from one of the Boston Harbor specimens. This value was less than one fifth the second lowest value reported for all the New England sites (2.2 ppm) and was an order of magnitude lower than the second lowest value for a Boston Harbor sample (4.7 ppm). When this exceptionally low value was excluded from the calculations, the Boston Harbor mean became 20.9±13.5 ppm. This was still the lowest mean for all the New England sites and there was no change in the statistical analysis results. No comparison could be made between Boston Harbor and the three northern-Maine sites; because a different species, longhorn sculpin (*M. octodecemspinosus*), was sampled at these sites. The Benthic Surveillance Project sampled winter flounder at four other sites during the same time frame: two in Long Island Sound and one each in Raritan and Great bays in New Jersey. All four site means were greater than the mean for Boston Harbor; they ranged from a low of 23.1±17.8 ppm (West Long Island Sound) to a high of 54.4±22.1 ppm (Great Bay).

Temporal Trends

No temporal trends in the copper levels of Boston Harbor biota could be determined based on the available data because of a lack of consistent data sets. The only internally consistent data sets sampling the same organism from the same locations over a number of years were the NS&T Program's Benthic Surveillance and Mussel Watch projects and the NEA Mussel Watch program. Data for these projects were only available for 2, 3, and 3, years respectively. Between 1984 and 1985 there was approximately a 60 percent increase in the level of copper in winter flounder livers (15.1±7.5 to 24.7±17.3 ppm) (Figure 6.17) which was significantly different at p=0.01. However, whether this indicates a trend in levels of

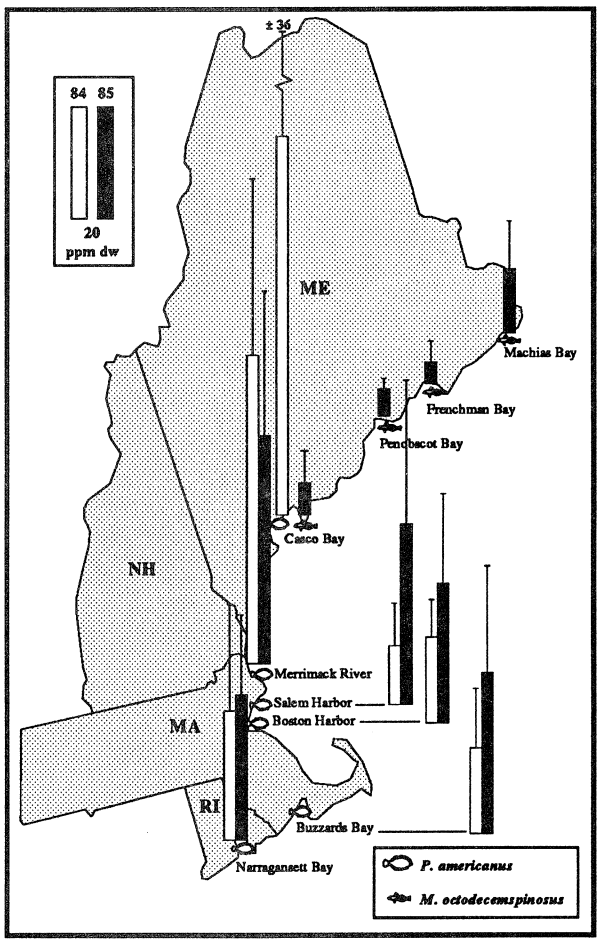


Figure 6.17. Mean copper concentrations (ppm dw) in the liver tissue of *P. americanus* and *M. octodecemspinosus* along the outer New England coast for 1984 and 1985 (NOAA, unpublished) (bars represent one standard deviation).

copper contamination in Boston Harbor biota or is just due to random sampling could not be determined based on only 2 years. Likewise, the 3 years of data for *M. edulis* from the NS&T Program Mussel Watch Project failed to indicate any trend with copper levels slightly increasing between 1986 and 1987 and then decreasing in 1988 (Figure 3.15). The yearly means were 12.3±1.4 for 1986, 15.2±1.8 for 1987, and 10.7±1.5 ppm for 1988. The yearly means for the NEA Mussel Watch Program showed no apparent trend, decreasing from 11.0±3.3 ppm (1987) to 8.0±0.7 ppm (1988) and then increasing to 10.1±1.7 ppm (1989). The EPA Deer Island site had a copper concentration in the soft parts of mussels of 6.5 ppm in 1976. It was compared to the NS&T Program Deer Island site (which is about 0.5 miles northwest of the EPA site) with yearly means of 12.7, 13.3, and 9.8 ppm in 1986, 1987, and 1988, respectively. There appeared to be an approximate twofold increase in copper concentrations in the 11 years between 1976 and 1987 although there appeared to be a decrease in copper levels between 1987 and 1988. However, this comparison needs to be viewed with caution because the EPA value was based on only one composite sample while the NS&T Program values were based on three composite samples each. Also, the difference between the EPA value and the NS&T Program values may be the result of differences in laboratory methodology.

Summary

Boston Harbor sediments were found to contain copper at levels that exceeded background levels by more than an order of magnitude. When the overall mean value of copper in Boston Harbor (105±91 ppm) was compared to the overall mean of San Francisco Bay (51±58 ppm) (Long *et al.*, 1988), it was found to be more than 2 times higher than the San Francisco Bay mean. When just the NS&T Program data for the two ports were compared, the Boston Harbor mean, 108±57 ppm, was more than 2 times higher than the San Francisco Bay mean, 49±24 ppm (Long *et al.*, 1988) (Table 6.8). The overall data set indicated a trend of decreasing copper concentrations in Boston Harbor surficial sediments from the inner harbor towards the southeastern harbor and towards the mouth. This trend was also apparent in four of the five individual data sets that covered most of the Harbor (White, 1972; Gilbert *et al.*, 1972; Massachusetts DEQE, 1986 and 1987; NOAA, unpublished). A fifth data set, Isaac and Delaney (1975), indicated a trend of decreasing copper concentrations from the northwest to the southeast harbor; but, the lowest value for copper was in the inner harbor. However, this low value was based on just one sample that may not be representative of the entire inner harbor. No clear temporal trends were apparent with regard to copper concentrations in the surficial sediment.

Table 6.8. Comparison of copper sediment statistics for Boston Harbor, NS&T Program Reference (based on the five New England sites with the lowest copper levels), and San Francisco Bay in ppm dw. Statistics for San Francisco Bay derived from Long *et al.*, 1988.

Area	Mean	Standard Deviation	Median	Range	Count
Boston	105	91	83	0.2 - 785	408
NS&T Program Boston	108	57	131	11.0 - 183	31
NS&T Program Reference	8	3	9	3.5 - 12	24
San Francisco Bay	51	58	46	1.0 - 1500	879
NS&T Program San Francisco Bay	49	24	52	9.1 - 130	40

Based on the available data, Boston Harbor biota appears to be moderately to highly contaminated with copper. Boston Harbor mussels (*M. edulis*) had some of the highest mean copper concentrations of all the New England NS&T Program sites sampled. When compared to all NS&T Program mussel sites sampled in the country, approximately 77 percent of the sites had means lower than Boston Harbor sites, while 8 percent had means higher than the Boston Harbor sites. However, the winter flounder (*P. americanus*) liver data suggested that Boston Harbor had only low levels of copper, since among the NS&T Program sites the Boston site had the lowest mean copper concentration among all the winter flounder sites. The winter flounder and lobster (*H. americanus*) tissue data suggested that copper tends to accumulate more in liver or liver-like tissue than in muscle tissue. There were no obvious geographic or temporal trends in copper content of biota within Boston Harbor based on the available data. This is because relative concentrations between different areas of the Harbor varied with the organism and tissue sampled. With the exception of the NS&T Program and the NEA Mussel Watch Program, none of the studies sampled the same organism from the same sites over a period of years.

CHROMIUM

Chromium is a naturally occurring element that functions both as an essential trace element and as a biocide. The majority of environmentally important chromium compounds are composed of either the trivalent (Cr^{+3}) or hexavalent (Cr^{+6}) form of chromium (Eisler, 1986). The trivalent form is the least toxic of the two and is the one that functions as an essential trace element (Eisler, 1986). In addition to being affected by the valency, chromium toxicity is also affected by environmental conditions including: temperature, pH, salinity, and alkalinity (Eisler, 1986). In a review of the literature, Long and Morgan (1990) found data suggesting that chromium levels in sediment below about 80 ppm have little or no effect on biota, while levels of 145 ppm or greater generally have either chronic or acute effects on biota.

As with lead, there is some concern over the reliability of chromium concentration data from biological samples (Eisler, 1986). In a study involving 87 laboratories (Fukai *et al.*, 1978), an oyster homogenate with an average concentration of 1.1 ppm was reported as having a concentration of from 0.6 to 1.6 ppm by 67 percent of the laboratories; while 33 percent of the laboratories reported concentrations outside this range.

Sediments

Since the late 1960s, over 400 surficial sediment samples from Boston Harbor have been analyzed for chromium concentrations. Based on this data, the overall mean concentration of chromium in the surficial sediments of the Harbor was 133 ppm with a standard deviation of 101 and a reported range of from 0.03 to 666 ppm (Table 7.1). The median concentration was 110 ppm. The large standard deviation and the difference between the mean and the median values are because approximately 6 percent of the samples analyzed had concentrations greater than 300 ppm. The vast majority of the samples, approximately 78 percent, had values between 10 and 200 ppm inclusive, and approximately 2 percent of the samples contained less than 10 ppm chromium.

Table 7.1. Means, standard deviations, medians, ranges, and number of samples (count) for chromium concentrations (ppm dw) in surficial sediments for all of Boston Harbor and the four regions of the harbor, based on all the available data sets.

	Mean	Standard Deviation	Median	Range	Count
OVERALL	133	101	110	0.03 - 666	404
INNER HARBOR	166	125	153	0.03 - 666	109
NORTHWEST HARBOR	145	96	125	12 - 480	147
CENTRAL HARBOR	107	81	85	4 - 433	85
SOUTHEAST HARBOR	86	54	70	18 - 234	63

Geographic Trends

When the combined data set was broken down into the four harbor divisions, both the means and medians suggested a trend of decreasing chromium concentrations in a northwest to southeast direction. The surficial sediments of the inner harbor had the highest levels of chromium (166 and 153 ppm). Those of the northwest harbor had the second highest (145 and 125 ppm), followed by the central harbor (107 and 85 ppm), and then the southeast harbor (86 and 70 ppm) (Table 7.1). The northwest harbor was subdivided into the Winthrop Bay area north of President Roads and the Dorchester Bay area south of President Roads. Based on the means, the Winthrop Bay area (152 ppm) had the second highest levels of chromium and the Dorchester Bay area (138 ppm) had the third.

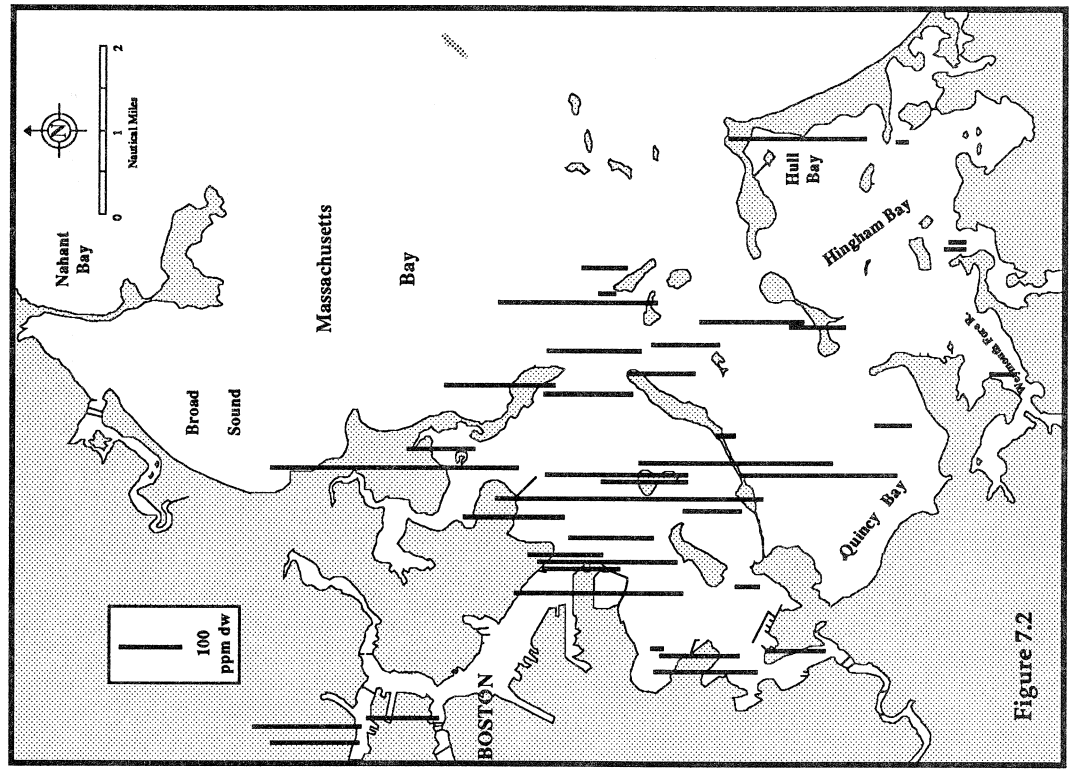
However, the medians (122 and 125 ppm, respectively) indicated virtually no difference between the two areas.

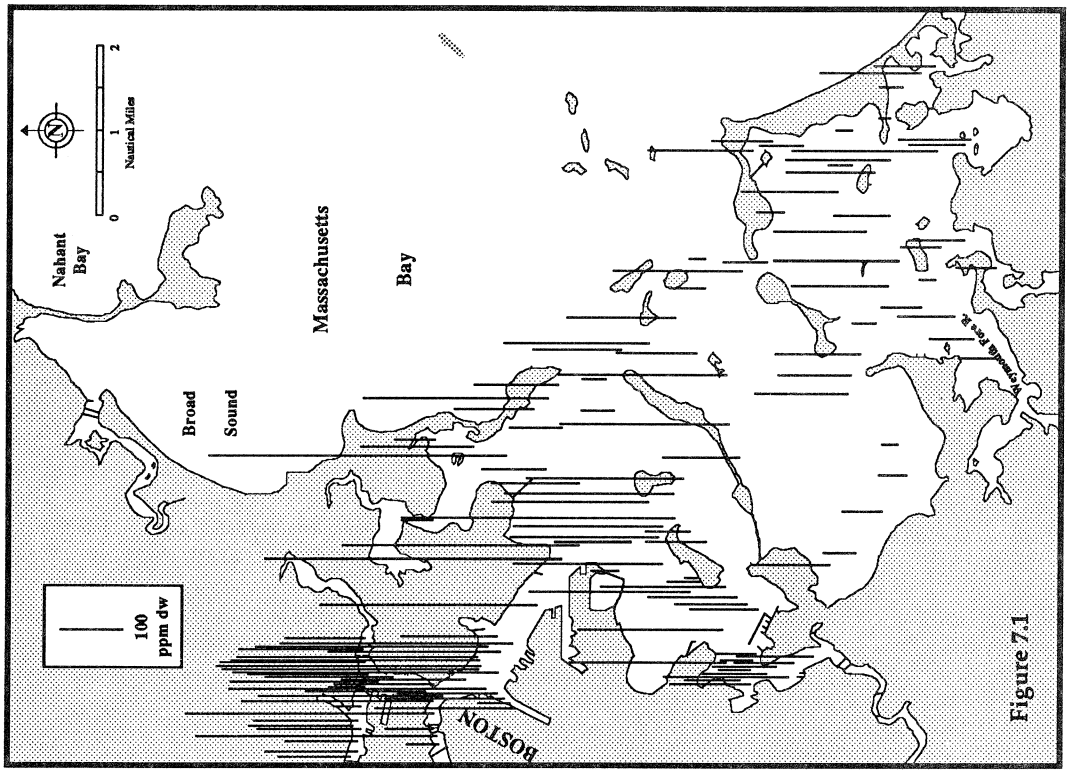
Around 1970, White (1972) collected and analyzed 130 surficial sediment samples from Boston Harbor for a variety of metals, including chromium. He found an overall mean chromium concentration in Boston Harbor surficial sediments of 165 ppm. Individual sample concentrations ranged from 18 ppm, in a sample taken off Worlds End, to 480 ppm, in a sample taken from Winthrop Bay near the mouth of the inner harbor (Figure 7.1). Figure 7.1 indicates that chromium concentrations in the surficial sediments decreased from northwest to southeast. The highest concentrations occurred in the inner harbor and Dorchester Bay. The lowest concentrations occurred in the central and southeastern harbor divisions. This trend of decreasing chromium in the surficial sediments from northwest to southeast was supported by the means for the individual harbor divisions which decreased from a high of 234 ppm in the inner harbor to a low of 98 ppm in the southeast harbor (Table 7.2). Statistical analysis of the log transformed data for the four harbor divisions indicated that the inner harbor was significantly different from the central and southeast harbor and the northwest harbor was significantly different from the southeast harbor at p=0.05. The inner and northwest harbor were significantly different from each other at p=0.10. When the data for the northwest harbor was subdivided, the Winthrop Bay area had the second highest mean concentration of chromium (195 ppm) followed by the Dorchester Bay area (154 ppm). Statistical analysis of the log transformed data for the five harbor areas indicated that the inner harbor was significantly different from the central and southeast harbor at p=0.05.

Table 7.2. Mean chromium concentrations in the surficial sediments of Boston Harbor and the four divisions of the harbor (ppm dw) based on the data of White (1972), Gilbert *et al.* (1972), Isaac and Delaney (1975), MA DEQE (1986 and 1987), and NOAA's NS&T Program (unpublished). The numbers in parentheses are the number of data points used to calculate the means.

	White 1970?	Gilbert *et al.* 1971	Isaac and Delaney 1972	MA DEQE 1985-86	NOAA NS&T 1984-87
OVERALL	165 (130)	141 (41)	89 (6)	121 (30)	184 (31)
INNER HARBOR	234 (38)	145 (3)	27 (1)	136 (8)	N/A
NORTHWEST HARBOR	168 (45)	155 (18)	160 (1)	123 (14)	213 (22)
CENTRAL HARBOR	118 (16)	152 (13)	120 (2)	113 (5)	224 (3)
SOUTHEAST HARBOR	98 (31)	84 (7)	54 (2)	85 (3)	57 (6)

In 1971, the NEA collected 55 cores of Boston Harbor sediments and analyzed various sections of the cores for heavy metal content (Gilbert *et al.*, 1972). Based on 41 samples of the upper surface of the cores that were analyzed for chromium, chromium concentrations ranged from a low of 4 ppm in a sample taken from Quincy Bay, off Wollaston Beach, to a high of 433 ppm in a sample also taken from Quincy Bay but south of Moon Head. The overall mean chromium concentration in the surficial sediments was 141±99 ppm (Table 7.2). Figure 7.2 indicates that the southeastern harbor generally had the lowest concentrations of chromium in the surficial sediments, although one sample had a concentration of over 200 ppm. Figure 7.2 also indicates that there were no clear trends in chromium concentrations in the other three harbor divisions. When the means were calculated for the four harbor divisions, the northwest harbor had the highest mean chromium concentration (155±128 ppm), closely followed by the central harbor (152±88 ppm), and then the inner harbor (145±29 ppm). The southeast harbor had the lowest mean chromium concentration (84±76 ppm). When the northwest harbor data was subdivided, the Winthrop Bay area had the highest mean (214±129 ppm) due largely to one of the four samples with a chromium concentration more than 400 ppm with the second highest sample concentration being 179





Figures 7.1 & 7.2. Chromium concentrations (ppm dw) in the surficial sediments of Boston Harbor for around 1970 based on data from White, 1972 (Fig. 7.1) and for 1971 based on data from Gilbert *et al.*, 1972 (Fig. 7.2).

ppm. When the log transformed data for the harbor divisions were compared statistically, there was no significant difference between any of the divisions at p=0.05.

Between 1971 and 1974, Massachusetts conducted a toxic element survey of the waters of the State (Isaac and Delaney, 1975). The survey included the analysis of sediment samples for volatile solids and a variety of heavy metals including chromium. Six surficial sediment samples from around Boston Harbor had a combined mean chromium concentration of 89±63 ppm, with a range of from 25 ppm to 170 ppm (Figure 7.3). Because so few samples were analyzed, no statistical comparison among harbor divisions could be made. The data did suggest a trend of decreasing chromium concentrations from northwest to southeast, although the second lowest chromium concentration was found in the single sample from the inner harbor (Table 7.2). This sample, located near the mouth of the inner harbor, also had relatively low concentrations of the other metals for which it was analyzed, as well as the lowest concentration of volatile solids in the Harbor.

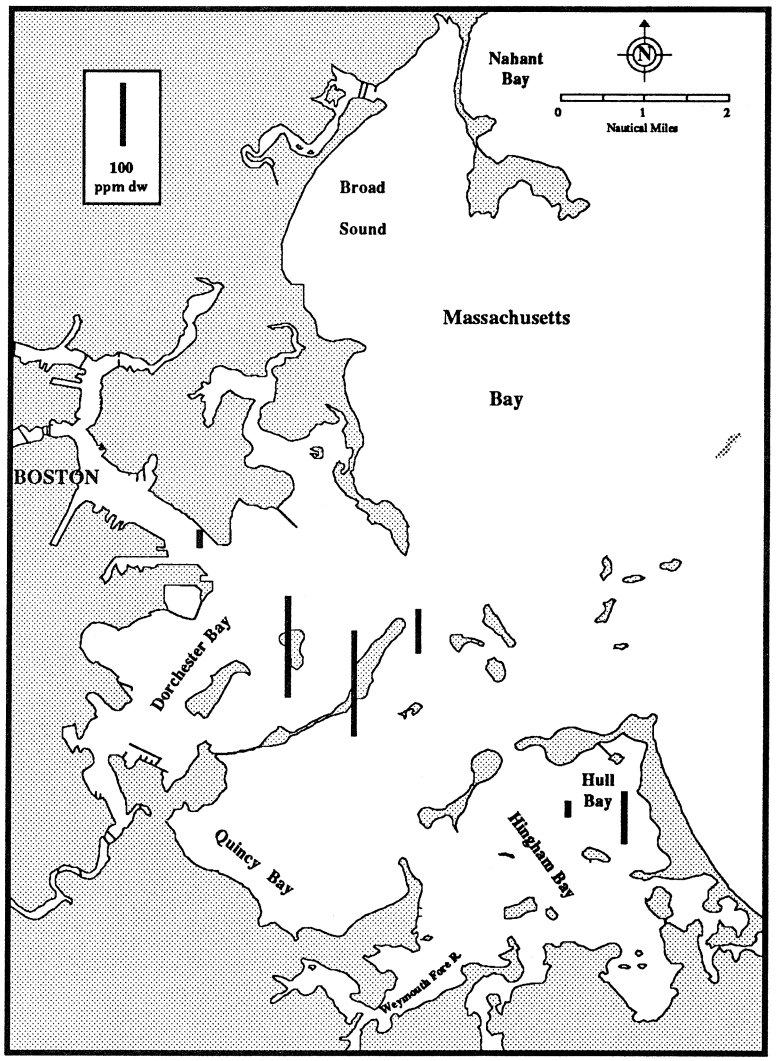


Figure 7.3. Chromium concentrations (ppm dw) in the surficial sediments of Boston Harbor in the early 1970s (Isaac & Delaney, 1975).

Data were obtained from the New England Division of the USACOE for dredging studies conducted in and around Boston Harbor from 1972 through 1988 (USACOE, 1972-88; 1981: Hubbard, 1987). The USACOE analyzed 126 samples during this time for chromium content. The overall mean chromium concentration for the Harbor based on this data was 107±95 ppm. This mean ranged from a low of 0.03 ppm, in a sample taken from the lower reaches of the Mystic River, to a high of 666 ppm, in a sample from the lower reaches of the Chelsea River. The main reason for the high standard deviation was that the vast majority of the samples (90%) had chromium concentrations between 10 and 200 ppm, inclusive. Approximately 2 percent of the samples had less than 10 ppm and only 8 percent of the samples had concentrations in excess of 200 ppm. When the data were grouped by harbor divisions, the means ranged between 59±63 ppm in the central harbor and 129±117 ppm in the inner harbor. The northwest harbor had a mean of 94±69 ppm while the southeast harbor had a mean of 76±50 ppm. When the northwest harbor data was subdivided, the Winthrop Bay area had a mean chromium concentration of 95±68 ppm (based on 33 samples), while the Dorchester Bay area had a

mean of 92±74 ppm (based on 14 samples). The division means suggested a trend of decreasing chromium concentration from the inner harbor to the central harbor and then a slight increase from the central harbor to the southeast harbor. However, statistical analysis of the log transformed data indicated no significant difference between any of the harbor divisions at p=0.05. It should be noted that the vast majority of the samples analyzed were from the inner and northwest harbor (59 and 47, respectively). Only 6 samples were from the central harbor and 14 from the southeast harbor.

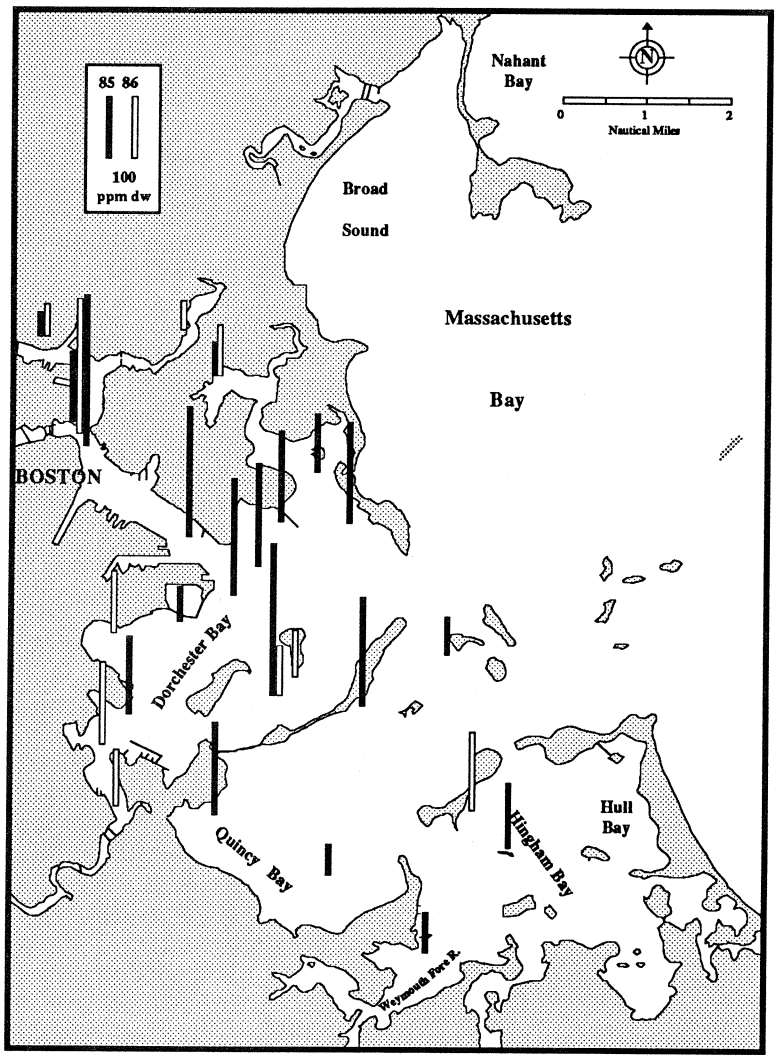


Figure 7.4. Chromium concentrations (ppm dw) in the surficial sediments of Boston Harbor in 1985 and 1986 (MA DEQE, 1986; 1987).

In 1985 and 1986, the Massachusetts DEQE, as part of their annual Boston Harbor Water Quality and Wastewater Discharge Survey analyzed 30 surficial sediment samples for chromium content. They found an overall mean chromium concentration of 121±61 ppm. The low end of the range was 40 ppm in a sample taken from the lower reaches of the Mystic River. The high end of the range was 245 ppm in two samples. One sample was from the mouth of the Fort Point Channel in the inner harbor and the other from north of Moon Head Point in Dorchester Bay (Figure 7.4). Only 13 percent of the samples had concentrations in excess of 200 ppm. The means for the harbor divisions ranged from a low of 85±20 ppm in the southeast harbor to 136±84 ppm in the inner harbor. The northwest and central harbors had means of 123±55 and 113±55 ppm, respectively. When the northwest harbor data was subdivided, the Winthrop Bay area had a mean chromium concentration of 136±51 ppm (based on six samples) and the Dorchester Bay area had a mean of 113±59 ppm (based on eight samples). While the means for the harbor divisions (Table 7.2) suggested a trend of decreasing chromium levels from the inner harbor to the southeast harbor, statistical analysis of the log transformed data indicated no significant difference between any of the divisions at p=0.05. This trend can also be seen in Figure 7.4 which graphically displays the data by site and year.

In 1987 a study, essentially restricted to Quincy Bay, was conducted under the auspices of the U. S. EPA (U.S. EPA, 1988). Figure 7.5 graphically displays the results of the grab sample analysis. Based on the analysis of 40 samples, the overall mean chromium

concentration in the surficial sediments for the study was 86±54 ppm with a range of 6 to 215 ppm.

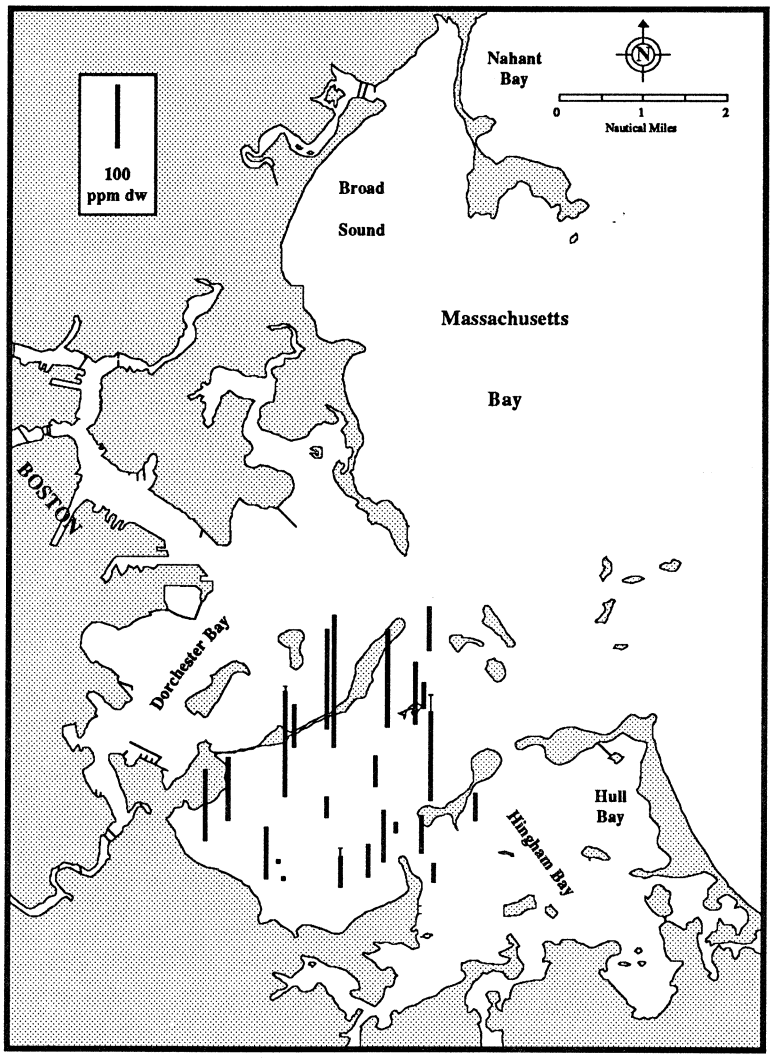
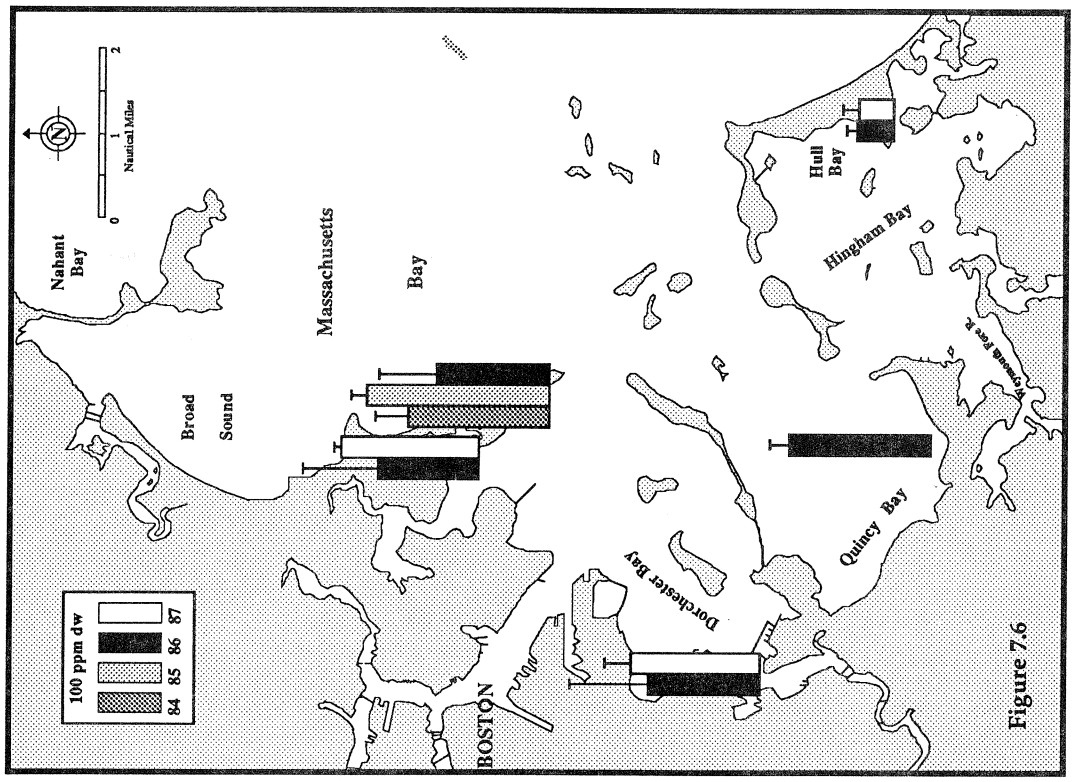
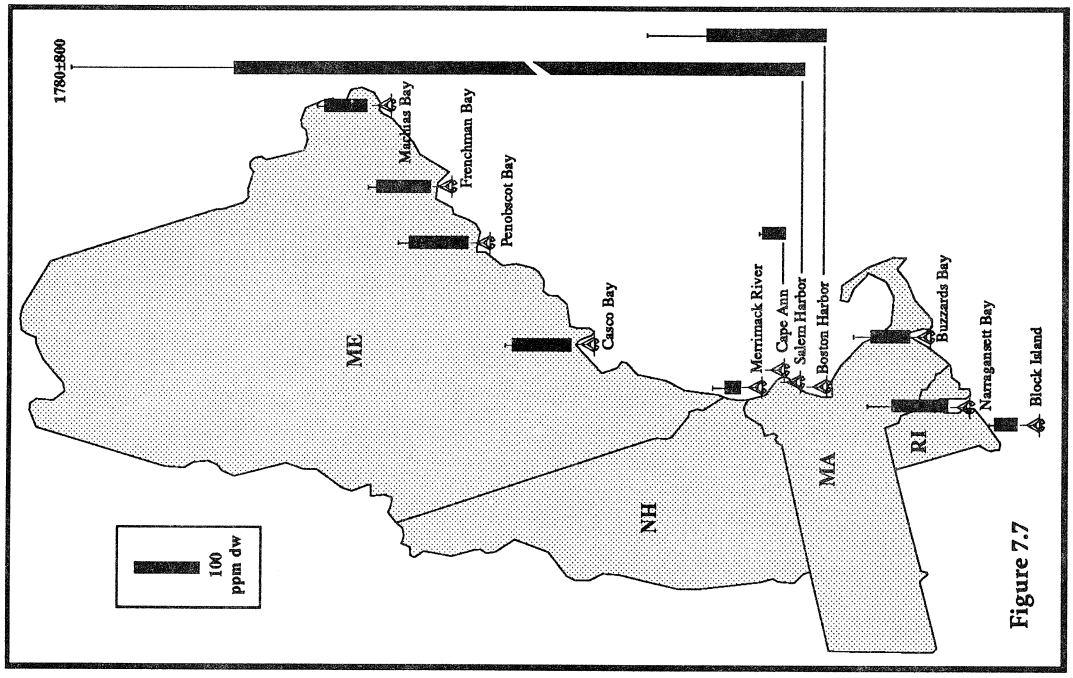


Figure 7.5. Chromium concentrations (ppm dw) in the surficial sediments of Quincy Bay and environs, based on 1987 grab sample data (U.S. EPA, 1988).

NOAA's NS&T Program has sampled and analyzed surficial sediments from several sites around Boston Harbor for several analytes, including chromium since 1984. Figure 7.6 portrays this data graphically by year and site. The overall mean chromium concentration in surficial sediments of the harbor was 184±92 ppm. Individual sample values ranged from 26 to 311 ppm. Site means, based on all 4 years of available data, ranged from 57±19 ppm, at the site off the northern tip of Worlds End, to 238±73 ppm, at the site southwest of Deer Island. The mean chromium concentrations in the surficial sediments of the other sites were: Quincy Bay, 224±32 ppm; Dorchester Bay, 192±86 ppm; and northwest of Deer Island, 191±82 ppm. Statistical comparison of the log transformed data indicated that the Worlds End site was significantly different from the southwest Deer Island and Quincy Bay sites at p=0.05. When the data were grouped by harbor divisions (Table 7.2). the means suggested that there was little difference in mean chromium concentrations in the northwest and central harbor (213±79 and 224±32, respectively). However, the chromium concentrations were significantly lower in the southeast harbor (57±19 ppm). When the northwest harbor data was subdivided, the Winthrop Bay area had a mean chromium concentration of 220±78 ppm (based on 16 samples). while the Dorchester Bay area had a mean of 192±86 ppm (based on 6 samples). Statistical analysis of the log transformed data indicated that the southeast harbor was significantly different from the other harbor divisions at p=0.05.

On a broader scale, between 1984 and 1987, the NOAA NS&T Program analyzed surficial sediment samples from 23 sites from 11 areas along the outer New England coast. From Figure 7.7, that displays the means and standard deviations for the 11 coastal areas, it is clear that the mean chromium concentration of the NS&T Program sites in Boston Harbor (184±92 ppm) was higher than the means for all other areas sampled in New England, except Salem Harbor (1780±797 ppm). It should be noted that the Salem Harbor mean is based on samples from only one site, while that for Boston Harbor was based on





Figures 7.6 & 7.7. Chromium concentrations (ppm dw) in the surficial sediments of Boston Harbor by site and year (Fig. 7.6), and the 11 areas sampled along the outer New England Coast (Fig. 7.7) for 1984-1987, based on NOAA's NS&T Program data (NOAA, unpublished) (bars represent one standard deviation).

samples from five sites. Statistical analysis of the log transformed data indicated that Boston Harbor was significantly different (p=0.05) from all the other areas of New England sampled except areas in Maine (Casco, Penobscot, Frenchman, and Machias bays).

A comparison of the mean chromium concentrations in the surficial sediments of the individual New England NS&T Program sites showed four of the five sites with the highest mean chromium concentrations were located in Boston Harbor (Table 7.3). In an attempt to determine a value for background chromium levels, the overall mean was calculated for the five NS&T Program sites in New England with the lowest chromium concentrations in their surficial sediments (Table 7.3). This mean was 35±15 ppm; the overall mean chromium concentration in the surficial sediments of Boston Harbor, based on the NS&T Program data, was more than 5 times greater than this reference mean. The four Boston Harbor sites with the highest chromium concentrations had means more than 5 times higher than the reference mean. However, the lowest Boston Harbor site mean chromium concentration (57±19 ppm, Worlds End) was only about 1 1/2 times higher than the reference mean.

Table 7.3. The five outer New England coast NOAA NS&T Program sites with the lowest and highest mean chromium concentrations (ppm dw) based on data from 1984 through 1987.

Site	Mean	Standard Deviation	Count
MERRIMAC RIVER	25	16	5
GOOSEBURY NECK, BUZZARDS BAY	33	12	6
BLOCK ISLAND, RHODE ISLAND	34	7	3
STRAITSMOUTH ISLAND, CAPE ANN	34	4	3
ANGELICA ROCK, BUZZARDS BAY	49	17	6
NORTHWESTERN DEER ISLAND	191	82	6
DORCHESTER BAY	192	86	6
QUINCY BAY	224	32	3
SOUTHWESTERN DEER ISLAND	238	73	10
SALEM HARBOR	1780	797	9

Temporal Trends

Figure 7.8 compares the yearly mean chromium concentrations in the surficial sediments of Boston Harbor based on all the available data sets (White, 1972: Gilbert *et al.*, 1972: Isaac & Delaney, 1975: USACOE, 1972-88; 1981; 1988: MA DEQE, 1986; 1987: U.S. EPA, 1988: NOAA, unpublished). While there is no overall temporal trend apparent from Figure 7.8, if just the 5 years with largest sample sizes are compared (1970, 1971, 1985, 1986, and 1987), it appears that chromium concentrations in the surficial sediments of Boston Harbor may have declined slightly since the early 1970s. The high mean chromium concentration for 1983 was the result of the small sample size and the inclusion of the two highest values reported for chromium concentrations in the surficial sediments.

Data were available from the USACOE on dredging studies for 1975 and most of the years from 1980 through 1988. When the yearly mean chromium concentrations in the surficial sediments based on this dat, were calculated and the log transformed data compared, only 1980 and 1987 were significantly different at p=0.05. One factor contributing to the lack of any statistically significant difference among most of the years was the variation in the number of sites sampled each year, from 1 in 1975 and 1988 to 59 in 1986 (Table 7.4). In addition to the variability in the number of sites sampled each year, the sites themselves varied from year to year. Therefore, while the data sets would be expected to be internally consistent with regard to methodology, any conclusions concerning temporal trends based on the data must be viewed with extreme caution.

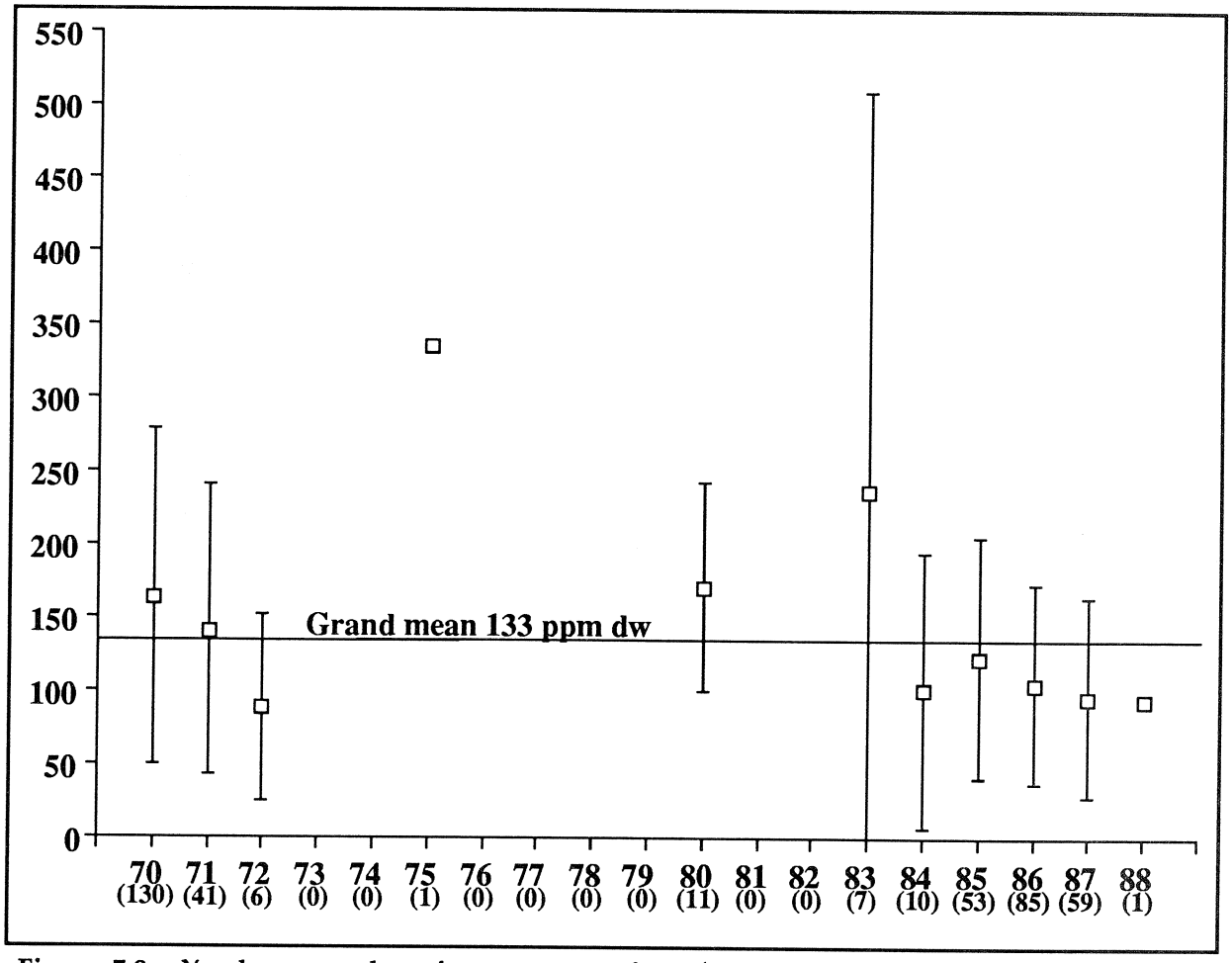


Figure 7.8. Yearly mean chromium concentrations (ppm dw) in the surficial sediments of Boston Harbor, based on White (1972), Gilbert *et al.* (1972), Isaac & Delaney (1975), USACOE (1972-88, 1981, 1988), MA DEQE (1986, 1987), U.S. EPA (1988), and NOAA (unpublished). The bars represent one standard deviation and the numbers in parenthesis are the number of samples analyzed each year.

Table 7.4. Yearly mean chromium concentrations (ppm dw) in Boston Harbor surficial sediments based on dredging study data from the USACOE.

Year	Mean	Standard Deviation	Count
1975	335	N/A	1
1980	172	71	11
1983	238	271	7
1984	49	40	7
1985	97	67	30
1986	91	56	59
1987	84	77	10
1988	95	N/A	1

The only other available data which spanned more than 2 years was that from NOAA's NS&T Program Benthic Surveillance (1984-86) and Mussel Watch (1986-87) projects. The yearly mean chromium concentrations in the surficial sediments of Boston Harbor based on this data ranged from a high of 293±24 ppm in 1985 to a low of 160±95 ppm in 1987. The yearly mean for 1984 was 224±55 ppm and for 1986 was 161±83 ppm. There was no indication of any temporal trends in chromium contamination. The difference in the yearly mean chromium concentrations can be explained by the difference in the sites sampled each year (Figure 7.6).

Biota

Since 1976 over 200 tissue samples from a variety of organisms in Boston Harbor have been analyzed for chromium content. Chromium concentrations ranged from 0.01 ppm in the muscle of a winter flounder (*P. americanus*) and a lobster (*H. americanus*) to 6.47 ppm in the hepatopancreas of a lobster. Table 7.5 gives the statistics on chromium contamination of biota by organism and tissue. The large difference between the mean and median chromium concentration and the standard deviation for winter flounder muscle was due to a single sample with an extraordinarily high reported chromium concentration, 1.69 ppm. This concentration was more than an order of magnitude higher than the second highest reported chromium concentration (0.13 ppm). If it was excluded from the calculations, the mean chromium concentration in winter flounder muscle would become 0.5±0.03 ppm. In addition, approximately 58 percent of the winter flounder muscle tissue samples had chromium levels which were below the limits of detection (0.03 to 0.24 ppm); while 22 percent of the lobster muscle and 38 percent of the lobster hepatopancreas samples had chromium levels below the detection limits (0.02 to 0.04 and 0.18 to 0.96 ppm). The data for winter flounder and lobster (Table 7.5) suggest that chromium tends to accumulate more in the liver or liver-like tissue than in muscle tissue.

Table 7.5. Harborwide means, standard deviations, medians, ranges, and sample sizes (count) for chromium concentrations (ppm dw) in biota by organism and tissues based on all the available data sets (* transplants).

		Mean	Standard Deviation	Median	Range	Count
P. americanus						
	liver	0.42	0.54	0.29	0.08-2.60	20
	muscle	0.12	0.34	0.04	0.01-1.69	24
H. americanus						
	hepatopancreas	1.60	2.27	0.34	0.20-6.47	8
	muscle	0.20	0.24	0.14	0.01-1.17	40
M. arenaria						
	soft parts	3.61	1.17	3.62	1.22-6.14	36
M. edulis						
	soft parts	1.54	0.84	0.85	0.55-5.60	85
*C. virginica**						
	soft parts	0.50	0.20	0.52	0.26-0.69	4

Geographic Trends.

Only lobster muscle tissue and mussel soft-part tissue were sampled from more than one division of the Harbor (Table 7.6). The mussel data suggested that the northwest harbor biota contained the highest levels of chromium, followed closely by the southeast harbor, then the inner harbor. The mussels in the central harbor had the lowest chromium levels. The lobster muscle data also suggested that the northwest harbor biota had higher levels of chromium than did the central harbor.

Table 7.6. Mean chromium concentrations (ppm dw) of the entire harbor and the four divisions in various organisms and tissues (the number in parentheses is the sample size).

	H. americanus muscle	*M. edulis* soft parts
OVERALL	0.20 (40)	1.54 (85)
INNER HARBOR	—	1.47 (29)
NORTHWEST HARBOR	0.26 (24)	2.05 (18)
CENTRAL HARBOR	0.10 (16)	1.17 (29)
SOUTHEAST HARBOR	—	1.91 (9)

In 1985 and 1986, lobster (*H. americanus*) and soft-shelled clams (*M. arenaria*) were collected from Boston and Salem harbors and analyzed for various analytes, including chromium, as part of a study of contaminants in marine resources

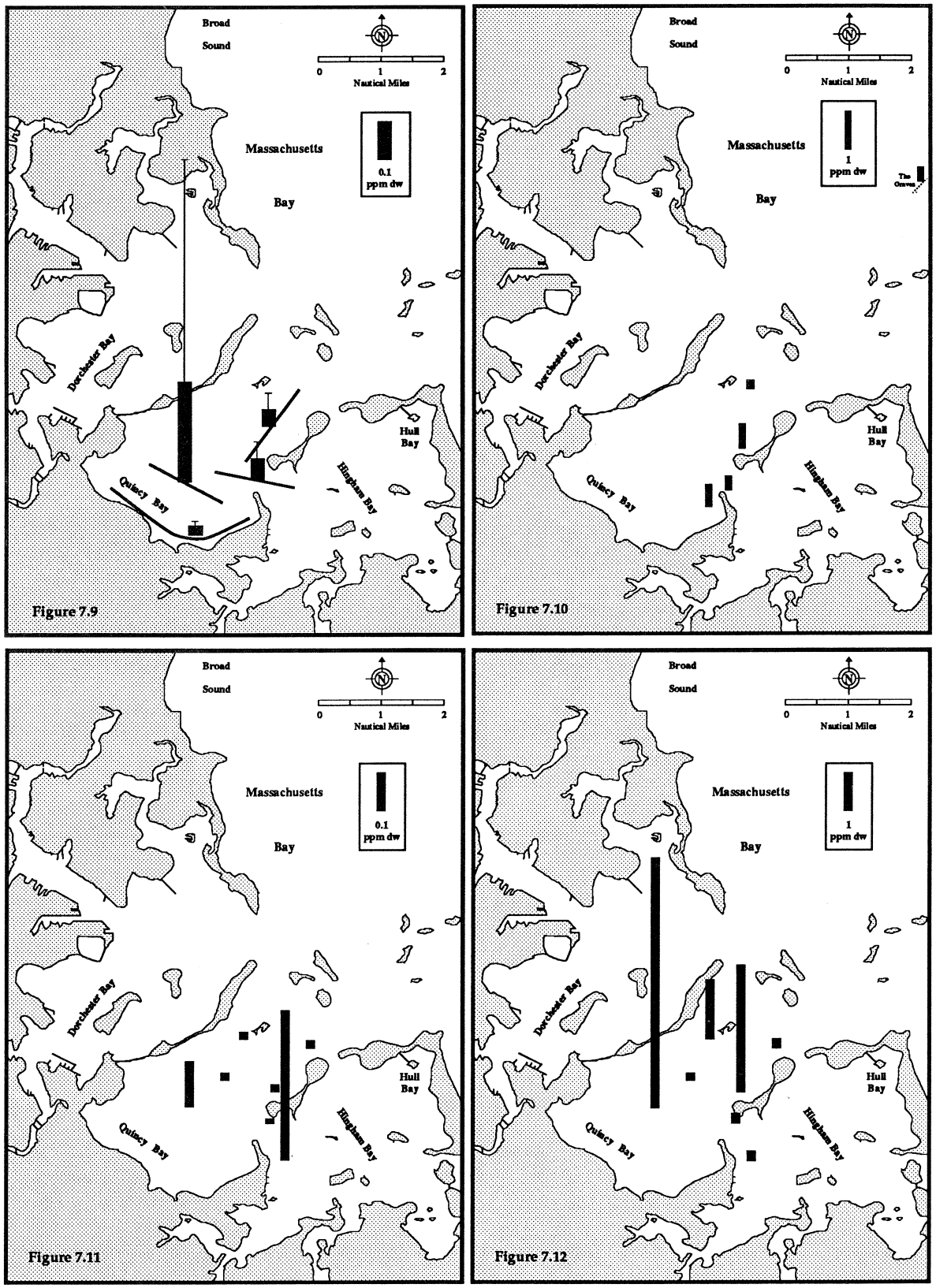
(Wallace *et al.*, 1988). The mean chromium concentration in the combined claw and tail-muscle tissue of 24 lobsters collected from around Deer Island was 0.26±0.22 ppm with a range of from 0.10 to 1.17 ppm. Lobsters were also collected from two sites in Salem Harbor, the treatment plant outfall and Willows Pier. The mean chromium concentrations in combined claw and tail muscle tissue based on the analysis of 25 lobsters per site were 0.25±0.22 and 0.24±0.51 ppm, respectively. Statistical analysis of the log transformed data indicated that chromium concentrations in the muscle tissue of Deer Island lobsters were significantly different from that for the Willows Pier site in Salem Harbor at p=0.05. The mean chromium concentration for 34 soft-shelled clams from Wollaston Beach in Quincy Bay was 3.73±1.08 ppm with a range of 1.49 to 6.14 ppm.

An intensive study of Quincy Bay was conducted in 1987 which included the analysis for chromium levels in the tissues of native winter flounder (*P. americanus*), lobsters (*H. americanus*), soft-shelled clams (*M. arenaria*), and transplanted oysters (*C. virginica*) (U.S. EPA, 1988). The muscle tissue of from five to seven winter flounder from each of four different trawl transects was analyzed for chromium content. The chromium concentrations in individual samples ranged from a low of 0.01 ppm to a high of 1.69 ppm; while 58 percent of the samples had chromium concentrations below detection limits which ranged from 0.03 to 0.24 ppm. The means for the individual trawls ranged from less than 0.48 to 0.26±0.58 ppm (Figure 7.9). Statistical analysis of the log transformed trawl data indicated no significant difference between any of the trawls at p=0.05.

Oysters (*C. virginica*) were collected from a commercial bed in Cotuit Bay, Cotuit, Massachusetts. They were deployed at four sites in Quincy Bay and one site located at The Graves in Massachusetts Bay from June 5 through July 16, 1987. The chromium concentrations in the oysters at the four sites ranged from 0.26 to 0.69 ppm. The oysters from The Graves had 0.41 ppm chromium, while those from the source bed in Cotuit Bay had a chromium concentration of 0.29 ppm (Figure 7.10). Two samples of the soft-shelled clam from around Moon Island, Quincy Bay also were analyzed for chromium and found to have concentrations of 1.22 and 1.71 ppm.

Both the tail muscle and the hepatopancreas of lobsters from seven sites were analyzed for levels of chromium content. Two replicate samples from the tail muscles of a total of 16 lobsters were analyzed, two to three from each of the seven sites. The chromium concentrations in the individual samples ranged from less than 0.02 to 0.98 ppm; 9 of the 16 lobster muscle tissue samples had chromium concentrations which were below the detection limits of 0.02 to 0.04 ppm. The mean tail muscle concentrations for the seven sites ranged from less than 0.02 to 0.37±0.52 ppm (Figure 7.11). There was no significant difference in tail-muscle chromium levels among sites based on statistical analysis of the log transformed data (p=0.05). Two replicate samples of hepatopancreas from 8 of the 16 lobsters (one each from six of the sites and two from the remaining site) were also analyzed for chromium. Chromium concentrations for the individual specimens ranged from less than 0.39 to 6.47 ppm (Figure 7.12). Three of the specimens had chromium concentrations in their hepatopancreas below the limits of detection that ranged from 0.18 to 0.96 ppm for the individual replicates.

NOAA's Mussel Watch Project, a part of the NS&T Program, has sampled mussels (*M. edulis*) on an annual basis from four sites in and around Boston Harbor since 1986. Three whole-body composite samples from each site were analyzed for a variety of analytes, including chromium. The overall mean concentration of chromium in the mussels for the three sites in Boston Harbor from 1986 through 1988 was 2.00±1.04 ppm with a range of from 0.62 to 5.60 ppm. The means for the individual sites were 1.88±0.61 ppm northwest of Deer Island, 1.91±1.56 ppm in Hingham Bay off Worlds End, and 2.22±0.80 ppm in southwestern Dorchester Bay. Mussels from the site outside the Harbor, Outer Brewster Island, had a mean chromium concentration of 1.97±0.47 ppm (Figure 7.13). Statistical analysis of the log transformed data for the four sites indicated that none of the sites was significantly different (p=0.05).



Figures 7.9-7.12. Chromium concentrations (ppm dw) in *P. americanus* muscle (Fig. 7.9), transplanted *C. virginica* (Fig. 7.10), and *H. americanus* muscle (Fig. 7.11) and hepatopancreas (Fig, 7.12) sampled in 1987 (U.S. EPA, 1988) (bars represent one standard deviation).

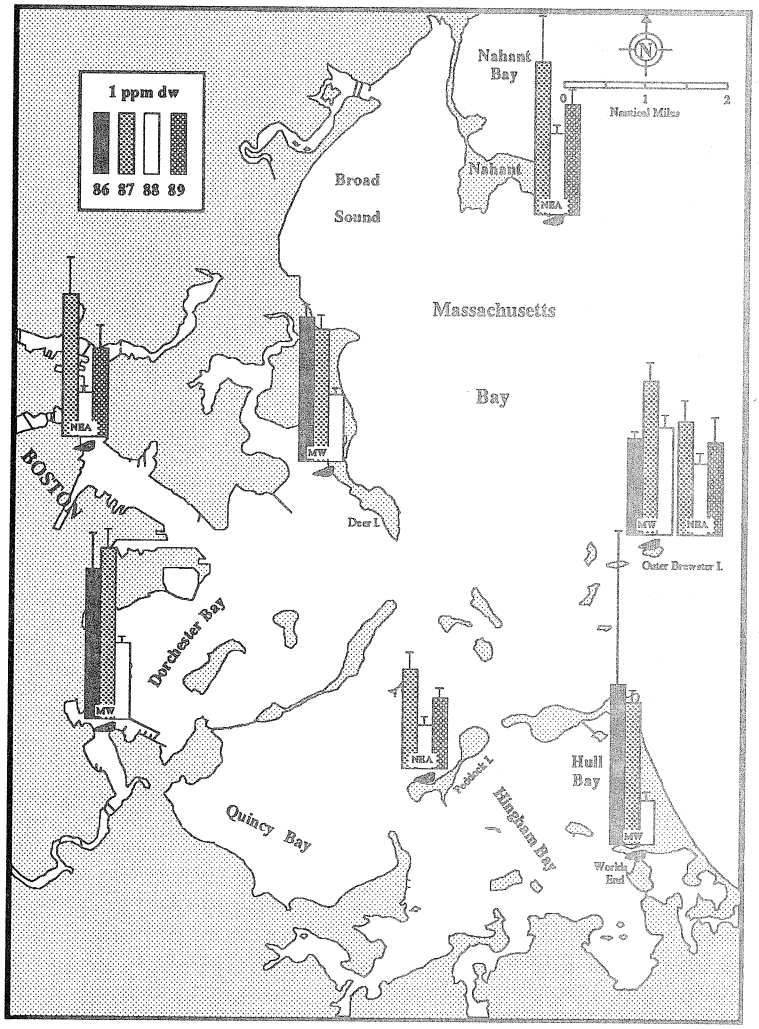


Figure 7.13. Mean chromium concentrations (ppm dw) in the soft-parts of *M. edulis* from 1986-89, based on data from NOAA's (MW) and the New England Aquarium's mussel watch projects (NOAA, unpublished; Robinson *et al.*, 1990) (bars represent one standard deviation).

Since 1987 the NEA has conducted their own Mussel Watch program (Robinson *et al.*, 1990). They sample mussels from two sites within Boston Harbor and two sites in Massachusetts Bay. These sites include the same site on Outer Brewster Island that NOAA's Mussel Watch Project samples. The mean chromium concentration in Boston Harbor, based on data from the two sites for the 3 years from 1987 through 1989, was 1.32±0.64 ppm with a range of from 0.55 to 3.23 ppm. The means for the two sites were 1.17±0.42 ppm at the Peddocks Island site and 1.47±0.78 ppm at the Central Wharf, Boston site. The two sites from Massachusetts Bay had means of 1.49±0.41 ppm at the Outer Brewster Island site and 1.89±0.66 ppm at the Pumphouse Beach, Nahant site. When the data for the four sites is log transformed and the sites statistically compared, the Pumphouse Beach site was found to be significantly different from the Central Wharf and the Peddocks Island sites at p=0.05. Figure 7.13 plots the NEA data alongside the NOAA Mussel Watch data.

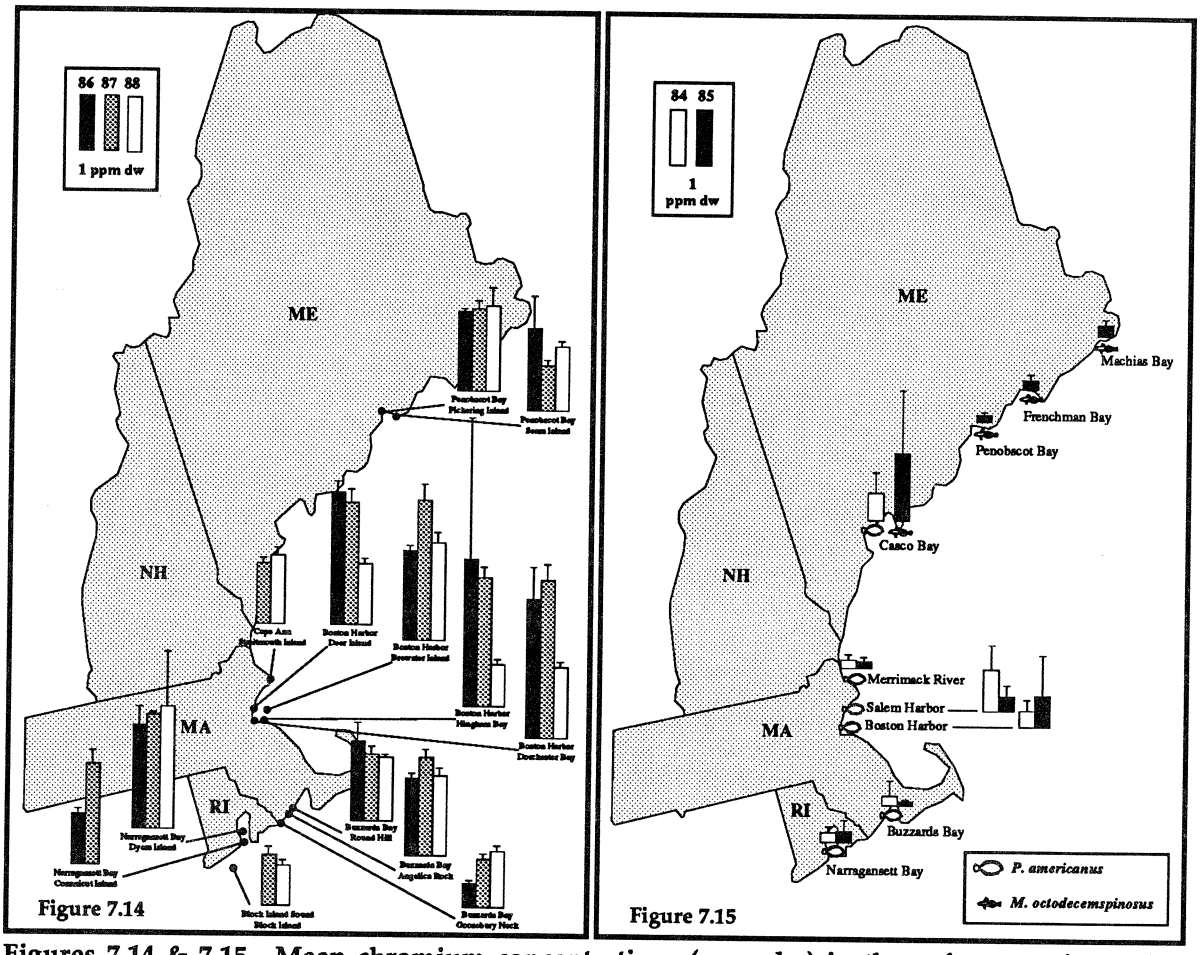
On a broader scale, when the chromium levels in mussels from the Boston Harbor NS&T sites were compared to those from the other outer New England coast NS&T Mussel Watch sites (Table 7.7 and Figure 7.14) and the log transformed data statistically analyzed, the Deer Island and Dorchester Bay sites were found to be significantly different from the Goosebury Neck site. In addition, the Dorchester Bay site was found to be significantly different from the Block Island site (p=0.05). The Goosebury Neck and Block Island sites were also found to be significantly different from the Brewster Island and Dyers Island sites (p=0.05) (Table 7.7). From this data, it appears that chromium levels in mussels vary little throughout New England with the range of means being a little less than a factor of 3. When a reference value is calculated based on the five sites with the lowest mean chromium concentrations in mussels, a value of 1.05±0.32 ppm is obtained. The Boston Harbor sites have mean chromium values of from 1.8 to 2.1 times higher than this reference value. On a national scale, the Mussel Watch sites where *M. edulis* was sampled had mean chromium concentrations ranging from 0.51 to 11.3 ppm with an overall mean for all the sites of 2.00±1.71 ppm, 67 percent of the sites had means less than 2.00 ppm, 24 percent had concentrations between 2.00 and 3.00 ppm, and one site (2%) had a mean chromium concentration in excess of 4.20 ppm. When the sites where *M. californianus* was sampled were included in the calculations, the overall mean became

1.92±1.46 ppm, with 70 percent of the sites having means less than 2.00 ppm, 23 percent of the sites had means between 2.00 and 3.00 ppm, and still, just the one site with a mean in excess of 4.20 ppm. Based on this data, Boston Harbor mussels appeared to be moderately contaminated with chromium since two of the harbor sites had means less than 2.00 ppm and one had a mean slightly over 2.00 ppm.

Table 7.7. The mean chromium concentrations (ppm dw) in *M. edulis* at the 13 outer New England coast NS&T Program Mussel Watch sites. The outlined means are for Boston Harbor sites.

Site	Mean	Standard Deviation	Count
DORCHESTER BAY, BOSTON HARBOR	2.22	0.8	9
DYERS ISLAND, NARRAGANSETT BAY	2.03	0.54	9
OUTER BREWSTER ISLAND	1.97	0.47	9
HINGHAM BAY, BOSTON HARBOR	1.91	1.56	9
DEER ISLAND, BOSTON HARBOR	1.88	0.61	9
PICKERING ISLAND, PENOBSCOT BAY	1.48	0.18	9
ANGELICA ROCK, BUZZARDS BAY	1.48	0.22	11
CONANICUT ISLAND NARRAGANSETT BAY	1.37	0.53	6
ROUND HILL, BUZZARDS BAY	1.24	0.24	9
CAPE ANN, STRAITSMOUTH ISLAND	1.17	0.14	6
SEARS ISLAND, PENOBSCOT BAY	1.15	0.41	9
GOOSEBURY NECK, BUZZARDS BAY	0.82	0.25	8
BLOCK ISLAND, RHODE ISLAND	0.79	0.16	6

NOAA's Benthic Surveillance Project, a part of the NS&T Program, has sampled winter flounder (*P. americanus*) from an area just west of Deer Island on an annual basis since 1984. The mean chromium concentration in the liver of the fish sampled in 1984 and 1985 was 0.42±0.54 ppm with a range of 0.08 to 2.60 ppm. The mean concentration of chromium in flounder livers for all of the New England Benthic Surveillance sites, excluding Boston Harbor, ranged from a low of 0.12±0.20 ppm at the Buzzards Bay site to a high of 0.51±0.41 ppm at the Salem Harbor site (Figure 7.15). The mean chromium concentration of winter flounder liver from Boston Harbor was exceeded by the means for the Salem Harbor and Casco Bay (0.49±0.36 ppm) sites. Statistical analysis of the log transformed data indicated that the Boston Harbor site, along with the Casco Bay and Salem Harbor sites, were significantly different from the two sites with the lowest mean chromium concentrations in winter flounder liver, Buzzards Bay and Merrimac River (0.13±0.10). In addition, the Salem Harbor site was significantly different from the Narragansett Bay site at $p=0.05$. The highest reported value for chromium in a single sample was 2.60 ppm from one of the Boston Harbor specimens. This value was almost 2 times as high as the second highest value reported for all the New England sites (1.48 ppm) and was more than 3.5 times higher than the second highest value for a Boston Harbor sample (0.71 ppm). When this exceptionally high value was excluded from the calculations, the Boston Harbor mean became 0.30±0.16 ppm. This was still the third highest mean for all the New England sites and there was no change in the statistical analysis results. No comparison could be made between Boston Harbor and the three northern-Maine sites, because a different species, longhorn sculpin (*Myoxcephalus octodecemspinosus*), was sampled at these sites. The Benthic Surveillance Project sampled winter flounder at four other sites during the same time frame: two in Long Island Sound and one each in Raritan and Great bays in New Jersey. The site means for Raritan and Great bays and east Long Island Sound (0.25±0.11, 0.07±0.06, and 0.32±0.30 ppm, respectively) were less than the mean for Boston Harbor. The mean for the west Long Island Sound site (0.54 ±0.63 ppm) was greater than the Boston Harbor mean.



Figures 7.14 & 7.15. Mean chromium concentrations (ppm dw) in the soft-parts of *M. edulis* (Fig. 7.14) and liver tissue of *P. americanus* (Fig. 7.15) along the outer New England coast (NOAA, unpublished) (bars represent one standard deviation.

Temporal Trends

No temporal trends in the chromium levels of Boston Harbor biota could be determined based on the available data. The only internally consistent data sets sampling the same organism from the same locations over a number of years were the NS&T Program's Benthic Surveillance and Mussel Watch projects and the NEA Mussel Watch Program. Data for these projects were only available for 2, 3, and 3 years, respectively. Between 1984 and 1985 there was approximately a 90 percent increase in the level of chromium in winter flounder livers (0.29±0.19 to 0.55±0.73 ppm) (Figure 7.15). If the extraordinarily high single sample chromium value (2.60 ppm) is excluded from the calculations, the 1985 mean becomes 0.32±0.14 ppm, less than a 10 percent increase over 1984. The 3 years of data for *M. edulis* from the NS&T Program Mussel Watch Project indicated no significant change between 1986 and 1987 (2.52±1.31 and 2.46±0.38 ppm, respectively). However, there was apparently more than a 50 percent reduction in chromium levels between 1987 and 1988 (1.04±0.25 ppm) (Figure 7.14). The yearly means for the NEA Mussel Watch Program also indicated an apparent greater than 50 percent reduction in chromium levels between 1987 and 1988 (1.99±0.60 to 0.73±0.10 ppm), although there was approximately an 80 percent increase between 1988 and 1989 (1.31±0.32 ppm).

Summary

Boston Harbor sediments were found to contain chromium at levels 5 times greater than background levels. When the overall mean value of chromium in Boston Harbor (133±101 ppm) was compared to the overall mean of San Francisco Bay (89±96 ppm) (Long *et al.*, 1988),

it was found to be approximately 1 1/2 times higher than the San Francisco Bay mean. However, when just the NS&T Program data for the two ports were compared, the Boston Harbor mean, 184±92 ppm, was only 3/4 as high as the San Francisco Bay mean, 241±154 ppm (Long *et al.*, 1988) (Table 7.8). San Francisco Bay chromium levels may not be representative of a typical harbor area because the NS&T Program data suggested that the sediments in the San Francisco Bay area, including reference sites outside the Bay (Bodega and Tomales bays), contain high levels of apparently naturally occurring chromium. The overall data set indicated a trend of decreasing chromium concentrations in Boston Harbor surficial sediments from the inner harbor towards the southeastern harbor and towards the mouth. This trend was also apparent in two of the five individual data sets which covered most of the Harbor (White, 1972; Massachusetts DEQE, 1986 and 1987). However, two of the data sets indicated that the inner harbor had lower chromium levels than the northwestern and central harbors. One of the two data sets suggested that the inner harbor had the lowest levels of chromium (Isaac and Delaney, 1975). However, this was based on only one sample from the inner harbor while the other data set (Gilbert *et al.*, 1972) only had three samples from the inner harbor. The NS&T Program data set suggested that the central harbor was slightly more contaminated with chromium than the northwestern harbor, and the southeastern harbor had the lowest levels of chromium. The data for the northwestern harbor were subdivided into that for the Winthrop Bay area and that for Dorchester Bay. The overall data sets and the individual data sets indicated that the Winthrop Bay area had higher levels of chromium than did Dorchester Bay.

Table 7.8. Comparison of chromium sediment statistics for Boston Harbor, NS&T Program Reference (based on the five New England sites with the lowest chromium levels), and San Francisco Bay in ppm dw. Statistics for San Francisco Bay derived from Long *et al.*,1988.

Area	Mean	Standard Deviation	Median	Range	Count
Boston	133	101	110	0.03-666	404
NS&T Program Boston	184	92	220	26-311	31
NS&T Program Reference	35	15	32	9.9-68	23
San Francisco Bay	89	96	63	8-769	396
NS&T Program San Francisco Bay	241	154	190	72-769	42

Neither the overall data nor individual data sets gave any indication of unequivocal temporal trends; because when the 5 years with the largest numbers of samples (1970, 1971, 1985, 1986, and 1987) were compared, there appeared to be a slight decrease in chromium levels between the early 1970s and the mid 1980s.

Based on the available data, Boston Harbor biota appear to be moderately to highly contaminated with chromium. Boston Harbor mussels (*M. edulis*) had some of the highest mean chromium concentrations of all the New England NS&T Program sites sampled. When compared to all NS&T Program mussel sites sampled in the country, approximately 60 percent of the sites had means lower than the lowest Boston Harbor site while 19 percent had means higher than the highest Boston Harbor site. The winter flounder (*P. americanus*) liver data also suggested that Boston Harbor had moderate to high levels of chromium since, among the NS&T Program sites, only three sites had higher mean chromium concentrations in winter founder liver than the Boston site. The winter flounder and lobster (*H. americanus*) tissue data suggested that chromium tends to accumulate more in liver or liver-like tissue than in muscle tissue. There were no obvious geographic or temporal trends in chromium content of biota within Boston Harbor based on the available data. This is because relative concentrations between different areas of the Harbor varied with the organism and tissue sampled. Also, with the exception of the NS&T Program and the NEA Mussel Watch Program, none of the studies sampled the same organism from the same sites over a period of years.

SILVER

Silver is considered to be one of the most toxic heavy metals in the aquatic environment (Bryan, 1971). In a survey of the literature, Long and Morgan (1990) found toxic effects associated with sediments having a silver concentration as low as 0.2±0.1 ppm. In all but two of the cases, looked-at toxic effects were reported for sediments with silver concentrations of 1.7 ppm or higher. Concentrations as high as 6.0 ppm have been reported for the soft parts of mussels and as high as 82 ppm for the soft parts of clams (Eisler, 1981).

Sediments

Little reliable data exists on the concentration of silver in the sediments of Boston Harbor before 1984. Between 1984 and 1988, four groups of researchers analyzed 82 sediment samples from around Boston Harbor for silver. The overall mean concentration of silver in Boston Harbor sediments for that period was 3.12 ppm, with a standard deviation of 2.04 ppm, and a range of from 0.27 to 9.12 ppm. The median concentration of silver was 2.80 ppm (Table 8.1). The vast majority of the samples analyzed (73%) had silver concentrations between 1.00 and 4.00 ppm inclusive, while 7 percent of the samples had concentrations less than 1.00 ppm and 20 percent had concentrations greater than 4.00 ppm.

Table 8.1. Means, standard deviations, medians, ranges, and number of samples (count) for silver concentrations (ppm dw) in sediments for all of Boston Harbor and the four harbor divisions, based on all the available data sets.

	Mean	SD	Median	Range	Count
OVERALL	3.12	2.04	2.80	0.27-9.12	82
INNER HARBOR	3.32	1.42	4.00	0.40-7.00	29
NORTHWEST HARBOR	3.40	2.46	2.50	0.27-9.12	36
CENTRAL HARBOR	3.21	2.10	2.70	1.00-6.04	8
SOUTHEAST HARBOR	1.22	0.32	1.20	0.67-1.60	9

Geographic Trends

Table 8.1 gives the combined means, standard deviations, medians, ranges, and number of samples analyzed for Boston Harbor and the four harbor divisions based on all the data sets reviewed for this report. From this table it can be seen that, with the exception of the southern harbor region, there is little difference in the mean concentrations of silver in harbor sediments. With a standard deviation of only 1.42, the inner harbor has a relatively uniform distribution of silver. The northern harbor, with a standard deviation of 2.46 and a range that includes both the lowest and highest recorded concentrations, has a rather heterogeneous distribution. When the data for the northwest harbor was subdivided into the Winthrop Bay area and Dorchester Bay area, the Winthrop Bay area mean silver concentration (4.02±2.88 ppm) was found to be more than 1 1/2 times higher than the mean for Dorchester Bay area (2.42±1.13 ppm). The lowest and highest recorded concentrations were from the Winthrop Bay area.

Between 1985 and 1986, the Massachusetts DEQE (1986; 1987) collected and analyzed 30 sediment samples from throughout Boston Harbor for silver content (Figure 8.1). Silver levels ranged from below the detection limit of 1 ppm (three samples) to 3 ppm. The mean silver concentration was 1.52 ppm with a standard deviation of 0.61. Figure 8.1 and Table 8.2 suggest that silver was relatively uniformly distributed throughout the harbor with the central and northwest harbor having slightly higher concentrations than either the inner or southeast harbor. However, when the data for the northwest harbor were subdivided into the Winthrop Bay area and Dorchester Bay area, the lowest mean silver concentration (1.17±0.54 ppm) was from the Winthrop Bay area and the highest mean (1.90±0.51 ppm)

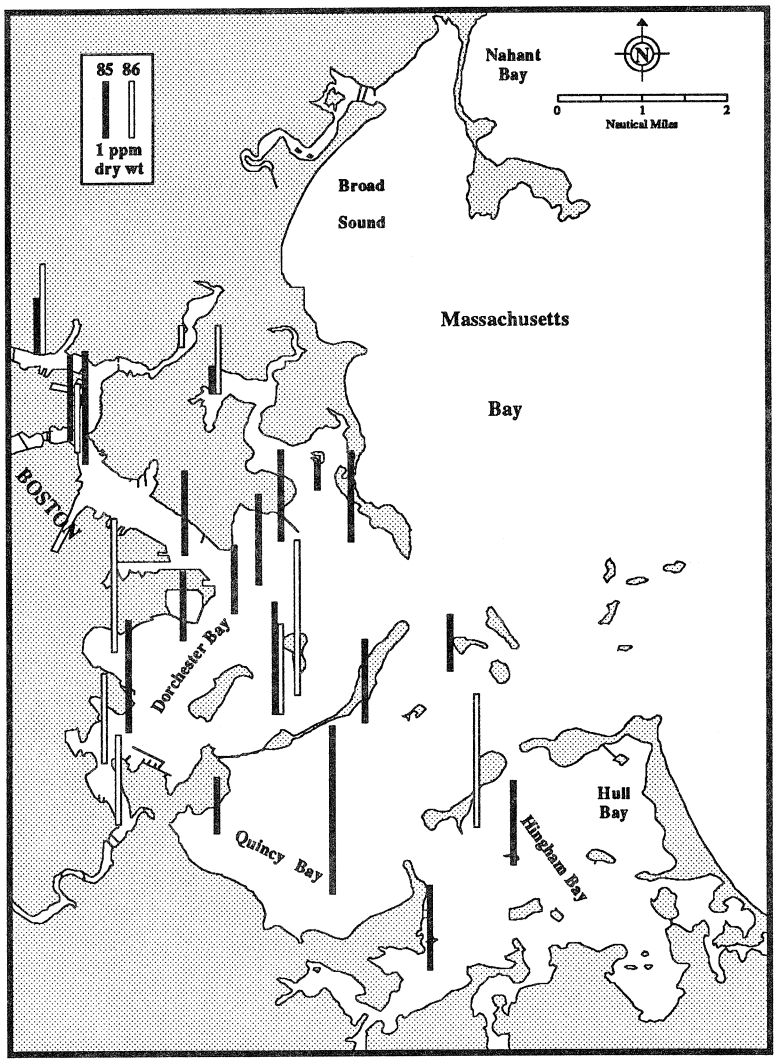


Figure 8.1. Silver concentrations (ppm dw) in the surficial sediments of Boston Harbor for 1985 and 1986 (MA DEQE, 1986, 1987).

Table 8.2. Mean silver concentrations in the surficial sediments of Boston Harbor and the four harbor divisions (ppm dw) based on the data of the MA DEQE (1986 and 1987) and NOAA's NS&T Program (unpublished). The numbers in parentheses are the number of data points used to calculate the means.

	MA DEQE 1985-86	NOAA NS&T 1984-87
OVERALL	1.52(30)	3.99(31)
INNER HARBOR	1.30 (8)	N/A
NORTHWEST HARBOR	1.59(14)	4.56(22)
CENTRAL HARBOR	1.78 (5)	5.60 (3)
SOUTHEAST HARBOR	1.40 (3)	1.12 (6)

was from the Dorchester Bay area. Statistical analysis of the log transformed data indicated no significant difference between any of the harbor divisions at p=0.05.

In 1986, the USACOE analyzed sediment samples from 21 sites in the inner harbor for a suite of analytes, including silver (USACOE, 1988). One site (in the Reserved Channel) had a reported silver concentration of 7 ppm while all the other sites had reported concentrations of less than 8 ppm.

NOAA's NS&T Program has sampled and analyzed surficial sediments from several sites around Boston Harbor for several analytes, including silver, since 1984. Figure 8.2 portrays this data graphically by year and site. The overall mean silver concentration in surficial sediments of the harbor was 3.99±2.56 ppm. Individual sample values ranged from 0.27 to 9.12 ppm. Site means, based on all 4 years of available data, ranged from 1.12±0.36 ppm at the site off the northern tip of Worlds End, to 6.30±2.21 ppm at the site southwest of Deer Island. The mean silver concentrations in the surficial sediments of the other sites were: Quincy Bay, 5.60±0.38 ppm; Dorchester Bay, 3.12±1.39 ppm; and northwest of Deer Island, 3.10±2.10 ppm. Statistical comparison of the log transformed data indicated that the Worlds End site was significantly different from the southwest Deer Island and Quincy Bay sites at p=0.05. When the data were grouped by harbor divisions (Table 8.2),

the means suggested that there was little difference in mean silver concentrations in the northwest and central harbor (4.56±2.50 and 5.60±0.38 ppm, respectively). The silver concentrations were significantly lower in the southeast harbor (1.12±0.36 ppm). When the northwest harbor data were subdivided, the Winthrop Bay area had a mean silver concentration of 5.10±2.64 ppm (16 samples) while the Dorchester Bay area had a mean of 3.12±1.39 ppm (6 samples). Statistical analysis of the log transformed data indicated that the southeast harbor was significantly different from the other harbor divisions at p=0.05.

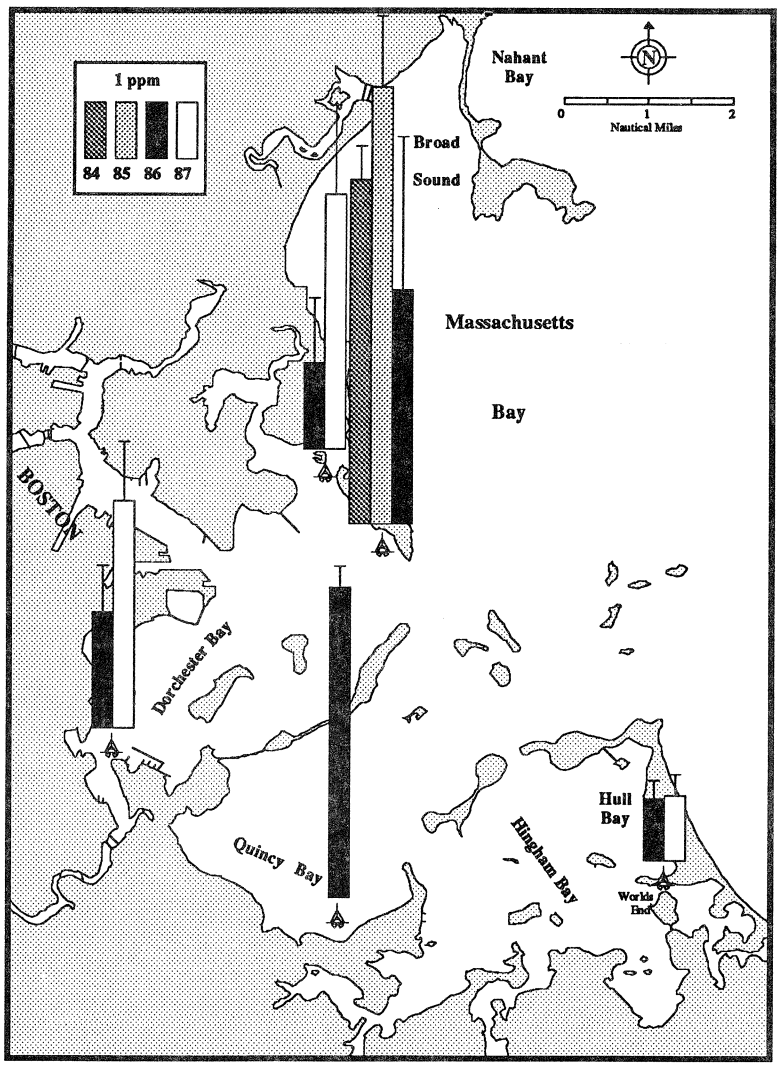


Figure 8.2. Mean silver concentrations (ppm dw) in the surficial sediments of Boston Harbor for 1984-87 (NOAA, unpublished) (bars represent one standard deviation).

On a broader scale, between 1984 and 1987, the NOAA NS&T Program analyzed surficial sediment samples from 23 sites from 11 areas along the New England coast. From Figure 8.3, that displays the means and standard deviations for the 11 coastal areas, it is clear that the mean silver concentration of the NS&T Program sites in Boston Harbor (3.99±2.56 ppm) was higher than the means for all other areas sampled in New England. The second most contaminated area was Salem Harbor (1.48±0.66 ppm), closely followed by Narragansett Bay (1.01±0.78 ppm). Statistical analysis of the log transformed data indicated that Boston Harbor was significantly different (p=0.05) from all the other areas of New England sampled except Salem Harbor.

When the mean silver concentrations in the surficial sediments of the individual New England NS&T Program sites were compared, the four sites with the highest mean silver concentrations were located in Boston Harbor (Table 8.3). In an attempt to determine a value for background silver levels, the overall mean was calculated for the five New England NS&T Program sites with the lowest silver concentrations in their surficial sediments (Table 8.3). This mean was 0.060±0.034 ppm; the overall mean silver concentration in the surficial sediments of Boston Harbor (3.99±2.56 ppm) based on the NS&T Program data, was more than 60 times greater than this reference mean. The four Boston Harbor sites with the highest silver concentrations had means more than 50 times higher than the reference mean. The lowest Boston Harbor site mean silver concentration (1.12±0.36 ppm, Worlds End) was more than 18 times higher than the reference mean.

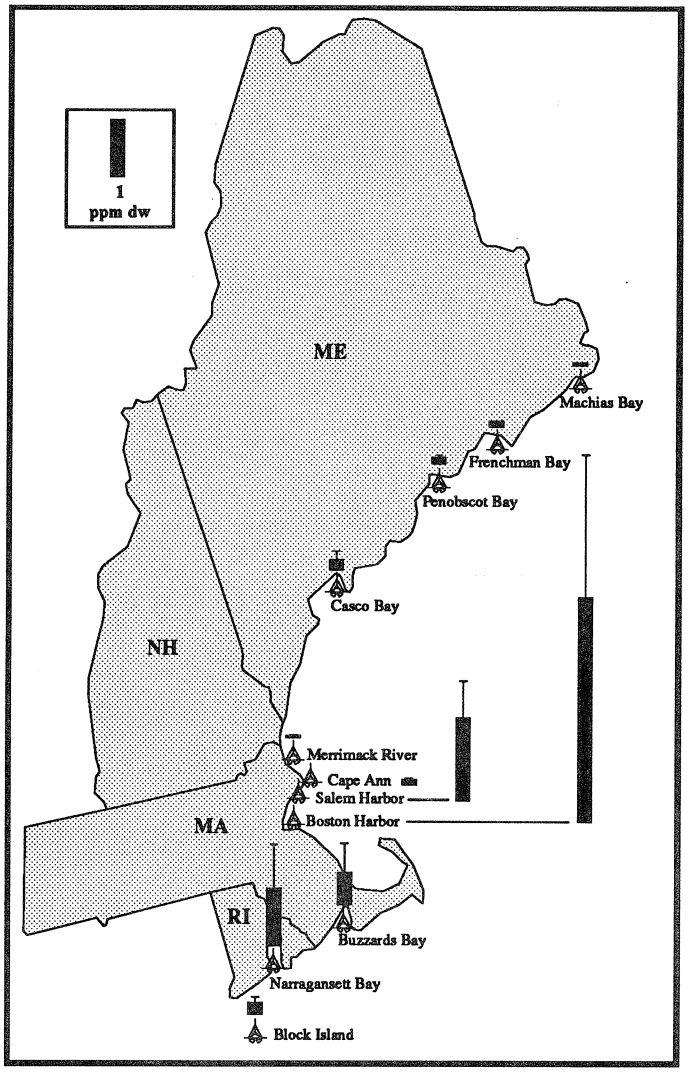


Figure 8.3. Mean silver concentrations in the surficial sediments of the outer New England coast for 1984-87 (NOAA, unpublished) bars represent one standard deviation).

Table 8.3. The five outer New England coast NOAA NS&T Program sites with the lowest and highest mean silver concentrations (ppm dw) based on data from 1984 through 1987.

Site	Mean	Standard Deviation	Count
MERRIMAC RIVER	0.027	0.021	5
MACHIAS BAY, MAINE	0.042	0.012	7
PICKERING ISLAND, PENOBSCOT BAY	0.069	0.045	3
STRAITSMOUTH ISLAND, CAPE ANN	0.084	0.040	3
FRENCHMAN BAY, MAINE	0.093	0.012	6
MOUNT HOPE, NARRAGANSETT BAY	2.20	0.10	3
NORTHWESTERN DEER ISLAND	3.10	2.10	6
DORCHESTER BAY	3.12	1.39	6
QUINCY BAY	5.60	0.38	3
SOUTHWESTERN DEER ISLAND	6.30	2.21	10

Temporal Trends

The only available data that spanned more than 2 years was that from NOAA's NS&T Program Benthic Surveillance (1984-86) and Mussel Watch (1986-87) projects. The yearly mean silver concentrations in the surficial sediments of Boston Harbor based on this data, ranged from a high of 7.91±1.27 ppm in 1985 to a low of 2.92±2.14 ppm in 1986. The yearly means for 1984 and 1987 were 6.20±0.64 ppm and 3.31±1.89 ppm, respectively. While the yearly means suggested a decrease in silver levels after 1985, the difference in the yearly mean silver concentrations can be explained by the difference in the sites sampled each year rather than a difference in overall silver concentrations (Figure 8.2). When the yearly means for the individual sites were compared, the Benthic Surveillance site (southwest of Deer Island) means suggested a decrease in silver levels from 1985 to 1986 (7.91±1.26 to 4.92±1.91 ppm). However, analysis of the log transformed data indicated no significant difference between the 2 years (p=0.05). When the yearly means of the individual Mussel Watch sites were compared, the means for the Dorchester Bay (2.10±0.82 to 4.13±1.02 ppm) and Deer Island (1.57±1.18 to 4.63±1.59 ppm) sites indicated an increase in silver levels between 1986 and 1987. Those for the Worlds End site (1.09±0.38 to 1.16±0.41 ppm) indicated no change between the 2 years (Figure 8.2). One-tailed t-tests of the log transformed data for the individual sites indicated a significant difference among years for the Dorchester Bay site only (p=0.05).

Biota

Since 1976, over 130 tissue samples from a variety of organisms in Boston Harbor have been analyzed for silver content. Silver concentrations ranged from a low of 0.05 ppm in the muscle of a winter flounder (*P. americanus*) to a high of 8.71 ppm in the soft parts of a mussel (*M. edulis*). Table 8.4 gives the statistics on silver contamination of biota by organism and tissue. The data for winter flounder suggest that silver tends to accumulate more in the liver than in muscle tissue.

Table 8.4 Harborwide means, standard deviations, medians, ranges, and sample sizes (count) for silver concentrations (ppm dw) in biota by organism and tissues based on all the available data sets.

		Mean	Standard Deviation	Median	Range	Count
P. americanus						
	liver	0.88	0.87	0.64	0.06-4.35	36
	muscle	0.15	0.12	0.11	0.05-0.28	3
H. americanus						
	muscle	1.42	0.58	1.29	0.74-2.48	8
M. edulis						
	soft parts	1.54	1.38	1.13	0.34-8.71	84

Geographic Trends.

Only lobster muscle tissue and mussel soft part tissue were sampled from more than one division of the Harbor (Table 8.5). The mussel data suggested that the central harbor biota contained the highest levels of silver, followed closely by the northwest and southeast harbors. The mussels in the inner harbor had the lowest silver levels. The lobster muscle data also suggested that the central harbor biota had the highest levels of silver, followed by the inner harbor and then the northwest harbor.

In 1976, the U. S. EPA sampled mussels and other bivalves from 107 sites nationwide and analyzed the samples for a variety of metals and organic analytes, including silver (Goldberg *et al.*, 1978). A composite sample of *M. edulis* from a site on the northwest side of

Table 8.5 Mean silver concentrations (ppm dw) of the entire harbor and the four divisions in lobster muscle and the soft parts of mussels (the number in parentheses is the sample size).

	H. americanus muscle	*M. edulis* soft parts
OVERALL	1.42 (8)	1.54 (84)
INNER HARBOR	1.48 (2)	0.85 (28)
NORTHWEST HARBOR	1.29 (4)	1.00 (19)
CENTRAL HARBOR	1.61 (2)	2.76 (28)
SOUTHEAST HARBOR	N/A	1.01 (9)

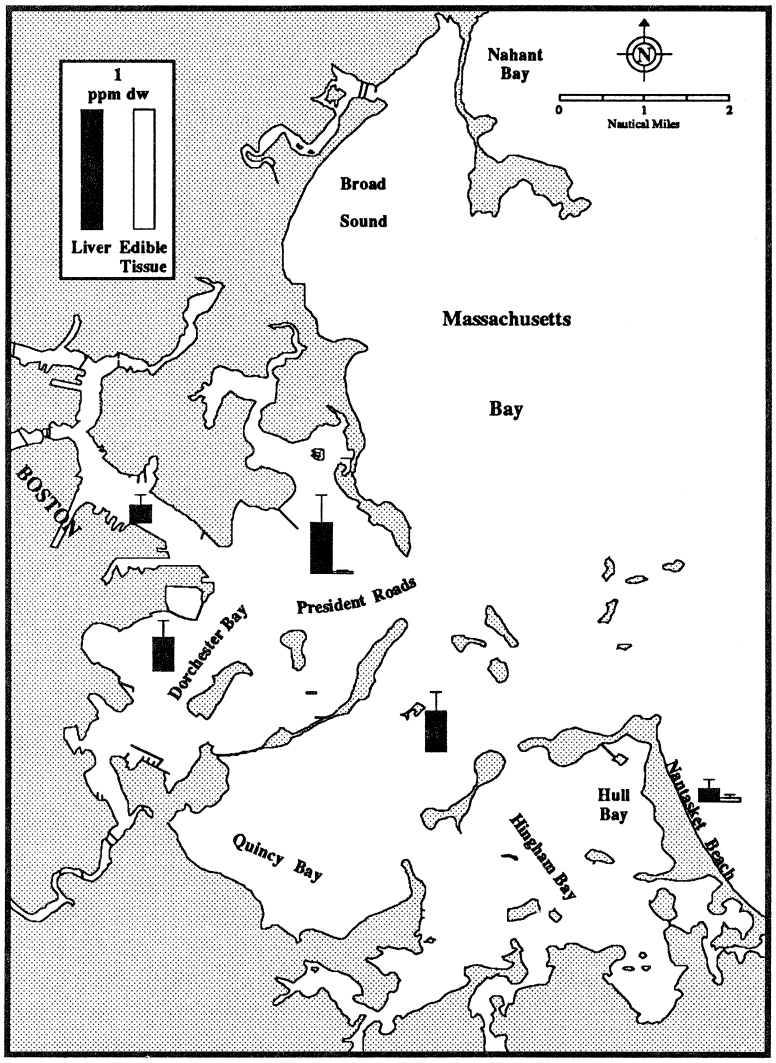


Figure 8.4. Mean silver concentrations in liver and edible tissue of *P. americanus* sampled from Boston Harbor in 1979 (Metcalf & Eddy, 1984) (bars represent one standard deviation).

Deer Island was found to have a silver concentration in the soft parts of 0.43 ppm. Between Block Island and the Canadian Border, 10 other New England sites were sampled. Silver concentrations in the soft parts of *M. edulis* were found to range from 0.04 ppm at Blue Hill Falls, Maine to 0.12 ppm at Plymouth, Massachusetts.

In 1979, as a part of the 301h waiver application for the Deer Island and Nut Island sewage treatment plants, winter flounder (*P. americanus*) and lobster (*H. americanus*) tissue samples from five sites in and around Boston Harbor were analyzed for levels of several analytes, including silver (Metcalf and Eddy, 1984). The livers of four winter flounder from each of four different sites in Boston Harbor and one site outside the harbor (Nantasket Beach) were analyzed for silver levels. The values for the individual samples ranged from 0.55 ppm from the President Roads site to 2.24 ppm from the Nantasket Beach site. The mean silver concentrations in livers for the five sites ranged from 0.34±0.27 ppm at the President Roads site to 1.28±0.745 ppm at the Nantasket Beach site (Figure 8.4). The Inner Harbor, Nut Island Discharge, and Dorchester Bay sites had means of 0.39±0.30, 0.96±0.47, and 1.05±0.74 ppm, respectively. When the data were log transformed and analyzed, none of the sites was significantly different at p=0.05. When the data were looked at with regard to the harbor divisions, the

means suggested that there was a trend of increasing silver going from the inner harbor to Massachusetts Bay. However, as the sites' means showed, when the northwest harbor was divided into the Winthrop Bay area and Dorchester Bay area, the Winthrop bay area had the lowest mean silver concentration in winter flounder liver, while Dorchester Bay area had the second highest mean. It should be noted that statistical analysis of the log transformed data indicated no significant difference between any of the harbor divisions (p=0.05). Unfortunately, only five edible tissue samples (three samples from President Roads and two from Nantasket Beach) were analyzed for silver. The silver concentrations in individual specimens ranged from 0.50 ppm in two specimens, one each from Nantasket Beach and President Roads, to 0.28 ppm in a specimen from the President Roads site. The mean silver concentrations in winter flounder edible tissue at the two sites were 0.08 ppm at the Nantasket Beach site and 0.15 ppm at the President Roads site (Figure 8.4).

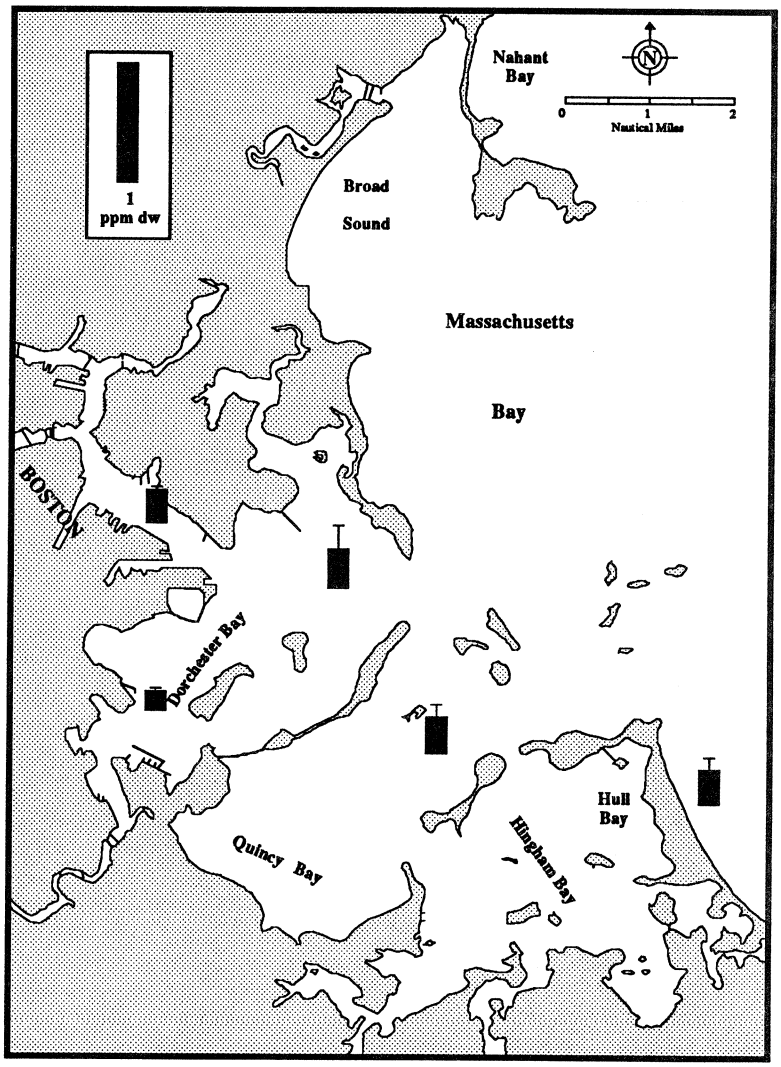


Figure 8.5. Mean silver concentrations (ppm dw) in lobster claw and tail muscle tissue sampled from Boston Harbor in 1979 (Metcalf & Eddy, 1984) (bars represent one standard deviation).

Two lobsters each were collected from the same five sites and the claw and tail muscle tissue was analyzed for levels of silver. Silver concentrations in the individual specimens ranged from less than 0.74 to 2.48 ppm. The means for the five sites ranged from lows of 0.84 ppm, at the Dorchester Bay site, to a high of 1.74 ppm at the President Roads site. The Inner Harbor, Nantasket Beach, and Nut Island Discharge sites had means of 1.48, 1.53, and 1.61 ppm, respectively (Figure 8.5). None of the sites were significantly different based on analysis of the log transformed data (p=0.05). When the lobster muscle data were grouped by division, the central harbor had the highest mean silver concentration (1.61 ppm), followed by Massachusetts Bay (1.53 ppm), then the inner harbor (1.48 ppm), and finally, the northwest harbor (1.29 ppm). Statistical analysis of the log transformed data indicated no significant difference between any of the divisions nor between any of the divisions at p=0.05. Concerning the subdivisions of the northwest harbor, the lobster muscle data indicated the reverse of the winter flounder liver data. The Dorchester Bay site had the lowest mean silver concentration (0.84 ppm) while the Winthrop Bay area site had the highest (1.74 ppm).

NOAA's Mussel Watch Project, a part of the NS&T Program, has sampled mussels (*M. edulis*) on an annual basis from four sites in and around Boston Harbor since 1986 (Figure 8.6). Three whole-body composite samples from each site were analyzed for a variety of analytes, including silver. The overall mean concentration of silver in the mussels for the three sites in Boston Harbor from 1986 through 1988 was 0.96±0.48 ppm with a range of from 0.26 to 1.90 ppm. The means for the individual sites were 0.91±0.43 ppm in southwestern Dorchester Bay, 1.01±0.38 ppm in Hingham Bay off Worlds End, and 1.51±0.56 ppm northwest of Deer Island. Mussels from the site outside the harbor, Outer Brewster Island, had a mean silver concentration of 0.76±0.54 ppm. Statistical analysis of the log transformed data for the four sites indicated that none of the sites were significantly different (p=0.05).

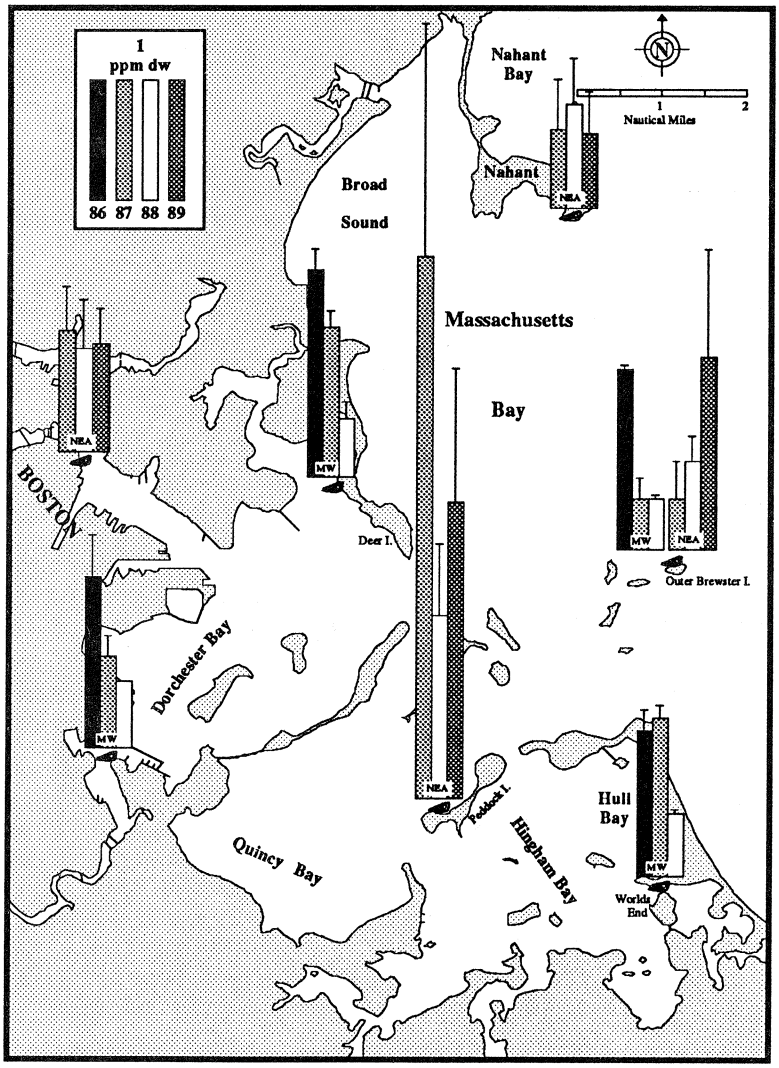


Figure 8.6. Mean silver concentrations (ppm dw) in the soft-parts of *M. edulis* from Boston Harbor and environs for 1986-89, based on data from the New England Aquarium (NEA) and NOAA (MW) mussel watch projects (Robinson *et al.*, 1990; NOAA, unpublished) (bars represent one standard deviation)

Since 1987, the NEA has conducted their own Mussel Watch Program (Robinson *et al.*, 1990). They sampled mussels from two sites within Boston Harbor and two sites in Massachusetts Bay. These sites included the same site on Outer Brewster Island that NOAA's Mussel Watch samples. The mean silver concentration in Boston Harbor, based on data from the two sites for the 3 years from 1987 through 1989, was 1.81±1.60 ppm with a range of from 0.37 to 8.71 ppm. The means for the two sites were 2.76±1.79 ppm at the Peddocks Island site and 0.85±0.32 ppm at the Central Wharf, Inner Harbor site. The two sites from Massachusetts Bay had means of 0.95±0.74 ppm at the Outer Brewster Island site and 0.70±0.385 ppm at the Pumphouse Beach, Nahant site. When the data for the four sites was log transformed and the sites statistically compared, the Peddocks Island site was found to be significantly different from the other three sites at p=0.05. Figure 8.6 plots the NEA data alongside the NOAA Mussel Watch data.

On a broader scale, the silver levels in mussels from the Boston Harbor NS&T sites were compared to those from the other New England NS&T Mussel Watch sites (Table

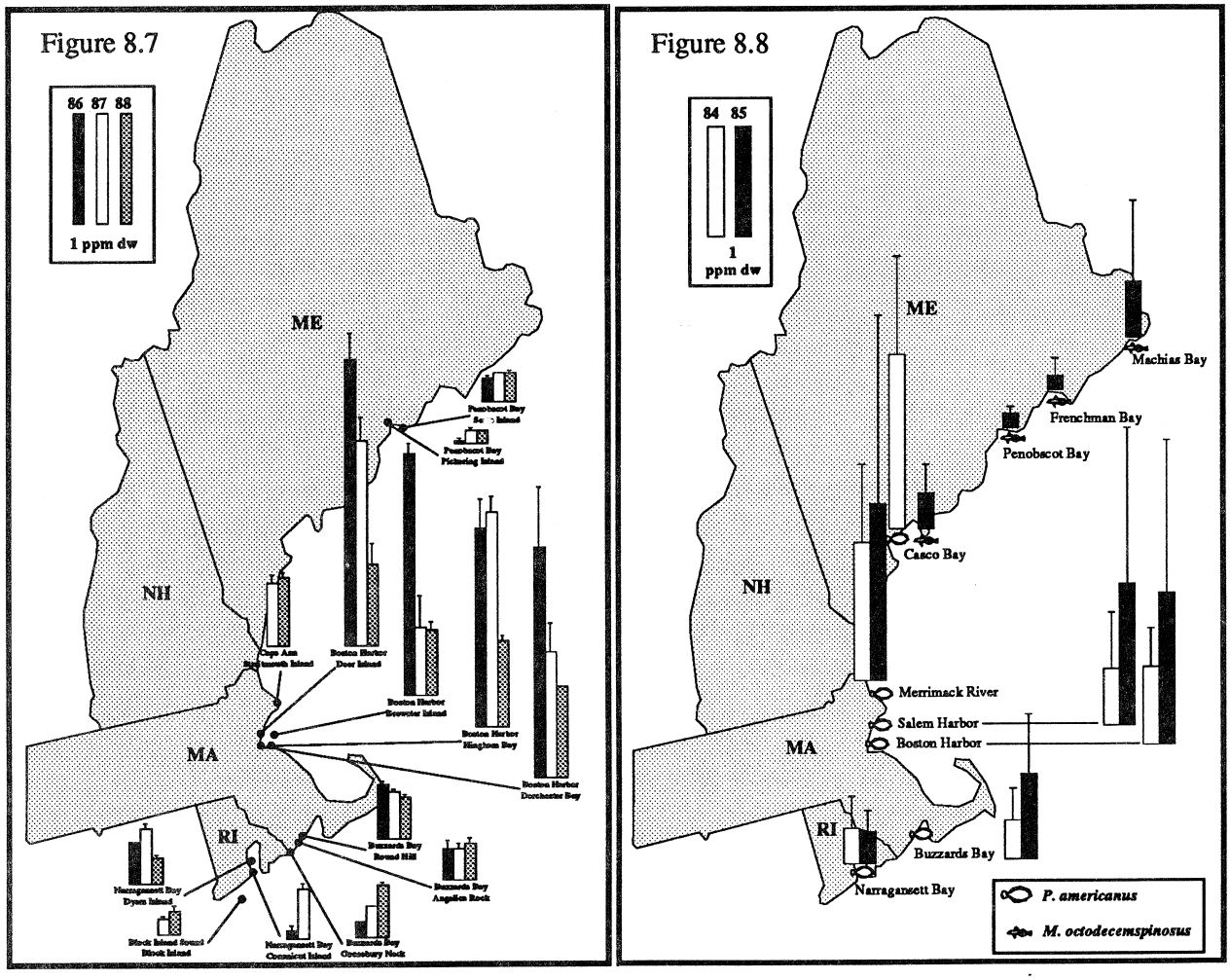
8.6 and Figure 8.7) and the log transformed data statistically analyzed. The Deer Island and Hingham Bay sites were significantly different from all the sites outside Boston Harbor, except for the Brewster Island and Cape Ann sites. The Dorchester Bay site was significantly different from all but the Brewster Island, Cape Ann, and Round Hill sites (p=0.05). This data suggests that silver levels in mussels were significantly higher in the vicinity of Boston Harbor than in the rest of New England. When a reference value was calculated based on the five sites with the lowest mean silver concentrations in mussels, a value of 0.14±0.08 ppm was obtained. The Boston Harbor sites had mean silver values of from 6.5 to 8.2 times higher than this reference value. On a national scale, the Mussel Watch sites where *M. edulis* was sampled had mean silver concentrations ranging from 0.012 to 1.74 ppm with an overall mean for all the sites of 0.32±0.41 ppm; 29 percent of the sites had means less than 0.10 ppm, while 64 percent had concentrations between 0.10 and 1.00 ppm, and only four sites (7%) had mean silver concentrations in excess of 1.00 ppm. The Boston Harbor Deer Island site had the second highest mean nationwide. When the sites where *M. californianus* was sampled were included in the calculations, the overall mean became 0.41±0.55 ppm, while 31 percent of the sites had means less than 0.10 ppm, 57 percent of the sites had means between 0.10 and 1.00 ppm, and 12 percent of the sites had means greater than 1.00 ppm. Based on this data, Boston Harbor mussels appeared to be relatively highly contaminated with silver since two of the Harbor sites were in the top 12 percent nationwide and the third site was in the top 14 percent of all sites sampled.

Table 8.6 The mean silver concentrations (ppm dw) in *M. edulis* at the 13 outer New England coast NS&T Program Mussel Watch sites. The outlined means are for Boston Harbor sites.

Site	Mean	Standard Deviation	Count
DEER ISLAND, BOSTON HARBOR	1.15	0.56	9
HINGHAM BAY, BOSTON HARBOR	1.01	0.40	9
DORCHESTER BAY, BOSTON HARBOR	0.91	0.43	9
OUTER BREWSTER ISLAND	0.76	0.54	9
CAPE ANN, STRAITSMOUTH ISLAND	0.39	0.04	6
ROUND HILL, BUZZARDS BAY	0.294	0.041	9
DYERS ISLAND, NARRAGANSETT BAY	0.25	0.08	9
GOOSEBURY NECK, BUZZARDS BAY	0.21	0.02	8
ANGELICA ROCK, BUZZARDS BAY	0.20	0.04	9
CONANICUT ISLAND NARRAGANSETT BAY	0.18	0.14	6
SEARS ISLAND, PENOBSCOT BAY	0.16	0.02	9
BLOCK ISLAND, RHODE ISLAND	0.12	0.03	6
PICKERING ISLAND, PENOBSCOT BAY	0.06	0.03	9

NOAA's Benthic Surveillance Project, a part of the NS&T Program, has sampled winter flounder (*P. americanus*) from an area just west of Deer Island annually since 1984. The mean silver concentration in the liver of the fish sampled in 1984 and 1985 was 1.04±1.04 ppm with a range of 0.08 to 4.35 ppm. The mean concentration of silver in flounder livers for all the New England Benthic Surveillance sites ranged from a low of 0.30±0.26 ppm, at the Narragansett Bay site, to a high of 1.58±0.88 ppm at the Casco Bay site (Figure 8.8). The mean silver concentration of winter flounder liver from Boston Harbor was exceeded by the means for the Casco Bay and Merrimac River sites (1.43±1.29 ppm). Statistical analysis of the log transformed data indicated that the Boston Harbor site, along with the Casco Bay and Merrimac River sites, were significantly different from the Narragansett Bay site at p=0.05. The highest reported value for silver in a single sample was 5.35 ppm from the Merrimac River site. The second highest value, 4.35 ppm was from the Boston Harbor site. No comparison could be made between Boston Harbor and the three northern-Maine sites; because a different species, longhorn sculpin (*M. octodecemspinosus*), was sampled at the Maine sites. The Benthic Surveillance Project sampled winter flounder at four other sites during the same time frame: two in Long Island Sound and one each in Raritan and Great

bays in New Jersey. The site means for Great Bay and east and west Long Island Sound (0.76±0.71, 0.62±0.70, and 0.33±0.36 ppm, respectively) were less than the mean for Boston Harbor. The mean for the Raritan Bay site (1.91 ±2.53 ppm) was greater than the Boston Harbor mean. As the high standard deviation suggests, the Raritan Bay mean was strongly influenced by a single specimen with a silver concentration of 8.80 ppm. Excluding this specimen from the calculations changed the Raritan Bay mean to 1.15±0.78, still higher than the Boston Harbor mean.



Figures 8.7 & 8.8. Mean silver concentrations (ppm dw) in the soft-parts of *M. edulis* (Fig. 8.7) and liver tissue of *P. americanus* and *M. octodecemspinosus* (Fig. 8.8) from the outer New England coast (NOAA, unpublished) (bars represent one standard deviation).

Temporal Trends

No long-term temporal trends in the silver levels of Boston Harbor biota could be determined based on the available data because of a lack of data sets. The only internally consistent data sets sampling the same organism from the same locations over a number of years were the NS&T Program's Benthic Surveillance and Mussel Watch projects and the NEA Mussel Watch program. Data for these projects were only available for 2, 3 and 3 years, respectively. Between 1984 and 1985 there was more than a 90 percent increase in the level of silver in winter flounder livers (0.70±0.37 to 1.38±1.38 ppm) (Figure 8.8). When the two extremely high sample silver values (4.35 and 3.15 ppm) were excluded from the calculations, the 1985 mean became 0.79±0.59 ppm, only a 13 percent increase over 1984. The

3 years of data for *M. edulis* from the NS&T Program Mussel Watch Project indicated approximately a 24 percent decrease in silver levels between 1986 and 1987 (1.44±0.32 to 1.10±0.28 ppm). The data also indicated a further 52 percent reduction in silver in 1988 (0.52±0.07) (Figure 8.6). The yearly means for the New England Mussel Watch program also indicated a greater than 50 percent reduction in silver levels between 1987 and 1988 (2.71±2.27 to 1.16±0.63 ppm). However, there was approximately a 37 percent increase between 1988 and 1989 (1.60±1.12 ppm). It is noteworthy that most of the yearly variation in the NEA Mussel Watch harborwide mean was largely due to fluctuations at the Peddocks Island site. Yearly means stayed relatively constant at the Central Wharf site in the inner harbor. The EPA Deer Island site had a silver concentration in the soft parts of mussels of 0.43 ppm in 1976. This was compared to the NS&T Program Deer Island site (which is about 0.5 miles northwest of the EPA site) with yearly means of 1.73, 1.23, and 0.49 ppm (1986, 1987, and 1988, respectively). There appeared to be an approximate fourfold increase in silver concentrations in the 11 years between 1976 and 1986, and then a decrease in silver levels between 1986 and 1988 back to approximately the 1976 level. However, this comparison needs to be viewed with caution because the EPA value was based on only one composite sample while the NS&T Program values were based on three composite samples each. Also the difference between the EPA value and the NS&T Program values may be the result of differences in laboratory methodology.

Summary

Boston Harbor sediments were found to contain silver at levels 5 times greater than background levels. The overall mean value of silver in Boston Harbor (3.12±2.04 ppm) was compared to the overall mean of San Francisco Bay (1.13±1.52 ppm) (Long *et al.*, 1988). It was found to be approximately 2.75 times higher than the San Francisco Bay mean. However, when just the NS&T Program data for the two ports were compared, the Boston Harbor mean, 3.99±2.03 ppm, was more than 4 times higher than the San Francisco Bay mean, 0.97±1.85 ppm (Long *et al.*, 1988) (Table 8.7). The large standard deviation for the NS&T Program San Francisco Bay mean was due to three samples from a highly contaminated channel, Islais Creek Waterway. These samples ranged from 4.00 to 8.60 ppm. Outside the channel, the highest value for an NS&T Program sample was 2.40 ppm. When the Islais Creek Waterway data was excluded from the calculations, the mean silver concentration in San Francisco Bay sediments analyzed by the NS&T Program was 0.51±0.59 ppm. This is approximately 1/8 the mean silver concentration in Boston Harbor sediments analyzed by the NS&T Program. The overall data set indicated little difference among the silver levels of the inner, northwest, and central harbor division sediments. The southeast harbor sediments had a mean silver concentration, less than 1/2 the other divisions. This trend was also apparent in the NOAA NS&T Program data set which covered the three outer harbor divisions; only, the difference between the southeast harbor mean silver concentration and those of the other two divisions was more extreme (1/4 to 1/5 lower). However, the Massachusetts DEQE data set indicated little difference between any of the four harbor divisions with less than a 30 percent difference between the highest and lowest division means (central harbor 1.78 ppm and inner harbor 1.30 ppm).

Table 8.7. Comparison of silver sediment statistics for Boston Harbor, NS&T Program Reference (based on the 5 New England sites with the lowest levels of silver) and San Francisco Bay in ppm dw. Statistics for San Francisco Bay derived from Long *et al.*, 1988.

Area	Mean	Standard Deviation	Median	Range	Count
Boston	3.12	2.04	2.80	0.27-9.12	82
NS&T Program Boston	3.99	2.03	2.8	0.27-9.12	31
NS&T Program Reference	0.06	0.03	0.05	0.01-0.13	24
San Francisco Bay	1.13	1.52	0.58	0.01-16.00	336
NS&T Program San Francisco Bay	0.97	1.85	0.34	0.01-8.60	42

The data for the northwestern harbor was subdivided into that for the Winthrop Bay area and that for Dorchester Bay. The NOAA NS&T Program data set indicated that the Winthrop Bay area had approximately a 60 percent higher mean sediment concentration of silver than did Dorchester Bay. The Massachusetts DEQE data indicated the reverse. The Dorchester Bay mean silver concentration was approximately 60 percent higher than that for the Winthrop Bay area.

Because no reliable historical data on silver levels in Boston Harbor sediments were available, no long -term temporal trends could be determined. NOAA NS&T Program data suggested a short-term trend of decreasing silver concentrations, but the differences in yearly silver means may more readily be explained by the differences in sites sampled each year.

Based on the available data, Boston Harbor biota appears to be moderately to highly contaminated with silver. Boston Harbor mussels (*M. edulis*) had the highest mean silver concentrations of all the New England NS&T Program sites sampled. When compared to all NS&T Program mussel sites sampled in the country, all three sites had means in the top 14 percent. The winter flounder (*P. americanus*) liver data suggested that Boston Harbor had moderate levels of silver, since, among the NS&T Program sites, two of the four New England sites and one middle Atlantic site had higher mean silver concentrations in winter flounder liver than the Boston site. There were no obvious geographic or temporal trends in silver content of biota within Boston Harbor based on the available data. This is because relative concentrations among different areas of the Harbor varied with the organism and tissue sampled. With the exception of the NS&T Program and the New England Mussel Watch Program, none of the studies sampled the same organism from the same sites over a period of years.

NICKEL

Nickel is a naturally occurring element that is believed to function as an essential trace element, although its specific function is unknown (Kirchgessner and Schnegg, 1980). Nickel is both acutely toxic (Birge and Black, 1980) and carcinogenic (Furst, 1980). In a review of the literature, Long and Morgan (1990) found data suggesting that nickel levels in sediment below about 17 ppm have little or no effect on biota, while levels of 150 ppm or greater generally have either a chronic or acute effect on the organisms tested.

Sediments

Since the late 1960s, over 350 surficial sediment samples from Boston Harbor have been analyzed for nickel concentrations. Based on this data, the overall mean concentration of nickel in the surficial sediments of the Harbor was 34 ppm with a standard deviation of 34 and a range of from 2.5 to 340 ppm (Table 9.1). The median concentration was 28 ppm. The large standard deviation and the difference between the mean and the median values are because approximately 2.5 percent of the samples analyzed had concentrations greater than 100 ppm. The vast majority of the samples, approximately 94 percent, had values between 10 and 100 ppm, inclusive. The remaining 4 percent of the samples contained less than 10 ppm nickel. Approximately 58 percent of the samples had concentrations in the relatively narrow range of 20 to 45 ppm.

Table 9.1. Means, standard deviations, medians, ranges, and number of samples (Count) for nickel concentrations (ppm dw) in surficial sediments of all of Boston Harbor and for the four regions of the harbor, based on all the available data sets.

	Mean	SD	Median	Range	Count
OVERALL	34	34	28	2.5-340	369
INNER HARBOR	52	49	42	4.0-340	109
NORTHWEST HARBOR	27	12	25	7.3- 74	147
CENTRAL HARBOR	33	44	25	2.5-293	45
SOUTHEAST HARBOR	24	11	22	8.0- 58	68

Geographic Trends

When the combined data set was broken down into the four harbor divisions, both the means and medians suggested that the surficial sediments of the inner harbor had the highest levels of nickel (52 and 42 ppm). The means suggested that the central harbor had the second highest nickel levels (33 ppm) followed by the northwest and southeast harbor (27 and 24 ppm, respectively). The medians suggested there was virtually no difference among nickel levels in the three outer harbor divisions (Table 9.1). The difference between the means and medians can be explained by the inclusion of two of the nine sediment samples with nickel concentrations in excess of 100 ppm (130 and 293 ppm) in the central harbor data set. The inclusion of these two samples, both of which came from marina sediments, also resulted in the high standard deviation for the central harbor. When these two samples were excluded from the calculations, the central harbor mean became 24 ppm with a standard deviation of 11. When the northwest harbor was subdivided, nickel levels in both subdivisions, Winthrop Bay area and Dorchester Bay, were virtually identical (27±13 and 27±9 ppm, respectively).

Around 1970, White (1972) collected and analyzed over 130 surficial sediment samples from Boston for a variety of metals, including nickel. He found an overall mean nickel concentration in Boston Harbor surficial sediments of 32 ppm. Individual sample concentrations ranged from a low of 8 ppm in two samples, one from southwest Thompson Island and one from eastern Hull Bay, to a high of 129 ppm in a sample taken from the

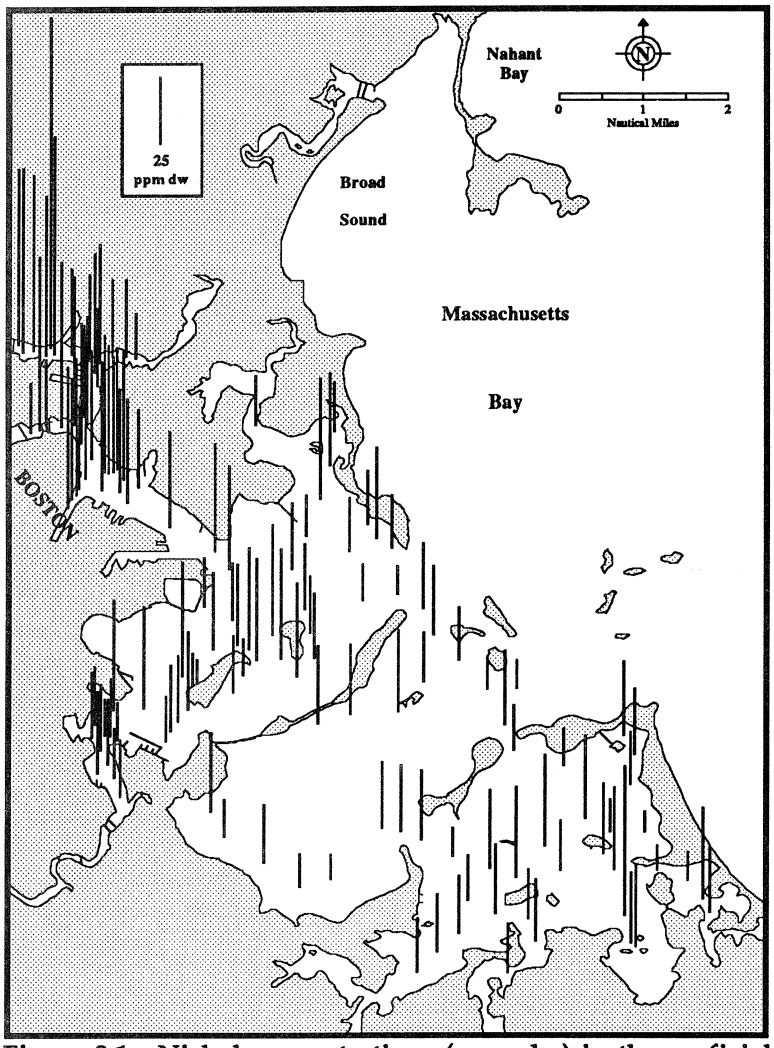


Figure 9.1. Nickel concentrations (ppm dw) in the surficial sediments of Boston Harbor from around 1970 (White, 1972).

lower reaches of the Mystic River (Figure 9.1). Figure 9.1 and Table 9.2 indicate that nickel concentrations in the surficial sediments were highest in the inner harbor with no clear trends in the outer harbor divisions. Statistical analysis of the log transformed data for the four harbor divisions indicated that the inner harbor was significantly different from the other three divisions at p=0.05. When the data for northwest harbor was subdivided, the Winthrop Bay area (16 samples) and the Dorchester Bay area (32 samples) had virtually identical levels of nickel (27 ppm).

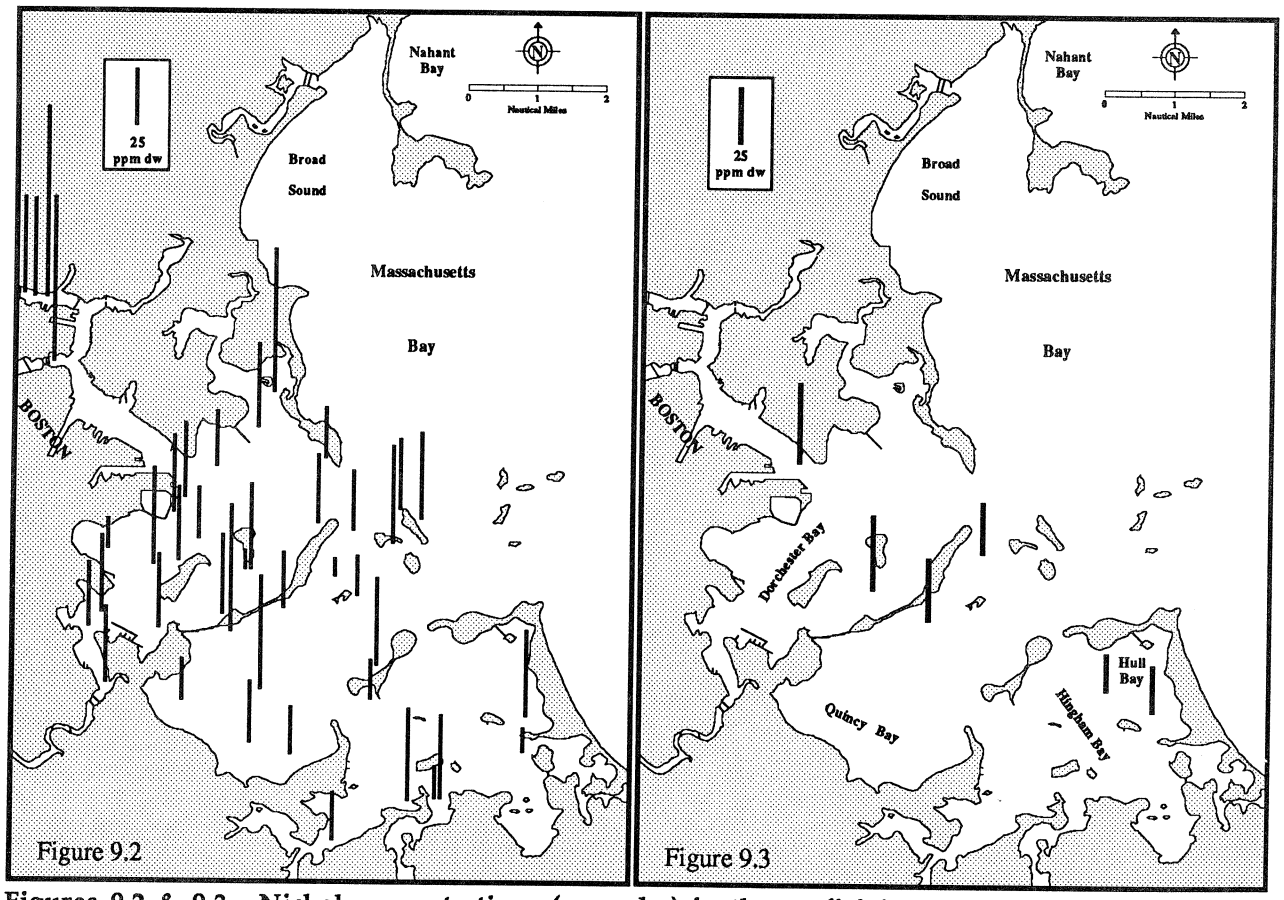
In 1971, the NEA collected 55 cores of Boston Harbor sediments and analyzed various sections of the cores for heavy metal content (Gilbert *et al.*, 1972). Based on 43 samples of the upper surface of the cores analyzed for nickel, they found nickel concentrations ranging from a low of 8 ppm in a sample taken between Long and Rainsford islands, to a high of 87 ppm in a sample taken from the lower reaches of the Mystic River (the same general locations as the high sample taken by White). The overall mean nickel concentration in the surficial sediments was 34±16 ppm (Table 9.2). As with the White data, a graphic representation (Figure 9.2) suggests that

Table 9.2. Mean nickel concentrations in the surficial sediments of Boston Harbor and the four divisions of the harbor, in ppm dw, based on the data of White (1972), Gilbert *et al.* (1972), Isaac and Delaney (1975), MA DEQE, 1986 & 1987) and NOAA's NS&T Program (unpublished). The numbers in parentheses are the number of data points used to calculate the means.

	White 1970?	Gilbert *et al.* 1971	Isaac and Delaney 1972	MA DEQE 1985-86	NOAA NS&T 1984-87
OVERALL	32 (133)	34 (43)	26 (6)	24 (30)	27 (31)
INNER HARBOR	49 (38)	63 (4)	36 (1)	31 (8)	N/A
NORTHWEST HARBOR	27 (48)	32 (18)	33 (1)	22 (14)	30 (22)
CENTRAL HARBOR	21 (16)	32 (13)	26 (2)	20 (5)	30 (3)
SOUTHEAST HARBOR	24 (31)	28 (8)	19 (2)	23 (3)	14 (6)

the inner harbor has the highest concentrations of nickel with little if any difference among the three outer harbor divisions. This is supported by the division means listed in Table 9.2. When the log transformed data for the harbor divisions were compared statistically the inner and southeast harbor divisions were found to be significantly different at p=0.05. When the data for the northwest harbor are subdivided, the Winthrop Bay area (4 samples) had a slightly higher mean nickel concentration (38±19 ppm) than did the Dorchester Bay area (16 samples; 31±9 ppm). The highest nickel concentration in the outer harbor was a sample from the Winthrop Bay area that was a large part of the difference between the two subdivisions. Excluding this sample, the Winthrop Bay area mean was 29±8 ppm.

Between 1971 and 1974, Massachusetts conducted a toxic element survey of the waters of the State (Isaac and Delaney, 1975). The survey included the analysis of sediment samples for volatile solids and a variety of heavy metals, including nickel. The combined mean nickel concentration from six surficial sediment samples from around Boston Harbor was 26±7 ppm. The range was from 17 to 36 ppm (Figure 9.3). Because so few samples were analyzed, no statistical comparison between harbor divisions could be made; but, the data did suggest a trend of decreasing nickel concentrations from northwest to southeast (Table 9.2).



Figures 9.2 & 9.3. Nickel concentrations (ppm dw) in the surficial sediments of Boston Harbor in 1971 (Gilbert *et al.*, 1972) (Fig. 9.2) and from 1971-74 (Isaac & Delaney, 1975) (Fig. 9.3).

Data were obtained from the New England Division of the USACOE for dredging studies conducted in and around Boston Harbor from 1972 through 1988 (USACOE, 1972-88; 1981; 1988). The USACOE analyzed over 125 samples during this period for nickel content. The overall mean nickel concentration for the Harbor based on this data was 42±53 ppm. The

range was from a low of 2.5 ppm in a sample taken from Squantum Point in Quincy Bay, to a high of 340 ppm in a sample taken from the lower reaches of the Mystic River. The main reason for the high standard deviation was that the vast majority of the of the samples (87%) had nickel concentrations between 10 and 100 ppm, inclusive. Approximately 7 percent of the samples had less than 10 ppm. Only 6 percent of the samples had concentrations in excess of 100 ppm. Approximately 43 percent were within the relatively narrow range of 20 to 45 ppm. When the data was grouped by harbor divisions, the means ranged between 24±12 ppm in the southeast harbor and 78±116 ppm in the central harbor. The northwest harbor had a mean of 24±15 ppm, while the inner harbor had a mean of 57±64 ppm. The high mean and extremely high standard deviation for the central harbor resulted from a small sample size (six) and the inclusion of two of the nine sediment samples that had nickel concentrations in excess of 100 ppm (130 and 293 ppm). Excluding these samples from the calculations resulted in a central harbor mean of 12±13 ppm. As with the previously cited studies, the division means indicate that the inner harbor had higher levels of nickel in its sediments than did the northwest and southeast harbor. However, no conclusions can be drawn about the relative level of nickel in the central harbor because of the small sample size and very wide range of individual sample concentrations. The subdivisions of the northwest harbor, the Winthrop Bay area (37 samples) and the Dorchester Bay area (7 samples) had virtually identical mean nickel concentrations (24±16 and 25±2, respectively). Statistical analysis of the log transformed data indicated that only the inner and northwest harbors were significantly different at p=0.05. It should be noted that the vast majority of the samples analyzed were from the inner and northwest harbor (58 and 44, respectively). Only 6 samples were from the central harbor and 18 from the southeast harbor.

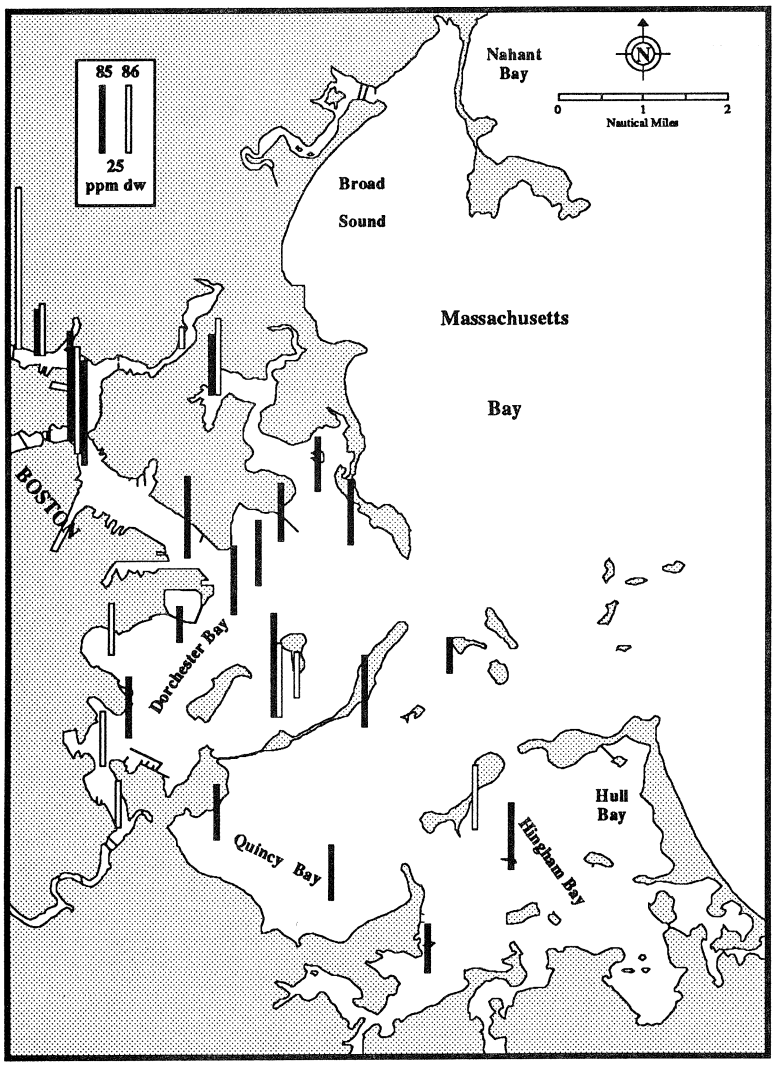


Figure 9.4. Nickel concentrations (ppm dw) in the surficial sediments of Boston Harbor in 1985 and 1986 (MA DEQE, 1986, 1987).

In 1985 and 1986 the Massachusetts DEQE, as part of their annual Boston Harbor Water Quality and Wastewater Discharge Survey, analyzed 30 surficial sediment samples for nickel content (Figure 9.4). They found an overall mean nickel concentration of 24±10 ppm ranging from a low of 8 ppm, in a sample taken from the lower reaches of the Chelsea River, to a high of 60 ppm in a sample taken from the lower reaches of the Mystic River. The vast majority

(93%) of the surficial sediment samples had nickel concentrations between 10 and 40 ppm, while 3 percent of the samples had concentrations less than 10 ppm and 3 percent of the samples had more than 40 ppm. While the means for the harbor divisions (Table 9.2) suggested that the inner harbor was slightly more contaminated than the other three harbor divisions with essentially the same levels of nickel in their surficial sediments, statistical analysis of the log transformed data indicated no significant difference between any of the divisions at p=0.05. As with the previously cited studies, there was virtually no difference among the subdivisions of the northwest harbor. The Winthrop Bay area had a mean nickel concentration of 23±2 ppm and the Dorchester Bay area had a mean of 22±8 ppm. The relatively homogeneous distribution of nickel throughout the harbor is apparent in Figure 9.4 that graphically displays the data by site and year.

NOAA's NS&T Program has sampled and analyzed surficial sediments from several sites around Boston Harbor for several analytes, including nickel, since 1984. Figure 9.5 portrays this data graphically by year and site. The overall mean nickel concentration in surficial sediments of the harbor was 27±9 ppm. Individual sample values ranged from 10 to 44 ppm. Site means, based on all 4 years of available data, ranged from 14±3 ppm at the site off the northern tip of Worlds End to 31±8 ppm at the site southwest of Deer Island and the Dorchester Bay site. The mean nickel concentrations in the surficial sediments of the other sites were: northwest of Deer Island, 29±8 ppm and Quincy Bay, 30±2 ppm. Statistical comparison of the log transformed data indicated that the Worlds End site was significantly different from all the other sites at p=0.05. When the data were grouped by harbor divisions (Table 9.2), the means suggested that there was no difference in nickel concentrations in the northwest and central harbor, but, the nickel concentrations were significantly lower in the southeast harbor. Statistical analysis of the log transformed data indicated that the southeast harbor was significantly different from both the northwest and central harbors at p=0.05.

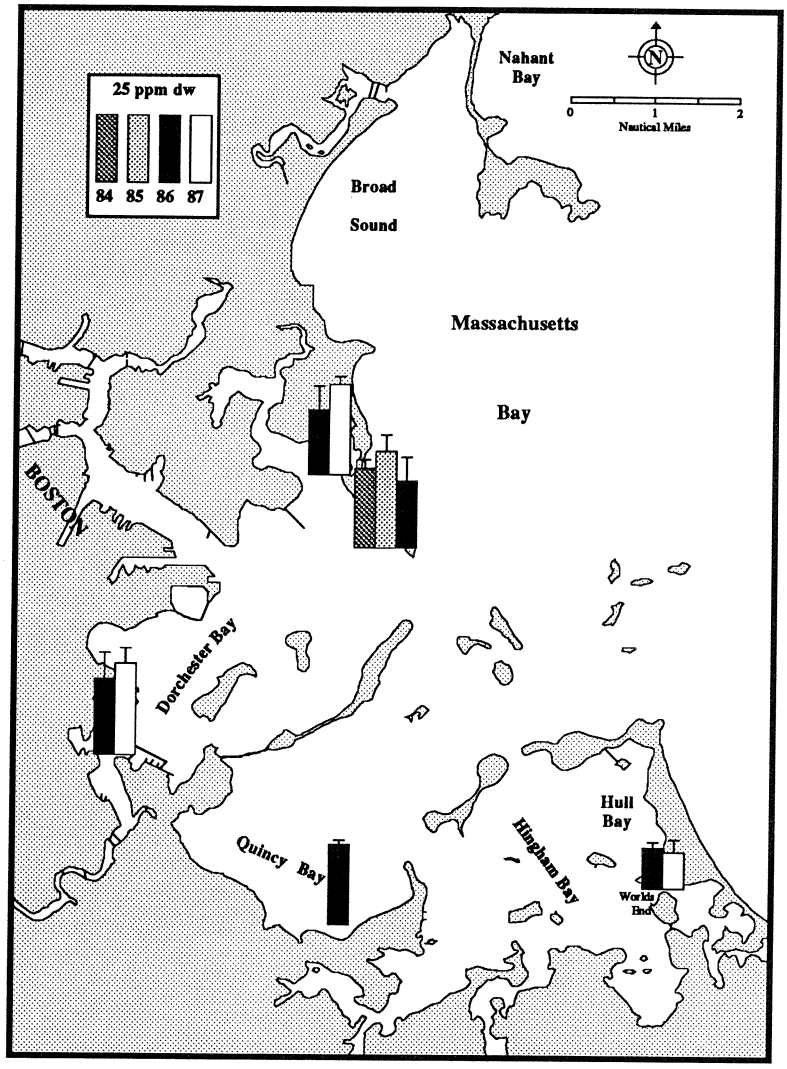


Figure 9.5. Mean nickel concentrations (ppm dw) in the surficial sediments of Boston Harbor by site and year for 1984-87 (NOAA, unpublished) (bars represent one standard deviation).

On a broader scale, between 1984 and 1987, the NOAA NS&T Program analyzed surficial sediment samples from 23 sites from 11 areas along the outer

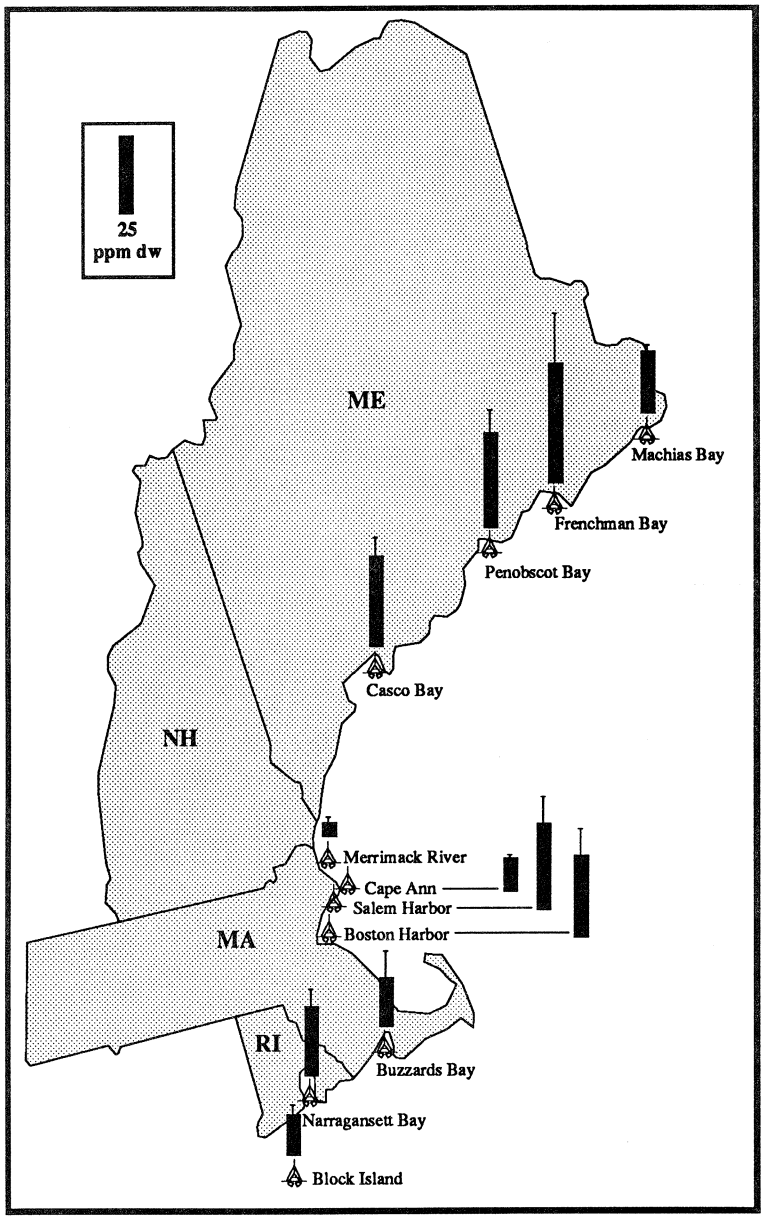


Figure 9.6. Mean nickel concentrations (ppm dw) in the surficial sediments along the outer New England coast for 1984-87 (NOAA, unpublished) (bars represent one standard deviation).

New England coast. The means and standard deviations for the 11 coastal areas are displayed in Figure 9.6. The overall mean NS&T Program site in Boston Harbor (27±9 ppm) was approximately in the middle of the range of means for all the areas in New England sampled by the NS&T Program. Statistical analysis of the log transformed data indicated that Boston Harbor was significantly different (p=0.05) from Buzzards Bay and the Merrimac River. In addition the Merrimac River was significantly different from all the areas sampled except Buzzards Bay and Cape Ann (p=0.05)

The mean nickel concentrations in the surficial sediments of the individual New England NS&T Program sites were compared. The Dorchester Bay and southwest Deer Island sites had the fourth highest mean nickel concentrations (Table 9.3). In an attempt to determine a value for background nickel levels, the overall mean was calculated for the five NS&T Program sites with the lowest nickel concentrations in their surficial sediments (Table 9.3). This mean was 8.5±3.5 ppm. The overall mean nickel concentration in the surficial sediments of Boston Harbor, based on the NS&T Program data, was approximately 3 times greater than this reference mean. The mean of the New England site with the highest nickel concentration, Frenchman's Island, was more than 4 1/2 times higher than this reference mean and approximately 33 percent higher than the highest Boston Harbor site.

Table 9.3. The five outer New England coast NOAA NS&T Program sites with the lowest and highest mean nickel concentrations (ppm dw) based on data from 1984 through 1987.

Site	Mean	Standard Deviation	Count
MERRIMAC RIVER	4.7	1.9	5
GOOSEBURY NECK, BUZZARDS BAY	8.1	3.5	6
ANGELICA ROCK, BUZZARDS BAY	8.4	1.8	6
STRAITSMOUTH ISLAND, CAPE ANN	10.9	1.1	3
BLOCK ISLAND, RHODE ISLAND	13.3	3.1	3
DORCHESTER BAY	31	8	6
SOUTHWESTERN DEER ISLAND	31	8	10
SEARS ISLAND, PENOBSCOT BAY	32	3	6
PENOBSCOT BAY	37	7	6
FRENCHMAN'S ISLAND	40	17	6

Temporal Trends

Figure 9.7 compares the yearly mean nickel concentrations in the surficial sediments of Boston Harbor based on all the available data sets (White, 1972: Gilbert *et al.*, 1972: Isaac and Delaney, 1975: USACOE, 1972-88; 1981, 1988: MA DEQE, 1986; 1987: NOAA, unpublished). There is no overall temporal trend apparent from Figure 9.7. When just the 4 years with largest sample sizes are compared (1970, 1971, 1985, and 1986), it appears that nickel concentrations in the surficial sediments of Boston Harbor were virtually unchanged since the early 1970s. The yearly fluctuations were more likely due to differences in the sites sampled than to any overall change in nickel concentrations.

Data were available from the USACOE on dredging studies for the mid 1970s and most of the years from 1980 through 1988. When the yearly mean nickel concentrations in the surficial sediments based on this data were calculated (Table 9.4) and the log transformed data compared, none of the years were found to be significantly different at $p=0.05$. One factor contributing to the lack of any statistically significant difference was the variation in the number of sites sampled each year, from 1 in 1975 and 1988 to 59 in 1986 (Table 9.4). In addition to the variability in the number of sites sampled each year, the sites themselves varied from year to year. Therefore, while the data sets would be expected to be internally consistent about methodology, any conclusions concerning temporal trends based on the data must be viewed with extreme caution.

The only other available data that spanned more than 2 years was that from NOAA's NS&T Program Benthic Surveillance (1984-86) and Mussel Watch (1986-87) projects. The yearly mean nickel concentrations in the surficial sediments of Boston Harbor based on this data, ranged from a high of 36±6 ppm in 1985 to a low of 25±8 ppm in 1987. The yearly means for 1984 and 1986 were 30±3 ppm and 27±11 ppm, respectively. There was no indication of any temporal trends in nickel contamination. Statistical analysis of the log transformed data found no significant difference between any of the years at $p=0.05$.

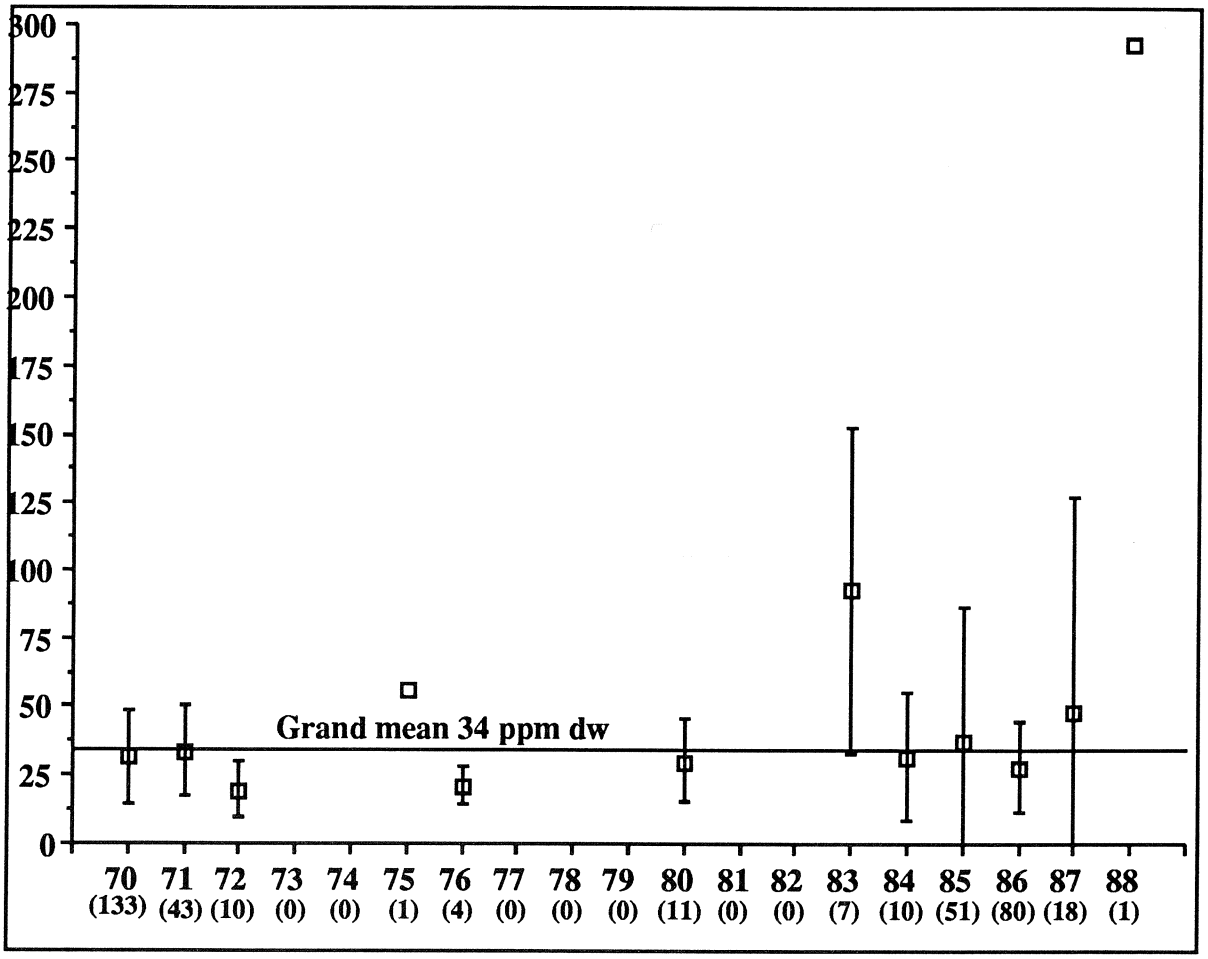


Figure 9.7 Yearly mean nickel concentrations (ppm) in the surficial sediments of Boston Harbor, based on White (1972), Gilbert *et al.* (1972), Isaac & Delaney (1975), USACOE (1972-88, 1981, 1988), MA DEQE (1986, 1987), and NOAA (unpublished). The numbers in parenthesis are the number of samples analyzed.

Table 9.4 Yearly mean nickel concentrations (ppm dw) in Boston Harbor surficial sediments based on dredging study data from the USACOE.

Year	Mean	Standard Deviation	Count
1972	10	0	4
1975	56	N/A	1
1976	22	7	4
1980	30	15	11
1983	93	59	7
1984	33	28	7
1985	48	63	28
1986	30	19	54
1987	71	108	9
1988	293	N/A	1

Biota

Since 1976, over 150 tissue samples from a variety of organisms in Boston Harbor have been analyzed for nickel content. Nickel concentrations ranged from a low of 0.04 ppm in the muscle of a lobster (*H. americanus*) to a high of 10.61 ppm in the soft parts of a composite sample of mussels (*M. edulis*). Table 9.5 gives the statistics on nickel contamination of biota by organism and tissue. The large difference between the mean and median nickel concentration and the standard deviation for the soft parts of mussels was due to the 1987 data from the NEA Mussel Watch Program. These 1987 values ranged from 3.76 to 10.61 ppm and because they were unrealistically high were considered suspect (Robinson, personal communication). When they were excluded from the calculations, the overall mean nickel concentration in the soft parts of mussels was 1.29 ±0.82. Only one sample exceeded a concentration of 2.51 ppm. It should be noted that, with the exception of the mussel data, the values in Table 9.5 for the different tissues were each derived from only one study and samples from one site. The mussel data was based on three studies with samples from six sites.

Geographic Trends

Table 9.5 Harborwide means, standard deviations, medians, ranges, and sample sizes (count) for nickel concentrations (ppm dw) in biota by organism and tissues based on all the available data sets.

		Mean	Standard Deviation	Median	Range	Count
P. americanus						
	liver	0.38	0.21	0.30	0.13-0.98	20
H. americanus						
	muscle	0.18	0.22	0.12	0.04-0.88	24
M. arenaria						
	soft parts	1.51	0.31	1.50	0.82-2.21	34
M. edulis						
	soft parts	2.40	2.44	1.24	0.57	86

There were no clear geographic trends in the nickel content of biota within Boston Harbor based on an overview of the mussel data broken down by division and excluding the 1987 NEA Mussel Watch data (Table 9.6). The data suggested that the inner harbor mussels contained slightly higher concentrations of nickel than did those from the outer harbor divisions. There was little difference among nickel levels in mussels from the three outer harbor divisions.

Table 9.6 Mean nickel concentrations (ppm dw) of the entire harbor and the four divisions in the soft parts of *M. edulis* (Goldberg *et al.*, 1978; Robinson *et al.*, 1990, and NOAA, unpublished). The number in parentheses is the sample size (excludes 1987 NEA data, see text).

	M. edulis soft parts
OVERALL	1.29 (66)
INNER HARBOR	1.58 (20)
NORTHWEST HARBOR	0.94 (18)
CENTRAL HARBOR	1.20 (20)
SOUTHEAST HARBOR	0.94 (8)

In 1976 the U. S. EPA sampled mussels and other bivalves from 107 sites nationwide and analyzed the samples for a variety of metals and organic analytes, including nickel (Goldberg *et al.*, 1978). A composite sample of *M. edulis* from a site on the northwest side of Deer Island was found to have a nickel concentration in the soft parts of 1.2 ppm. Between Block Island and the Canadian Border, 11 other New England sites were sampled. Nickel concentrations in the soft parts of *M. edulis* ranged from 0.4 ppm from Blue Hill Falls, Maine to 1.6 ppm at Sakonnet Point, Rhode Island. Boston mussels had the second highest concentration of nickel among the 11 sites.

In 1985 and 1986, lobster (*H. americanus*) and soft-shelled clams (*M. arenaria*) were collected from Boston and Salem Harbors and analyzed for various analytes, including nickel, as part of a study of contaminants in marine resources (Wallace *et al.*, 1988). The combined claw and tail muscle tissue of 24 lobsters collected from around Deer Island had a mean nickel concentration of 0.18±0.22 ppm with a range of from 0.04 to 0.88 ppm. Lobsters were collected from two sites in Salem Harbor, the treatment plant outfall and Willows Pier. The mean nickel concentrations in combined claw and tail muscle tissue based on the analysis of 25 lobsters per site were 0.15±0.07 and 0.16±0.10 ppm, respectively. Statistical analysis of the log transformed data indicated that there was no significant difference among any of the three sites at p=0.05. The mean nickel concentration for 34 soft-shelled clams from Wollaston Beach in Quincy Bay was 1.51±0.31 ppm with a range of 0.82 to 2.21 ppm.

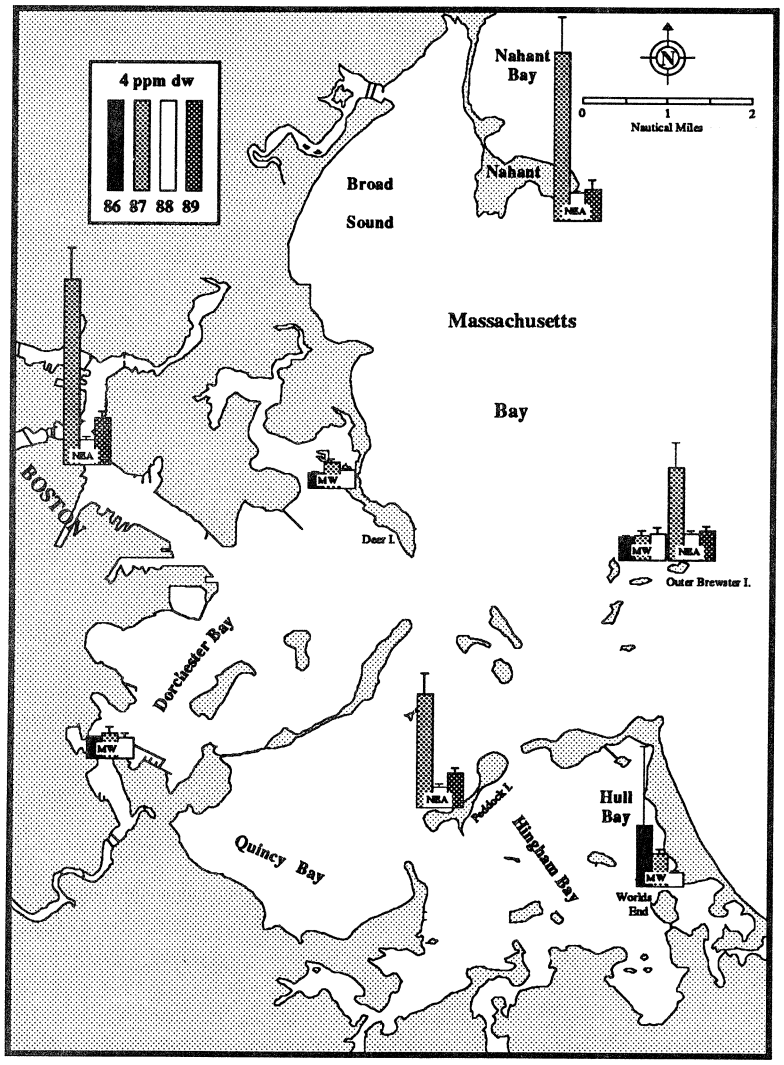


Figure 9.8. Mean nickel concentrations in the soft-parts of *M. edulis* from Boston Harbor and environs for 1986-89, based on data from the New England Aquarium's (NEA) and NOAA (MW) musel watch projects (Robinson *et al.*, 1990; NOAA, unpublished) (bars represent one standard deviation)>

NOAA's Mussel Watch Project, a part of the NS&T Program, has sampled mussels (*M, edulis*) on an annual basis from four sites in and around Boston Harbor since 1986. Three whole-body composite samples from each site were analyzed for a variety of analytes, including nickel. The overall mean concentration of nickel in the mussels for the three sites in Boston Harbor from 1986 through 1988 was 1.15±1.14 ppm with a range of from 0.57 to 6.70 ppm. When the single, extraordinarily high value of 6.70 ppm was excluded from the calculations, the overall mean for the harbor became 0.94±0.28 ppm with a range of 0.57 to 1.60 ppm. The means for the individual sites were 0.89±0.23 ppm northwest of Deer Island, 0.99±0.18 ppm in southwestern Dorchester Bay, and 1.58±1.96 ppm in Hingham Bay off Worlds End. However, the Hingham Bay site included the sample with a reported 6.70 ppm. When this sample was excluded, the site mean became 0.94±0.43 ppm. Mussels from the site outside the Harbor, Outer Brewster Island, had a mean nickel concentration of 1.12±0.19 ppm (Figure 9.8). Statistical analysis of the

log transformed data for the four sites indicated no significant difference between any of the sites (p=0.05).

Since 1987, the NEA has conducted their own Mussel Watch Program, sampling mussels from two sites within Boston Harbor and two sites in Massachusetts Bay (Robinson *et al.*, 1990). These sites include the same site on Outer Brewster Island that NOAA's Mussel Watch Project samples. Reported nickel concentrations for 1987 ranged from 3.21 to 10.61, while after 1987 no sample had a reported nickel concentration greater than 2.51. Because these 1987 values appear to be unreasonably high, they have been excluded from subsequent analyses. The remainder of this discussion is based only on 1988 and 1989 data. The mean nickel concentration in Boston Harbor, based on data from the two sites for 1988 and 1989, was 1.39±0.50 ppm with a range of from 0.66 to 2.51 ppm. The means for the two sites were 1.20±0.38 ppm at the Peddocks Island site and 1.58±0.54 ppm at the Central Wharf, Boston site. The two sites from Massachusetts Bay had means of 1.30±0.32 ppm at the Pumphouse Beach, Nahant site and 1.27±0.18 ppm at the Outer Brewster Island site. When the data for the four sites is log transformed and the sites statistically compared, the Central Wharf site was found to be significantly different from the Peddocks Island site at p=0.05. Figure 9.8 plots the NEA data alongside the NOAA Mussel Watch data.

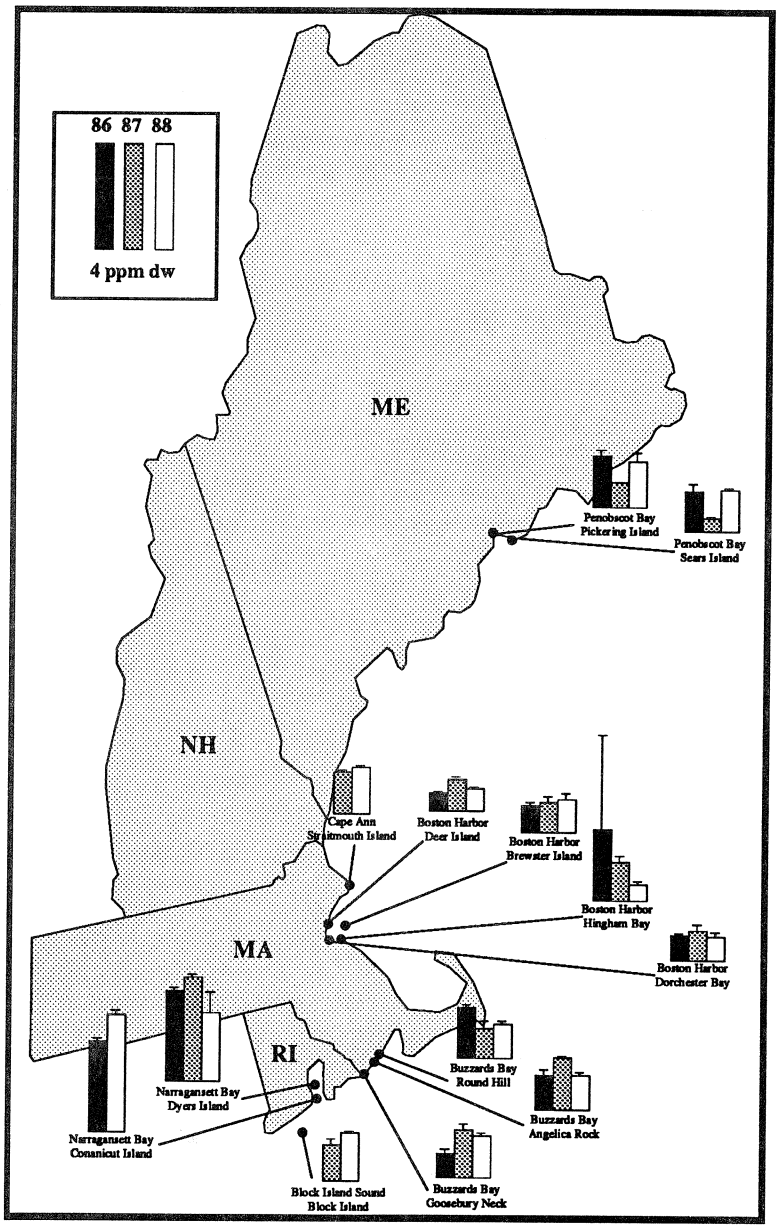


Figure 9.9. Mean nickel concentrations (ppm dw) in the soft-parts of *M. edulis* from the outer New England coast by site and year for 1986-88 (NOAA, unpublished) (bars represent one standard deviation).

On a broader scale, when the Boston Harbor NS&T sites were compared to the other New England NS&T Mussel Watch sites (Figure 9.9 and Table 9.7), the mussels from the Deer Island and Dorchester Bay sites had the lowest and second lowest mean nickel concentrations, respectively. The mussels from the Hingham Bay site had the fourth highest mean nickel concentration. However, when the sample with 6.70 ppm nickel was excluded from the calculations for Hingham Bay, the mussels from Hingham Bay had the second lowest mean nickel concentration. When the log transformed data were

statistically analyzed, only the two sites with the highest mean nickel concentrations (Conanicut and Dyers islands in Narragansett Bay) were found to be significantly different from the three Boston Harbor sites (p=0.05). The two Narragansett Bay sites, Conanicut and Dyers islands, were also significantly different from most of the other New England sites (p=0.05) with the following exceptions. Neither was significantly different from the Cape Ann and Block Island sites. Also, the Dyers Island site was not significantly different from the Angelica Rock and Goosebury Neck sites in Buzzards Bay; and, they were not significantly different from each other. Because the Boston Harbor mussels had the lowest mean nickel concentrations, no reference mean was calculated. On a national scale, the Mussel Watch sites where *M. edulis* was sampled had mean nickel concentrations ranging from 0.89 to 6.51 ppm with an overall mean for all the sites of 2.38±1.43 ppm. Approximately 4 percent of the sites had means less than 1.0 ppm (Deer Island and Dorchester Bay) while 69 percent had concentrations between 1.00 and 3.00 ppm, and 27 percent had mean nickel concentrations greater than 3.00 ppm. When the sites where *M. californianus* was sampled were included in the calculations, the overall mean became 2.46±1.46 ppm. Approximately 4 percent of the sites had means less than 1.0 ppm, 70 percent had means between 1.00 and 3.00 ppm, and 26 percent had mean nickel concentrations greater than 3.00 ppm. Based on this data Boston Harbor mussels appeared to have relatively low levels of nickel.

Table 9.7 The mean nickel concentrations (ppm dw) in *M. edulis* at the 13 outer New England coast NS&T Program Mussel Watch sites. The outlined means are for Boston Harbor sites.

Site	Mean	Standard Deviation	Count
CONANICUT ISLAND NARRAGANSETT BAY	3.867	0.572	6
DYERS ISLAND, NARRAGANSETT BAY	3.289	0.697	9
CAPE ANN, STRAITSMOUTH ISLAND	1.65	0.105	6
HINGHAM BAY, BOSTON HARBOR	1.583	1.96	9
BLOCK ISLAND, RHODE ISLAND	1.55	0.274	6
PICKERING ISLAND, PENOBSCOT BAY	1.52	0.499	9
ANGELICA ROCK, BUZZARDS BAY	1.493	0.358	9
GOOSEBURY NECK, BUZZARDS BAY	1.479	0.388	8
ROUND HILL, BUZZARDS BAY	1.439	0.382	9
SEARS ISLAND, PENOBSCOT BAY	1.186	0.541	9
OUTER BREWSTER ISLAND	1.118	0.189	9
DORCHESTER BAY, BOSTON HARBOR	0.993	0.176	9
DEER ISLAND, BOSTON HARBOR	0.887	0.231	9

NOAA's Benthic Surveillance Project, a part of the NS&T Program, has sampled winter flounder (*P. americanus*) from an area just west of Deer Island on an annual basis since 1984. The mean nickel concentration in the liver of the fish sampled in 1984 and 1985 was 0.38±0.21 ppm with a range of 0.13 to 0.98 ppm. The mean concentration of nickel in flounder livers for all the New England Benthic Surveillance sites, excluding Boston Harbor, ranged from a low of 0.47±0.40 ppm at the Salem Harbor site to a high of 1.71±0.49 ppm at the Casco Bay site (Figure 9.10). The mean nickel concentration of winter flounder liver from Boston Harbor was lower than the mean for any other New England site. Statistical analysis of the log transformed data indicated that the Casco Bay site was significantly different from all the other New England sites at p=0.05. No comparison could be made between Boston Harbor and the three northern-Maine sites. A different species, longhorn sculpin (*M. octodecemspinosus*), was sampled at these sites. The Benthic Surveillance Project sampled winter flounder at four other sites during the same time; two in Long Island Sound and one each in Raritan and Great bays in New Jersey. All but the Great Bay site (0.12±0.07 ppm) had means greater than the mean for Boston Harbor. They were: West Long Island Sound, 1.23±1.14 ppm; East Long Island Sound, 1.07±0.91 ppm; and Raritan Bay, 0.61±0.32 ppm.

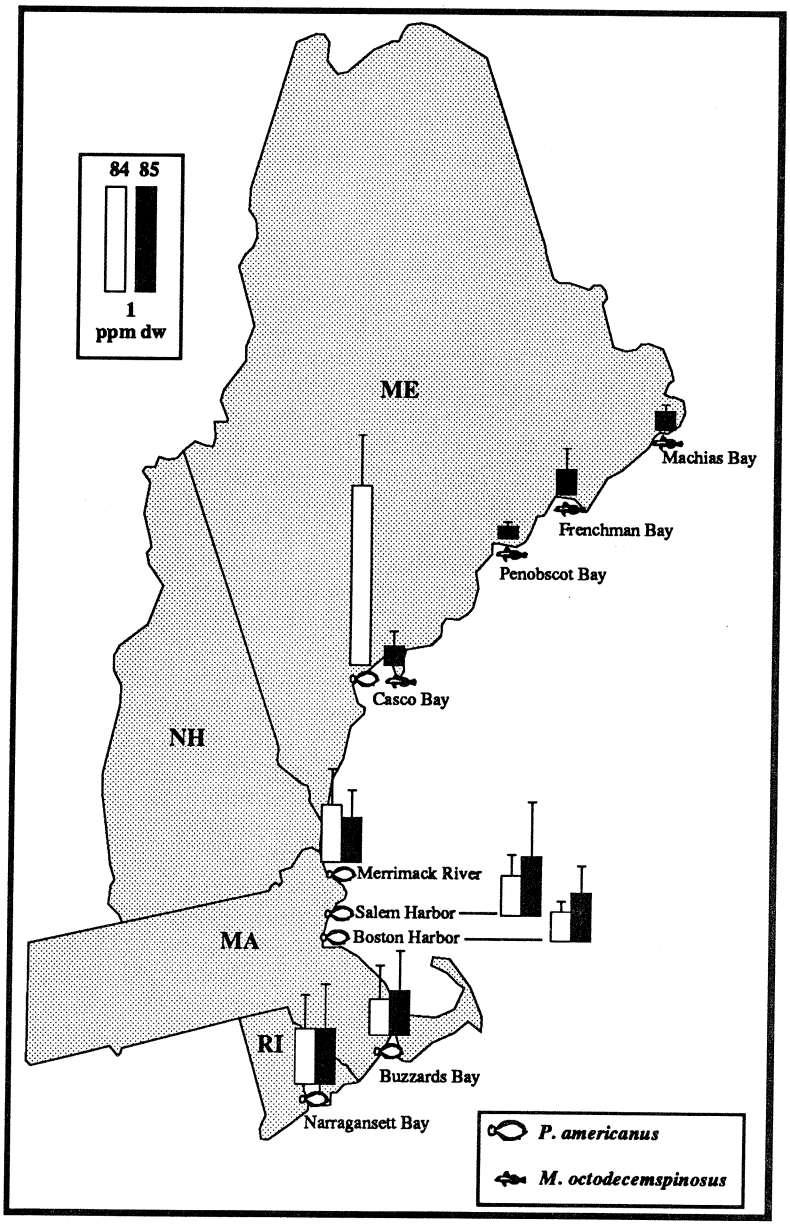


Figure 9.10. Mean nickel concentrations (ppm dw) in the liver tissue of *P. americanus* and *M. octodecemspinosus* caught along the outer New England coast from 1984-85 (NOAA, unpublished) (bars represent one standard deviation).

Temporal Trends

No temporal trends in the nickel levels of Boston Harbor biota could be determined based on the available data. The only internally consistent data sets sampling the same organism from the same locations over a number of years were the NS&T Program's Benthic Surveillance and Mussel Watch projects and the NEA Mussel Watch Program. Data for these projects were only available for 2, 3, and 3 years, respectively. Between 1984 and 1985 there was approximately a 60 percent increase in the level of nickel in winter flounder livers (0.29±0.9 to 0.47±0.26 ppm) (Figure 9.10) that was significantly different at p=0.05. However, whether this indicates a trend in levels of nickel contamination in Boston Harbor biota or was just due to random sampling could not be determined based on only 2 years. Likewise the 3 years of data for *M. edulis* from the NS&T Program Mussel Watch Project failed to indicate any trend with nickel levels slightly decreasing between 1986 and 1987 and further decreasing in 1988 (Figure 9.8). The yearly means were 1.44±1.98, 1.23±0.23, and 0.89±0.26 ppm, respectively. The yearly means for the NEA Mussel Watch Program showed a sharp decrease between 1987 (6.56±1.98 ppm) and 1988 (0.987 ppm), but, as mentioned above, during the first year of the program there were some problems determining nickel concentrations (Robinson, 1990). Between 1988 and 1989 (1.80±0.37 ppm) there was almost a doubling of mean nickel concentrations in mussels. When the EPA Deer Island site, which had a nickel concentration in the soft parts of mussels of 1.2 ppm in 1976, was compared to the NS&T Program Deer Island site (which is about 0.5 miles northwest of the EPA site) with yearly means of 1.17, 0.82, and 0.67 ppm (1986, 1987, and 1988, respectively) there appeared to be an approximate twofold decrease in nickel concentrations in the 11 years between 1976 and 1988. However, this comparison needs to be viewed with caution because the EPA value was based on only one composite sample. The NS&T Program values were based on three composite samples

each. Also, the difference between the EPA value and the NS&T Program values may be the result of differences in laboratory methodology.

Summary

Boston Harbor sediments were found to contain nickel at levels approximately 2 to 4 times that of reference levels. The mean sediment concentrations for the Boston Harbor NS&T Program sites were compared to 91 NS&T Program Mussel Watch sites on the East and West coasts. Approximately 21 percent of the sites had means lower than the lowest Boston site mean (Hingham Bay, 14±3 ppm). Approximately 34 percent of the sites had means higher than the highest Boston Harbor site mean (southwest Deer Island 31±8 ppm). Approximately 7 percent of the sites had mean nickel concentrations in excess of 100 ppm including four of the five sites sampled in San Francisco Bay. The overall data set indicated a trend of decreasing nickel concentrations in Boston Harbor surficial sediments from the inner harbor to the outer harbor with little if any difference among the outer harbor divisions. This trend was also apparent in four of the five individual data sets that covered most of the Harbor (White, 1972; Gilbert *et al.*, 1972; Isaac and Delaney, 1975; Massachusetts DEQE, 1986 and 1987). The fifth data set, NOAA (unpublished), did not include samples from the inner harbor. While it indicated no difference between the northwest and central harbor, it suggested that the southwest harbor had a somewhat lower mean concentration of nickel in its surficial sediments. No clear temporal trends were apparent with regard to nickel concentrations in the surficial sediment.

Based on the available data, Boston Harbor biota appears to be slightly contaminated with nickel. Boston Harbor mussels (*M. edulis*) had some of the lowest mean nickel concentrations of all the New England NS&T Program sites sampled. When compared to all NS&T Program mussel sites sampled in the country, the only two sites with means less than 1.00 ppm were from Boston Harbor, Deer Island, and Dorchester Bay, (0.89 and 0.99, respectively), while 62 percent had means higher than the Boston Harbor site with the highest mean of the three (Hingham Bay, 1.58 ppm). Likewise, the winter flounder (*P. americanus*) liver data suggested that Boston Harbor had only low levels of nickel, since, among the NS&T Program sites, the Boston site had the lowest mean nickel concentration among all the winter flounder sites. There were no obvious geographic or temporal trends in nickel content of biota within Boston Harbor based on the available data because relative concentrations among different areas of the Harbor varied with the organism and tissue sampled. With the exception of the NS&T Program and the NEA Mussel Watch Program, none of the studies sampled the same organism from the same sites over a period of years.

ZINC

Zinc is a naturally occurring element that functions as an essential trace element, but in excess it can be toxic because it has lethal and sublethal effects (Eisler, 1981). In a review of the literature, Long and Morgan (1990) found data suggesting that zinc levels in sediment below about 50 ppm have little or no effect on biota. Biological effects are usually observed at levels of 260 ppm or greater.

Sediments

Since the late 1960s, over 370 surficial sediment samples from Boston Harbor have been analyzed for zinc concentrations. Based on this data, the overall mean concentration of zinc in the surficial sediments of the Harbor was 219 ppm with a standard deviation of 201 and a range of from 1 to 1750 ppm (Table 10.1). The median concentration was 83 ppm. The large standard deviation and the difference between the mean and the median values are because approximately 25 percent of the samples analyzed had concentrations less than 100 ppm. The vast majority of the samples, approximately 69 percent, had values between 100 and 500 ppm, inclusive. The remaining 6 percent of the samples contained more than 500 ppm zinc including four samples (1%) with concentrations greater than 1000 ppm.

Table 10.1. Means (ppm dw), standard deviations, medians, ranges, and number of samples (count) for zinc concentrations in surficial sediments for all of Boston Harbor and the four regions of the harbor, based on all the available data sets.

	Mean	Standard Deviation	Median	Range	Count
OVERALL	219	201	165	1 - 1750	373
INNER HARBOR	348	291	275	2 - 1750	110
NORTHWEST HARBOR	184	124	162	1 - 890	150
CENTRAL HARBOR	151	95	154	16 - 455	45
SOUTHEAST HARBOR	134	76	126	17 - 334	68

Geographic Trends

When the combined data set was broken down into the four harbor divisions, both the means and medians suggested that the surficial sediments of the inner harbor had the highest levels of zinc (348 and 275 ppm). Those of the northwest harbor had the second highest (184 and 162 ppm), followed by the central harbor (151 and 154 ppm), and then the southeast harbor (134 and 126 ppm) (Table 10.1). When the data for the northwest harbor were subdivided, the Dorchester Bay area (73 samples) had the second highest mean and median (210 and 195 ppm, respectively). The Winthrop Bay area had virtually the same levels of zinc as the central harbor (mean, 158 ppm and median, 154 ppm).

Around 1970, White (1972) collected and analyzed over 130 surficial sediment samples from Boston for a variety of metals, including zinc. He found an overall mean zinc concentration in Boston Harbor surficial sediments of 267±235 ppm. Individual sample concentrations ranged from a low of 32 ppm, in a sample taken in eastern Hull Bay to a high of 1750 ppm, in a sample taken from the lower reaches of the Charles River (Figure 10.1). The extremely high standard deviation was due to two samples with zinc concentrations in excess of 1000 ppm. When these two samples were excluded from the calculations, the mean became 247±172 ppm with a high sample concentration of 750 ppm. Figure 10.1 suggests that zinc concentrations in the surficial sediments decreased from the inner harbor to the outer harbor with zinc being heterogeneously distributed throughout the outer harbor. The trend of decreasing zinc in the surficial sediments from inner to outer harbor was supported by the

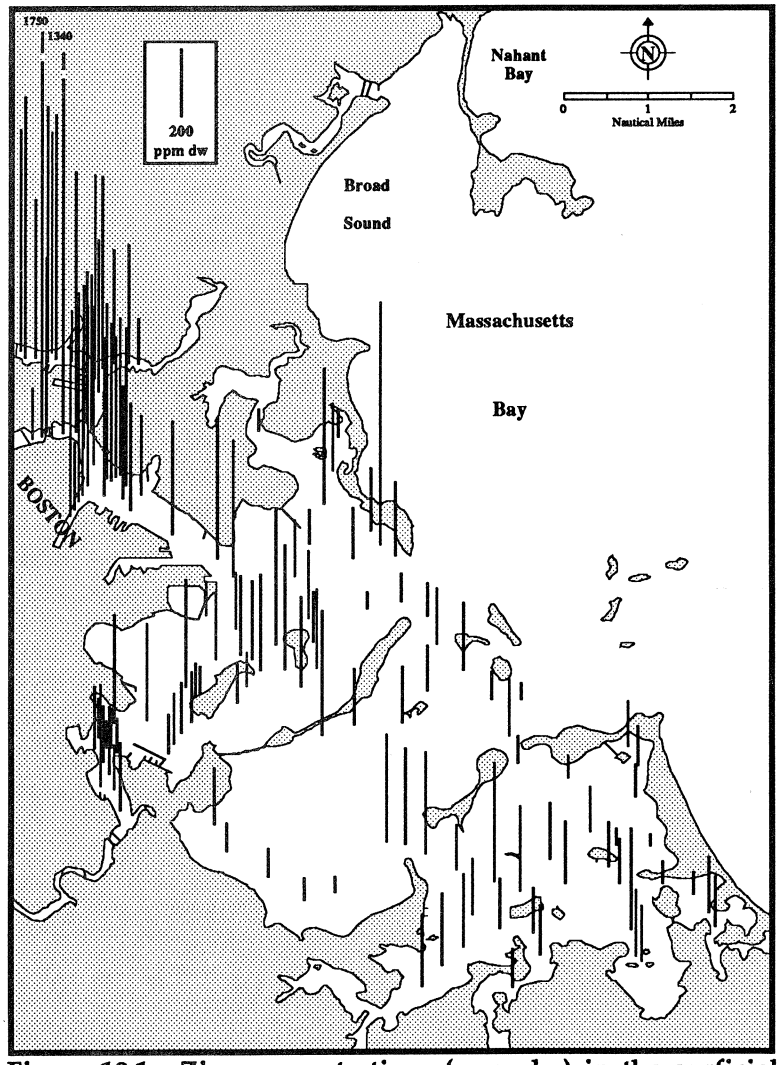


Figure 10.1. Zinc concentrations (ppm dw) in the surficial sediments of Boston Harbor from around 1970 (White, 1972).

means for the individual harbor divisions that decreased from a high of 500 ppm in the inner harbor to a low of 140 ppm in the central harbor (Table 10.2). Statistical analysis of the log transformed data for the four harbor divisions indicated that the inner harbor was significantly different from the other three divisions (p=0.05). The data for the northwest harbor subdivisions were analyzed. The Winthrop Bay area (15 samples) with a mean of 229 ppm and the Dorchester Bay area (32 samples) with a mean of 184 ppm, were found to be significantly different only from the inner harbor at p=0.05.

In 1971, the NEA collected 55 cores of Boston Harbor sediment sand and analyzed various sections of the cores for heavy metal content (Gilbert *et al.*, 1972). The upper surface of 43 cores were analyzed for zinc. Zinc concentrations were found ranging from a low of 30 ppm in a sample taken off Worlds End, to a high of 1360 ppm in a sample taken from the lower reaches of the Charles River (the same general locations as the high sample taken by White). The overall mean zinc concentration in the surficial sediments was 270±279 ppm (Table 10.2). The extremely high standard deviation was due to two samples with zinc concentrations more than 1000 ppm. When these two samples were excluded from the calculations, the mean became 220±161 ppm with a high sample concentration of 985 ppm. A graphic representation of the data (Figure 10.2) suggests a trend of decreasing zinc concentrations in the surficial sediments from the inner harbor to the southeast harbor. When the data were grouped by the four harbor divisions, the inner harbor had the highest mean zinc concentration (1005 ppm) and the southeast harbor had the lowest (137 ppm). The northwest and central harbor divisions had intermediate levels of zinc (231 and 179 ppm, respectively). When the log transformed data for the harbor divisions were compared statistically the inner harbor was found to be significantly different from the other three harbor divisions (p=0.05). The data for the northwest harbor subdivisions were analyzed. The Winthrop Bay area (4 samples), with a mean of 221 ppm, and the Dorchester Bay area (14 samples), with a mean of 234 ppm, were found to be significantly different from only the inner harbor at p=0.05.

Table 10.2. Mean zinc concentrations (ppm dw) in the surficial sediments of Boston Harbor and the four divisions of the harbor based on the data of White (1972), Gilbert *et al.* (1972), Isaac and Delaney (1975), MA DEQE, (1986 and 1987), and NOAA's NS&T Program (unpublished). The numbers in parentheses are the number of data points used to calculate the means.

	White	Gilbert *et al.*	Isaac and Delaney	MA DEQE	NOAA NS&T
YEAR SAMPLED	**1970?**	**1971**	**1972**	**1985-86**	**1984-87**
OVERALL	267 (133)	270 (43)	148 (6)	226 (28)	171 (31)
INNER HARBOR	500 (38)	1005 (4)	81 (1)	336 (8)	N/A
NORTHWEST HARBOR	199 (48)	231 (18)	350 (1)	209 (12)	198 (22)
CENTRAL HARBOR	140 (16)	179 (13)	144 (2)	141 (5)	192 (3)
SOUTHEAST HARBOR	151 (13)	137 (8)	86 (2)	144 (3)	58 (6)

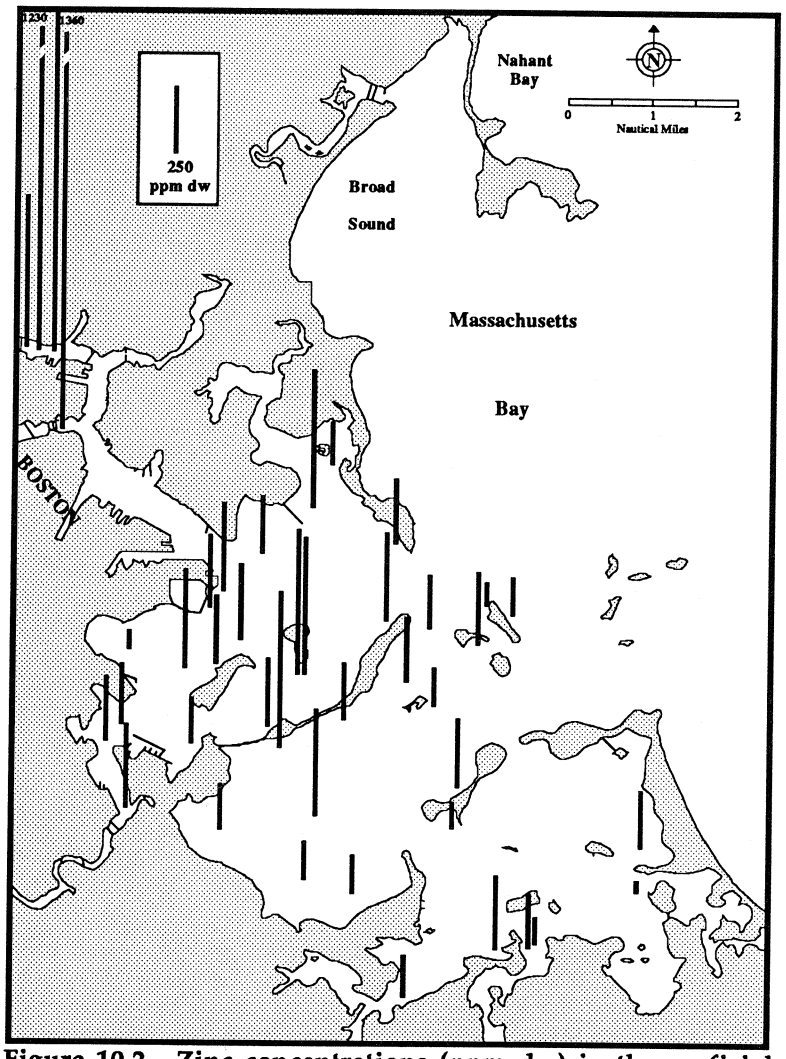


Figure 10.2. Zinc concentrations (ppm dw) in the surficial sediments of Boston Harbor in 1971 (Gilbert *et al.*, 1975).

Between 1971 and 1974, Massachusetts conducted a toxic element survey of the waters of the State (Isaac and Delaney, 1975). The survey included the analysis of sediment samples for volatile solids and a variety of heavy metals, including zinc. Six surficial sediment samples from around Boston Harbor had a combined mean zinc concentration of 148±109 ppm with a range of from 51 ppm to 350 ppm (Figure 10.3). Because so few samples were analyzed, no statistical comparison among harbor divisions could be made; but, the data did suggest a trend of decreasing zinc concentrations from northwest to southeast. Although, the second lowest zinc concentration was found in the single sample from the inner harbor (Table 10.2), this sample, located near the mouth of the inner harbor, also had relatively low concentrations of the other metals for which it was analyzed, as well as the lowest concentration of volatile solids in the harbor.

Data were obtained from the New England Division of the USACOE for dredging studies conducted in and around Boston Harbor from 1972 through 1988 (USACOE, 1972-1988, 1981; 1988). The USACOE analyzed 132 samples during this period for zinc content. The overall mean zinc concentration for the harbor based on this

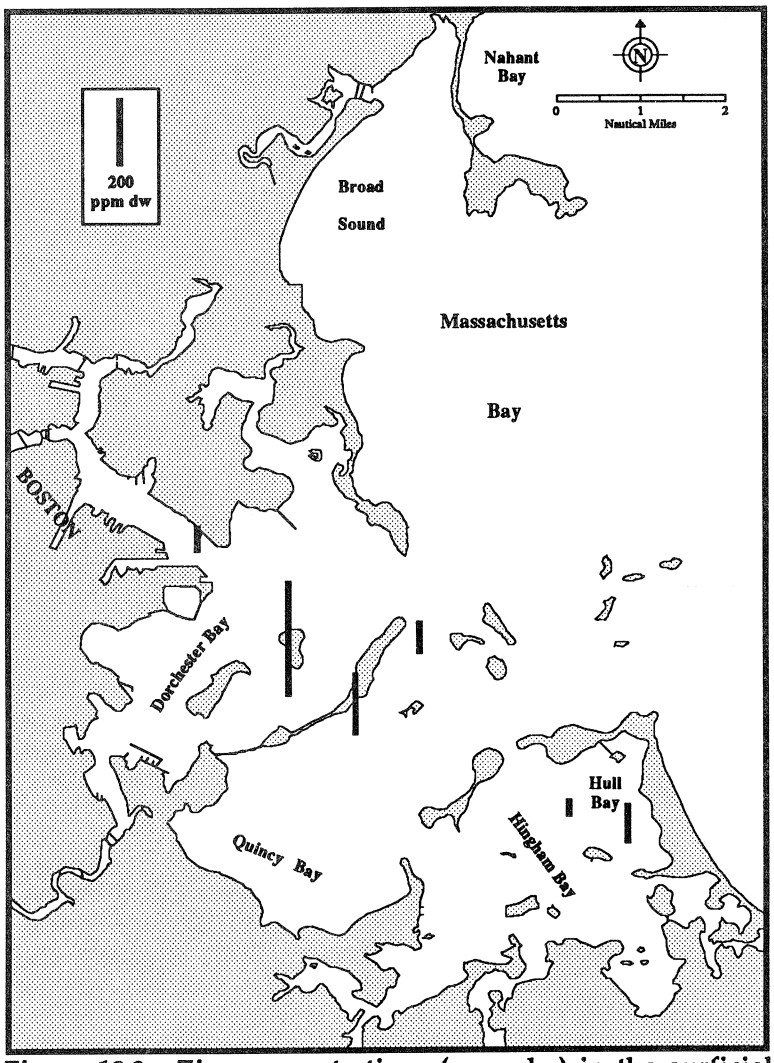


Figure 10.3. Zinc concentrations (ppm dw) in the surficial sediments of Boston Harbor in the early 1970's (Isaac & Delaney, 1975).

data was 168±146 ppm. The range was from a low of 1 ppm, in four samples taken from the Winthrop Harbor area to a high of 890 ppm, in a sample from western Dorchester Bay near the John F. Kennedy Library. The majority of the samples (81%) had zinc concentrations between 10 and 300 ppm, inclusive. Approximately 5 percent of the samples had less than 10 ppm, only 14 percent of the samples had concentrations more than 300 ppm, and 2 percent had zinc concentrations greater than 600 ppm. When the data were grouped by harbor divisions, the means ranged between 112±133 ppm in the central harbor (6 samples) and 212±156 ppm in the inner harbor (59 samples). The northwest harbor (49 samples) had a mean of 135±139 ppm, while the southeast harbor (18 samples) had a mean of 132±90 ppm. The division means suggested a trend of decreasing zinc concentration from the inner to the outer harbor with little difference among the outer harbor divisions. This apparent trend was supported by statistical analysis of the log transformed data that indicated a significant difference among the inner harbor and the northwest harbor divisions at p=0.05. The lack of any significant difference among the inner harbor and the other two outer harbor divisions was probably the result of the small sample sizes and relatively high standard deviations of the data from the central and southeast harbor. When the northwest harbor data were subdivided, the Dorchester Bay area (12 samples) had a mean zinc concentration of 237±233 ppm while the Winthrop Bay area (33 samples) mean was 101±68 ppm. The large difference between the two subdivision means and the large standard deviation of the Dorchester Bay area data was due to one sample from Dorchester bay area that had zinc concentration of 890 ppm and four samples (all from Winthrop Harbor in 1972) from the Winthrop Bay area that had zinc concentrations of 1 ppm. When these extraordinarily high and low values were excluded from the calculations, the means became 179±115 ppm for the Dorchester Bay area and 114±62 ppm for the Winthrop Bay area.

In 1985 and 1986, the Massachusetts DEQE, as part of their annual Boston Harbor Water Quality and Wastewater Discharge Survey, analyzed 30 surficial sediment samples for zinc content. They found an overall mean zinc concentration of 226±143 ppm. The range was from a low of 60 ppm, in a sample taken from northwestern Dorchester Bay to a high of 640 ppm,

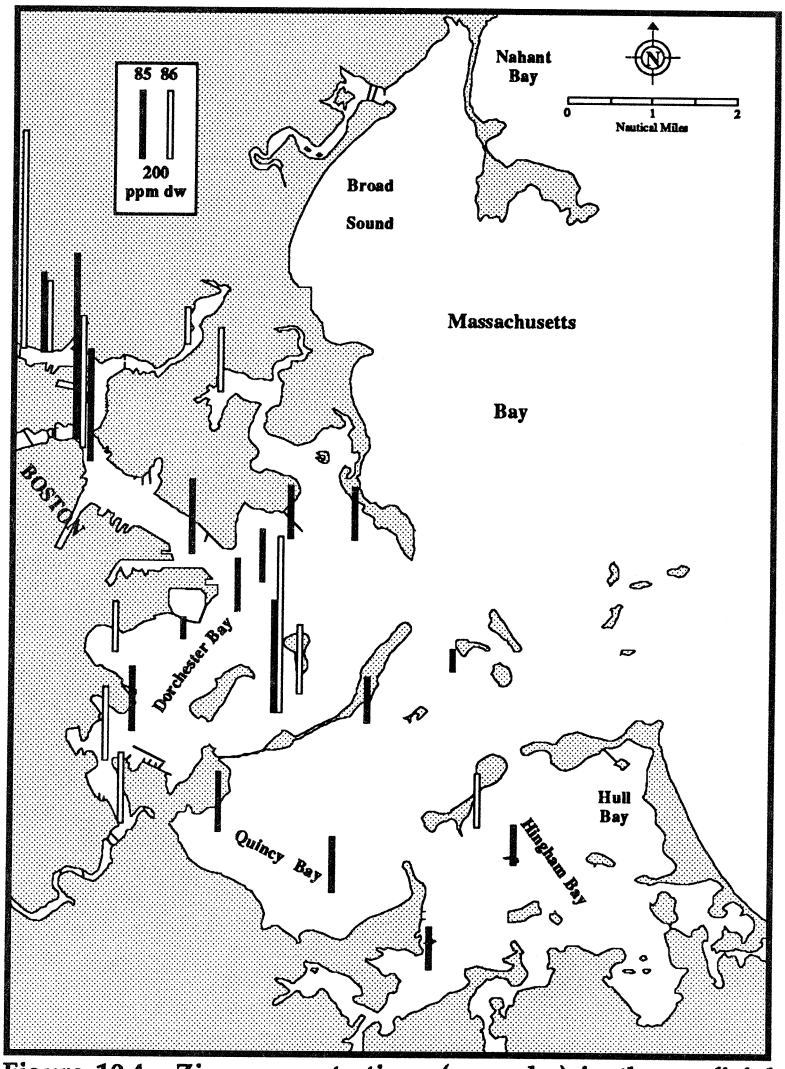
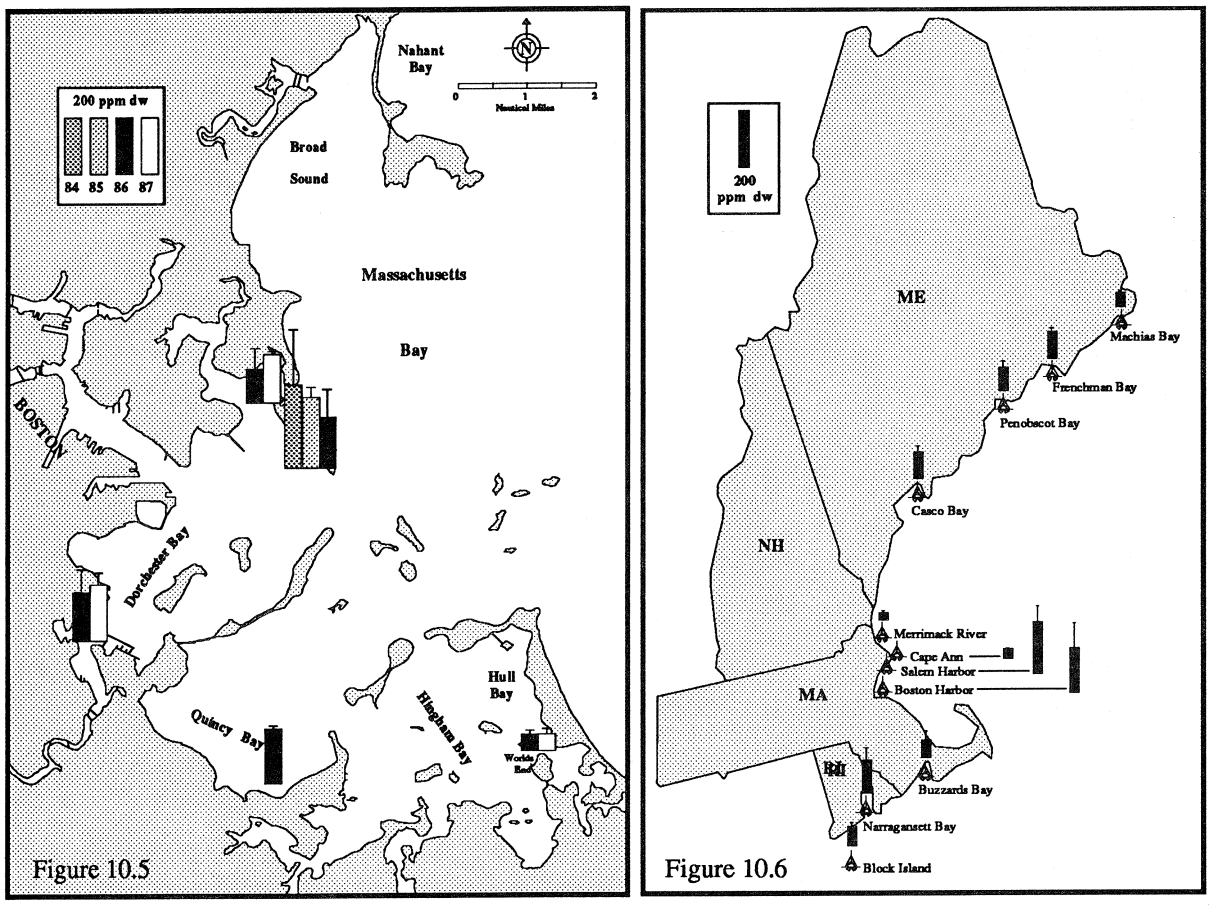


Figure 10.4. Zinc concentrations (ppm dw) in the surficial sediments of Boston Harbor in 1985 and 1986. (MA DEQE, 1986, 1987).

in a sample taken from the lower reaches of the Mystic River. The vast majority (approximately 71%) of the surficial sediment samples had zinc concentrations between 100 and 300 ppm; while approximately 21 percent of the samples had concentrations in excess of 300 ppm. While the means for the harbor divisions (Table 10.2) suggested a trend of decreasing zinc levels from the inner harbor to the central and southeast harbor, statistical analysis of the log transformed data indicated that only the inner harbor was significantly different from the other three harbor divisions at p=0.05. This trend can also be seen in Figure 10.4 that graphically displays the data by site and year. When the data for the northwest harbor subdivisions were analyzed, the Winthrop Bay area (four samples) with a mean of 156 ppm and the Dorchester Bay area (eight samples) with a mean of 236 ppm, were found not to be significantly different from any of the harbor divisions at p=0.05.

NOAA's NS&T Program has sampled and analyzed surficial sediments from several sites around Boston Harbor for several analytes, including zinc since 1984. Figure 10.5 portrays this data graphically by year and site. The overall mean zinc concentration in surficial sediments of the harbor was 171±97 ppm. Individual sample values ranged from 38 to 516 ppm. Site means, based on all 4 years of available data, ranged from 58±15 ppm at the site off the northern tip of Worlds End to 240±115 ppm at the site southwest of Deer Island. The mean zinc concentrations in the surficial sediments of the other sites were: northwest of Deer Island, 145±53 ppm; Dorchester Bay, 183±60 ppm; and Quincy Bay, 192±10 ppm. Statistical comparison of the log transformed data indicated that the Worlds End site was significantly different from all the other sites except the northwest Deer Island site at p=0.05. When the data were grouped by harbor divisions (Table 10.2), the means suggested that there was little difference in mean zinc concentrations in the northwest and central harbor; but, the zinc concentrations were significantly lower in the southeast harbor. Statistical analysis of the log transformed data indicated that the southeast harbor was significantly different from both the northwest and central harbors at p=0.05.

On a broader scale, between 1984 and 1987, the NOAA NS&T Program analyzed surficial sediment samples from 23 sites from 11 areas, along the New England coast. Figure 10.6 clearly displays the means and standard deviations for the 11 coastal areas. This figure it is clearly shows that the mean zinc concentration of the NS&T Program sites in Boston Harbor (171±97 ppm) was only exceeded by the mean for Salem Harbor (197±63 ppm). It should be noted that the Salem Harbor mean was based on samples from only one site while that for Boston Harbor was based on samples from five sites. Statistical analysis of the log transformed data indicated that Boston Harbor was significantly different (p=0.05) from only the four New England areas with the lowest mean zinc concentrations (Buzzards Bay, Merrimack River, Cape Ann, and Machias Bay).



Figures 10.5 & 10.6. Mean zinc concentrations (ppm dw) in the surficial sediments of Boston Harbor by site and year (Fig. 10.5) and along the outer New England coast for 1984-1987 (NOAA, unpublished).

When the mean zinc concentrations in the surficial sediments of the individual outer New England coast NS&T Program sites were compared, four of the five sites with the highest mean zinc concentrations were located in Boston Harbor (Table 10.3). In an attempt to determine a value for background zinc levels, the overall mean was calculated for the five New England NS&T Program sites with the lowest zinc concentrations in their surficial sediments (Table 10.3). This mean was 41±13 ppm. The overall mean zinc concentration in the surficial sediments of Boston Harbor, based on the NS&T Program data, was more than 4 times greater than this reference mean. The Boston Harbor site with the highest zinc concentration had a mean almost 6 times higher than the reference mean. The Boston Harbor site with the lowest mean zinc concentration (Worlds End) was less than 1 1/2 times higher than the reference mean.

Table 10.3. The five outer New England Coast NOAA NS&T Program sites with the lowest and highest mean zinc concentrations (ppm dw) based on data from 1984 through 1987.

Site	Mean	Standard Deviation	Count
MERRIMACK RIVER	27	8	5
GOOSEBURY NECK, BUZZARDS BAY	36	11	6
STRAITSMOUTH ISLAND, CAPE ANN	40	2	3
ANGELICA ROCK, BUZZARDS BAY	42	11	6
MACHIAS BAY, MAINE	54	8	7
DORCHESTER BAY	183	60	6
MOUNT HOPE, NARRAGANSETT BAY	190	10	3
QUINCY BAY	192	10	3
SALEM HARBOR	197	63	9
SOUTHWESTERN DEER ISLAND	240	115	10

Temporal Trends

Figure 10.7 compares the yearly mean zinc concentrations in the surficial sediments of Boston Harbor based on all the available data sets (White, 1972: Gilbert *et al.*, 1972: Isaac and Delaney, 1975: USACOE, 1972-1988; 1981, 1988: MA DEQE, 1986; 1987: NOAA, unpublished). Because of the large yearly standard deviations, there is no overall temporal trend in zinc concentrations apparent from Figure 10.7. However, when just the 4 years with the largest sample sizes are compared (1970, 1971, 1985, and 1986), the data suggests that zinc concentrations in the surficial sediments of Boston Harbor have declined slightly since the early 1970s.

Some data were available from the USACOE on dredging studies for the mid 1970s and most of the years from 1980 through 1988. When the yearly mean zinc concentrations in the surficial sediments based on this data were calculated (Table 10.4) and the log transformed data compared, not surprisingly, 1972 was found to be significantly different from any of the other years at $p=0.05$. None of the other years were found to be significantly different from each other at $p=0.05$. It should be noted that all four samples from 1972 were from the same area, Winthrop Harbor, and were not representative of the harbor as a whole. One factor contributing to the lack of any statistically significant difference was the variation in the number of sites sampled each year, from 1 in 1975 and 1988 to 59 in 1986 (Table 10.4). In addition to the variability in the number of sites sampled each year, the sites themselves varied from year to year. Therefore, while the data sets would be expected to be internally consistent concerning methodology, any conclusions concerning temporal trends based on the data must be viewed with extreme caution.

The only other available data that spanned more than 2 years was that from NOAA's NS&T Program Benthic Surveillance (1984-86) and Mussel Watch (1986-87) projects. The yearly mean zinc concentrations in the surficial sediments of Boston Harbor based on this data ranged from a high of 292±195 ppm in 1984 to a low of 141±68 ppm in 1987. The yearly means for 1985 and 1986 were 246±37 ppm and 144±75 ppm, respectively. Statistical analysis of the log transformed data indicated no significant difference among any of the years at $p=0.05$; and, while the means suggest a trend of decreasing zinc concentrations, the difference in the yearly means can be explained by the difference in the sites sampled each year (Figure 10.6).

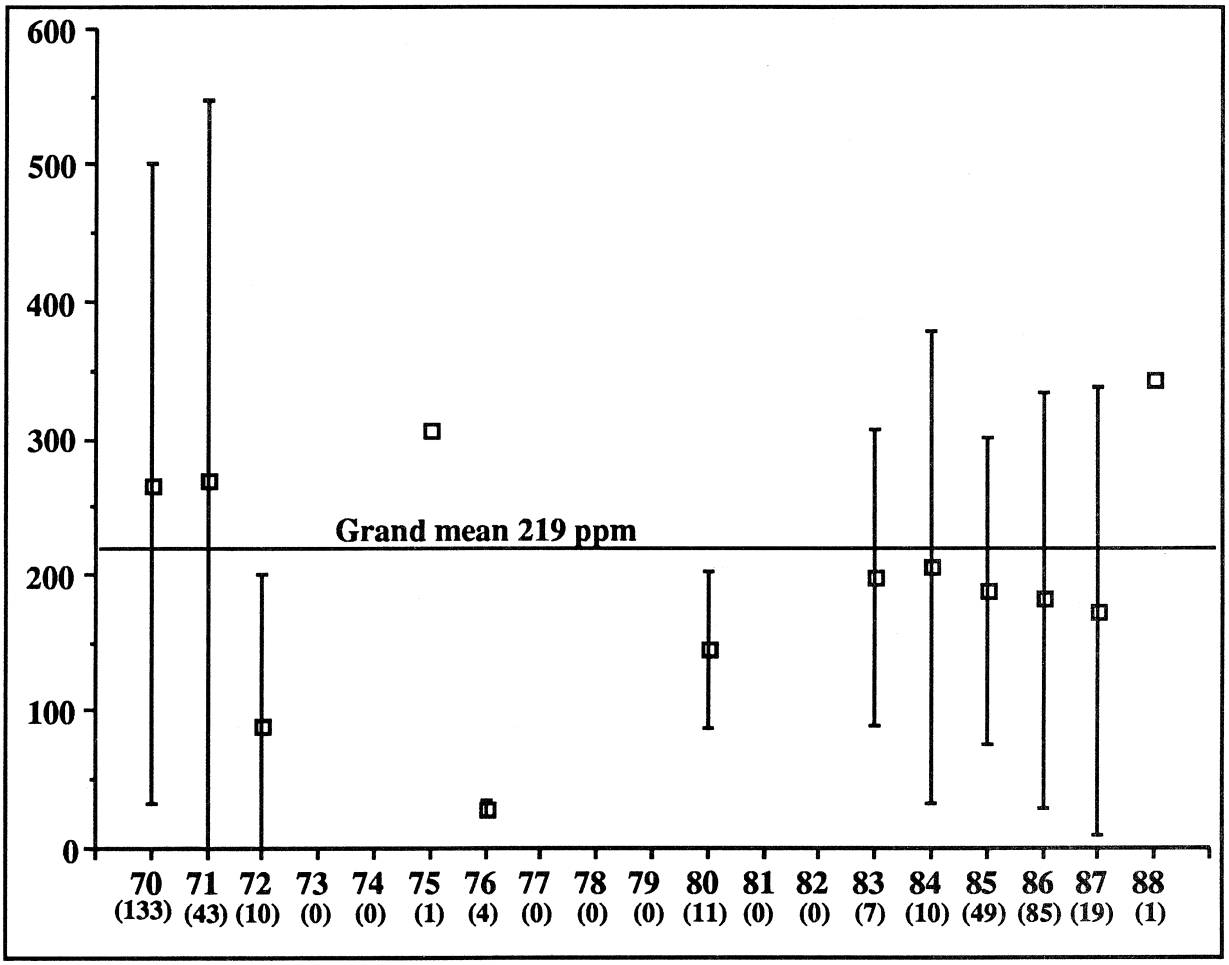


Figure 10.7 Yearly mean zinc concentrations (ppm) in the surficial sediments of Boston Harbor, based on White (1972), Gilbert *et al.* (1972), Isaac and Delaney (1975), USACOE (1972-1988, 1981, 1988), MA DEQE (1986, 1987), and NOAA (unpublished). The numbers in parenthesis are the number of samples analyzed.

Table 10.4 Yearly mean zinc concentrations (ppm dw) in Boston Harbor surficial sediments based on dredging study data from the USACOE.

Year	Mean	Standard Deviation	Count
1972	1	0	4
1975	306	N/A	1
1976	30	5	4
1980	145	57	11
1983	198	109	7
1984	169	164	7
1985	175	116	28
1986	174	158	59
1987	203	218	10
1988	344	N/A	1

Biota

Since 1976, over 160 tissue samples from a variety of organisms in Boston Harbor have been analyzed for zinc content. Zinc concentrations ranged from a low of 46 ppm in the soft parts of soft-shelled clams (*M. arenaria*) to a high of 297 ppm in the soft parts of mussels (*M. edulis*). Table 10.5 gives the statistics on zinc contamination of biota by organism and tissue. The statistics for winter flounder (*P. americanus*) (NOAA, unpublished), lobster (*H. americanus*) (Wallace *et al.*, 1988), and soft-shelled clams (Wallace *et al.*, 1988) are each based on single data sets while those for mussels are based on three different data sets (Goldberg *et al.*, 1978, Robinson *et al.*, 1990, NOAA, unpublished).

Geographic Trends

The only biota data available for more than one harbor division were zinc concentration in the soft parts of mussels. This data suggested that the inner harbor biota contained higher levels of zinc than did the biota of any of the outer harbor divisions. It further suggested that there was little difference in zinc levels in the biota of the three outer harbor divisions (Table 10.6). Little difference was found between zinc levels in mussels from the two subdivisions of the northwest harbor. The Winthrop Harbor area mussels had a mean zinc concentration of 125 ppm while the Dorchester Bay area mussels had a mean of 128 ppm.

Table 10.5 Harborwide means, standard deviations, medians, ranges and sample sizes (count) for zinc concentrations (ppm dw) in biota by organism and tissues based on all the available data sets.

		Mean	SD	Median	Range	Count
P. americanus						
	liver	93	25	90	51-139	20
H. americanus						
	muscle	95	19	98	58-131	24
M. arenaria						
	soft parts	85	20	78	46-140	34
M. edulis						
	soft parts	136	43	123	66-297	86

In 1976, the U. S. EPA sampled mussels and other bivalves from 107 sites nationwide and analyzed the samples for a variety of metals and organic analytes, including zinc (Goldberg *et al.*, 1978). A composite sample of *M. edulis* from a site on the northwest side of Deer Island was found to have a zinc concentration in the soft parts of 114 ppm. Between Block Island and the Canadian Border, 11 other New England sites were sampled and had zinc concentrations in the soft parts of *M. edulis* ranging from 67 ppm at Bailey Island, Maine to 146 ppm at Cape Ann. Boston mussels had the third highest concentration of zinc among the 11 sites. Sakonnet Point, Rhode Island mussels had the second highest zinc concentration (122 ppm).

Table 10.6 Mean zinc concentrations (ppm dw) of the entire harbor and the four divisions in the soft parts of *M. edulis* (the number in parentheses is the sample size).

	M. edulis soft parts
OVERALL	136 (86)
INNER HARBOR	170 (29)
NORTHWEST HARBOR	126 (19)
CENTRAL HARBOR	114 (29)
SOUTHEAST HARBOR	115 (9)

In 1985 and 1986, lobster (*H. americanus*) and soft-shelled clams (*M. arenaria*) were collected from Boston and Salem harbors and analyzed for various analytes, including zinc, as part of a study of contaminants in marine resources (Wallace *et al.*, 1988). The mean zinc concentration in the combined claw and muscle

tissue of 24 lobsters collected from around Deer Island was 95±19 ppm with a range of from 58 to 131 ppm. Lobsters were collected from two sites in Salem Harbor, the treatment plant outfall and Willows Pier. The mean zinc concentrations in combined claw and tail muscle tissue based on the analysis of 25 lobsters per site were 107±18 and 97±19 ppm, respectively. Statistical analysis of the log transformed data indicated that the Deer Island lobsters were not significantly different from those from the two sites in Salem Harbor at p=0.05. The mean zinc concentration for 34 soft-shelled clams from Wollaston Beach in Quincy Bay was 85±20 ppm with a range of 46 to 140 ppm.

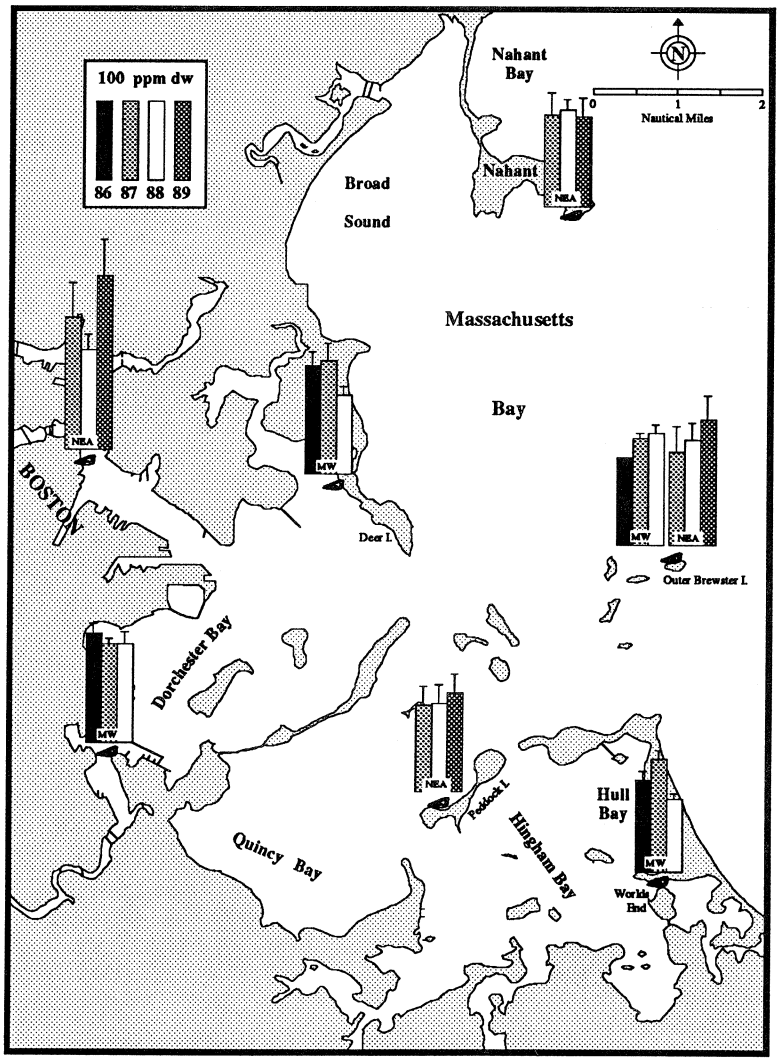


Figure 10.8. Mean zinc concentration (ppm dw) in the soft-parts of *M. edulis* from Boston Harbor and environs for 1986-89, based on data from the New England Aquarium's (NEA) and NOAA's mussel watch projects (Robinson *et al.*, 1990; NOAA, unpublished) (bars represent one standard deviation).

NOAA's Mussel Watch Project, a part of the NS&T Program, has sampled mussels (*M. edulis*) on an annual basis from four sites in and around Boston Harbor since 1986. Three whole-body composite samples from each site were analyzed for a variety of analytes, including zinc. The overall mean concentration of zinc in the mussels for the three sites in Boston Harbor from 1986 through 1988 was 123±21 ppm with a range of from 85 to 160 ppm. The means for the individual sites were 126±25 ppm northwest of Deer Island, 128±12 ppm in southwestern Dorchester Bay, and 115±23 ppm in Hingham Bay off Worlds End. Mussels from the site outside the harbor, Outer Brewster Island, had a mean zinc concentration of 128±15 ppm (Figure 10.8). Statistical analysis of the log transformed data for the four sites indicated that none of the four sites was significantly different (p=0.10).

Since 1987, the NEA has conducted their own Mussel Watch Program (Robinson *et al.*, 1990). They sampled mussels from two sites within Boston Harbor and two sites in Massachusetts Bay, including the same site on Outer Brewster Island that NOAA's Mussel Watch Project samples. The mean zinc concentration in Boston Harbor, based on data from the two sites for the 3 years from 1987 through 1989, was 142±49 ppm with a range of 66 to 297 ppm. The means for the two sites were 114±23 ppm at the Peddocks Island site and 170±53 ppm at the Central Wharf, Boston site. The two sites from Massachusetts Bay had means of 116±22

ppm at the Pumphouse Beach, Nahant site and 137±32 ppm at the Outer Brewster Island site. The data for the four sites was log transformed and the sites statistically compared. The Central Wharf site was found to be significantly different from the other three sites (p=0.05). Figure 10.8 plots the NEA data alongside the NOAA Mussel Watch data.

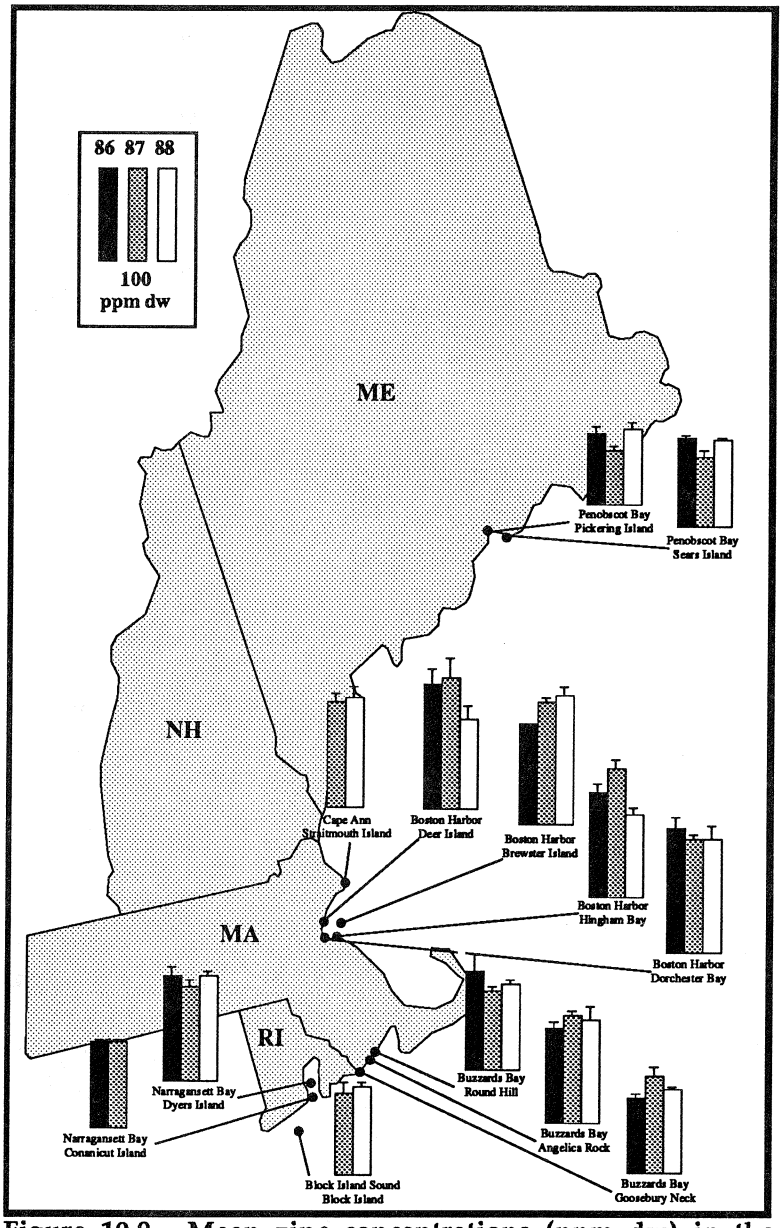


Figure 10.9. Mean zinc concentrations (ppm dw) in the soft-parts of *M. edulis* from the outer New England coast for 1986-88 (NOAA, unpublished) (bars represent one standard deviation).

On a broader scale, when the Boston Harbor NS&T sites were compared to the other New England NS&T Mussel Watch sites (Figure 10.9 and Table 10.7), the sites in Boston Harbor had the second, third, and fifth highest mean zinc concentrations. All three Boston Harbor sites were found to be significantly different from the New England site with the lowest mean zinc concentration in mussels, Pickering Island (p=0.05). In addition, the Deer Island site was found to be significantly different from the Sears Island site (the site with the second lowest mean zinc concentration in mussels) (p=0.05). The Dorchester Bay site was also significantly different from the Sears Island, Goosebury Neck, and Round Hill sites (p=0.05). The Pickering Island site was significantly different from the seven New England sites with the highest mean zinc concentrations in mussels at p=0.05. From this data it appears that zinc levels in mussels vary little throughout New England with the range of means being less than a factor of 2. When a reference value is calculated based on the five sites with the lowest mean zinc concentrations in mussels, a value of 88±13 ppm is obtained. The Boston Harbor sites have mean zinc values of from 1.3 to 1.5 times higher than this reference value. On a national scale, the Mussel Watch sites where *M. edulis* was sampled had mean zinc concentrations ranging from 71 to 284 ppm with an overall mean for all the sites of 131±55 ppm. Means at 36 percent of the sites were less than 100 ppm, while 51 percent had concentrations between 100 and 200 ppm. Only 13 percent had means more than 200 ppm. When the sites where *M. californianus* was sampled were included in the calculations, the

overall mean became 138±51 ppm. Means from 24 percent of the sites had means of less than 100 ppm, while 68 percent had concentrations between 100 and 200 ppm. Only 8 percent had means in excess of 200 ppm. Based on this data, Boston Harbor mussels appeared to be only moderately contaminated with zinc since all the harbor sites had means between 115 and 128 ppm and 51 percent of all the *M. edulis* sites had means greater than the Boston Harbor sites.

Table 10.7 The mean zinc concentrations (ppm dw) in *M. edulis* at the 13 outer New England coast NS&T Program Mussel Watch sites. The outlined means are for Boston Harbor sites.

Site	Mean	Standard Deviation	Count
DORCHESTER BAY, BOSTON HARBOR	128	12	9
OUTER BREWSTER ISLAND	128	15	9
DEER ISLAND, BOSTON HARBOR	126	25	9
CAPE ANN, STRAITSMOUTH ISLAND	117	10	6
HINGHAM BAY, BOSTON HARBOR	115	23	9
ANGELICA ROCK, BUZZARDS BAY	111	10	9
DYERS ISLAND, NARRAGANSETT BAY	109	10	9
ROUND HILL, BUZZARDS BAY	95	14	9
GOOSEBURY NECK, BUZZARDS BAY	94	12	8
CONANICUT ISLAND NARRAGANSETT BAY	93	2	6
BLOCK ISLAND, RHODE ISLAND	91	8	6
SEARS ISLAND, PENOBSCOT BAY	90	11	9
PICKERING ISLAND, PENOBSCOT BAY	74	13	9

NOAA's Benthic Surveillance Project, a part of the NS&T Program, has sampled winter flounder (*P. americanus*) from an area just west of Deer Island on an annual basis since 1984. The mean zinc concentration in the liver of the fish sampled in 1984 and 1985 was 93±25 ppm with a range of 51 to 139 ppm. The mean concentration of zinc in flounder livers for all the New England Benthic Surveillance sites, excluding Boston Harbor, ranged from a low of 103±30 ppm at the Salem Harbor site to a high of 184±29 ppm at the Casco Bay site (Figure 10.10). The mean zinc concentration of winter flounder liver from Boston Harbor was lower than the mean for any other New England site. Statistical analysis of the log transformed data indicated that the Boston Harbor site was significantly different from all but the Salem Harbor site at p=0.05. The Salem Harbor site was significantly different from the Merrimack River site at p=0.05. No comparison could be made between Boston Harbor and the three northern-Maine sites; because, a different species, longhorn sculpin (*M. octodecemspinosus*), was sampled at these sites. The Benthic Surveillance Project sampled winter flounder at four other sites during the same time frame: two in Long Island Sound and one each in Raritan and Great bays in New Jersey. All four site means were greater than the mean for Boston Harbor. They ranged from a low of 119±29 ppm (Great Bay) to a high of 150±34 ppm (East Long Island Sound).

Temporal Trends

No temporal trends in the zinc levels of Boston Harbor biota could be determined based on the available data. The only internally consistent data sets sampling the same organism from the same locations over a number of years were the NS&T Program's Benthic Surveillance and Mussel Watch projects and the NEA Mussel Watch Program. Data for these projects were only available for 2, 3, and 3 years, respectively. Between 1984 and 1985 there was approximately a 16 percent increase in the reported level of zinc in winter flounder livers (86±30 to 100±17 ppm) (Figure 10.10) which was not significantly different at p=0.05. Likewise, the 3 years of data for *M. edulis* from the NS&T Program Mussel Watch Project are insufficient to indicate any trend; but, these data show zinc levels slightly increasing between 1986 and 1987 and then decreasing in 1988 (Figure 10.8). The yearly

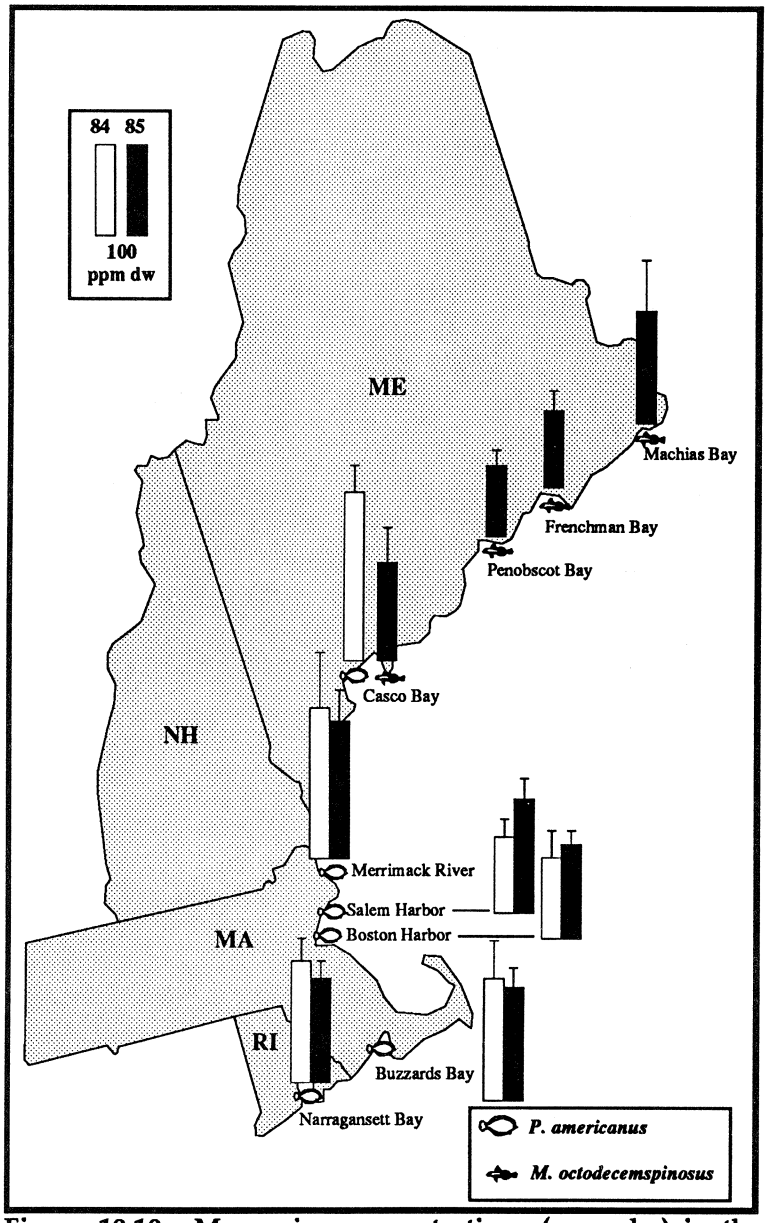


Figure 10.10. Mean zinc concentrations (ppm dw) in the liver tissue of *P. americanus* and *M. octodecemspinosus* from the outer New England coast in 1984 and 1985 (NOAA, unpublished) (bars represent one standard deviation).

means were 129±16, 136±15, and 104±18 ppm, respectively. However, statistical analysis of the log transformed NS&T Program Mussel Watch data did indicate a significant difference between 1988 and the two earlier years. The yearly means for the New England Aquarium Mussel Watch Program showed no apparent trend, decreasing from 138±44 ppm (1987) to 118±23 ppm (1988) and then increasing to 171±59 ppm (1989). Statistical analysis of the log transformed NEA Mussel Watch data did indicate a significant difference between 1988 and 1989 at p=0.05. It is interesting that while neither the NS&T Program nor the NEA Mussel Watch projects indicate any long-term temporal trends, both data sets indicate that zinc levels were lower in mussels in 1988 than in the other years sampled.

When the EPA Deer Island site, which had a zinc concentration in the soft parts of mussels of 114 ppm in 1976, was compared to the NS&T Program Deer Island site (which is about 0.5 miles northwest of the EPA site) with yearly means of 137, 98, and 143 ppm (1986, 1987, and 1988, respectively), there appeared to be an approximate 25 percent increase in zinc concentrations in the 11 years between 1976 and 1987 although there appeared to be a decrease in zinc levels between 1987 and 1988. However, this comparison needs to be viewed with caution because the EPA value was based on only one composite sample while the NS&T Program values were based on three composite samples each. Also, the difference between the EPA value and the NS&T Program values may be the result of differences in laboratory methodology.

Summary

The mean zinc concentrations in Boston Harbor sediments were found to exceed background levels by more than a factor of 4. Individual samples exceeded background levels by more than a factor of 400. When the NS&T Program data mean value of zinc in Boston Harbor (171±97 ppm) was compared to the NS&T Program data mean for San Francisco Bay (126±52 ppm) (Long *et al.*, 1988), it was found to be approximately 36 percent higher than the San Francisco Bay mean (Table 10.8). The overall data set indicated a trend of decreasing zinc concentrations in Boston Harbor surficial sediments from the inner harbor towards the southeastern harbor and towards the mouth. This trend was also apparent in four of the five individual data sets that covered most of the Harbor (White, 1972; Gilbert *et al.*, 1972; Massachusetts DEQE, 1986 and 1987; NOAA, unpublished). The fifth data set, Isaac and Delaney (1975), indicated a trend of decreasing zinc concentrations from the northwest to the southeast harbor but the lowest value for zinc was in the inner harbor. However, this low value was based on just one sample that may not be representative of the entire inner harbor. No clear temporal trends were apparent with regard to zinc concentrations in the surficial sediment.

Table 10.8. Comparison of zinc sediment statistics for Boston Harbor, NS&T Program Reference (based on the five NS&T Program sites in New England with the lowest zinc levels), and San Francisco Bay in ppm dw. Statistics for San Francisco Bay derived from Long *et al.*, 1988.

Area	Mean	Standard Deviation	Median	Range	Count
Boston	219	201	165	1 - 1750	373
NS&T Program Boston	171	97	180	38 - 516	31
NS&T Program Reference	45	12	43	26 - 71	25
NS&T Program San Francisco Bay	126	52	126	13 - 321	36

Based on the available data, Boston Harbor biota appears to be slightly to moderately contaminated with zinc. Boston Harbor mussels (*M. edulis*) had some of the highest mean zinc concentrations of all the New England NS&T Program sites sampled. When compared to all NS&T Program mussel sites sampled in the country, approximately 51 percent of the sites had means greater than the Boston Harbor sites. Only 30 percent had means lower than the lowest Boston Harbor site mean. The winter flounder (*P. americanus*) liver data suggested that Boston Harbor had only low levels of zinc. Among the NS&T Program sites, the Boston site had the lowest mean zinc concentration among all the winter flounder sites. The NEA data suggested that inner harbor mussels had higher concentrations of zinc than did outer harbor mussels; but, other than this one example, there were no obvious geographic or temporal trends in zinc content of biota within Boston Harbor based on the available data.

ARSENIC

Arsenic is commonly found in sediments, seawater, and biota, including humans. The toxicity of arsenic has been known for centuries (it was the poison of choice during the Middle Ages). It is a known teratogen and carcinogen, although there is evidence suggesting that it is nutritionally essential or beneficial in trace amounts (Eisler, 1988b). Arsenic is found in inorganic and organic form. The inorganic forms are generally more toxic than the organic forms (Eisler, 1988b). Arsenic concentration in the earth's crust ranges between 1.5 and 2.0 ppm (GESAMP, 1986a) and is found in shales and clays at approximately 14.5 ppm (Eisler, 1988). In a review of the literature, Long and Morgan (1990) found data suggesting that arsenic levels in sediment below about 33 ppm have little or no effect on biota while biological effects are usually observed at levels of 70 ppm or greater.

Sediments

Since 1972, over 170 surficial sediment samples from Boston Harbor have been analyzed for arsenic concentrations. Based on this data, the overall mean concentration of arsenic in the surficial sediments of the Harbor was 14.2 ppm with a standard deviation of 20.5 and a range of from 0.32 to 143 ppm (Table 11.1). The median concentration was 8.4 ppm. Approximately 1 percent of the samples analyzed had concentrations less than 1.0 ppm. The vast majority of the samples, approximately 84 percent, had values between 1.0 and 20.0 ppm, inclusive. The remaining 15 percent of the samples contained more than 20.0 ppm arsenic including 2 percent (three samples) with concentrations greater than 100 ppm. All three samples with arsenic concentrations greater than 100 ppm were taken from the same site in the inner harbor (USACOE, data sheets); and, if they are excluded from the calculations, the mean arsenic concentration would become 12.3±14.7 ppm with a maximum value of 89 ppm and a median of 8.3 ppm.

Table 11.1. Means (ppm dw), standard deviations, medians, ranges, and number of samples (count) for arsenic concentrations in surficial sediments for all of Boston Harbor and the four regions of the harbor based on all the available data sets.

	Mean	Standard Deviation	Median	Range	Count
OVERALL	14.2	20.5	8.4	0.32 - 142.7	178
INNER HARBOR	20.3	28.2	9.6	1.30 - 142.7	62
NORTHWEST HARBOR	9.7	8.5	7.8	1.00 - 55.0	77
CENTRAL HARBOR	11.3	13.1	10.4	0.92 - 53.0	14
SOUTHEAST HARBOR	14.4	24.4	4.6	0.32 - 86.7	25

Geographic Trends

When the combined data set was broken down into the four harbor divisions, the means and medians suggested different patterns of arsenic distribution. The means suggested that the highest levels of arsenic were found in the inner harbor (20.3±28.2 ppm) and the second highest levels in the southeast harbor (14.4±24.4 ppm). There was little difference between arsenic levels in the central and northwest harbor (11.3±13.1 and 9.7±8.5 ppm, respectively). The medians, on the other hand, suggest that the highest levels of arsenic were in the central (10.4 ppm) and inner (9.6 ppm) harbor divisions. The northwest harbor had only slightly lower levels (7.8 ppm) while the lowest levels were in the southwest harbor (4.6 ppm) (Table 11.1). This difference between the means and medians, as well as the large

standard deviation was because in each harbor division there was one site with significantly higher concentrations of arsenic than the rest of the sites in the division. Three samples from a single site in the inner harbor had concentrations more than 100 ppm while the next highest sample was 89 ppm. The northwest and central harbor divisions each had a single sample with an arsenic concentration greater than 50 ppm, while the second highest sample concentrations were 33 and 18 ppm, respectively. Three samples from a single site in the southeast harbor division (actually from the Fore River) had concentrations in excess of 70 ppm while the next highest sample was 21 ppm. When these high samples were excluded from the calculations, the means for the four harbor divisions became: inner, 15.0±15.8; northwest, 9.1±6.7; central, 8.1 ±5.5; and southeast, 5.8±4.6, ppm, respectively. This data suggests that, with the exception of a few individual hot spots, there was a general trend of decreasing arsenic concentrations from the inner to the southeast harbor. When the data for the northwest harbor were subdivided, the Dorchester Bay area (21 samples), which included the highest single sample for the northwest harbor (55 ppm), had a higher mean arsenic concentration (12.5±13.1 ppm) than the Winthrop Bay area (8.7±5.5 ppm). Excluding the single high sample from the calculations gave a mean arsenic concentration for the Dorchester Bay area of 10.5±9.3 ppm, still higher than that for the Winthrop Bay area.

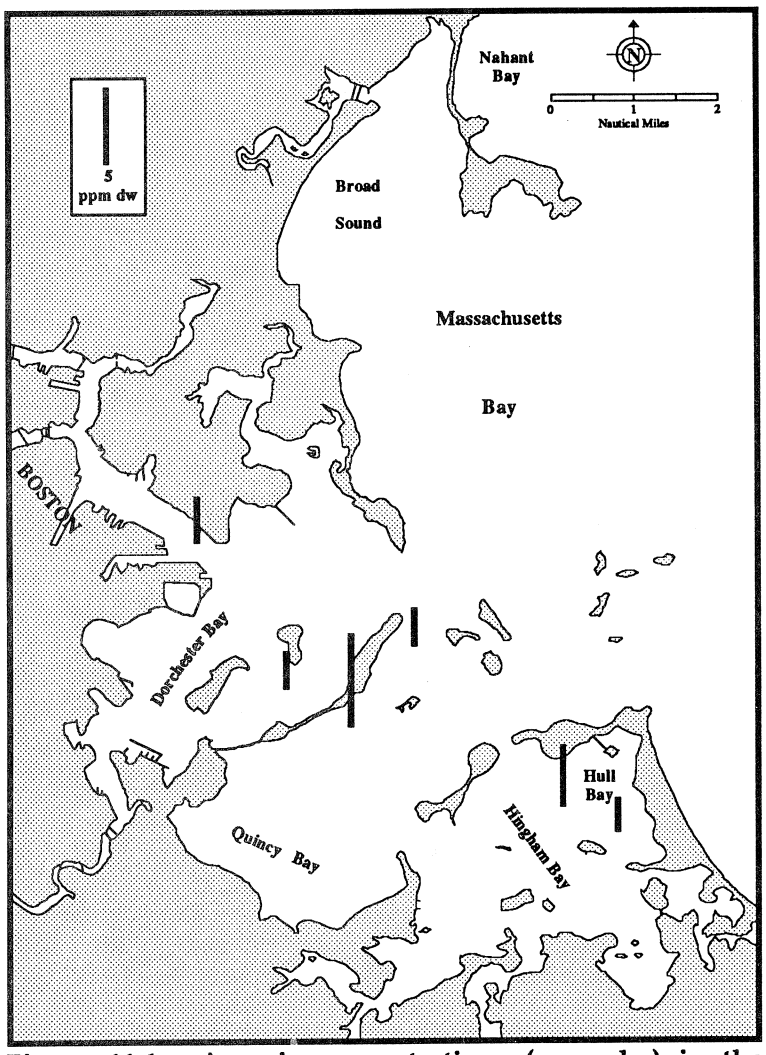


Figure 11.1. Arsenic concentrations (ppm dw) in the surficial sediments of Boston Harbor in the early 1970s (Isaac & Delaney, 1975)

Between 1971 and 1974, Massachusetts conducted a toxic element survey of the waters of the State (Isaac and Delaney, 1975). The survey included the analysis of sediment samples for volatile solids and a variety of analytes, including arsenic. The combined mean arsenic concentration for six surficial sediment samples from around Boston Harbor was 3.3±1.5 ppm with a range of from 2.2 to 6.0 ppm (Figure 11.1). Because so few samples were analyzed, no statistical comparison among harbor divisions could be made and the data did not suggest any trend in arsenic concentrations throughout the Harbor (Table 11.2).

Data were obtained from the New England Division of the USACOE for dredging studies conducted in and around Boston Harbor from 1975 through 1988 (USACOE, 1975-1988, 1981; 1988). The USACOE analyzed 122 samples during this period for arsenic content. The overall mean arsenic concentration for the harbor based on this data was 15.7±24.1 ppm. The range was from a low of 0.32

Table 11.2. Mean arsenic concentrations (ppm dw) in the surficial sediments of Boston Harbor and the four divisions of the harbor based on the data of Isaac and Delaney (1975), USACOE (1975-1988, 1981) and Hubbard (1987), MA DEQE (1986 and 1987), and NOAA's NS&T Program (unpublished). The numbers in parentheses are the number of data points used to calculate the means.

SAMPLING YEAR(S)	Isaac and Delaney 1972	USACOE 1975-88	MA DEQE 1985-86	NOAA NS&T 1984-87
OVERALL	3.3 (6)	15.7 (122)	15.9 (19)	9.3 (31)
INNER HARBOR	3.0 (1)	20.9 (57)	15.6 (4)	N/A
NORTHWEST HARBOR	2.4 (1)	8.7 (45)	13.4 (9)	10.6 (22)
CENTRAL HARBOR	4.2 (2)	3.5 (6)	23.4 (4)	11.7 (3)
SOUTHEAST HARBOR	3.1 (2)	22.0 (14)	13.0 (2)	3.4 (6)

ppm in a sample from the Town River, Quincy (southeast harbor division) to a high of 142 ppm in a sample from the inner harbor. The majority of the samples (80%) had arsenic concentrations between 1 and 20 ppm inclusive. Approximately 1.6 percent of the samples had less than 1 ppm. Only 19 percent of the samples had concentrations more than 30 ppm, with 2.4 percent greater than 100 ppm. When the data was grouped by harbor divisions, the means ranged between 4.2±4.5 ppm in the central harbor (5 samples) to 20.9±30.7 ppm in the inner harbor (57 samples). The northwest harbor (45 samples) had a mean of 8.7±10.2 ppm, while the southeast harbor (15 samples) had a mean of 20.6±30.1 ppm. The high means and standard deviations for the inner and southeast harbor divisions were the result, in both cases, of the inclusion of three samples from a single site with exceptionally high concentrations of arsenic. In the case of the inner harbor, the three samples had reported arsenic concentrations more than 100 ppm while those from the southeast harbor had concentrations more than 70 ppm. Excluding these exceptionally high values from the calculations resulted in a mean for the inner harbor of 15.2±16.4 ppm and a mean for the southeast harbor of 6.3±5.1 ppm. These modified division means suggested a trend of decreasing arsenic concentration from the inner to the outer harbor with the central harbor having the lowest mean arsenic concentration of the three outer harbor divisions. The log transformed modified data indicated that the inner harbor was significantly different from the other three harbor divisions at $p=0.05$. When the northwest harbor data was subdivided, the Dorchester Bay area (12 samples) had a mean arsenic concentration of 13.1±17.4 ppm while the Winthrop Bay area (33 samples) mean was 7.1±5.4 ppm. The large difference between the two subdivision means and the large standard deviation of the Dorchester Bay area data was because one sample from Dorchester bay area had an arsenic concentration of 55 ppm. When this extraordinarily high value was excluded from the calculations. the mean became 9.3±12.0 ppm for the Dorchester Bay area.

In 1985, the Massachusetts DEQE, as part of their annual Boston Harbor Water Quality and Wastewater Discharge Survey, analyzed 19 surficial sediment samples for arsenic content. They found an overall mean arsenic concentration of 15.9±10.4 ppm ranging from a low of 5.2 ppm, in a sample taken from northwestern Dorchester Bay, to a high of 53.0 ppm, in a sample taken from southeastern Quincy Bay. The second highest sample was 23.0 ppm taken from a site north of Logan Airport. The majority of the surficial sediment samples (approximately 79%) had arsenic concentrations between 5.0 and 20.0 ppm. Approximately 21 percent of the samples had concentrations more than 20.0 ppm including one sample with a concentration of 53.0 ppm. The division means ranged from 13.0 ppm for the southeast harbor to 23.4±20.1 ppm for the central harbor. The inner harbor had the second highest mean, 15.6±5.9 ppm, while the northwest harbor mean was 13.4±6.6 ppm (Table 11.2). The high mean for the central harbor was the result of a single extraordinarily high arsenic value of 53.0 ppm while the second highest value in the central harbor area was 18.0 ppm. When this high value was excluded from the calculations, the mean arsenic concentration in

the central harbor was 13.5±4.3 ppm. The division data, excluding the 53.0 ppm sample, suggested that the inner harbor had the highest levels of arsenic in the sediments and that there was little difference in arsenic levels among the outer harbor divisions. However, the log transformed data indicated no significant difference among any of the harbor divisions at p=0.05. Figure 11.2 graphically displays the data by site and year. The data for the northwest harbor subdivisions were analyzed. The Winthrop Bay area (six samples), with a mean of 14.0±7.0 ppm, and the Dorchester Bay area (three samples), with a mean of 12.1±6.9 ppm, were found not to be significantly different from any of the harbor divisions at p=0.05.

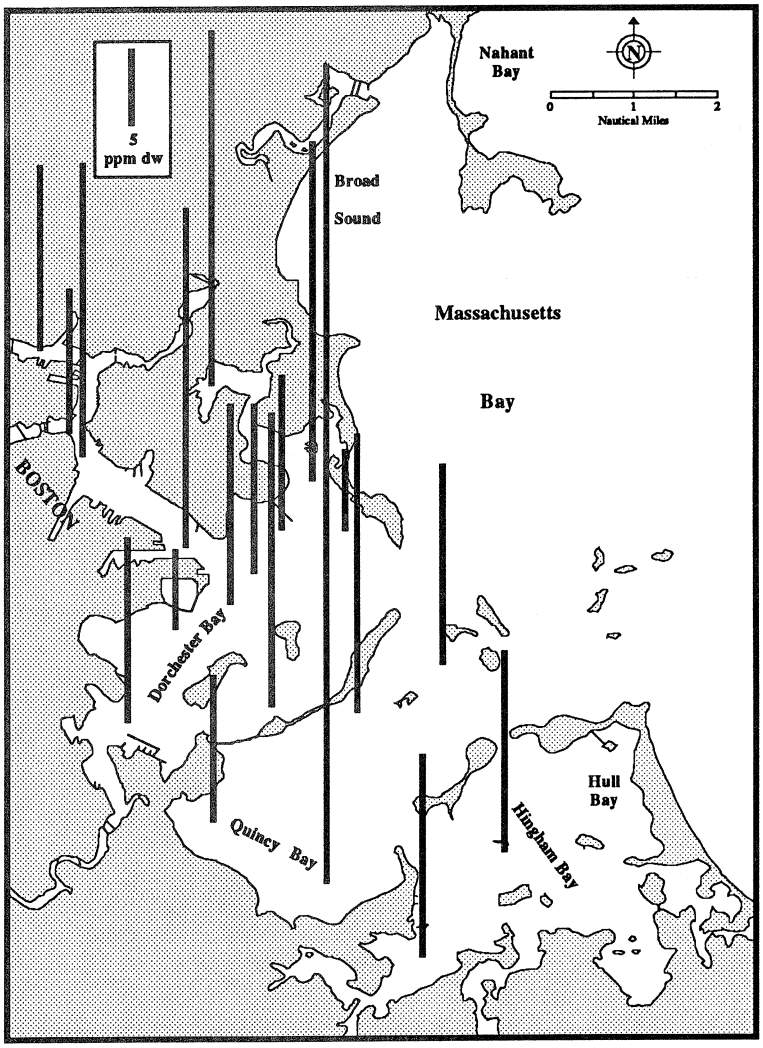
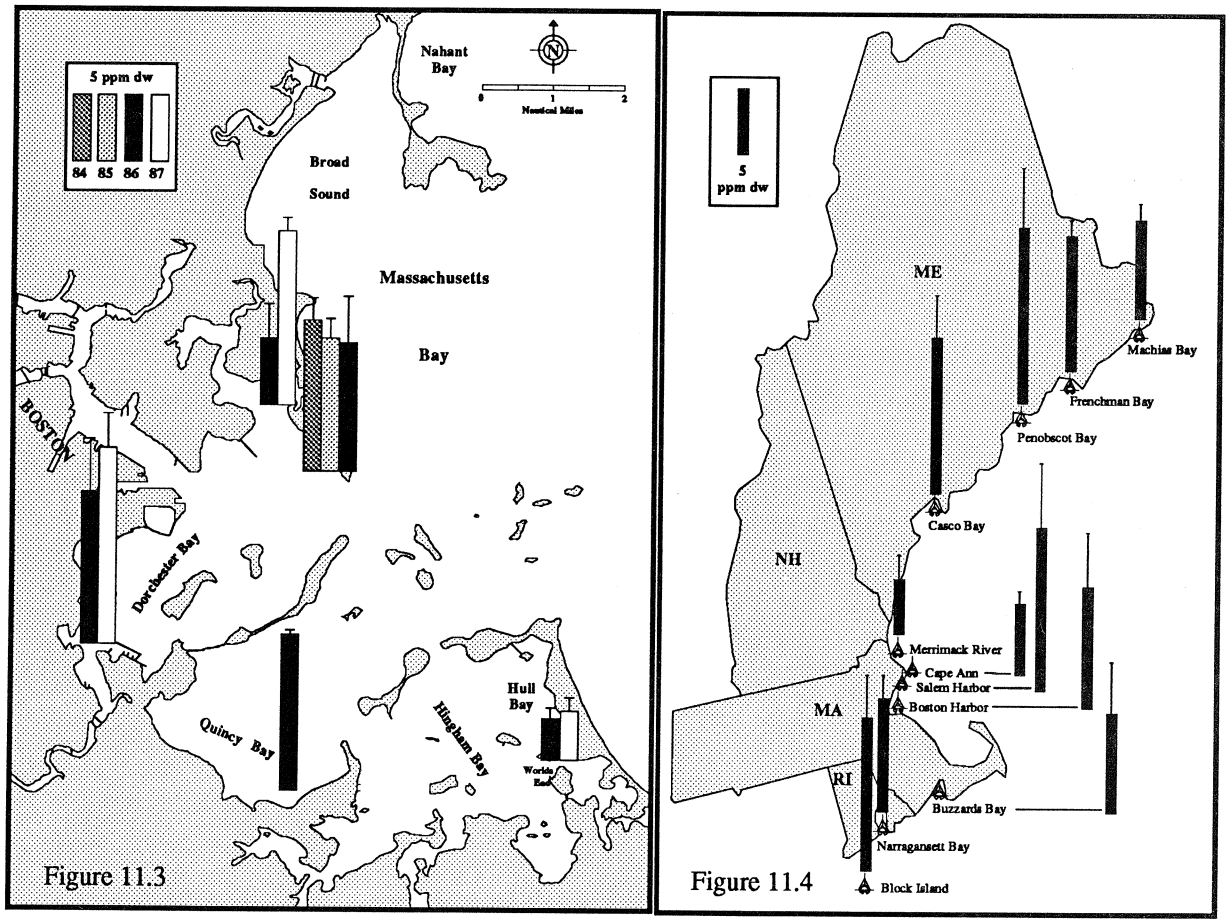


Figure 11.2. Arsenic concentrations (ppm dw) in the surficial sediments of Boston Harbor in 1985, based on data from the Massachusetts DEQE (1986).

NOAA's NS&T Program has sampled and analyzed surficial sediments from several sites around Boston Harbor for several analytes, including arsenic, since 1984. Figure 11.3 portrays this data graphically by year and site. The overall mean arsenic concentration in surficial sediments of the harbor was 9.3±4.2 ppm. Individual sample values ranged from 2.4 to 17.0 ppm. Site means, based on all 4 years of available data, ranged from 3.4±0.8 ppm at the site off the northern tip of Worlds End to 13.0±3.5 ppm at the site in southwestern Dorchester Bay. The mean arsenic concentrations in the surficial sediments of the other sites were: northwest of Deer Island, 9.0±4.7 ppm; southwest of Deer Island, 10.2±2.1 ppm; and Quincy Bay, 11.7±0.3 ppm. Statistical comparison of the log transformed data indicated that the Worlds End site was significantly different from all the other sites at p=0.05. When the data were grouped by harbor divisions (Table 11.2), the means suggested that there was little difference in mean arsenic concentrations in the northwest and central harbor; but, the arsenic concentrations were significantly lower in the southeast harbor. Statistical analysis of the log transformed data indicated that the southeast harbor was significantly different from both the northwest and central harbors at p=0.05.

On a broader scale, between 1984 and 1987, the NOAA NS&T Program analyzed surficial sediment samples from 23 sites from 11 areas along the outer New England coast. Figure 11.4 displays the means and standard deviations for the 11 coastal areas. This figure

clearly shows that the mean arsenic concentration of the NS&T Program sites in Boston Harbor (9.3±4.2 ppm) was right in the middle of the 11 areas sampled. Statistical analysis of the log transformed data indicated that the Merrimack River (the area with the lowest mean arsenic concentration) was significantly different from the three New England areas with the highest mean arsenic concentrations (Penobscot Bay, Salem Harbor, and Casco Bay). The area with the third lowest mean arsenic concentration, Buzzards Bay, was significantly different from Penobscot Bay, which had the highest mean arsenic concentration at p=0.05.



Figures 11.3 & 11.4. Mean arsenic concentrations (ppm dw) in the surficial sediments of Boston Harbor, by site and year (Fig. 11.3) and along the outer New England coast for 1985-87 (NOAA, unpublished) (bars represent one standard deviation).

When the mean arsenic concentrations in the surficial sediments of the individual New England NS&T Program sites were compared, only one of the five sites with the highest mean arsenic concentration was located in Boston Harbor; and, the site with the lowest mean arsenic concentration, Hingham Bay, was also located in Boston Harbor (Table 11.3). In an attempt to determine a value for background arsenic levels, the overall mean was calculated for the five NS&T Program sites with the lowest arsenic concentrations in their surficial sediments (Table 11.3). This mean was 4.1±1.6 ppm; the overall mean arsenic concentration in the surficial sediments of Boston Harbor, based on the NS&T Program data, was just over 2 times greater than this reference mean. The Boston Harbor site with the highest arsenic concentration had a mean just under 3 times higher than the reference mean. The Boston Harbor site with the lowest mean arsenic concentration (Worlds End) was only about 0.8 times the reference mean.

Table 11.3 The five outer New England Coast NOAA NS&T Program sites with the lowest and highest mean arsenic concentrations (ppm dw) based on data from 1984 through 1987.

Site	Mean	Standard Deviation	Count
HINGHAM BAY	3.40	0.82	6
ANGELICA ROCK, BUZZARDS BAY	3.68	1.57	6
MERRIMACK RIVER	4.18	1.95	5
GOOSEBURY NECK, BUZZARDS BAY	4.32	1.88	6
STRAITSMOUTH ISLAND, CAPE ANN	5.50	1.04	3
BUZZARDS BAY	11.77	1.65	11
CASCO BAY	11.91	3.23	9
SALEM HARBOR	12.67	4.91	9
DORCHESTER BAY	13.05	3.45	6
SEARS ISLAND, PENOBSCOT BAY	17.83	3.60	6

Temporal Trends

Figure 11.5 compares the yearly mean arsenic concentrations in the surficial sediments of Boston Harbor based on all the available data sets (USACOE, 1972-1988; 1981, 1988: MA DEQE, 1986; 1987: NOAA, unpublished). Because of the large yearly standard deviations, nothing could be said about temporal trends in arsenic concentrations when all the sample concentrations were used. In an attempt to reduce the standard deviation, by eliminating the outliers, the sample concentrations below 1.0 ppm (2 samples) and above 50 ppm (11 samples) were excluded and the yearly means calculated based on the remaining 93 percent of the total sample concentrations. When these outliers were excluded the range of sample values became 1 to 33 ppm, and as Figure 11.5 shows the yearly standard deviations were greatly reduced. With the exception of 1972, the yearly means fell within the relatively narrow range of 7.2 to 13.3 ppm (Figure 11.5). The modified data set suggests that arsenic concentrations in the surficial sediments might have increased since the early 1970s but have remained relatively constant since 1980. However, the possible increase in arsenic must be viewed with extreme caution because of the extremely small number of samples (seven) analyzed in the early and mid 1970s.

Some data were available from the USACOE on dredging studies for 1975 and most of the years from 1980 through 1988. When the yearly mean arsenic concentrations in the surficial sediments based on this data were calculated (Table 11.4) and the log transformed data compared, only the 2 years with the highest and lowest means were found to be significantly different at $p=0.05$, despite the wide range in yearly means. This lack of significant difference was probably due to the very large yearly standard deviations and the relatively small sample sizes for many of the years. Therefore, while the data sets would be expected to be internally consistent concerning methodology, any conclusions concerning temporal trends based on the data must be viewed with extreme caution.

The only other available data that spanned more than 2 years was that from NOAA's NS&T Program Benthic Surveillance (1984-86) and Mussel Watch (1986-87) projects. The yearly mean arsenic concentrations in the surficial sediments of Boston Harbor based on this data ranged from a high of 11.2±1.7 ppm in 1984 to a low of 8.1±4.2 ppm in 1986. The yearly means for 1985 and 1987 were 9.9±1.3 ppm and 10.5±5.3 ppm, respectively. Statistical analysis of the log transformed data indicated no significant difference between any of the years at $p=0.05$. What difference there was between means could readily be explained by difference in sites sampled each year.

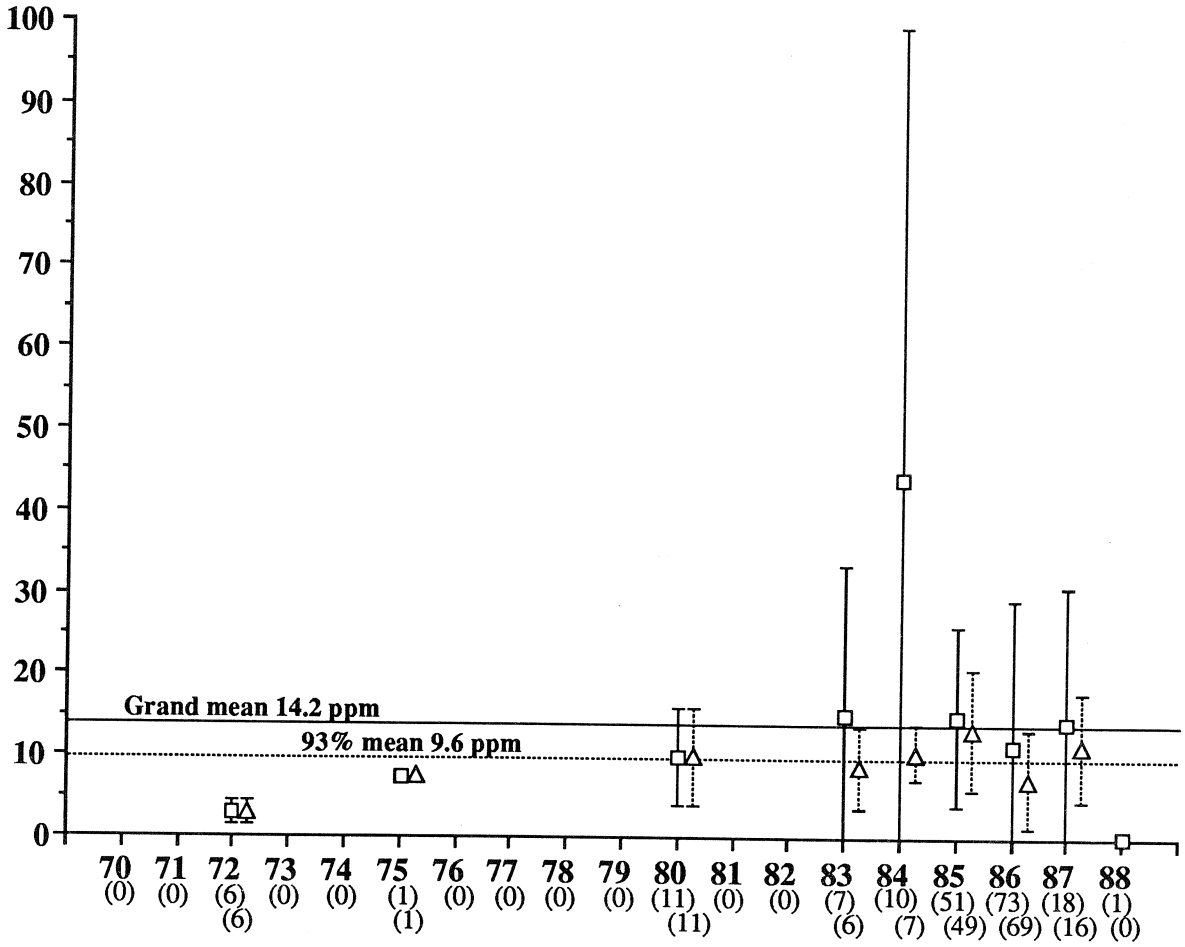


Figure 11.5 Yearly mean arsenic concentrations (ppm) in the surficial sediments of Boston Harbor, based on Isaac and Delaney (1975), USACOE (1972-1988, 1981, 1988), MA DEQE (1986, 1987), and NOAA (unpublished) and all samples analyzed (squares and solid lines). Also based on 93 percent of the samples analyzed from the same data sets (triangles and dotted lines) excluding those samples below 1 ppm and above 50 ppm. The bars represent one standard deviation. The numbers in parenthesis are the number of samples analyzed.

Table 11.4. Yearly mean arsenic concentrations (ppm dw) in Boston Harbor surficial sediments based on dredging study data from the USACOE.

Year	Mean	Standard Deviation	Count
1975	7.6	N/A	1
1980	10.0	6.0	11
1983	15.3	18.1	7
1984	58.5	61.4	7
1985	15.0	12.2	28
1986	12.0	19.9	58
1987	20.1	23.5	8
1988	0.32	N/A	1

Biota

The only available data on arsenic concentrations in biota were for winter flounder (*P. americanus*) liver and mussel (*M. edulis*) soft parts from NOAA's NS&T Program. The overall mean concentration for winter flounder liver (7.36 ppm) was about half that for mussel soft parts (8.90 ppm) (Table 11.5).

Table 11.5 Harborwide means, standard deviations, medians, ranges, and sample sizes (count) for arsenic concentrations (ppm dw) in biota by organism and tissues based NOAA's NS&T Program Benthic Surveillance and Mussel Watch data sets.

		Mean	Standard Deviation	Median	Range	Count
P. americanus	liver	3.73	2.62	2.91	0.74-8.42	16
M. edulis	soft parts	8.90	0.63	8.70	7.80-10.0	27

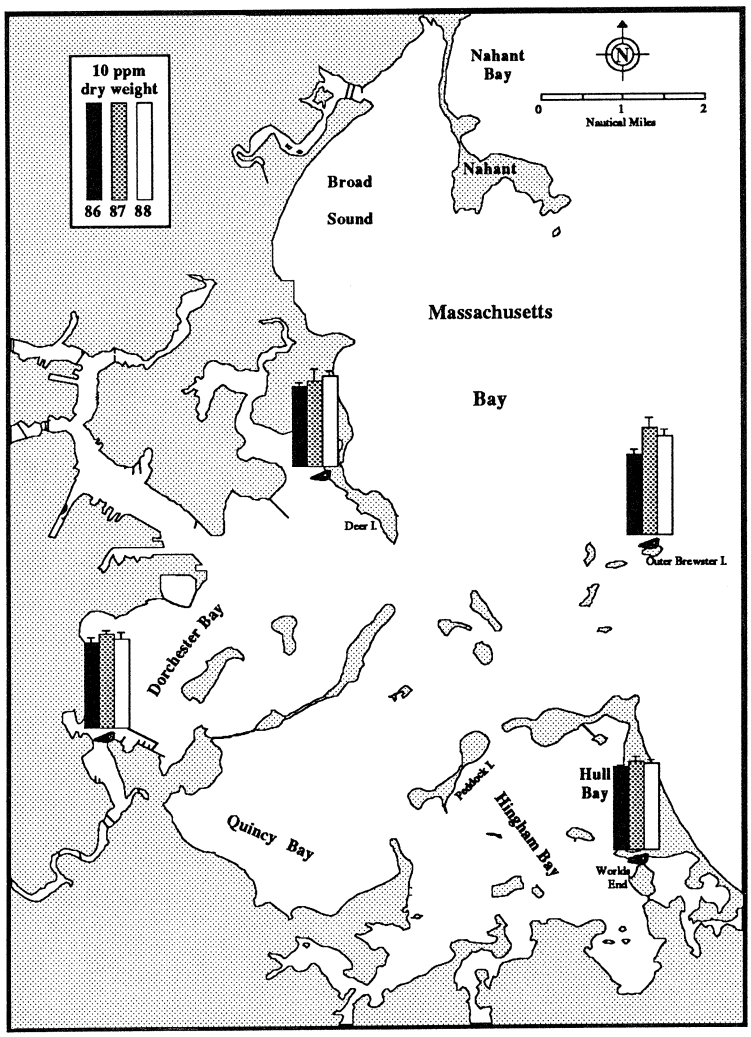


Figure 11.6. Mean arsenic concentrations (ppm dw) in the soft-parts of *M. edulis* from in and around Boston Harbor by site and year for 1986-88 (NOAA, unpublished) (bars represent one standard deviation).

Geographic Trends

NOAA's Mussel Watch Project, a part of the NS&T Program, has sampled mussels (*M. edulis*) on an annual basis from four sites in and around Boston Harbor since 1986. Three whole-body composite samples from each site were analyzed for a variety of analytes, including arsenic. The overall mean concentration of arsenic in the mussels for the three sites in Boston Harbor from 1986 through 1988 was 8.90±0.63 ppm with a range of from 7.80 to 10.0 ppm. The means for the individual sites were: 8.81±0.80 ppm, northwest of Deer Island; 9.18±0.59 ppm, southwestern Dorchester Bay; and 8.72±0.42 ppm, Hingham Bay off Worlds End. Mussels from the site just outside the harbor, Outer Brewster Island, had a mean arsenic concentration of 9.78±1.38 ppm (Figure 11.6). Statistical analysis of the log transformed data for the four sites indicated that none of the four sites was significantly different (p=0.05).

On a broader scale, when the Boston Harbor sites were

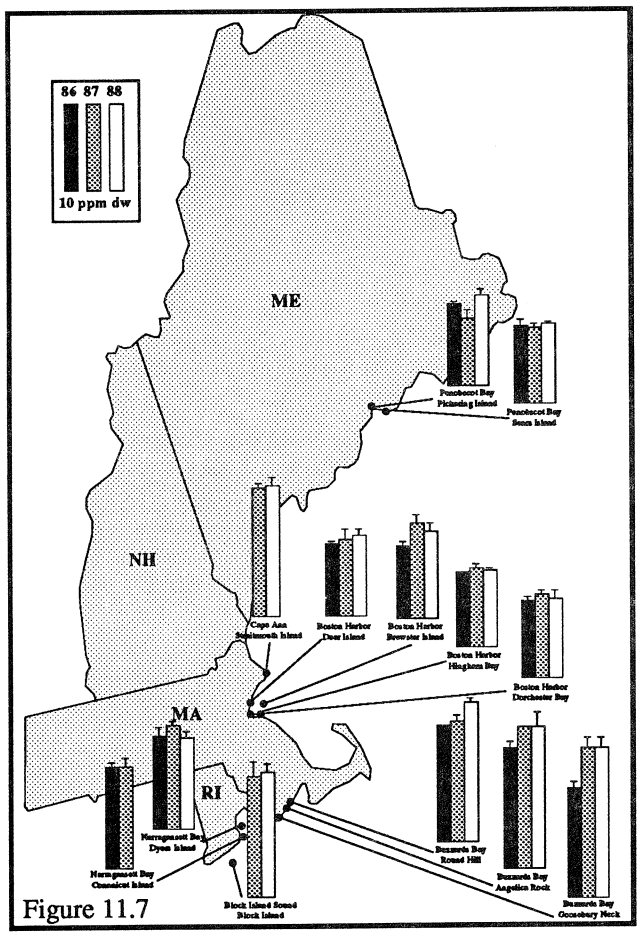
compared to the other New England Mussel Watch sites (Table 11.6 and Figure 11.7), the sites in Boston Harbor had the second, third, and fifth lowest mean arsenic concentrations. The sixth lowest mean was for the site just outside Boston Harbor, Outer Brewster Island. The six New England sites with the lowest means, including all three Boston Harbor sites, were found to be significantly different from the five New England sites with the highest mean arsenic concentrations in mussels (p=0.05). In addition, the Conanicut Island site was found to be significantly different from the three sites with the lowest means and the three sites with the highest means (p=0.05) (Table 11.6). The seventh ranked site, Dyers Island, was significantly different from the four highest ranked sites (p=0.05) (Table 11.6). From this data, it appears that arsenic levels in mussels vary little throughout New England with the range of means being less than a factor of 2. When a reference value was calculated based on the five sites with the lowest mean arsenic concentrations in mussels, a value of 8.91±0.77 ppm was obtained. This reference mean is virtually identical to the Boston Harbor mean. This is not surprising since three of the five sites with the lowest means were the Boston Harbor sites. On a national scale, the Mussel Watch sites where *M. edulis* was sampled had mean arsenic concentrations ranging from 4.63 to 15.8 ppm. The overall mean for all the sites was 131±55 ppm. There were 53 percent of the sites with means lower than Hingham Bay (8.72 ppm), the Boston Harbor site with the lowest mean arsenic concentration; while 33 percent of the sites had means higher than Dorchester Bay (8.72 ppm), the Boston Harbor site with the highest mean. The five sites with the highest means were the same five New England sites. When the sites where *M. californianus* was sampled were included in the calculations, the overall mean became 138±51 ppm. Individual site means ranged from 4.63 to 33.1 ppm and 36 percent of the sites had means lower than the Boston Harbor site with the lowest mean arsenic concentration and 52 percent of the sites had means higher than the Boston Harbor site with the highest mean. Based on this data, while Boston Harbor mussels had relatively low levels of arsenic compared to other New England sites, they appeared to be moderately contaminated with arsenic when compared to the sites nationwide.

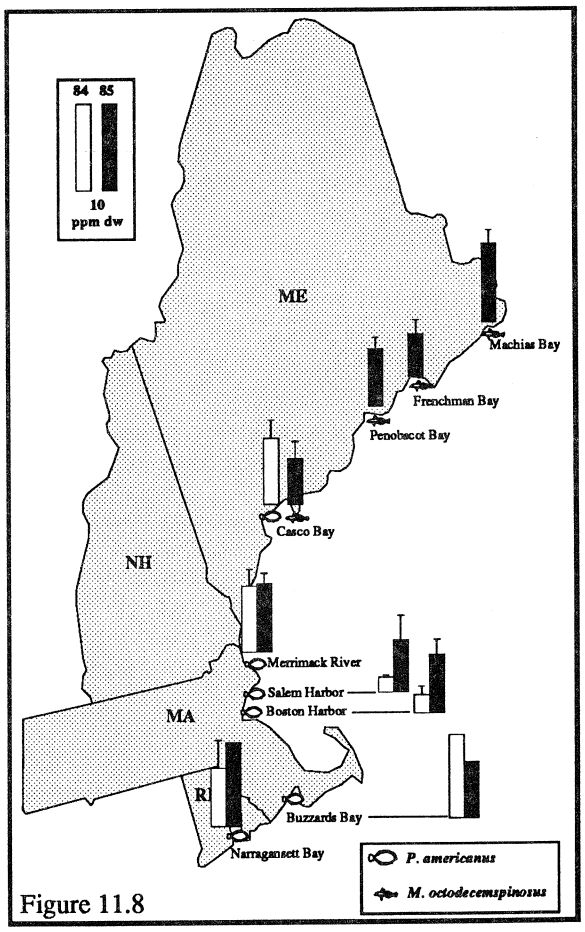
Table 11.6 The mean arsenic concentrations (ppm dw) in *M. edulis* at the 13 outer New England coast NS&T Program Mussel Watch sites. The outlined means are for Boston Harbor sites.

Site	Mean	Standard Deviation	Count
GOOSEBURY NECK, BUZZARDS BAY	15.88	2.23	8
ANGELICA ROCK, BUZZARDS BAY	15.22	1.48	9
CAPE ANN, STRAITSMOUTH ISLAND	14.83	0.75	6
ROUND HILL, BUZZARDS BAY	14.11	1.27	9
BLOCK ISLAND, RHODE ISLAND	13.83	1.17	6
CONANICUT ISLAND NARRAGANSETT BAY	11.33	0.82	6
DYERS ISLAND, NARRAGANSETT BAY	10.84	0.85	9
OUTER BREWSTER ISLAND	9.78	1.38	9
DORCHESTER BAY, BOSTON HARBOR	9.18	0.59	9
PICKERING ISLAND, PENOBSCOT BAY	9.04	1.3	9
DEER ISLAND, BOSTON HARBOR	8.81	0.8	9
SEARS ISLAND, PENOBSCOT BAY	8.8	0.46	9
HINGHAM BAY, BOSTON HARBOR	8.72	0.42	9

NOAA's Benthic Surveillance Project, a part of the NS&T Program, has sampled winter flounder (*P. americanus*) from an area just west of Deer Island on an annual basis since 1984. The mean arsenic concentration in the liver of the fish sampled in 1984 and 1985 was 3.72±2.62 ppm with a range of 0.74 to 8.42 ppm. The mean concentration of arsenic in flounder livers for all the New England Benthic Surveillance sites, excluding Boston Harbor, ranged from a low of 3.41±2.77 ppm at the Salem Harbor site to a high of 7.76±2.11 ppm at the Buzzards Bay site. The other three sites had means of: 7.04±2.98 ppm, Narragansett Bay; 7.53±2.02 ppm, Casco Bay; and 7.53±1.70 ppm, Merrimack River (Figure 11.8). The mean arsenic concentration of winter flounder liver from Boston Harbor was lower than the

mean for any other New England site except Salem Harbor. Statistical analysis of the log transformed data indicated that both the Boston Harbor and Salem Harbor sites were significantly different from all but the Casco Bay site at p=0.05. The low means for Boston and Salem harbors winter flounder were due to exceptionally low reported concentrations in 1984. The 1984 means were 2.00±1.01 ppm for Boston Harbor and 1.64±0.26 ppm for Salem Harbor; while those for 1985 were 6.61±1.70 and 5.94±2.77 ppm respectively. No comparison could be made among Boston Harbor and the three northern-Maine sites; because a different species, longhorn sculpin (*M. octodecemspinosus*), was sampled at these sites. The Benthic Surveillance Project sampled winter flounder at four other sites during the same time frame: two in Long Island Sound and one each in Raritan and Great bays in New Jersey. The mean arsenic concentrations at all four sites were higher than the mean for Boston Harbor. They ranged from a low of 4.95±1.61 ppm (Great Bay) to a high of 6.11±2.21 ppm (East Long Island Sound).





Figures 11.7 & 11.8. Mean arsenic concentrations (ppm dw) in the soft-parts of *M. edulis* for 1986-88 (Fig. 11.7) and in the liver tissue of *P. americanus* and *M. octodecemspinosus* for 1984-85 (Fig. 11.8) along the outer New England coast by site and year (NOAA, unpublished) (bars represent one standard deviation).

Temporal Trends

No temporal trends in the arsenic levels of Boston Harbor biota could be determined based on the available data. The only internally consistent data sets sampling the same organism from the same locations over a number of years were the NS&T Program's Benthic Surveillance and Mussel Watch projects. Data for these projects were only available for 2 and 3 years, respectively. Between 1984 and 1985 there was over a 300 percent increase in

the reported level of arsenic in winter flounder livers (2.00±1.01 to 6.61±1.70 ppm) (Figure 11.8) which was significantly different at p=0.01. However, since the data only covers 2 years, no conclusion can be drawn from it regarding long-term trends. Likewise, the 3 years of data for *M. edulis* from the NS&T Program Mussel Watch project are insufficient to indicate any trend. Arsenic levels increased between 1986 and 1987 and then decreased very slightly in 1988 (Figure 11.7). The yearly means were 8.52±0.42, 9.14±0.71, and 9.04±0.60 ppm, respectively. Statistical analysis of the log transformed NS&T Program Mussel Watch indicated no significant difference between any of the years.

Summary

The mean arsenic concentration in Boston Harbor sediments was found to exceed reference levels by just over a factor of 2. However, individual site means ranged from 0.82 of the reference mean to more than 3 times the reference mean. The mean for Boston Harbor proved to be less than half the San Francisco Bay mean when the NS&T Program data mean value of arsenic in Boston Harbor (9.3±4.2 ppm) was compared to the NS&T Program data mean for San Francisco Bay (22.3±20.7 ppm) (NOAA, unpublished) (Table 11.8). However, when the medians were compared, the Boston median (10.9 ppm) was 0.84 that of the San Francisco Bay median (13.0 ppm) (Table 11.8). The overall data set indicated that the highest mean arsenic concentration in Boston Harbor surficial sediments was in the inner harbor. With the exception of a single hot spot, the lowest mean arsenic concentration was in the southeast harbor. There was little difference in mean arsenic concentrations between the northwest and central harbor. The medians, on the other hand, indicated that there was little difference among the inner, northwest, and central harbor divisions. The southeast harbor had the lowest levels of arsenic in the surficial sediments. Because of individual hot spots and the difference in sites sampled, there was no general agreement among the individual data sets on relative arsenic levels. Based on the overall data, no clear temporal trends were apparent concerning arsenic concentrations in the surficial sediment. However, when only 93 percent of the overall data excluding these extremes were analyzed, there appeared to be a slight increase in arsenic concentrations since the early 1970s but only slight yearly fluctuations since 1980.

Table 11.8. Comparison of arsenic sediment statistics for Boston Harbor, NS&T Program Reference (based on the five NS&T Program sites in New England with the lowest arsenic levels), and San Francisco Bay in ppm dw. Statistics for San Francisco Bay derived from Long *et al.*, 1988.

Area	Mean	Standard Deviation	Median	Range	Count
Boston	14.2	20.5	8.4	0.32 - 143	178
NS&T Program Boston	9.3	4.2	10.9	2.40 - 17.0	31
NS&T Program Reference	4.1	1.6	3.7	2.00 - 8.00	26
NS&T Program San Francisco Bay	22.3	20.7	13.0	2.78 - 72.0	42

Based on the available data, Boston Harbor biota appears to be slightly to moderately contaminated with arsenic. Boston Harbor mussels (*M. edulis*) had some of the lowest mean arsenic concentrations of all the New England NS&T Program sites sampled. When compared to all NS&T Program mussel sites sampled in the country, approximately 53 percent of the sites had means greater than the Boston Harbor sites and only 36 percent had means lower than the lowest Boston Harbor site mean. The winter flounder (*P. americanus*) liver data suggested that Boston Harbor had only low levels of arsenic since, among the NS&T Program sites, the Boston site had the second lowest mean arsenic concentration.

DDT

DDT is a synthetically produced chlorinated hydrocarbon used as an insecticide. Commercial grade DDT is composed of various amounts of the paired isomers (o,p' and p,p') of DDT, DDD, and DDE. These six isomers have varying rates of decomposition; and, while o,p' DDT comprises approximately 20 percent of commercial grade DDT, it is seldom found in the natural environment (Anderson *et al.*, 1982). The most abundant of the six isomers in the marine environment is p,p'DDE (Risebrough, 1971). The most comprehensive way of determining total DDT (tDDT) concentration in a sample is by measuring the concentrations of the six individual isomers and summing them. The data sets used in this report reported DDT concentrations as the values for the six individual isomers, as the values for the three compounds (DDE, DDD, DDT) with and without reference to the isomers measured, and as DDT with no reference to isomers measured. Because of this variability in reporting methods, extreme caution is needed when comparing the DDT values from different data sets.

Since DDT is a synthetically produced pesticide, background levels should be zero. However, because of the pesticide's past widespread use, it has been difficult to find uncontaminated ecosystems. However, since the early 1970s, when the use of DDT was banned in the United States, levels of DDT in the environment have dramatically decreased (Mearns *et al.*, 1988). Long and Morgan (1990) found toxic effects reported for sediments containing DDT concentrations as low as 1.6 ppb.

Sediments

The available data sets reported DDT concentrations from only 84 sediment samples taken from Boston Harbor between 1970 and 1987. The majority of these samples were taken between 1984 and 1987 with only 31 of the samples taken before 1980.

Geographic Trends

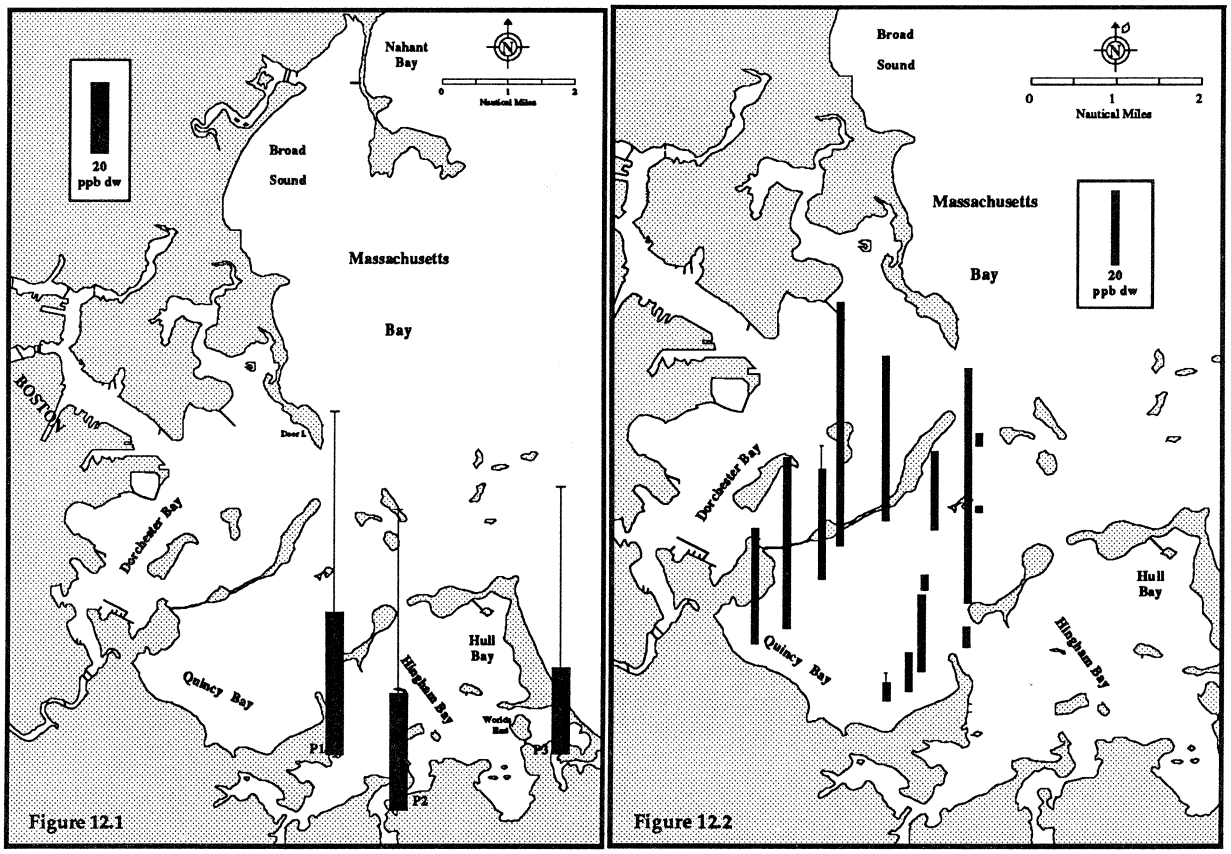
In 1970, the Massachusetts Department of Natural Resources (DNR) Division of Marine Fisheries (DMF) conducted a survey of Hingham Bay that included the analysis of sediment samples for DDE, DDD, and DDT (Iwanowicz *et al.*, 1973). During the year, 31 samples from three sites were taken and analyzed. In 19 of the samples, the concentrations of all three compounds were below the detection limit of 1.0 ppb. At least one of the three compounds was present at a concentration greater than the detection limit in the other 12 samples. Based on all the samples analyzed, the mean concentration of tDDT (tDDT=DDE+DDD+DDT) for Hingham Bay was 31 ppb with a standard deviation of 50.0 and a range of from less than 3.0 ppb to 150 ppb (Table 12.1). The mean tDDT concentrations for the individual sites were Hough's Neck (P1) 39±55 ppb, Weymouth Back River (P2) 32±50 ppb, and Weir River (P3) 23±49 ppb (Figure 12.1). Statistical analysis of the log transformed data indicated no significant difference between any of the sites at p=0.05.

Table 12.1. Mean standard deviation, median, range, and number of samples (count) for tDDT concentrations (ppb dw) in the surficial sediments of Boston Harbor based on the data of Iwanowicz *et al.* (1973), USACOE (1975-88, 1981), EPA (1988), and NOAA's NS&T Program (unpublished).

Data Set	Years	Mean	Standard Deviation	Median	Range	Count
Iwanowicz *et al.*	1970	31	50	<3.0	<3.0-150	31
USACOE	1980, 1983	22	41	8	1.0-105	6
Gardner *et al.*	1987	29	36	20	1.9-170	22
NOAA NS&T	1984-87	48	117	26	1.0-600	24

The New England Division of the USACOE analyzed two surficial sediment samples from the inner harbor and one sample from President Roads for DDT in 1980. In 1983 they analyzed three surficial sediment samples from Winthrop Harbor for DDE, DDD, and DDT. This data showed that the overall mean tDDT concentration for the inner and northwestern area of Boston Harbor was 22 ppb with a standard deviation of 41 and a range of from 1.0 to 105 ppb (Table 12.1). However, when the one sample from Winthrop Harbor that exceeded 100 ppb was excluded from the calculations, the mean became 5.2±2.3 ppb with a range of from 1.0 to 13 ppb. All three of the samples with the highest tDDT concentrations (9, 13, and 105 ppb) were taken from Winthrop Harbor. No statistical analysis could be done among sites because of the small sample size.

In 1987 a study of Quincy Bay, essentially restricted to the central harbor area, was conducted under the auspices of the US EPA (EPA, 1988). The study measured the concentrations of DDE, DDD, and DDT in 22 samples of the surficial sediments. Figure 12.2, which graphically displays the results of the grab sample analysis, suggests that tDDT was more concentrated along the northwestern side of Quincy Bay than elsewhere in the bay, with one exception. The one exception was just north of the southwestern end of Peddocks Island. The overall mean tDDT concentration in the surficial sediments for the study was 29±36 ppb with a range of 1.9 to 170 ppb (Table 12.1). When the single sample with a tDDT concentration in excess of 100 ppb was excluded from the calculations, the mean tDDT concentration became 22±20 ppb with a high value of 66 ppb.



Figures 12.1 & 12.2. Mean tDDT concentrations (ppb dw) in the surficial sediments of Hingham Bay in 1970 (Fig. 12.1) (Iwanowicz et al., 1973) and in Quincy Bay and environs in 1987 (Fig. 12.2) (US EPA, 1988) (the bars represent one standard deviation).

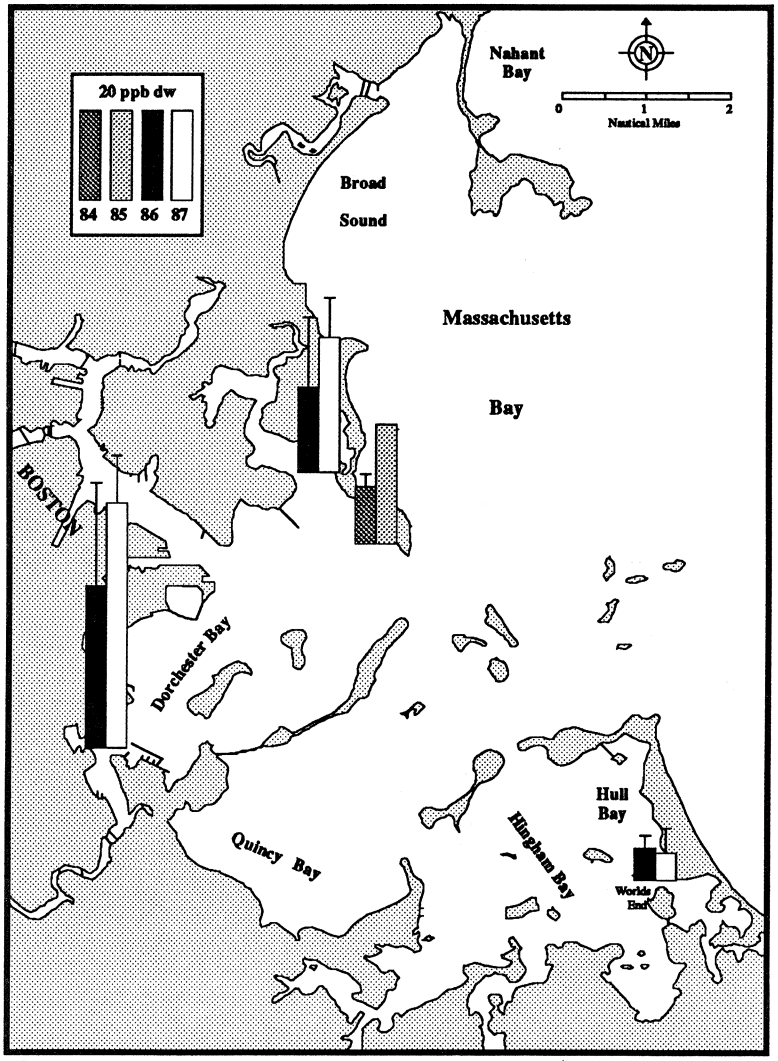


Figure 12.3. Mean tDDT concentrations (ppb dw) in the surficial sediments of Boston Harbor from 1984 through 1987 (NOAA, unpublished) (bars represent one standard deviation).

Since 1984 NOAA's NS&T Program has sampled and analyzed surficial sediments from several sites around Boston Harbor for several analytes, including the six isomers composing the DDT family of chemicals. The overall mean tDDT concentration in surficial sediments of the harbor was 48±120 ppb. Individual sample values ranged from 1.0 to 600 ppb (Table 12.1). However, when the single sample with a tDDT concentration of 600 ppb was excluded from the calculations, the overall mean tDDT concentration became 24±18 ppb and the high end of the range changed to 67 ppb. Figure 12.3 portrays mean tDDT concentrations graphically by year and site excluding the 600 ppb sample from the 1984 mean for the site off southwestern Deer Island. The individual site means, based on all 4 years of available data were: 6.7±4.0 ppb off the northern tip of Worlds End, 24±13 ppb northwest of Deer Island, 45±19 ppb in southwestern Dorchester Bay, and 105±220 ppb (22±7 ppb (when the 600 ppb sample was excluded from the calculations) southwest of Deer Island. Statistical comparison of the log transformed data indicated that at p=0.05 there was no significant difference between any of the sites with or without including the 600 ppb sample. When the data were grouped by harbor divisions, the means suggested that the northwest harbor, both with and without the inclusion of the 600 ppb sample (61±130 and 30±17 ppb, respectively), had higher tDDT concentrations than did the southeast harbor (6.7±4.0 ppb). Statistical analysis of the log transformed data, using an unpaired t-test, indicated no significant difference between the two divisions at p=0.05 when the 600 ppb sample was included in the calculations; but, did indicate a significant difference between the two divisions at p=0.01 when the 600 ppb sample was excluded. When the northwest harbor division was subdivided into the Winthrop Bay area (mean 23±10 ppb, excluding the 600 ppb sample) and the Dorchester Bay area (mean 45±19 ppb), statistical analysis of the log transformed data indicated a significant difference among all three harbor areas at p=0.05.

On a broader scale, between 1984 and 1987, the NOAA NS&T Program analyzed surficial sediment samples from 23 sites from 11 areas, along the outer New England Coast.

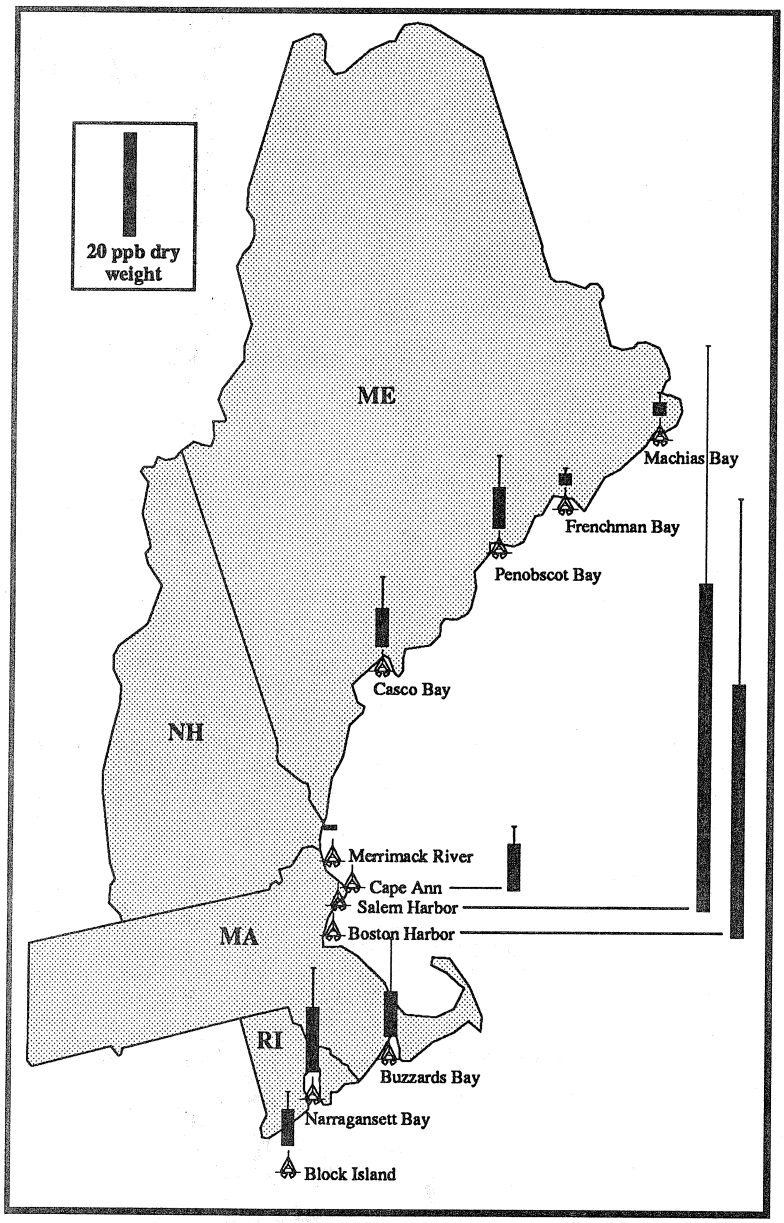


Figure 12.4. Mean tDDT concentrations (ppb dw) in the surficial sediments along the outer New England coast based on 1984 through 1987 data (NOAA, unpublished) (bars represent one standard deviation).

Figure 12.4 displays the means and standard deviations for the 11 coastal areas. It clearly shows that the mean tDDT concentration of the NS&T Program sites in Boston Harbor, even excluding the single sample with 600 ppb (24±18 ppb), was higher than all other areas sampled except for Salem Harbor (32±23 ppb). However, when the 600 ppb was included in the calculations, the Boston Harbor mean tDDT concentration (105±220 ppb) was clearly higher than all the other New England areas sampled. Statistical analysis of the log transformed data (excluding the 600 ppb sample) indicated that Boston Harbor was significantly different from only four of the other ten areas (Penobscot Bay, Merrimack River, Buzzards Bay, and Narragansett Bay) at p=0.05. Salem Harbor was found to be significantly different from all but three areas (Boston Harbor, Cape Ann, and Block Island) at p=0.05. Two points should be noted: 1) when the 604 ppb sample was included in the calculations, no significant difference between any of the areas was found; and, 2) the Salem Harbor mean was based on samples from only one site in Salem Harbor while the Boston Harbor mean was based on samples from four harbor sites.

When the mean tDDT concentrations in the surficial sediments of the individual New England NS&T Program sites were compared, three of the five sites with the highest mean tDDT concentrations were located in Boston Harbor (Table 12.2). Because DDT is a synthetically produced compound, background levels should be zero. By this rational, all of NOAA's NS&T Program sites sampled in New England had elevated levels of DDT with the possible exception of the Merrimack River site. All samples taken from this site had DDT levels below the detection limits (Table 12.2). Despite these facts, a regional background reference concentration was determined by calculating the overall mean for the five New England sites with the lowest mean tDDT concentrations; this overall mean was

1.2±0.8 ppb. The overall mean concentration of tDDT in Boston Harbor based on NS&T Program data, even excluding the 600 ppb sample (24 ppb), was 20 times higher than the regional background reference concentration.

Table 12.2. The five outer New England Coast NOAA NS&T Program sites with the lowest and highest mean tDDT concentrations (ppb dw) based on data from 1984 through 1987 (*excluding (including) 604 ppb sample, see text).

Site	Mean	Standard Deviation	Count
MERRIMACK RIVER	<0.59	0.22	5
FRENCHMAN BAY, MAINE	1.0	0.4	4
MACHIAS BAY, MAINE	1.1	1.0	4
PENOBSCOT BAY, MAINE	1.6	0.8	5
GOOSEBURY NECK, BUZZARDS BAY	1.8	0.7	6
MOUNT HOPE BAY, RHODE ISLAND	10	2	3
SOUTHWESTERN DEER ISLAND*	22 (105)	7 (220)	6 (7)
NORTHWESTERN DEER ISLAND	24	13	6
SALEM HARBOR	32	23	7
DORCHESTER BAY	45	19	6

Temporal Trends

Because of the sparsity of data, little can be said with confidence about temporal trends of DDT contamination in Boston Harbor sediments. Table 12.3 gives the yearly means of tDDT in the surficial sediments of Boston Harbor based on all the available data sets. The yearly means fluctuate from a low of 2.7 ppb to a high of 42 ppb. These fluctuations can probably be more readily attributed to differences in sites sampled and analytical methodologies than to any actual differences in yearly concentrations. It is interesting that the earliest year (1970) and latest year (1987) sampled, which coincidentally have the largest numbers of samples analyzed, had nearly identical mean tDDT concentrations (31 and 29 ppb). This suggests that over the 18 years spanned by the data there was no change in the tDDT levels in the surficial sediments of Boston Harbor.

The only single data set which spanned more than 1 year was that from NOAA's NS&T Program (NOAA, unpublished). It covered the 4 years from 1984 through 1987, although the same sites were not sampled in each of the 4 years. Excluding the 604 ppb sample from the calculations resulted in a mean tDDT concentration for 1984 of 13±3 ppb. The mean tDDT concentration increased in 1985 to 26±2 ppb, decreased to 21±19 ppb in 1986, and again increased in 1987 to 30±22 ppb. Based on this data, there was no consistent trend of tDDT contamination levels during the 4 years covered by NOAA's data.

Table 12.3. Yearly mean tDDT concentrations (ppb dw) in Boston Harbor surficial sediments based on all available data sets (* excludes 600 ppb sample, see text).

Data Set	Year	Mean	Standard Deviation	Count
Iwanowicz *et al.*, 1973	1970	31	50	31
USACOE, 1981	1980	2.7	2.9	3
USACOE, 1975-1988	1983	42	54	3
NOAA, unpublished*	1984	13	2.9	2
NOAA, unpublished	1985	26	1.6	4
NOAA, unpublished	1986	21	19	9
NOAA, unpublished and EPA, 1988	1987	29	32	31

Biota

The data used in this report includes the concentrations of DDT and associated chemicals from 150 tissue samples taken from specimens captured in Boston Harbor. Table 12.4 gives the statistics based on this data broken down by species and tissue type. The extremely large standard deviation and difference between the mean and the median concentrations for winter flounder (*P. americanus*) muscle given in this table are due to the inclusion of a single extraordinarily high reported concentration of 8,400 ppb for a single sample. This value is more than an order of magnitude higher than the second highest reported DDT concentration, 570 ppb. When this high concentration is excluded from the calculations, the overall mean concentration of DDT in winter flounder muscle becomes 89 ppb with a standard deviation of 152. The median remains unchanged. The individual samples with the lowest DDT concentrations were taken from winter flounder muscle. The highest DDT concentration reported for a single sample was 11,100 ppb from the soft parts of the soft-shelled clam.

Geographic Trends

In the 1960s and early 1970s, the Massachusetts DNR DMF conducted studies of the marine resources of the state that included the analysis of winter flounder (*P. americanus*) and soft-shelled clams (*M. arenaria*) for levels of several analytes, including DDT (Chesmore *et al.*, 1971; Iwanowicz *et al.*, 1973; and Jerome *et al.*, 1966). The two earlier reports (Chesmore *et al.*, 1971 and Jerome *et al.*, 1966) reported values for DDT and a mixture of dieldrin and DDE for specimens taken from Dorchester Bay (1967-68) and Quincy Bay (1964), respectively. The Iwanowicz *et al.*, 1973 study reported individual values for levels of DDE, DDD, and DDT for specimens taken from Hingham Bay in 1970. All three reports gave concentrations in ppm wet weight that was converted to ppb dry weight based on conversion factors derived from other sources (EPA, 1988 and Wallace *et al.*, 1987). The data for the mixture of dieldrin and DDE were not used in this report.

Table 12.4. Harborwide means, standard deviations, medians, ranges, and sample sizes (count) for tDDT concentrations (ppb dw) in biota by organism and tissues based on all the available data sets (* transplants).

		Mean	Standard Deviation	Median	Range	Count
P. americanus						
	liver	726	160	704	488-964	6
	intestine	118	220	33	<10-611	7
	muscle	349	1477	27	8-8400	32
H. americanus						
	hepatopancreas	2700	700	2786	1400-3700	8
	muscle	25	7	25	13-37	16
M. arenaria						
	soft parts	1500	3100	128	<16-11000	44
M. edulis						
	soft parts	100	75	80	13-260	38
*C. virginica**						
	soft parts	53	7	49	43-60	4

The DMF analyzed seven samples of winter flounder muscle from specimens taken from Dorchester Bay in 1967 and 1968 (Chesmore *et al.*, 1971) and found an overall mean DDT concentration of 1,500 ppb with a standard deviation of 3,100. Individual sample concentrations ranged from a low of 26 ppb to a high of 8,400 ppb. However, when the sample with the highest reported concentration of DDT was excluded from the calculations, the overall mean became 320 ppb with a standard deviation of 240 and a high single sample concentration of 570 ppb.

Total DDT concentrations were reported by the DMF for 42 composite samples of the soft parts of soft-shelled clams taken from the three bays (Figure 12.5). The overall mean tDDT concentration based on these samples was 1,600 ppb with a standard deviation of 3,100 and a range of from less than 16 ppb to 11,100 ppb. The median concentration was 480 ppb. When the data is broken down by harbor divisions, the means for the individual divisions sampled were: central harbor (Quincy Bay), 140±110 ppb; northwest harbor (Dorchester Bay), 390±630 ppb, and southeast harbor (Hingham Bay), 2,100±3,500 ppb. Despite the large differences among division means, statistical analysis of the log transformed data indicated no significant difference between any of the divisions at p=0.05. It should be noted that the mean concentrations for the central and northwest harbor divisions were based on reported values for only DDT, while that for the southeast harbor was based on the sum of reported values for DDE, DDD, and DDT

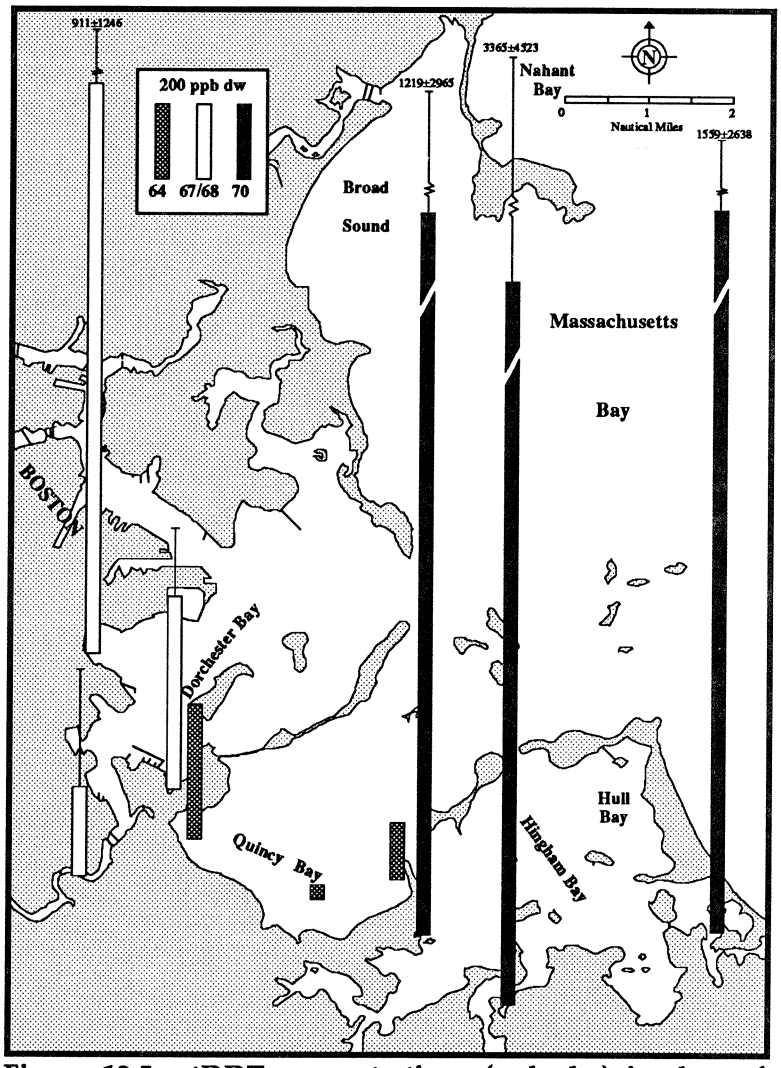


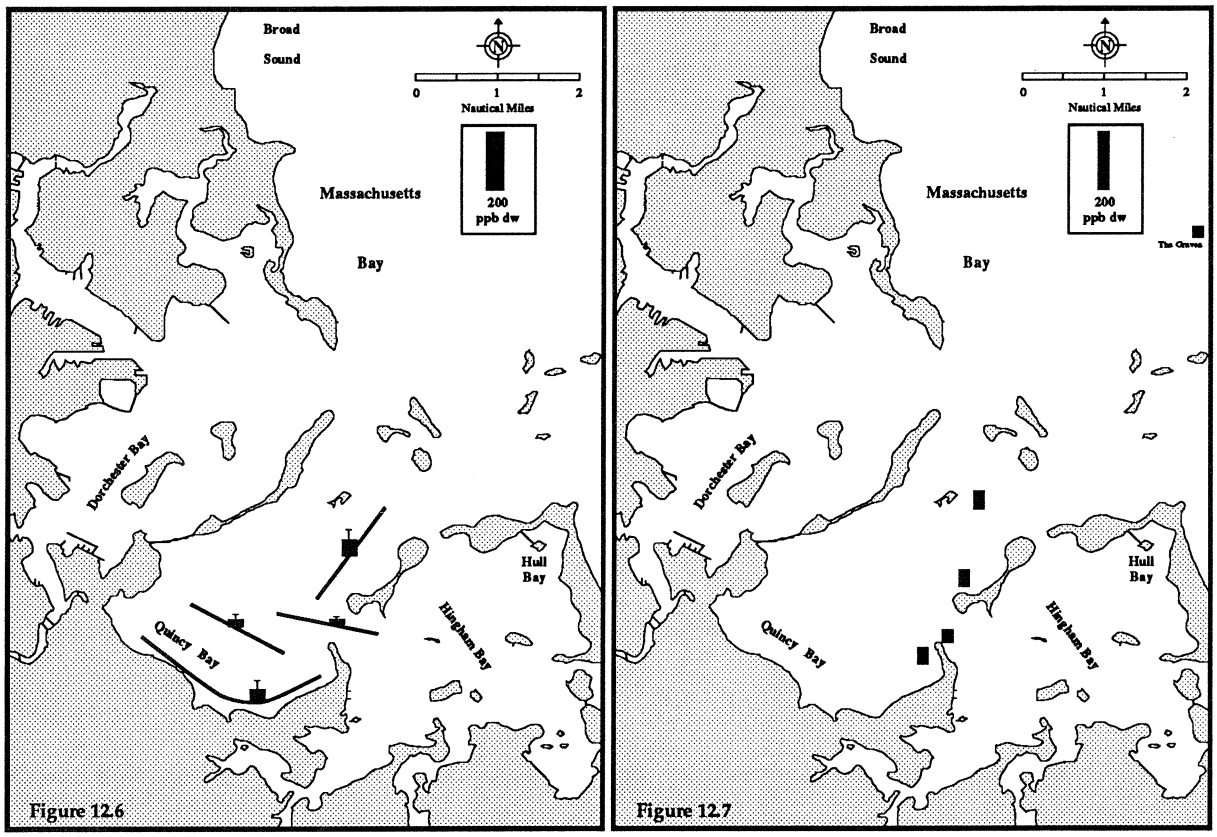
Figure 12.5. tDDT concentrations (ppb dw) in the soft parts Mya arenaria based on 1964-1970 data from the Massachusetts DMF (Jerome et al., 1966; Chesmore et al., 1971, and Iwanowicz et al., 1973) (bars represent one standard deviation).

In 1976 and 1977, the U. S. EPA sampled mussels and other bivalves from 107 sites nationwide and analyzed the samples for a variety of metals and organic analytes, including DDE (Goldberg *et al.*, 1978). Composite samples of *M. edulis* from a site on the northwest side of Deer Island were reported to have DDE concentrations in the soft parts of less than 44 ppb (1976) and less than 26 ppb (1977). Between Block Island and the Canadian border, 10 other New England sites were each sampled once in 1976 and 1977. DDE concentrations in 8 of the 20 samples of the soft parts of *M. edulis* were reported as less than values that ranged from 5 to 17 ppb. The other 12 samples had DDE concentrations ranging from 3.1 to 8.8 ppb.

An intensive study of Quincy Bay was conducted in 1987 that included the analysis for p,p'DDE, p,p'DDD, and p,p'DDT levels in the tissues of native winter flounder (*P. americanus*), lobsters (*H. americanus*), and soft-shelled clams (*M. arenaria*), as well as, transplanted oysters (*C. virginica*) (EPA, 1988). The muscle tissues of from five to seven winter flounder from each of four different trawl transects was analyzed for p,p'DDE, p,p'DDD, and p,p'DDT levels. The tDDT

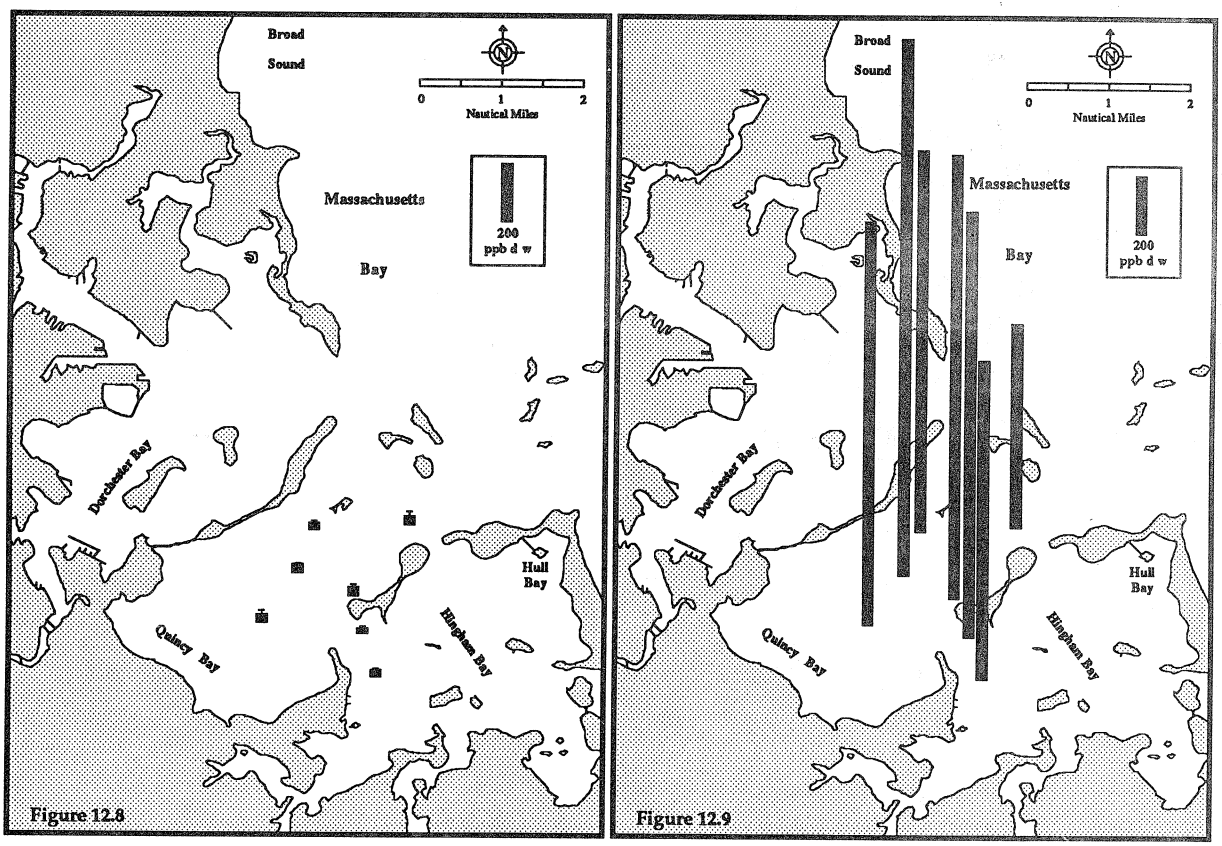
concentration, based on the sum of the concentrations of the three isomers, ranged for the individual samples from 8 to 101 ppb with an overall mean of 34±27 ppb. The tDDT means for the four trawl transects ranged from 17±9 ppb to 58±33 ppb (Figure 12.6). Statistical analysis of the log transformed data indicated that only the trawls with the lowest and highest mean tDDT concentrations were significantly different (p=0.05).

Oysters (*C. virginica*) were collected from a commercial bed located in Cotuit Bay, Massachusetts and deployed at four sites in Quincy Bay and one site located at The Graves in Massachusetts Bay from June 5 through July 16, 1987. The tDDT concentrations in the oysters at the four sites ranged from 43 to 59 ppb. The oysters from The Graves had 38 ppb tDDT while those from the source bed in Cotuit Bay had a tDDT concentration of 30 ppb (Figure 12.7). Two samples of the soft-shelled clam from around Moon Island, Quincy Bay also were analyzed for DDT and were found to have tDDT concentrations of 32 and 41 ppb.



Figures 12.6 & 12.7. tDDT concentrations (ppb dw) in muscle tissue of *P. americanus* from Quincy Bay (Fig. 12.6) and in the soft parts of transplanted *C. virginica* (Fig. 12.7) in 1987 (US EPA, 1988) (bars represent one standard deviation).

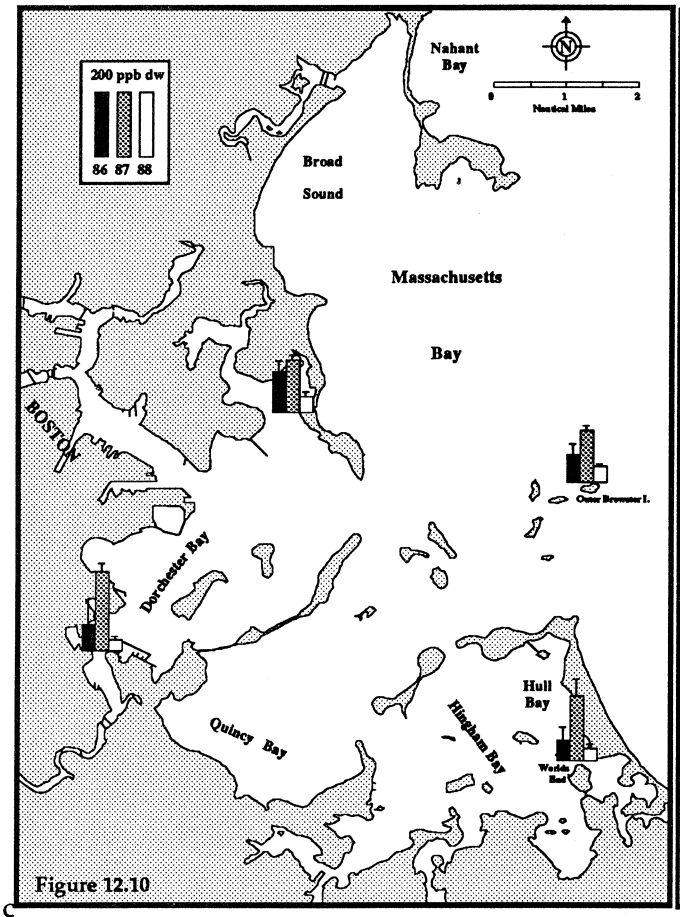
Both the tail muscle and the hepatopancreas of lobsters from seven sites were analyzed for levels of the three isomers. Two replicate samples from the tail muscles of a total of 16 lobsters; 1 to 3 from each of the seven sites were analyzed. The overall mean tDDT concentration in the lobster tail muscle was 25±7 ppb. The tDDT concentrations in the individual samples ranged from 13 to 37 ppb. The mean tail muscle concentrations for the seven sites ranged from 17±6 ppb to 30±7 ppb (Figure 12.8). There was no significant difference in tail muscle tDDT levels among sites based on statistical analysis of the log transformed data (p=0.05). Two replicate samples of the hepatopancreas of 8 of the 16 lobsters were also analyzed for DDT. Total DDT concentrations for the eight hepatopancreases ranged from less than 1,400 to 3,700 ppb (Figure 12.9). The overall mean tDDT concentration in the lobster hepatopancreases was 2,700±700 ppb.

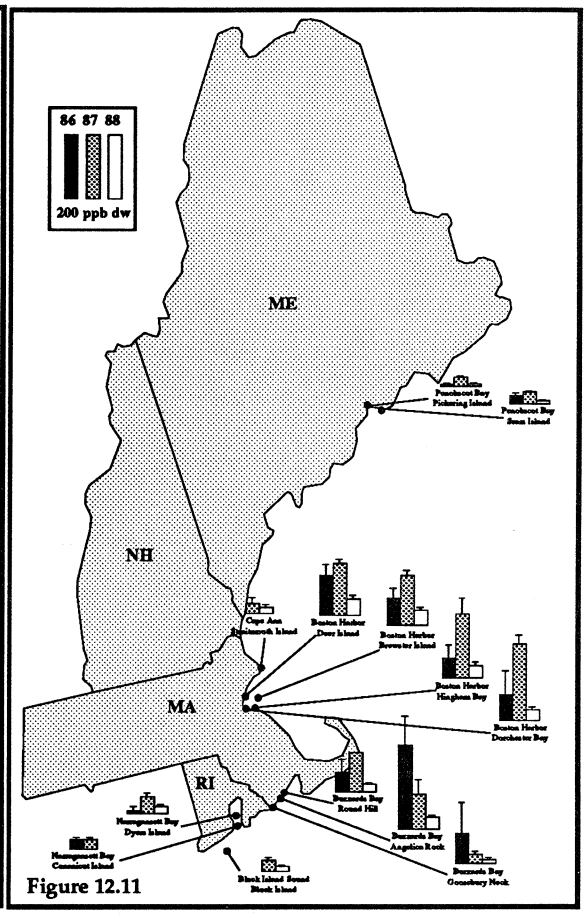


Figures 12.8 & 12.9. tDDT concentrations (ppb dw) in *H. americanus* muscle tissue (Fig. 12.8) and hepatopancreas tissue (Fig. 12.9) from Boston Harbor in 1987 (US EPA, 1988) (bars represent one standard deviation).

Since 1986, NOAA's Mussel Watch Project, a part of the NS&T Program, has sampled mussels (*M. edulis*) on an annual basis from four sites in and around Boston Harbor. Three whole-body composite samples from each site were analyzed for a variety of analytes including the paired isomers (o,p' and p,p') of DDE, DDD, and DDT. The overall mean concentration of tDDT (based on the sum of the six isomers) in the mussels for the three sites in Boston Harbor from 1986 through 1988 was 110±80 ppb with a range of from 21 to 260 ppb. The means for the individual sites were 110±50 ppb northwest of Deer Island, 120±110 ppb in southwestern Dorchester Bay, and 100±80 ppb in Hingham Bay off Worlds End. Mussels from the site just outside the Harbor, Outer Brewster Island, had a mean tDDT concentration of 100±50 (Figure 12.10). Statistical analysis of the log transformed data for the four sites indicated that none of the four sites was significantly different (p=0.05).

On a broader scale, when the Boston Harbor sites were compared to the other New England Mussel Watch sites (Table 12.5; Figure 12.11), the sites in Boston Harbor had the second, third, and fourth highest mean tDDT concentrations. The fifth highest mean was from the site just outside Boston Harbor (Outer Brewster Island). The New England site with the highest mean concentration was Angelica Rock in southeastern Buzzards Bay. The site at Pickering Island, in Penobscot Bay, had the lowest mean tDDT concentration. Statistical analysis of the log transformed data indicated that the site with the lowest mean tDDT concentration was significantly different from the sites with the five highest means (Table 12.5). From this data it appears that tDDT levels in mussels vary over an order of magnitude throughout New England. Although natural background levels of tDDT should be zero, an attempt was made to determine a regional background reference





Figures 12.10 & 12.11. Mean tDDT concentrations in the soft-parts of *M. edulis* in Boston Harbor (Fig. 12.10) and along the outer New England coast in 1986-88 (NOAA, unpublished) (bars represent one standard deviation).

Table 12.5. The mean DDT concentrations (ppb dw) in *M. edulis* at the 13 outer New England coast NS&T Program Mussel Watch sites. The outlined means are for Boston Harbor sites.

Site	Mean	Standard Deviation	Count
ANGELICA ROCK, BUZZARDS BAY	140	120	9
DORCHESTER BAY, BOSTON HARBOR	120	110	9
DEER ISLAND, BOSTON HARBOR	110	50	9
HINGHAM BAY, BOSTON HARBOR	100	80	9
OUTER BREWSTER ISLAND	98	52	9
ROUND HILL, BUZZARDS BAY	72	50	8
GOOSEBURY NECK, BUZZARDS BAY	45	63	9
CONANICUT ISLAND NARRAGANSETT BAY	32	6	6
DYERS ISLAND, NARRAGANSETT BAY	30	21	9
CAPE ANN, STRAITSMOUTH ISLAND	26	14	6
BLOCK ISLAND, RHODE ISLAND	26	12	6
SEARS ISLAND, PENOBSCOT BAY	24	13	9
PICKERING ISLAND, PENOBSCOT BAY	14	11	9

oncentration for tDDT in mussels by calculating the overall mean for the five New England sites with the lowest means. This overall mean was 27±18 ppb. The overall mean for Boston Harbor's concentration of tDDT (110 ppb) was more than four times greater than the calculated regional background reference concentration.

On a national scale, the Mussel Watch sites where *M. edulis* was sampled had mean tDDT concentrations ranging from 1.4 to 1,100 ppb. Means lower than the Boston Harbor site with the lowest mean tDDT concentration (Hingham Bay, 100 ppb) were found at 62 percent of the sites, while 29 percent of the sites had means higher than the Boston Harbor site with the highest mean (Dorchester Bay, 120 ppb). When the sites where *M. californianus* was sampled were included in the calculations, the individual site means ranged from 1.4 to 1,300 ppb, and 62 percent of the sites had means lower than the Boston Harbor site with the lowest mean tDDT concentration, while 30 percent of the sites had means higher than the Boston Harbor site with the highest mean. Based on this data, Boston Harbor mussels were moderately to highly contaminated with DDT when compared to the nationwide sites.

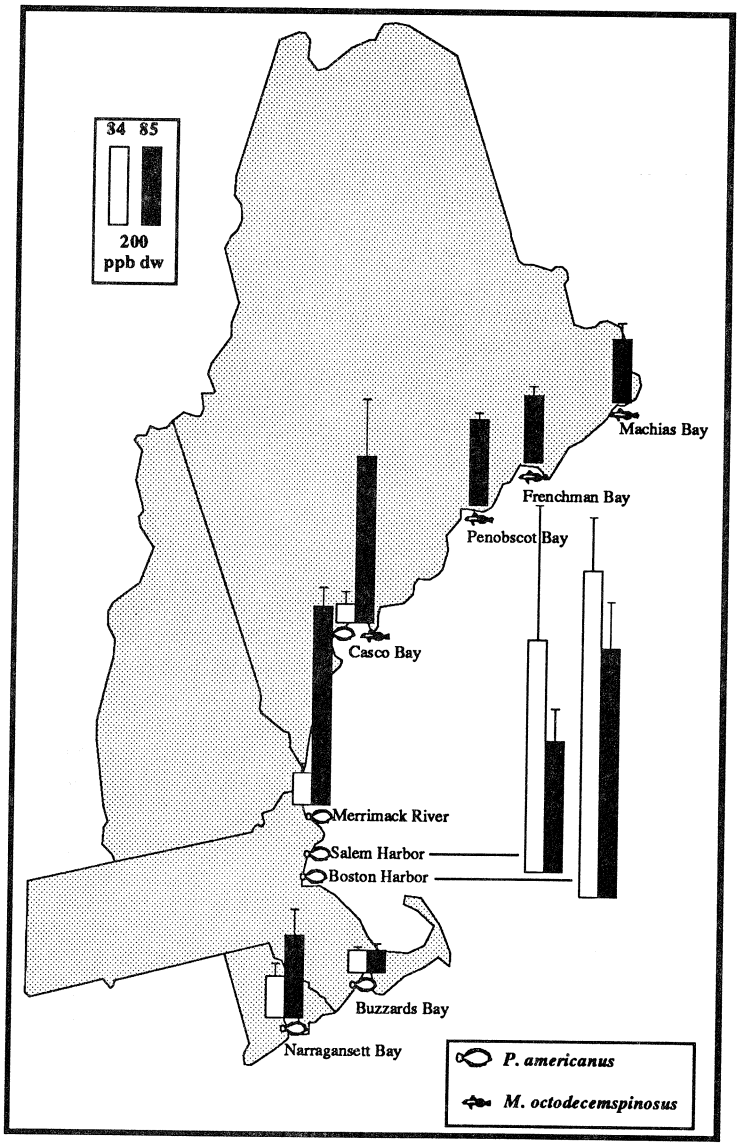


Figure 12.12. Mean tDDT concentrations (ppb dw) in liver tissue of *P. americanus* and *M. octodecemspinosus* from the outer New England coast in 1984 and 1985 (NOAA, unpublished) (bars represent one standard deviation).

Since 1984, NOAA's Benthic Surveillance Project, a part of the NS&T Program, has sampled winter flounder (*P. americanus*) from an area just west of Deer Island on an annual basis. The mean tDDT concentration in the liver of the fish sampled in 1984 and 1985 was 730±160 ppb with a range of 490 to 960 ppb. The mean concentration of tDDT in flounder livers for all the New England Benthic Surveillance sites, excluding Boston Harbor, ranged from a low of 58±10 ppb at the Buzzards Bay site to a high of 460±260 ppb at the Salem Harbor site. The other three sites had means of: 160±70 ppb, Narragansett Bay; 240±230 ppb, Casco Bay, and 290±240 ppb, Merrimack River (Figure 12.12). The mean tDDT concentration of winter flounder liver from Boston Harbor was higher than the mean for any other New England site. Statistical analysis of the log transformed data indicated that both the Boston Harbor and Salem Harbor sites were significantly different from all but the Buzzards Bay site. The Boston Harbor site was significantly different from the Casco Bay site at p=0.05. No

comparison could be made between Boston Harbor and the three northern-Maine sites because a different species; longhorn sculpin (*M. octodecemspinosus*), was sampled at these sites. The Benthic Surveillance Project sampled winter flounder at four other sites during the same time frame: two in Long Island Sound and one each in Raritan and Great bays in New Jersey. The mean tDDT concentrations at all four sites were lower than the mean for Boston Harbor. They ranged from a low of 140±100 ppb (East Long Island Sound) to a high of 680±270 ppb (Great Bay).

Temporal Trends

In the 1960s and early 1970s, the DMF found DDT concentrations in soft-shelled clams ranging from below the detection limit to over 11,000 ppb. The mean tDDT concentrations for Quincy, Dorchester, and Hingham bays were 140, 390, and 2,100 ppb, respectively (Chesmore *et al.*, 1971; Iwanowicz *et al.*, 1973; and Jerome *et al.*, 1966). The DMF also found DDT in winter flounder muscle ranging from 26 to 8,400 ppb. When the high value was excluded from the calculations, the mean DDT concentration was 320 ppb. In 1987, the EPA analyzed two composite samples of soft-shelled clams from a site in Quincy Bay and found a mean tDDT concentration of 37 ppb. They also analyzed the muscle tissue of 25 winter flounder in 1987 and found a mean tDDT concentration of 34 ppb (EPA, 1988). Caution is needed when comparing the results of different studies. The DMF only measured DDT in the Quincy Bay clams and winter flounder, while the EPA measured the p,p' isomers of DDE, DDD, and DDT. This apparent 5- to 10-fold reduction in DDT levels agrees with the 10-fold reduction of DDT levels in biota on a nationwide basis by 1977 reported by Mearns *et al.* (1988).

The only multiyear data sets available were the NS&T Program's Benthic Surveillance and Mussel Watch projects. The Benthic Surveillance data indicated a slight decrease in mean tDDT concentrations in winter flounder liver from 830±140 ppb in 1984 to 630±120 ppb in 1985. An unpaired one-tailed t-test on log transformed data indicated no significant difference between 1984 and 1985 at p=0.05. No apparent trend was indicated by the Mussel Watch data with mean tDDT concentrations in mussels more than doubling from 1986 to 1987 (90±49 to 190±45 ppb) and then undergoing an approximate fivefold reduction between 1987 and 1988 (190±45 to 43±12) (Figure 12.11). Because statistical analysis of the log transformed Mussel Watch data indicated a significant difference among all 3 years, this yearly fluctuation appears to be real. If the yearly fluctuation is real, it would take several years of data to determine any trend of increasing or decreasing tDDT contamination. The same pattern of yearly fluctuations was observed at most of the other Mussel Watch sites in New England (Figure 12.11).

The EPA Deer Island site had a DDE concentration in the soft parts of mussels of less than 44 ppb in 1976 and less than 26 ppb in 1977. The NS&T Program Deer Island site (which is about 0.5 miles northwest of the EPA site) had yearly mean tDDE (o,p' DDE + p,p' DDE) concentrations in mussels of 49, 39, and 19 ppb in 1986, 1987, and 1988, respectively. When the two data sets were compared, they suggested a yearly fluctuation in tDDE levels in mussels with no clear long-term trend.

Summary

Boston Harbor sediments were found to contain tDDT at levels more than an order of magnitude higher than regional background levels (not natural background levels that should be zero). This was true whether or not the 600 ppb sample was included in the calculation of the Boston Harbor mean. In some cases, tDDT levels in Boston Harbor exceeded other sites by more than an order of magnitude. When the overall mean value of tDDT in Boston Harbor (35±18 ppb) was compared to the overall mean of San Francisco Bay (100±280 ppb) (Long *et al.*, 1988) it was found to be approximately one-third as high as the San Francisco Bay mean. However, when just the NS&T Program data for the two ports were compared, the Boston Harbor mean, 48±120 ppb, was more than 9 times higher than the San Francisco Bay mean, 5.3±9.4 ppb (Long *et al.*, 1988) (Table 12.8). Even when the 600 ppb was excluded, the Boston Harbor mean tDDT concentration in the surficial sediments,

24±13 ppb, was more than 4 times higher than the San Francisco Bay mean. Based on the available data, no clear geographic or temporal trends were apparent concerning tDDT concentrations in the surficial sediment of Boston Harbor.

Table 12.8. Comparison of tDDT sediment statistics for Boston Harbor, NS&T Program Reference (based on the five New England sites with the lowest levels of tDDT), and San Francisco Bay in ppb. Statistics for San Francisco Bay derived from Long *et al.*, 1988.

Area	Mean	Standard Deviation	Median	Range	Count
Boston	35	18	12	1.0 - 600	84
NS&T Boston	48	120	26	1.0 - 600	25
NS&T Reference	1.2	0.8	1.1	<0.2- 2.9	24
San Francisco Bay	100	280	7	<0.5 - 1960	153
NS&T San Francisco Bay	5.3	9.4	1.4	<0.1 - 46	51

The available data shows Boston Harbor biota moderately to highly contaminated with DDT. Boston Harbor mussels (*M. edulis*) had some of the highest mean tDDT concentrations of all the New England NS&T Program sites sampled; but, when compared to all NS&T Program mussel sites sampled in the country, the Boston Harbor sites fall into the upper 30 percent. The winter flounder (*P. americanus*) liver data also suggested that Boston Harbor had high levels of DDT. Among the NS&T Program sites, the Boston site had the highest mean tDDT concentration among all the NS&T Program winter flounder sites. The winter flounder and lobster (*H. americanus*) data suggested that DDT tends to accumulate more in liver and liver-like tissue than in muscle tissue. There were no obvious geographic trends in DDT content of biota within Boston Harbor based on the available data. The lobster muscle and soft-shelled clam data suggested a possible 5- to 10-fold reduction in DDT levels between the late 1960s early 1970s and again in the late 1980s.

PCB

PCBs are a class of synthetically produced chlorinated aromatic hydrocarbons with a high degree of stability and low flammability. PCBs were commercially produced in this country between 1929 and 1977 and were marketed as mixtures of some of the 209 different congeners that make up this class of compounds. Early attempts to measure PCBs in the environment were directed at measuring the presence of the most common commercial mixtures that went by the names of Aroclor 1242, 1254, 1260, etc. More recent attempts have been directed at grouping the congeners by chlorination level (di through non or dec) and then determining the concentrations of the different chlorination levels. Another currently used method for PCB analysis is determining the concentrations of individual congeners. When this is done, only a select few congeners are measured and, therefore, the sum of the congeners is less than the total PCBs (tPCBs) present. NOAA's NS&T Program currently determines the concentration of 19 congeners. The sum of these congeners is equal to roughly half the PCB concentration determined by analyzing for chlorination levels and summing the results. As a result of these various methodologies, extreme caution must be taken when comparing reported PCB concentrations from various data sets. Since PCBs are synthetically produced, background levels should be zero. However, because of their past widespread use, it has been difficult to find uncontaminated ecosystems.

Long and Morgan (1990) found toxic effects reported for sediments containing PCB concentrations as low as 2.9 ppb. However, individual PCB congeners have varying degrees of toxicity, therefore, toxicity is not solely dependent on tPCB concentrations but also depends on the individual congeners and their concentrations which make up the mixture.

Sediments

The available data sets reported PCB concentrations from 182 sediment samples taken from Boston Harbor between 1980 and 1987. The majority of these samples were taken between 1984 and 1987. Only 45 of the samples taken before 1984 The grand mean tPCB concentration in Boston Harbor, based on all the available data sets, was 830 ppb with a standard deviation of 3800 and a range of from a low 2.5 ppb to a high of 51,000 ppb. The median was 260 ppb. Approximately 29 percent of the samples had PCB concentrations less than 100 ppb, while approximately 59 percent of the samples had concentrations between 100 and 1000 ppb. Only one sample (less than 1%) had a mean in excess of 10,000 ppb. When the sample with the highest concentration of PCBs was excluded from the calculations, the grand mean PCB concentration became 560 ppb with a standard deviation of 960, a high value of 7000 ppb, and a median of 260 ppb (Table 13.1).

Table 13.1. Means, standard deviations, medians, ranges, and number of samples (count) for tPCB concentrations (ppb dw) in surficial sediments of all of Boston Harbor and for the four regions of the harbor, based on all the available data sets (* excludes 51,000 ppb sample, see text).

	Mean	Standard Deviation	Median	Range	Count
OVERALL*	560	960	260	2.5-7000	181
INNER HARBOR	750	1300	350	2.5-7000	39
NORTHWEST HARBOR*	670	1100	270	2.5-5600	75
CENTRAL HARBOR	370	370	270	5.0-1700	46
SOUTHEAST HARBOR	170	210	65	5.0-640	21

When the combined data set was broken down by harbor division, the highest mean tPCBs concentration was found in the sediments of the inner harbor, 750±1300 ppb, followed by those of the northwest harbor, 670±1300 ppb (excluding the 51,000 ppb sample) (Table 13.1). The central harbor sediments had a mean concentration of 370±370 ppb, while the southeast harbor sediments had the lowest mean concentration of tPCBs, 170±210 ppb (Table 13.1). Note the similarity in median concentrations for the entire harbor and the northwest and central harbor divisions (260, 270, and 270, respectively). When the northwest harbor data were further subdivided, the Dorchester Bay area sediments had the highest mean concentration of tPCBs, 990±1400 ppb, while the Winthrop Bay area sediments had the third highest, 450±810 ppb.

Geographic Trends

Between 1980 and 1987 the New England Division of the USACOE analyzed 80 sediment samples from Boston Harbor for PCBs (USACOE, 1972-1988; 1981). The results of these analyses were generally reported as concentrations of PCBs; although, in the case of eight samples, the results were reported as concentrations of individual Aroclor mixtures, either Aroclor 1242 or Aroclor 1254. Based on all 80 samples, the overall mean tPCB concentration for Boston Harbor was 550 ppb (Table 13.2) with a standard deviation of 960 and a range of from 2.5 to 5600 ppb. The median concentration was 160 ppb. The eight samples with concentrations reported for individual Aroclor mixtures had concentrations ranging from 5 to 500 ppb. Approximately 38 percent of the samples had tPCB concentrations of less than 100 ppb while 15 percent of the samples had concentrations in excess of 1000 ppb.

Table 13.2. Mean tPCB concentrations in the surficial sediments of Boston Harbor and the four divisions of the harbor, in ppb dw, based on the data of MA DEQE (1986, 1987), USACOE (1975-1988; 1981), EPA (1988), and NOAA's NS&T Program (unpublished). The numbers in parentheses are the number of data points used to calculate the means (*excludes 51,000 ppb sample, see text).

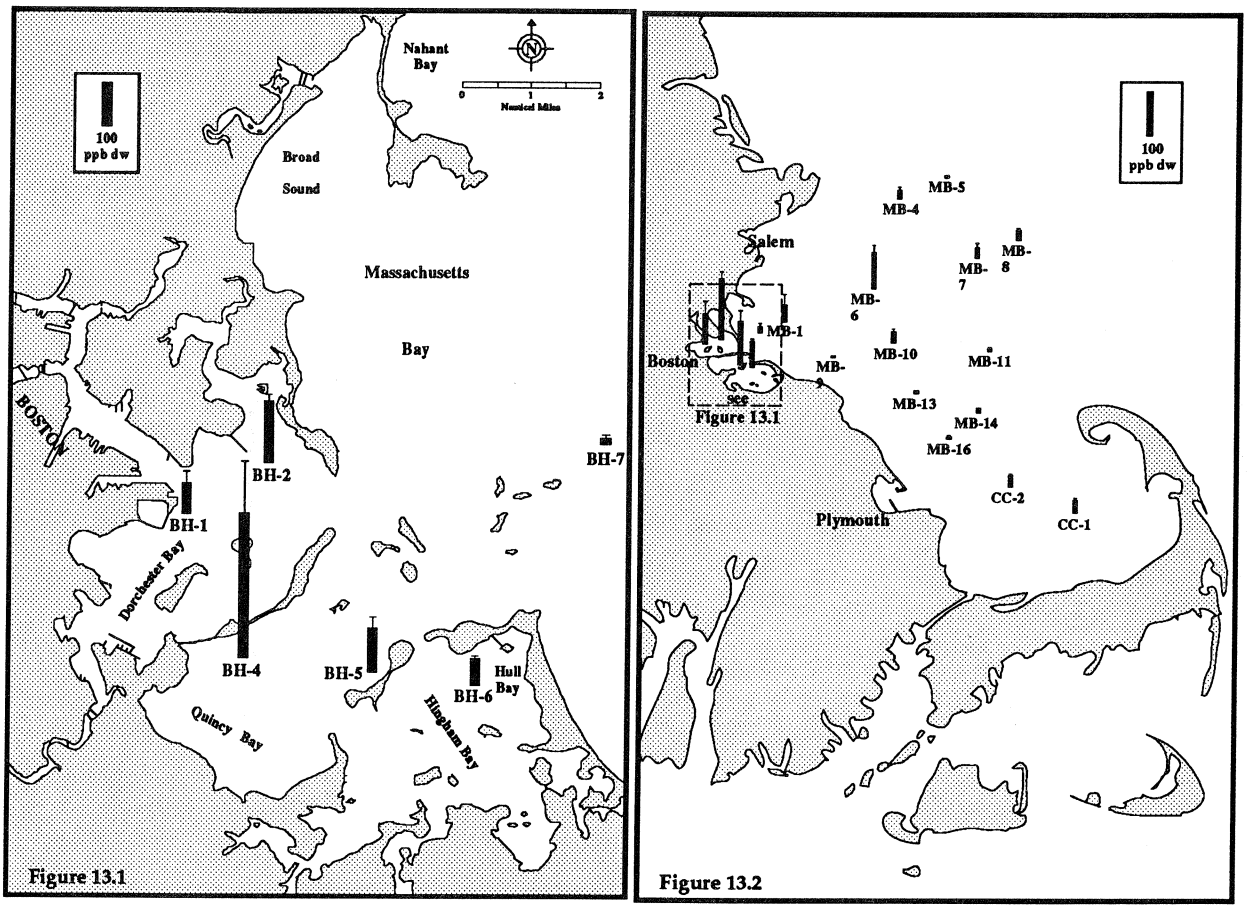
	USACOE	Boehm *et al.*	MA DEQE	EPA	NOAA NS&T
SAMPLING YEAR(S)	**1980-87**	**1983**	**1985-86**	**1987**	**1984-87**
OVERALL	550 (80)	140 (25)	1000 (30)	600 (22)	420 (24)*
INNER HARBOR	480 (31)	N/A	1800 (8)	N/A	N/A
NORTHWEST HARBOR	780 (33)	100 (10)	1000 (14)	N/A	540 (18)*
CENTRAL HARBOR	39 (8)	210 (10)	230 (6)	600 (22)	N/A
SOUTHEAST HARBOR	330 (8)	61 (5)	100 (2)	N/A	66 (6)

When the USACOE data were broken down by harbor division, the sediments in the northwest harbor had the highest mean concentration of tPCBs, 780±1300 ppb; followed by those of the inner harbor, 480±610 ppb; and then the sediments of the southeast harbor with a mean concentration of 330±270 ppb. The central harbor sediments had approximately an order of magnitude lower mean concentration (39±47 ppb) than did the other three divisions. When the northwest harbor was further subdivided, the Dorchester Bay area had the highest mean concentration of tPCBs in its sediments, 1200±1600 ppb and the Winthrop Bay area had the second highest, 540±1100 ppb. Statistical analysis of the log transformed data for the four divisions indicated that the central harbor was significantly different from both the inner and northwest harbor divisions at $p=0.05$. When the five divisions were analyzed the central harbor was significantly different from only the Dorchester Bay area at $p=0.05$.

In 1983, NOAA sponsored a study of organic pollution in Boston Harbor, Massachusetts Bay, and Cape Cod Bay which included the analysis of surficial sediment samples for PCBs (Boehm *et al.*, 1984). PCBs were quantified both as commercial Aroclor mixtures and by chlorination level. Five replicate samples were taken from five sites in Boston Harbor. The overall mean tPCB concentration in the Harbor was 140 ppb with a standard deviation of 110 (Table 13.1) and a range for the individual samples of 38 to 450 ppb; the median was 110 ppb. The means for the five sites ranged from a low of 61±5 ppb in Hull Bay (BH-6) to a

high of 330±120 ppb south of Moon Head in Quincy Bay (BH-4) (Figure 13.1). Statistical analysis of the log transformed data indicated that BH-4 was significantly different from the other four sites and BH-2, the site with the second highest mean (140±15 ppb), was also significantly different from the two sites with the lowest means, BH-6 and BH-1 (70±27 ppb), at p=0.05. When the data were grouped by harbor division, the central harbor had the highest levels of tPCBs (210±140 ppb), followed by the northwest harbor (100±42 ppb), and then the southeast harbor (61±5 ppb) (Table 13.1). When the northwest harbor was subdivided, the Dorchester Bay area had lower levels of tPCBs (70±27 ppb) than did the Winthrop Bay area (140±15 ppb). Statistical analysis of the log transformed data indicated that the central harbor was significantly different from the southeast harbor and the Dorchester Bay area at p=0.05.

In addition to the 5 sites in Boston Harbor, 13 sites in Massachusetts Bay and 2 in Cape Cod Bay had their surficial sediments analyzed for PCBs (Boehm *et al.*, 1984). From three to seven replicate samples were analyzed at each site. The site means ranged from a low of 2.3±0.7 ppb (MB-9) to a high of 83±16 ppb (MB-6) (Figure 13.2). The MB-6 site was in the vicinity of the disposal site referred to as the "Foul Area" which could account for its relatively high levels of tPCBs. The second highest site mean was 39±24 ppb (MB-1). The combined mean for Massachusetts and Cape Cod bays was 22±21 ppb. The mean was 18±14 ppb, excluding MB-6 that was approximately 7 times lower than the Boston Harbor mean of 140±110 ppb. Statistical analysis of the log transformed data indicated that five of these sites (MB-9, -11, -13, -14, and -16) were significantly different from all the Boston Harbor sites at p=0.05. The Boston Harbor site with the highest levels of tPCBs, BH-4, was significantly different from all but the Foul Area site, MB-6. The second most contaminated



Figures 13.1 & 13.2. Mean tPCB concentrations (ppb dw) in the surficial sediments of from Boston Harbor, Massachusetts and Cape Cod bays in 1983 (Boehm *et al.*, 1984) (bars represent one standard deviation).

Boston Harbor site, BH-2, was significantly different from all but three of the sites outside of the Harbor (MB-1, -6, and CC-1) at p=0.05.

Between 1985 and 1986 the Massachusetts DEQE, as part of their annual Boston Harbor Water Quality and Wastewater Discharge Survey, analyzed 30 surficial sediment samples for PCBs. The results of the 1985 analyses were reported as concentrations of Aroclor 1254 and 1260 while those for 1986 were reported as concentrations of Aroclor 1242, 1254, and 1260. Based on all 30 samples, the overall mean tPCB concentration for Boston Harbor was 1000 ppb (Table 13.2) with a standard deviation of 1600 and a range of from 25 to 7000 ppb. The median concentration was 350 ppb. The majority, approximately 67 percent, of the samples had tPCB concentrations between 100 and 1000 ppb. Approximately 13 percent of the samples had tPCB concentrations of less than 100 ppb and 20 percent of the samples had concentrations in excess of 1000 ppb. Figure 13.3 graphically displays the DEQE data by station and year.

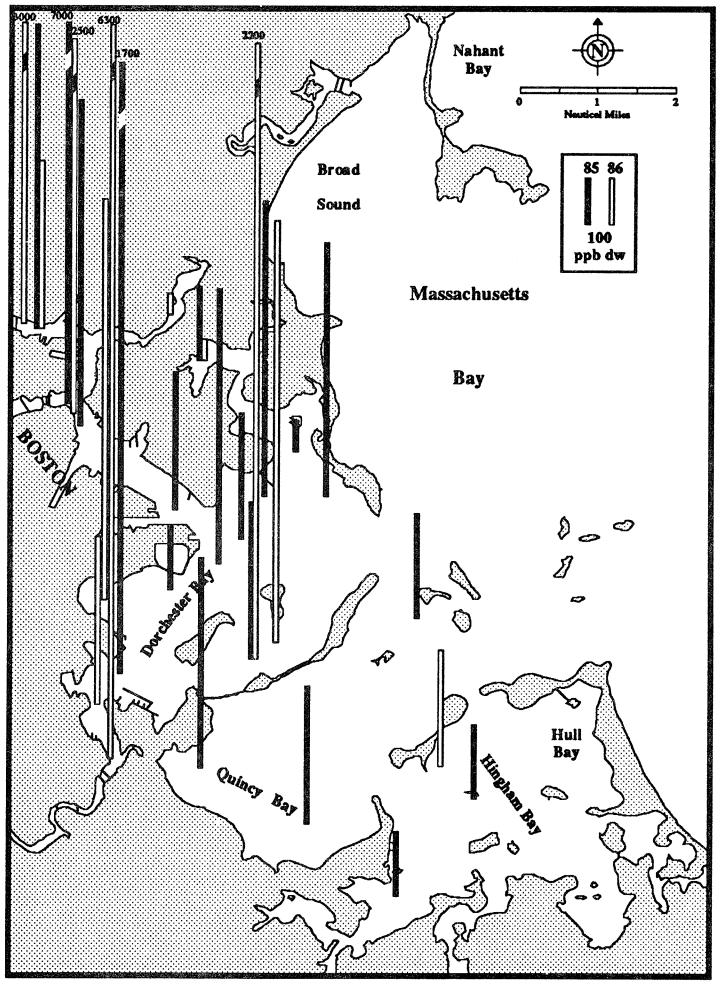
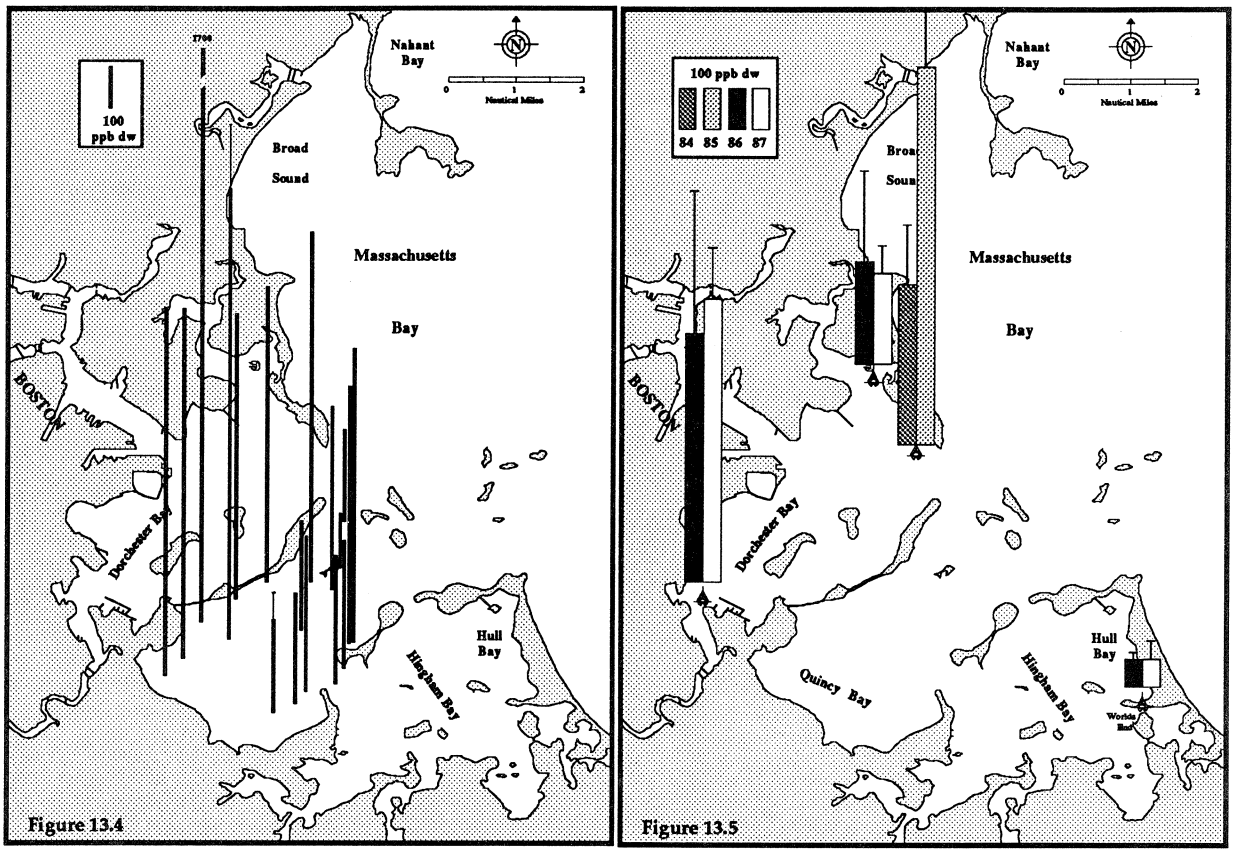


Figure 13.3. PCB concentrations (ppb dw) in the surficial sediments of Boston Harbor in 1985 and 1986 (MA DEQE, 1986, 1987).

When the DEQE data were broken down by harbor division, the surficial sediments in the inner harbor had the highest mean concentration of tPCBs, 1800±2400 ppb; followed by those of the northwest harbor, 1000±1400 ppb; and then the sediments of the central harbor, 230±140 ppb. The southeast harbor sediments had the lowest mean tPCB concentration, 100±80 ppb. When the northwest harbor was further subdivided, the Dorchester Bay area had the second highest mean concentration of tPCBs in its surficial sediments, 1500±1700 ppb and the Winthrop Bay area had the third highest, 370±240 ppb. These means and Figure 13.3 suggest a trend of decreasing levels of PCBs from the inner harbor to the southeast harbor. However, statistical analysis of the log transformed data for the four divisions and for the three divisions plus the two subdivisions of the northwest harbor indicated no significant difference among the divisions at p=0.05. When the data for Aroclor 1242 is excluded from the calculations basing the tPCB concentrations for all sites on the sum of Aroclor 1254 and 1260, the overall harbor mean was reduced by 30 percent to 700±1300 ppb and the median was reduced by 14 percent to 300 ppb. The range remained unchanged. The division means were reduced by 10 percent to 40 percent; but, the relative degree of contamination between the harbor divisions remained unchanged.

In 1987, a study of Quincy Bay, essentially restricted to the central harbor area, was conducted under the auspices of the U. S. EPA (EPA, *1988*). The study measured the

concentrations of Aroclor 1242 and 1254 in 22 samples of the surficial sediments. Figure 13.4 graphically displays the results of the grab sample analysis and suggests that tPCB may have been more concentrated along the northwestern side of Quincy Bay than elsewhere in the bay. The overall mean tPCB concentration in the surficial sediments for the study was 600±400 ppb (Table 13.2) with a range of 130 to 1700 ppb. The median was 540 ppb. Only three (14%) of the samples had tPCB concentrations in excess of 1000 ppb.



Figures 13.4 & 13.5. Mean tPCB concentrations (ppb dw) in the surficial sediments of from Boston Harbor in 1987 (US EPA, 1988) (Fig. 13.4) and in 1984-87 (NOAA, unpublished) (Fig. 13.5) (bars represent one standard deviation).

Since 1984, NOAA's NS&T Program has sampled and analyzed surficial sediments from several sites around Boston Harbor for several analytes, including PCBs. PCB concentrations were reported as values for the various chlorination levels from di- to non-, and tPCBs equaled the sum of the values for the individual chlorination levels. In 1984, one surficial sediment sample from the southwest Deer Island site was reported to have a tPCB concentration of 51,000 ppb. This value was approximately 50 times higher than the second highest concentration reported for any of the other NS&T Program sites; therefore, this sample was excluded from all calculations in the following discussion. The overall mean tPCB concentration in surficial sediments of the Harbor was 420±340 ppb (Table 13.2), while individual sample values ranged from 13 to 1000 ppb and the median was 280 ppb. Only one sample (4%) had a concentration of 1000 ppb or higher, while 25 percent of the samples had concentrations of less than 100 ppb. Figure 13.5 portrays mean tPCB concentrations graphically by year and site. The individual site means, based on all 4 years of available data were: 66±30 ppb off the northern tip of Worlds End, 230±150 ppb northwest of Deer Island, 640±240 ppb in southwestern Dorchester Bay, and 740±300 ppb southwest of Deer Island. Statistical analysis of the log transformed data indicated that the southwest Deer Island site was significantly different from the northwest Deer Island and Worlds End sites,

and the Worlds End site was significantly different from the Dorchester Bay site, all at p=0.05. When the data were grouped by harbor divisions, the means suggested that the northwest harbor, 540±320 ppb, had higher tPCB concentrations than did the southeast harbor, 66±30 ppb. Statistical analysis of the log transformed data, using an unpaired t-test, indicated a significant difference between the two divisions at p=0.05. When the northwest harbor division was subdivided into the Winthrop Bay area (mean 480±350 ppb) and the Dorchester Bay area (mean 640±240 ppb), statistical analysis of the log transformed data indicated a significant difference among the southeast harbor and the other two areas at p=0.05.

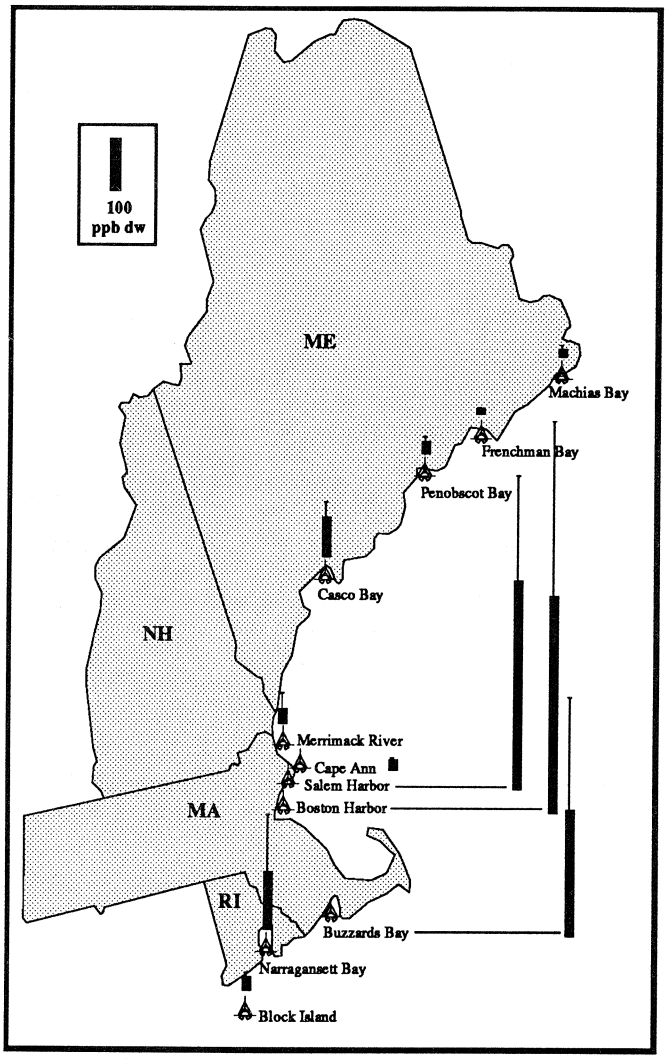


Figure 13.6. Mean tPCB concentrations (ppb dw) in the surficial sediments of the outer New England coast for 1984-87 (NOAA, unpublished).

On a broader scale, between 1984 and 1987, the NOAA NS&T Program analyzed surficial sediment samples from 23 sites from 11 areas along the outer New England coast. From Figure 13.6, which displays the means and standard deviations for the 11 coastal areas, it is clear that the mean tPCB concentration of the NS&T Program sites in Boston Harbor, even excluding the single sample with 51,000 ppb (420±340 ppb), was higher than all other areas sampled (although the mean for Salem Harbor, 400±210 ppb, was almost as high). Only two other areas had mean concentrations in excess of 100 ppb, Buzzards Bay (240±220 ppb) and Narragansett Bay (110±110 ppb). Statistical analysis of the log transformed data indicated that Boston and Salem harbors were significantly different from only four of the other nine areas (Machias Bay, Frenchman Bay, Penobscot Bay, and Merrimack River) at p=0.05. At p=0.10, Boston and Salem harbors were also significantly different from Cape Ann and Narragansett Bay. It should be noted that the Salem Harbor mean was based on samples from only one site. The Boston Harbor mean was based on samples from four sites.

When the mean tPCB concentrations in the surficial sediments of the individual New England NS&T Program sites were compared, the two sites with the highest mean tPCB concentrations were located in Boston Harbor (Table 13.3). Since PCB is a synthetically produced compound, background levels should be zero. By this rational, all of NOAA's NS&T Program sites sampled in New England had elevated levels of PCB (Table 13.3) with mean concentrations of tPCBs ranging over more than an order of magnitude. Despite these facts a regional background reference concentration was determined by calculating the overall mean for the five New England sites with the lowest mean tPCB concentrations; this overall mean was 17±8 ppb. The overall mean concentration of tPCB in Boston Harbor based on NS&T

Table 13.3 The five outer New England Coast NOAA NS&T Program sites with the lowest and highest mean tPCB concentrations (ppb dw) based on data from 1984 through 1987 (*excludes 51,000 ppb sample, see text).

Site	Mean	Standard Deviation	Count
FRENCHMAN BAY, MAINE	11	3	4
MACHIAS BAY, MAINE	15	9	4
PICKERING ISLAND, PENOBSCOT BAY	18	10	3
CAPE ANN	20	3	3
SEARS ISLAND, PENOBSCOT BAY	21	9	6
ROUND HILL, BUZZARDS BAY	230	60	6
SALEM HARBOR	400	200	7
ANGELICA ROCK, BUZZARDS BAY	530	190	6
DORCHESTER BAY	640	240	6
SOUTHWESTERN DEER ISLAND*	740	300	6

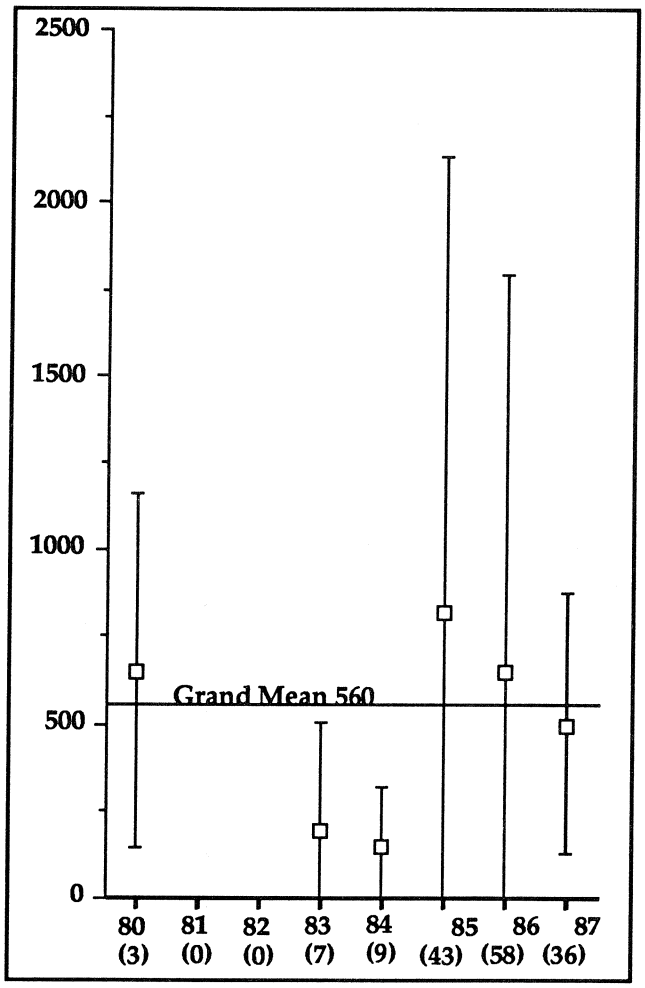


Figure 13.7. Yearly mean tPCB concentrations (ppb) in the surficial sediments of Boston Harbor, based on USACOE (1972-1988, 1981,), Boehm *et al.* (1984), MA DEQE (1986, 1987), U.S. EPA (1988), and NOAA (unpublished) (numbers in () are sample sizes).

Program data, even excluding the 51,000 ppb sample (420±340 ppb), was approximately 25 times higher than the regional background reference concentration.

Temporal Trends

Little can be said with confidence about temporal trends of PCB contamination in Boston Harbor sediments because of the sparsity of data. Figure 13.7 gives the yearly means of tPCB in the surficial sediments of Boston Harbor based on all the available data sets. The yearly means fluctuated from a low of 150 ppb in 1984 (excluding the 51,000 ppb sample) to a high of 820 ppb in 1985. These fluctuations can probably be more readily attributed to differences in sites sampled and analytical methodologies used than to any actual difference in yearly concentrations.

The only single data set which spanned more than one year was that from NOAA's NS&T Program (NOAA, unpublished). It covered the 4 years from 1984 through 1987, although the same sites were not sampled in each of the 4 years. The yearly mean tPCB concentration ranged from a low of 310 ppb in 1986 to a high of 910 in 1985. However, only the southwest Deer Island site was sampled in 1985 while the northwest Deer Island, Dorchester Bay, and Worlds End sites were sampled in 1986 (Figure 13.5). The mean for 1984 was 380 ppb; while that for 1987 was 320 ppb. Based on this data, there was no apparent trend of tPCB contamination levels during the 4 years covered by NOAA's data.

Biota

The data utilized in this report includes the concentrations of PCBs from 255 tissue samples from specimens taken from Boston Harbor between 1976 and 1988. Table 13.4 gives the statistics based on this data broken down by species and tissue type. Individual samples with the lowest concentrations of PCBs were muscle tissue taken from winter flounder (*P. americanus*), 140 ppb and lobster (*H. americanus*), 53 ppb. The highest concentrations of PCBS reported for a single sample was 110,000 ppb from lobster hepatopancreas. The overall data for winter flounder and lobster suggest that PCBs tend to accumulate more in liver or liver-like tissue than in muscle tissue.

Table 13.4 Harbor-wide means, standard deviations, medians, ranges, and sample sizes (count) for tPCB concentrations (ppb dw) in biota by organism and tissues based on all the available data sets (* transplants).

		Mean	Standard Deviation	Median	Range	Count
P. americanus						
	liver	22,000	15,000	20,000	4,200-62,000	38
	muscle	1,800	1,400	1,500	140-8,000	97
H. americanus						
	hepatopancreas	86,000	20,000	88,000	48,000-110,000	8
	muscle	550	470	280	53-1,900	49
C. borealis						
	soft parts	1,000	190	980	880-1,250	3
M. arenaria						
	soft parts	550	170	510	310-1,000	27
M. edulis						
	soft parts	920	550	740	220-2,400	29
*C. virginica**						
	soft parts	480	61	470	420-560	4

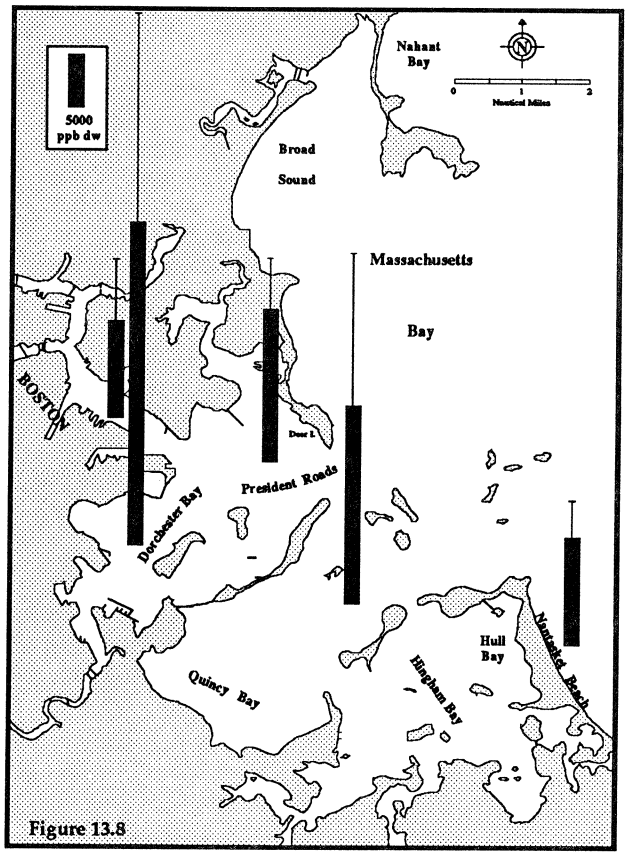
Geographic Trends

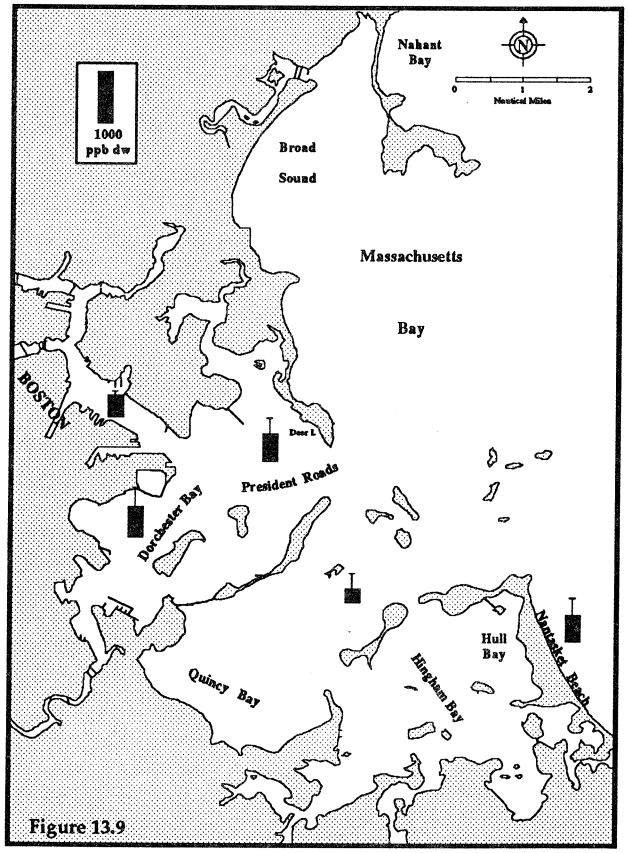
In 1976 and 1977 the U. S. EPA sampled mussels and other bivalves from 107 sites nationwide and analyzed the samples for a variety of metals and organic analytes, including PCBs as a mixture of Aroclor 1254 (Farrington *et al.*, 1982). Two composite samples of *M. edulis* from a site on the northwest side of Deer Island were found to have a mean PCB concentration in the soft parts of 685 ppb. Between Block Island and the Canadian Border, 10 other New England sites were sampled and had mean PCB concentrations in the soft parts of *M. edulis* ranging from 24 ppb at the site at Blue Hill Falls, Maine to 300 ppb at Plymouth, Massachusetts.

In 1979, as a part of the 301h waiver application for the Deer Island and Nut Island sewage treatment plants, winter flounder (*P. americanus*) and lobster (*H. americanus*) tissue samples from five sites in and around Boston Harbor were analyzed for levels of several analytes, including PCBs as a mixture of Aroclor 1254 (Metcalf and Eddy, 1984). The livers of four winter flounder from each of four different sites in Boston Harbor and one site outside the Harbor (Nantasket Beach) were analyzed for levels of PCBs. The values for the individual samples ranged from 4200 to 51,000 ppb with the low sample coming from near Nut Island and the high from Dorchester Bay. The mean PCB concentrations in livers for the five sites ranged from 8900±5700 ppb at the Inner Harbor site to 30,000±19,000 ppb at the Dorchester Bay site (Figure 13.8). When the data were log transformed and analyzed, none of the sites were significantly different at $p=0.05$. When the data were looked at with regard to the harbor divisions, they suggested that the northwestern harbor had the highest level of PCB contamination in winter flounder livers, followed by the central

harbor, and then the inner harbor. It also suggested that the Nantasket Beach site biota had levels of PCBs only slightly higher than the inner harbor biota (Figure 13.8). When the northwest harbor was subdivided, the Dorchester Bay area had higher levels of PCBs (30,000 ppb) than did the Winthrop Bay area (14,000 ppb). However, statistical analysis of the log transformed data found no significant difference between any of the harbor divisions nor between any of the divisions and the Nantasket Bay site. Unfortunately, only five edible tissue samples (three samples from President Roads and two samples from Nantasket Beach) were analyzed for PCBs. The mean concentration of PCBs for the samples from President Roads was 820±710 ppb, while that for Nantasket Beach was 520±50 ppb.

Two lobsters each were collected from the same five sites and the claws and tails were analyzed for levels of PCBs. Concentrations of PCBs in the individual specimens ranged from less than 53 to 844 ppb. The means for the five sites ranged from a low of 260 ppb at the Nut Island Discharge site to a high of 580 ppb at the Dorchester Bay site. The means for the other three sites were: President Roads, 530 ppb; Nantasket Beach, 500 ppb; and Inner Harbor, 420 ppb (Figure 13.9). None of the sites were significantly different based on analysis of the log transformed data (p=0.05). As with the winter flounder liver data, when the lobster muscle data were grouped by division, the northwest harbor had the highest mean concentration of PCBs (550 ppb); and, when the northwest harbor was subdivided, the Dorchester Bay area had a slightly higher mean concentration of PCBs (580 ppb) than did the Winthrop Bay area (530 ppb). Statistical analysis of the log transformed data indicated no significant difference between any of the divisions nor between any of the divisions and the Nantasket Beach site at p=0.05.

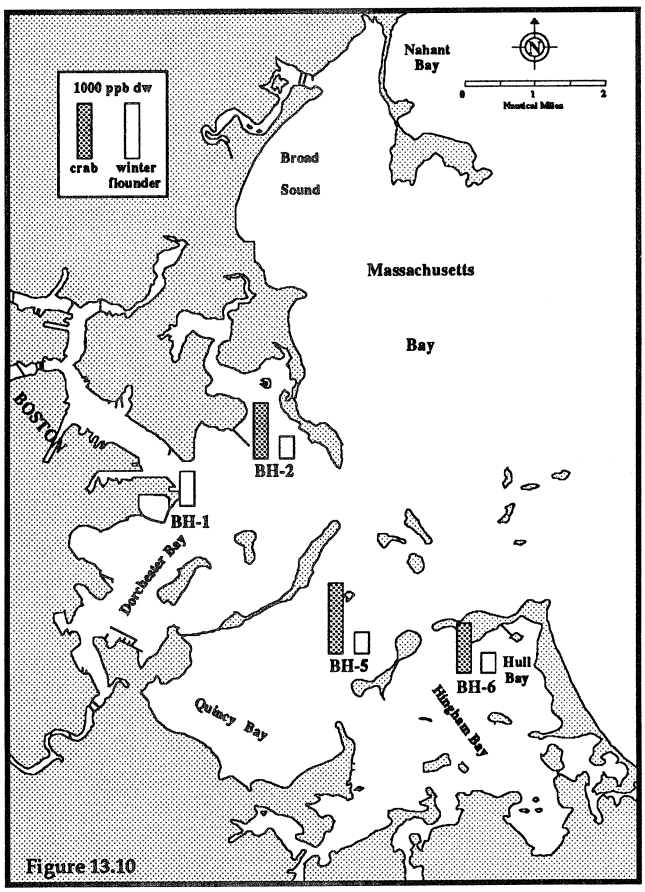


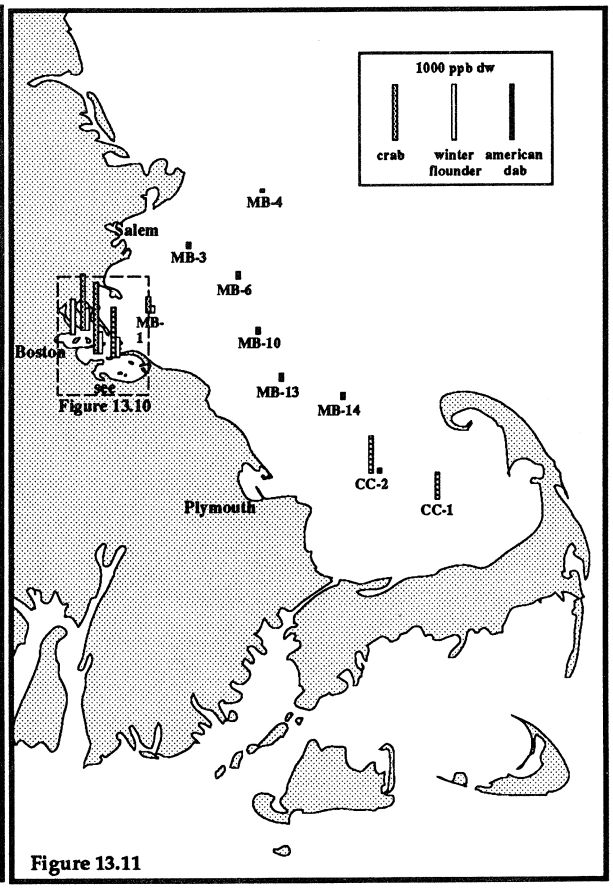


Figures 13.8 & 13.9. Mean PCB concentrations (ppb dw) in the liver of *P. americanus* (Fig. 13.8) and in the claw and muscle tissue of *H.americanus* (Fig. 13.9) in and around Boston Harbor in 1979 (Metcalf & Eddy, 1984).

In 1983, as part of a NOAA-sponsored study of organic pollution in Boston Harbor, Massachusetts Bay, and Cape Cod Bay, composite samples (at least three specimens per composite) of crab (*Cancer borealis)* soft parts and winter flounder (*P. americanus*) muscle tissue were analyzed for PCBs (Boehm *et al.*, 1984). PCBs were quantified both as commercial Aroclor mixtures and by chlorination level. Three composite samples of crab soft parts from three sites in Boston Harbor, one each from the three outer harbor divisions, had an overall mean tPCB concentration of 1000±190 ppb with a range of 880 to 1200 ppb. The sample with the highest concentration was from the central harbor, northwest of Peddocks Island (BH-5). The sample with the lowest concentration was from Hull Bay in the southeast harbor (BH-6) (Figure 13.10). Four composite samples of winter flounder muscle tissue from three sites in Boston Harbor were analyzed, two from the northwest harbor (BH-1 and 2), and one each from the central (BH-5) and southeast (BH-6) harbor divisions. The overall mean tPCB concentration was 430±120 ppb with a range of 353 (BH-6) to 613 (BH-1) ppb for individual samples. The sample with the highest concentration came from Dorchester Bay while that with the second highest (385 ppb) came from the Winthrop Bay area (BH-2) (Figure 13.10). The sample with the lowest concentration of tPCB was from Hull Bay in the southeast harbor (BH-6). Both the crab and flounder data suggests that the southeast harbor biota had the lowest levels of PCBs, but while the crab data suggests that the central harbor biota had the highest levels the flounder data suggests that the northwest harbor biota, in particular that from Dorchester Bay, had the highest levels.

In addition to the samples from Boston Harbor, three crab, one winter flounder, and seven American dab samples from sites in Massachusetts and Cape Cod bays were also analyzed for PCBs (Figure 10.11). The three crab soft parts samples had a mean tPCB concentration of 460±190 ppb, less than 1/2 the mean for Boston Harbor crab soft parts,





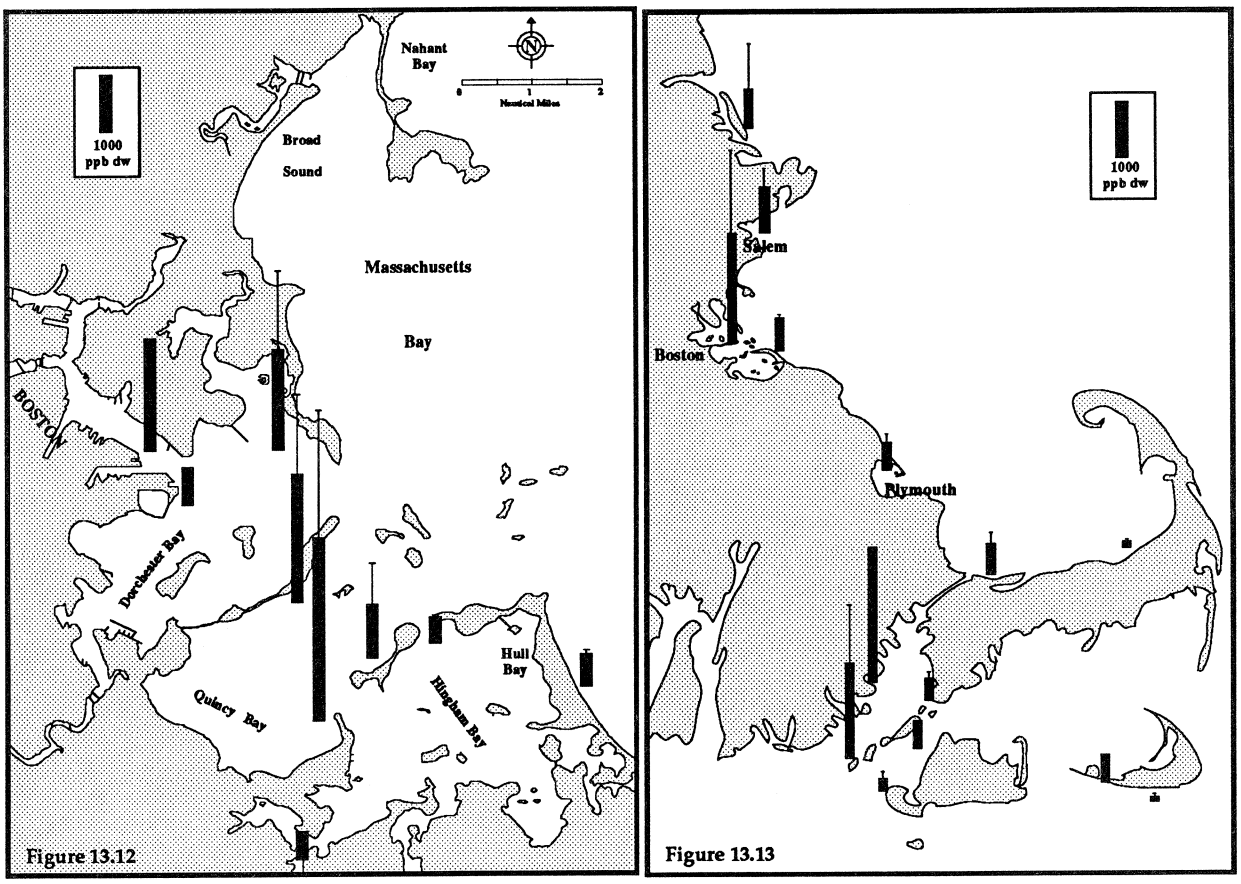
Figures 13.10 & 13.11. tPCB concentrations (ppb dw) in *C. borealis, P. americanus* and *H. plattessoides* in Boston Harbor, Massachusetts and Cape Cod bays in 1983 (Boehm *et al.*, 1984).

1000±190 ppb. The single winter flounder muscle tissue sample contained 116 ppb tPCB which was less than 1/3 the concentration of the least contaminated sample from Boston Harbor, 353 ppb. Although no direct comparison can be made between winter flounder muscle tissue concentrations and American dab muscle tissue concentrations of tPCBs, it should be noted that the mean for the seven American dab samples from Massachusetts and Cape Cod bays was 103±31. This mean, which was comparable to the single Massachusetts Bay winter flounder sample, was less than 1/4 the mean for Boston Harbor winter flounder muscle tissue. Based on this data, it appears that Boston Harbor biota were significantly more contaminated with PCBs than were biota outside of the Harbor.

Between 1983 and 1986, Massachusetts Department of Natural Resources Division of Marine Fisheries (DMF) analyzed winter flounder (*P. americanus*) muscle tissue, taken from the coastal waters of the state for PCBs in the form of Aroclor 1254 (Schwartz,1987). The muscle tissue of 69 winter flounders from seven sites in Boston Harbor were analyzed and PCB concentrations ranging from 250 to 8000 ppb were found. The overall mean for the Harbor was 2000 ppb with a standard deviation of 1500. The median concentration was 1500 ppb. The means for the seven sites ranged from a low of 480±35 ppb (Hingham Bay) to 3300±2300 ppb (west of Nut Island) (Figure 13.12). The highest single value, 8000 ppb, was from west of Deer Island. Despite the wide range of site means, statistical analysis of the the log transformed data indicated no significant difference between any of the sites at p=0.05. This lack of significant difference was probably due to the small sample size at several of the sites (three sites had only one sample, two sites had two samples) and the relatively large standard deviations of the three sites with the largest sample sizes (40, 14, and 6). When the data were grouped by harbor divisions, the divisions' means ranged from at low of 480±30 ppb in the southeast harbor to a high of 2600±1600 ppb in the central harbor. The northwest harbor had a mean of 1700±1400 ppb, while the single sample from the inner harbor had a PCB concentration of 2000 ppb. Statistical analysis of the log transformed data indicated that only the central and southeast harbors were significantly different at p=0.05. Only one sample was analyzed from the Dorchester Bay area of the northwest harbor, just off Castle Island; it had a PCB concentration of 677 ppb. From the Winthrop Bay area of the northwest harbor east of Deer Island, 40 samples were analyzed and had a mean PCB concentration of 1800±1400 ppb.

In addition to the samples from Boston Harbor, the DMF analyzed the muscle tissue of 62 winter flounders for PCB content from 13 other coastal areas throughout the state (Figure 13.13). Sample sizes ranged from 1 to 7, except for the Beverly-Salem Harbor area, which had 22 samples from four sites. The mean concentration of PCBs in winter flounder muscle tissue throughout the state's coastal waters, excluding Boston Harbor, was 660±540 ppb with a range of 50 to 2500 ppb. Only 12 (19%) of the samples had concentrations of 1000 ppb or greater and 7 of these were from the Beverly-Salem Harbor area, while 4 were from Buzzards Bay including 3 (5%) samples with concentrations of 2500 ppb. This compares to 51 (74%) of the samples from Boston Harbor which had means of 1000 ppb or greater and 22 (32%) of the samples which had means of 2000 ppb or greater. When the Beverly-Salem Harbor area and Buzzards Bay samples were excluded, the mean PCB concentrations in Massachusetts' coastal waters was 380±250 ppb, less than 1/5 the mean for Boston Harbor. The means for the 13 areas ranged from a low of 90±41 ppb, south of Nantucket, to a high of 2500 ppb for two samples from Mattapoisset (Figure 13.13). Statistical analysis of the log transformed data indicated that Boston Harbor was significantly different from only two of the other areas sampled, Gay Head and south of Nantucket Island.

In 1984 the DMF analyzed the liver of 16 winter flounders from west of Deer Island for PCBs. The mean PCB concentration for the 16 samples was 32,000±14,000 ppb with a range of 16,000 to 62,000 ppb. This is 16 times higher than the mean PCB concentration of 2000±1800 ppb in the muscle tissue of the 16 winter flounders taken from west of Deer Island that year. This data clearly suggests that PCBs are principally stored in the liver rather than in the muscle tissue.



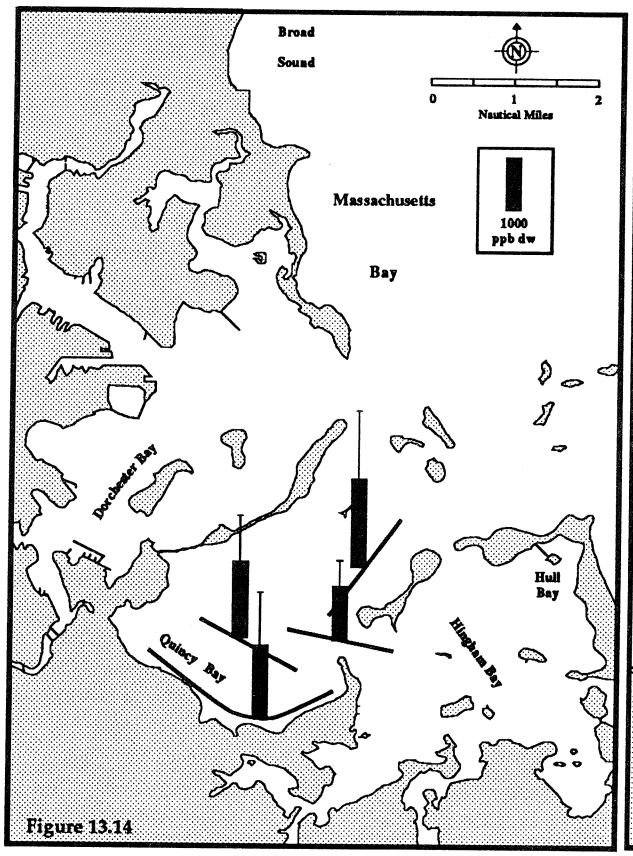
Figures 13.12 & 13.13. Mean PCB concentrations (ppb dw) in *P. americanus* muscle tissue from Boston Harbor (Fig. 13.12) and Massachusetts coastal waters (Fig. 13.13) based on 1983-1986 DMF data (Schwartz, 1987) (bars represent one standard deviation).

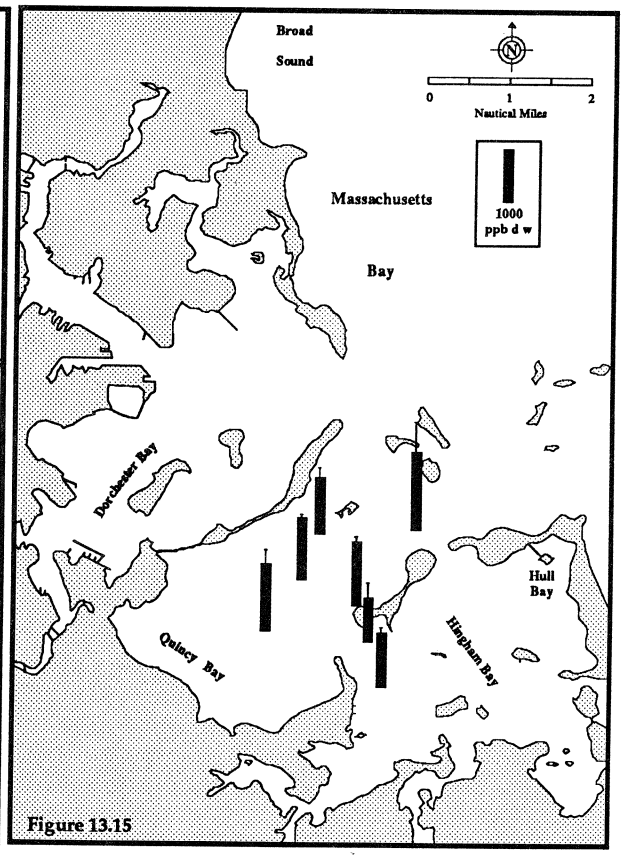
In 1985 and 1986, lobster (*H. americanus*) and soft-shelled clams (*M. arenaria*) were collected from Boston and Salem Harbors and analyzed for various analytes, including PCBs, as part of a study of contaminants in marine resources (Wallace *et al.*, 1988). PCB concentrations were reported by concentrations of individual congeners as well as by chlorination number. The mean tPCB concentration in the combined claw and tail muscle tissue of 25 lobsters collected from around Deer Island was 200±50 ppb with a range of from 120 to 380 ppb. Lobsters were collected from two sites in Salem Harbor, the treatment plant outfall and Willows Pier. The mean PCB concentrations in combined claw and tail muscle tissue based on the analysis of 25 lobsters per site were 90±27 and 120±100 ppb, respectively. Statistical analysis of the log transformed data indicated that the Deer Island site was significantly different from both the Salem harbor sites at p=0.05. The mean tPCB concentration for 25 soft-shelled clams from Wollaston Beach in Quincy Bay was 510±110 ppb with a range of 310 to 850 ppb.

An intensive study of Quincy Bay was conducted in 1987 which included the analysis for PCB levels in the tissues of native winter flounder (*P. americanus*), lobsters (*H. americanus*) and soft-shelled clams (*M. arenaria*), as well as transplanted oysters (*C. virginica*) (EPA,1988). The concentrations were reported both as concentrations of the Aroclor mixtures 1242 and 1254 and as concentrations of individual congeners. The muscle tissue of from five to seven winter flounder from each of four different trawl transects was analyzed for PCB levels. The tPCB (Aroclor 1242+Aroclor 1254) concentration ranged from 310 to 3900 ppb, for the individual samples, with an overall mean of 1400±920 ppb. The tPCB means for the four trawl transects ranged from 1000±490 to 1700±1300 ppb (Figure 13.14). Statistical

analysis of the log transformed data indicated no significant difference between any of the trawls (p=0.05).

The tail muscle and the hepatopancreas of lobsters from seven sites were analyzed for levels of PCBs. Two replicate samples from the tail muscles of a total of 16 lobsters, 1 to 3 from each of the seven sites were analyzed. The overall mean tPCB concentration in the lobster tail muscle was 1200±270 ppb. The tPCB concentrations in the individual samples ranged from 640 to 1900 ppb. The mean tail muscle concentrations for the seven sites ranged from 850±290 to 1500±580 ppb (Figure 13.15). There was no significant difference in tail muscle tPCB levels between sites based on statistical analysis of the log transformed data (p=0.05). Two replicate samples of the hepatopancreas of 8 of the 16 lobsters were also analyzed for PCBs. The tPCB concentrations for the eight hepatopancreases ranged from 48,000 to 113,000 ppb (Figure 13.16). The overall mean tPCB concentration in the lobster hepatopancreases was 86,000±20,000 ppb; more than 75 times the mean tPCB concentration in the muscle tissue of the same eight lobsters. This indicates that PCBs are preferentially stored in the hepatopancreas of lobsters.

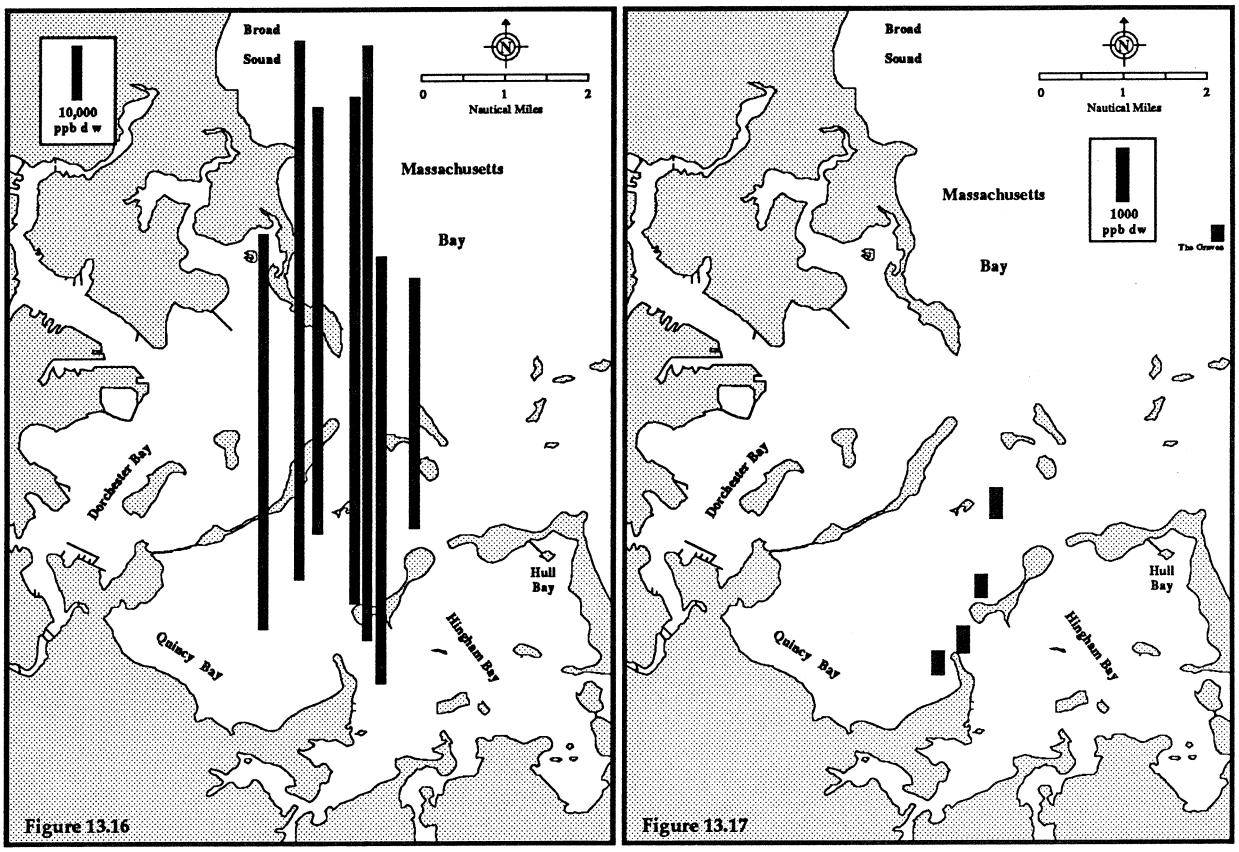




Figures 13.14 & 13.15. Mean tPCB concentrations in muscle tissue of *P. americanus* (Fig. 13.14) and *H. americanus* (Fig. 13.15) from Quincy Bay in 1987 (US EPA, 1988) (bars represent one standard deviation).

Oysters (*C. virginica*) were collected from a commercial bed located in Cotuit Bay, Massachusetts and deployed at four sites in Quincy Bay and one site located at The Graves in Massachusetts Bay from June 5 through July 16, 1987. The tPCB concentrations in the oysters at the four sites ranged from 420 to 560 ppb. The oysters from The Graves had 300 ppb tPCB, while those from the source bed in Cotuit Bay had a tPCB concentration of 280

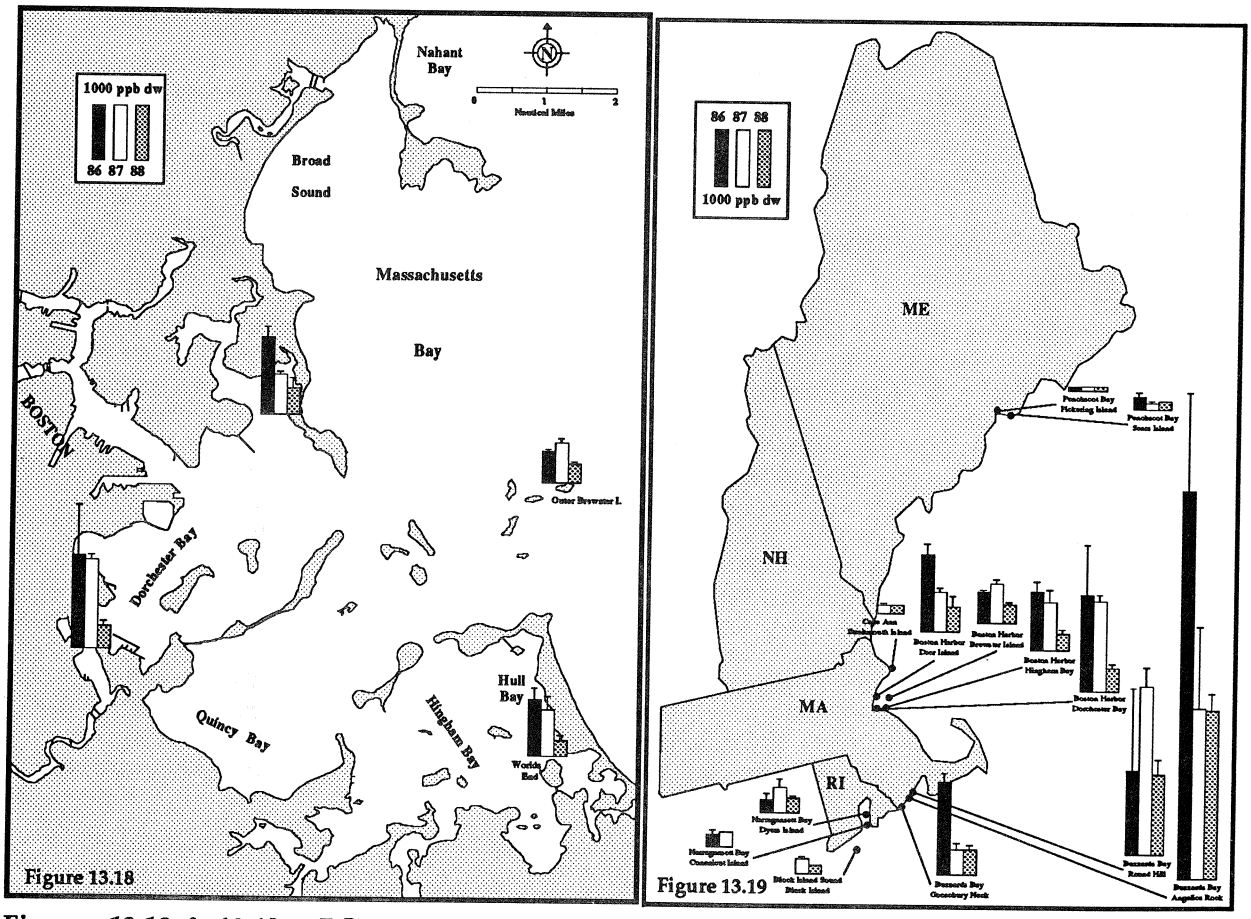
ppb (Figure 13.17). Two samples of the soft-shelled clam from around Moon Island, Quincy Bay also were analyzed for PCB and had tPCB concentrations of 1000 ppb.



Figures 13.16 & 13.17. Mean tPCB concentrations (ppb dw) in hepatopancreas tissue of *H. americanus* (Fig. 13.16) from Quincy Bay and environs and transplanted *C. virginica* (Fig. 13.17) in 1987 (US EPA, 1988) (bars represent one standard deviation) (note the difference in scales).

Since 1986, NOAA's Mussel Watch Project, a part of the NS&T Program, has sampled mussels (*M. edulis*) annually from four sites in and around Boston Harbor. Three whole-body composite samples from each site were analyzed for a variety of analytes, including PCBs. In 1986, PCB concentrations were reported for the 8 chlorination levels, di to non; in 1987 they were reported for the 8 chlorination levels as well as for 19 individual congeners; and, in 1988, concentrations were reported only for the 19 individual congeners. In 1987 the sum of the individual congener concentration was approximately 1/2 the sum of the nine chlorination levels for the same sample. Based on this relationship, the sum of the congeners for each sample in 1988 was converted to a value which approximately equals the the sum of the chlorination levels if they had been measured. For all the NS&T Program data in this report, tPCB equals the sum of the eight chlorination levels; or, in the case of 1988, the converted sum of the congeners. The overall mean concentration of tPCB in the mussels for the three sites in Boston Harbor from 1986 through 1988 was 930±570 ppb with a range of from 200 to 2400 ppb. The means for the individual sites were 710±370 ppb in Hingham Bay off World's End, 840±430 ppb northwest of Deer Island, and 1200±760 ppb in southwestern Dorchester Bay; mussels from the site just outside the Harbor, Outer Brewster Island, had a mean tPCB concentration of 530±160 ppb (Figure 13.18). Statistical analysis of the log transformed data for the four sites indicated that none of the four sites were significantly different (p=0.05).

On a broader scale, when the Boston Harbor sites were compared to the other New England Mussel Watch sites (Figure 13.19 and Table 13.5), the sites in Boston Harbor had the third, fourth, and sixth highest mean tPCB concentrations. The seventh highest mean was from the site just outside of Boston Harbor (Outer Brewster Island). The New England sites with the first, second, and fifth highest mean concentrations were all from Buzzards Bay; Angelica Rock, Round Hill, and Goosebury Neck, respectively. The site at Pickering Island in Penobscot Bay had the lowest mean tPCB concentration. Figure 13.19 suggests that tPCB levels in Boston Harbor mussels was significantly higher than in mussels from any other New England site except those in Buzzards Bay. This is largely supported by statistical analysis of the log transformed data which indicated that all three Boston Harbor sites were significantly different from the three sites with the lowest mean tPCB concentrations (Pickering Island, Sears Island, and Cape Ann) at p=0.05 (Table 12.5). The Deer Island and Dorchester Bay sites were also significantly different from the Block Island site and the Dorchester Bay site was significantly different from the two Narragansett Bay sites all at p=0.05. The Angelica Rock site was significantly different from all other sites, including the Boston Harbor sites, with the exception of the Round Hill site, at p=0.05. From this data, it appears that tPCB levels in mussels varies by almost 2 orders of magnitude throughout New England. In spite of the fact that natural background levels of tPCB should be zero, an attempt was made to determine a regional background reference concentration for tPCB in mussels by calculating the overall mean for the five New England sites with the lowest means. This overall mean was 150±80 ppb. The overall mean for Boston Harbor concentrations of tPCB (930±570 ppb) was more than 6 times greater than the calculated regional background reference concentration.



Figures 13.18 & 13.19. tPCB concentrations (ppb) in the soft parts of mussels (Mytilus edulis) from Boston Harbor (Fig.13.18) and the outer New England coast (Fig.13.19) (NOAA, unpublished) (bars represent one standard deviation).

Table 13.5 The mean tPCB concentrations (ppb) in *M. edulis* at the 13 outer New England Coast NS&T Program Mussel Watch sites. The outlined means are for Boston Harbor sites.

Site	Mean	Standard Deviation	Count
ANGELICA ROCK, BUZZARDS BAY	4300	2200	9
ROUND HILL, BUZZARDS BAY	2000	980	8
DORCHESTER BAY, BOSTON HARBOR	1200	760	9
DEER ISLAND, BOSTON HARBOR	840	430	9
GOOSEBURY NECK, BUZZARDS BAY	830	600	9
HINGHAM BAY, BOSTON HARBOR	710	370	9
OUTER BREWSTER ISLAND	530	160	9
DYERS ISLAND, NARRAGANSETT BAY	310	150	9
CONANICUT ISLAND NARRAGANSETT BAY	240	63	6
BLOCK ISLAND, RHODE ISLAND	190	71	6
SEARS ISLAND, PENOBSCOT BAY	150	71	9
CAPE ANN, STRAITSMOUTH ISLAND	140	27	6
PICKERING ISLAND, PENOBSCOT BAY	63	16	9

On a national scale, the Mussel Watch sites where *M. edulis* was sampled had mean tPCB concentrations ranging from 31 to 4300 ppb; 71 percent of the sites had means lower than the Boston Harbor site with the lowest mean tDDT concentration (Hingham Bay, 710 ppb); while 16 percent of the sites had means higher than the Boston Harbor site with the highest mean (Dorchester Bay, 1200 ppb). When the sites where *M. californianus* was sampled were included in the calculations, the range of the individual site means remained the same, while 80 percent of the sites had means lower than the Boston Harbor site with the lowest mean tPCB concentration, and only 11 percent of the sites had means higher than the Boston Harbor site with the highest mean. Based on this data, Boston Harbor mussels were fairly highly contaminated with PCBs when compared to the nationwide sites.

Since 1984 NOAA's Benthic Surveillance Project, a part of the NS&T Program, has sampled winter flounder (*P. americanus*) from an area just west of Deer Island annually. The mean tPCB concentration in the liver of the fish sampled in 1984 and 1985 was 8000±3000 ppb with a range of 4400 to 12,000 ppb. The mean concentration of tPCB in flounder livers for all of the New England Benthic Surveillance sites, excluding Boston Harbor, ranged from a low of 1100±530 ppb at the Casco Bay site to a high of 2900±490 ppb at the Buzzards Bay site. The other three sites had means of: 160±70 ppb, Narragansett Bay; 2500±2100 ppb, Salem Harbor, and 2600±1400 ppb, Merrimack River (Figure 13.20). As Figure 13.20 shows, the mean tPCB concentration of winter flounder liver from Boston Harbor was significantly higher than the mean for any other New England site. Statistical analysis of the log transformed data indicated that the Boston Harbor site was significantly different from Casco Bay and Salem Harbor sites at $p=0.05$. No comparison could be made between Boston Harbor and the three northern-Maine sites because a different species, longhorn sculpin (*Myoxcephalus octodecemspinosus*), was sampled at these sites; although, the mean tPCB concentrations at all these sights was distinctly lower than at the Boston Harbor site (Figure 13.20). The Benthic Surveillance Project sampled winter flounder at four other sites during the same time frame, two in Long Island Sound and one each in Raritan and Great bays in New Jersey. The mean tPCB concentrations at all four sites were lower than the mean for Boston Harbor; they ranged from a low of 1700±460 ppb (East Long Island Sound) to a high of 4000±1300 ppb (Raritan Bay).

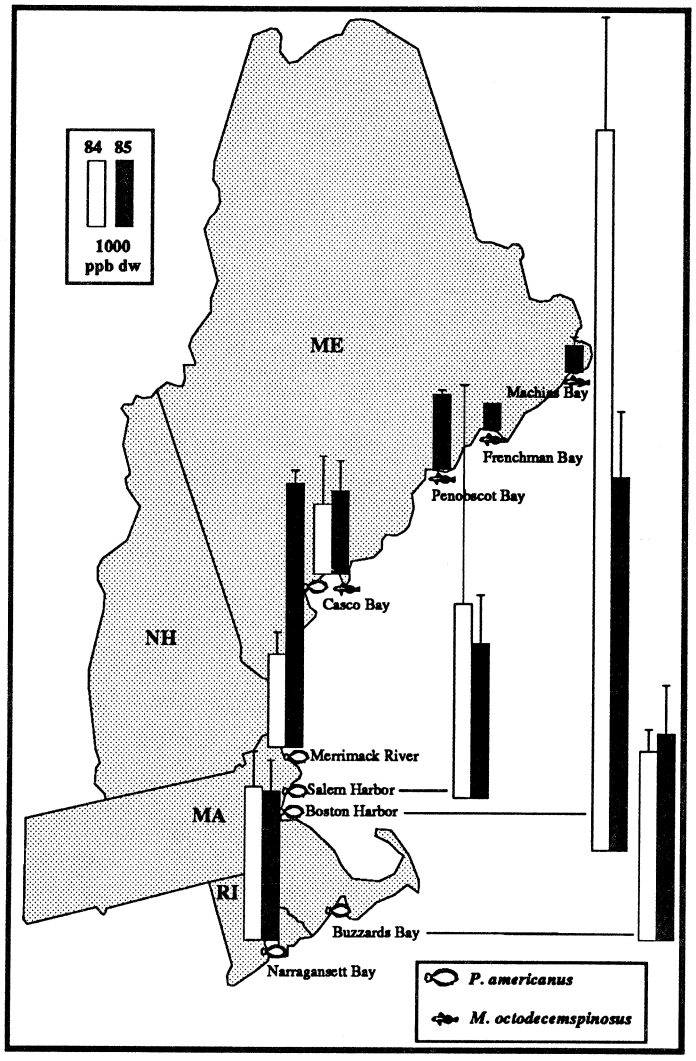


Figure 13.20. Mean tPCB concentrations (ppb dw) in *P. americanus* and *M. octodecemspinosus* liver tissue from the outer New England coast (NOAA, unpublished) (bars represent one standard deviation).

Temporal Trends

From 1983 through 1986, the DMF analyzed flounder muscle tissue samples for PCBs in the form of Aroclor 1254. The mean PCB concentrations for the 4 years ranged from of low of 1300±580 ppb in 1985 to a high of 2900±1500 ppb in 1986 (Table 13.6). The 4 years of data suggest a trend of increasing PCB concentrations in winter flounder muscle tissue. This suggestion is strengthened when the 1985 mean is excluded from consideration due to the small sample size (five). When the log transformed data for all 4 years were statistically compared, 1983, with a mean of 1700±1200 ppb, was significantly different from 1986, with a mean of 2900±1500 ppb, at p=0.05. The lack of any significant difference among 1985 and the other 3 years was possibly due to the small sample size in 1985.

Other available multiyear data sets were the NS&T Programs Benthic Surveillance and Mussel Watch projects. The Benthic Surveillance data indicated a decrease in mean tPCB concentrations in winter flounder liver tissue from 10,000±1700 ppb in 1984 to 5500±920 ppb in 1985. An unpaired, one-tailed t-test in the log transformed data indicated a significant difference between 1984 and 1985 at p=0.05. The Mussel Watch data also suggested a possible trend of decreasing tPCB concentrations. The tPCB concentrations in mussels decreased each year from 1986 through 1988 with means of: 1400±560 ppb in 1986, 1000±440 ppb in 1987, and 410±130 ppb in 1988 (Figure 13.18). Statistical analysis of the log transformed Mussel Watch data indicated a significant difference among 1988 and the two earlier years at p=0.05.

Table 13.6. Means, standard deviations, medians, ranges, and number of samples (count) for tPCB concentrations (ppb dw) in winter flounder muscle tissue samples from Boston Harbor for 1983-86. based on the DMF data.

Year	Mean	Standard Deviation	Median	Range	Count
1983	1700	1200	1500	500-5000	26
1984	2000	1800	1800	250-8000	16
1985	1300	570	1500	500-2000	5
1986	2900	1500	2900	750-6500	18

The EPA Deer Island site had PCB (Aroclor 1254) concentrations in the soft parts of mussels of 635 and 735 ppb in 1976 and 1977, respectively. The NS&T Program Deer Island site (which is about 0.5 miles northwest of the EPA site) had yearly mean tPCB concentrations (sum of eight chlorination levels) in mussels of 1400, 700, and 480 ppb in 1986, 1987, and 1988, respectively. When the two data sets were compared, there appeared to be a slight decrease in PCB levels between the mid 1970s and 1988.

Summary

Boston Harbor sediments were found to contain tPCB at levels which were more than an order of magnitude higher than regional background levels (not natural background levels which should be zero). In some cases, tPCB levels in Boston Harbor exceeded other sites by more than an order of magnitude. The only New England sites which approached the most contaminated Boston Harbor sites in levels of PCBs in sediments were in Salem Harbor and Buzzards Bay (Table 13.3). When the NS&T Program data for the Boston Harbor and San Francisco Bay were compared, the Boston Harbor mean, 420±340 ppb (excluding the 51,000 ppb sample), was more than 4 times higher than the San Francisco Bay mean, 99±159 ppb (Long *et al.*, 1988) (Table 13.7).

Table 13.7. Comparison of tPCB sediment statistics for Boston Harbor, NS&T Program Reference (based on the five New England sites with the lowest levels of tPCB), and San Francisco Bay in ppm. Statistics for San Francisco Bay derived from Long *et al.*, 1988 (* excludes 51,000 ppb sample).

Area	Mean	Standard Deviation	Median	Range	Count
Boston*	560	960	260	2.5 - 7000	181
NS&T Boston*	420	340	280	13.0 - 1000	24
NS&T Reference	17	8	14	6.4 - 32	20
NS&T San Francisco Bay	99	159	50	5.0 - 824	64

While the overall combined data set suggested a trend of decreasing PCB levels going from the inner harbor to the southeast harbor (Table 13.1), this trend was not clearly supported by the individual data sets (Table 13.2). However, in all cases where the data existed, the northwest harbor had higher PCB concentrations in the surficial sediments than did the southeast harbor (Table 13.2). The NS&T Program data indicated approximately an order of magnitude difference among the Boston Harbor site with the lowest mean PCB concentration (Hingham Bay, 66±30 PPB) located in the southeast harbor and the two harbor sites with the highest means (southwestern Deer Island and Dorchester Bay, 740±300 and 640±240, respectively) located in the northwest harbor. The overall data, as well as three of the four individual data sets that included data for the northwest harbor (USACOE, 1972-88; 1981;DEQE, 1986; 1987; and NOAA, unpublished) indicated that the Dorchester Bay area of the northwest harbor had higher levels of PCBs than did the Winthrop Bay area. No clear temporal trend in sediment contamination was apparent based on the available data.

Based on the available data, Boston Harbor biota appears to be highly contaminated with PCBs. Boston Harbor mussels had some of the highest mean tPCB concentrations of all the New England NS&T Program sites sampled, although, the sites in the upper reaches of Buzzards Bay had even higher levels of PCBs. When compared to all NS&T Program mussel sites sampled in the country, the Boston Harbor sites fall into the upper 20 percent. The winter flounder liver data also suggested that Boston Harbor had high levels of PCBs since, among the NS&T Program sites, the Boston site had the highest mean tPCB

concentration among all the NS&T Program winter flounder sites. The winter flounder and American dab muscle tissue data indicated that PCB levels were significantly lower in Massachusetts Bay and other state coastal waters than in Boston Harbor, except for Buzzards Bay and the Beverly-Salem Harbor area. There were no obvious geographic trends in the PCB content of biota within Boston Harbor based on the available data. While the winter flounder muscle data indicated only yearly fluctuations in PCB levels between 1983 and 1986, the mussel data suggested a possible trend of decreasing PCB levels between 1986 and 1988.

PAH

Polynuclear aromatic hydrocarbons (PAHs) (sometimes referred to as polycyclic aromatic hydrocarbons) are ubiquitous in marine sediments with concentrations roughly correlated to the proximity and amount of anthropogenic activity (Windsor and Hite, 1979). The two principle sources of PAHs are petroleum and combustion products (Boehm, 1983). PAHs have variable degrees of solubility and toxicity. Solubility decreases and toxicity increases with an increase in molecular weight either due to methylation or an increase in the number of rings (Boehm, 1983). Above about four rings PAHs become less soluble in water and thus less readily available to biota; however, many of the five-ring PAHs (*i.e.*, dibenz(ah)anthracene and benzo(b)fluoranthene) are carcinogenic once introduced to biota (Boehm, 1983).

Different researchers have measured various combinations and numbers of individual PAHs. Table 14.1 lists the PAHs analyzed by the various researchers whose data sets were used in this report. As Table 14.1 shows, only six PAHs (phenathrene, fluoranthene, pyrene, chrysene, benz(a)anthracene, and benzo(a)pyrene (B(a)p) were common to all the sediment analyses and only four PAHs (phenathrene, fluoranthene, pyrene, and chrysene) were common to all the biota analyses. Because of this difference in PAHs measured by the various researchers, the following discussion will report the overall mean for each data set based on the total number of PAHs in the data set and the common PAHs (six for sediment and four for biota).

Because the following discussion is restricted to the summed concentrations of various individual PAHs and not to the concentrations of the individual PAHs, no statistical comparisons were performed. Statistical comparisons were not considered to be justified because any analysis based on the means and standard deviations of sums of independent variables (*i.e.*, tPAH) does not account for the difference in variability of the individual variables (*i.e.*, individual PAHs) and their contribution to the variability of the total. The only justifiable statistical analysis of the data would be based on the concentrations of the individual PAHs.

Sediments

Between 1982 and 1987 over 110 surficial sediment samples were analyzed for PAH content. Based on the six PAHs which were common to all the data sets (Table 14.1), the overall mean total PAH ($tPAH^6$) concentration in Boston Harbor was 17,000 ppb with a standard deviation of 73,000 and a range of 16 to 680,000 ppb. The median was 2800 ppb. When the three samples which had reported PAH concentrations greater than 200,000 ppb were excluded from the calculations, the mean became 6000 ppb with a standard deviation of 12,000 ppb and a range of 16 to 93,000 ppb. The median was 2700 (Table 14.2). The majority of the samples, approximately 59 percent, had $tPAH^6$ concentrations between 1000 and 10,000 ppb. Approximately 28 percent of the samples had $tPAH^6$ concentrations of less than 1000 ppb; while 11 percent had concentrations between 10,000 and 100,000 ppb. Only three samples (approximately 3%) had $tPAH^6$ concentrations greater than 100,000 ppb.

Geographic Trends

When the combined data were broken down by harbor division, both the means and medians indicated a trend of decreasing $tPAH^6$ concentrations from the inner harbor (18,000 and 17,000 ppb, respectively) to the southeast harbor (1700 and 630 ppb, respectively) (Table 14.2). When the northwest harbor was further subdivided, the Dorchester Bay area had a mean $tPAH^6$ concentration of 8100±21,000 ppb while the Winthrop Bay area had a mean of 3600±4000 ppb. The medians for the two areas were 3000 and 3400 ppb, respectively. The large standard deviations and large difference between the means and the medians suggest a heterogeneous distribution of PAHs in Boston Harbor. In comparison, 83 samples from New England coastal waters (*i.e.*, not from harbors or Narragansett Bay) had a mean $tPAH^6$ concentration of 1100±1100 ppb with a range of 29 to 5300 ppb and a median of 680 ppb.

Table 14.1. The PAHs analyzed by the various researchers; boldface type denotes those PAHs common to all sediment analyses while those underlined are common to all biota analyses (^ sediment only; * biota only; ** biota in 88 only, ° sediment in 86 only)

	NOAA BS^ 84-85	NOAA MW 86-88	EPA* 76-77	Boehm *et al.*, 83	EPA 87	Mass. DEQE^ 85-86	Shiaris/ Jambard-Sweet^ 82
Acenaphthylene		X**				X°	
Napthalene	X	X	X	X			X
2-Methylnapthalene	X	X					
1-Methylnapthalene	X	X					
C1N (142)			X	X			
Dimethnaphthalene	X	X	X				
C2N (156)				X			
2,3,5-Trimethylnaphthalene		X					
C3N (170)				X			
C4N (184)				X			
Fluorene	X	X		X	X	X°	
C1F (180)				X			
C2F (194)				X			
C3F (208)				X			
Acenap+Fluorene							X
Acenapthene	X	X				X°	
Biphenyl	X	X					
Phenathrene	X	X	X	X	X	X	X
1-Methylphenathrene	X	X	X				
C1P (192)				X			
C2P (206)			X	X			
C3P (220)				X			
C4P (234)				X			
Anthracene	X	X			X	X	X
C1PA					X		
C2PA					X		
C3PA					X		
C4PA					X		
Fluoranthene	X	X	X	X	X	X	X
Pyrene	X	X	X	X	X	X	X
Benz(a)anthracene	X	X		X	X	X	
Chrysene+ Benz(a)anthracene							X
Chrysene	X	X	X	X	X	X	
Benzo(b)fluoranthenes		X**				X	X
Benzo(k)fluoranthenes		X**				X	
Benzofluoranthenes				X	X		
Benzopyrene			X		X*		
Benzo(e)pyrene	X	X		X	X		
Benzo(a)pyrene	X	X		X	X	X	X
Perylene	X	X		X	X		
Indeno(1,2,3-c,d)pyrene		X**			X		
Benzo[ghi]perylene		X**			X	X°	
Dibenz[ah]anthracene	X	X			X	X°	
S276					X		
Dibenzothiophene(184)			X	X			
C1DBT(198)			X	X			
C2DBT(212)				X			
C3DBT(226)				X			
S278					X		
Coronene					X		
S302					X		

C1N, C2N, C3N and C4N - alkylated naphthalenes
C1F, C2F, C3F and C4F - alkylated fluorenes
C1P, C2P, C3P and C4P - alkylated phenanthrenes
C1PA, C2PA, C3PA and C4PA - alkylated phenanthrenes and anthracenes
C1DBT, C2DBT, C3DBT and C4DBT - alkylated benzothiophenes
S276, S278 and S302 - sum of PAHs with molecular weights of 276, 278 and 302 respectively
numbers in parentheses are molecular weights.

Table 14.2. Means, standard deviations, medians, ranges, and number of samples (count) for $tPAH^6$ concentrations (ppb dw) in surficial sediments of all of Boston Harbor and for the four regions of the Harbor, based on all the available data sets (*excludes the three samples over 200,000 ppb, see text).

	Mean	SD	Median	Range	Count
OVERALL*	6000	12,000	2700	16 - 93,000	109
INNER HARBOR*	18,000	17,000	17,000	300 - 59,000	11
NORTHWEST HARBOR*	5800	14,000	3300	56 - 93,000	40
CENTRAL HARBOR	4700	8600	2400	16 - 45,000	43
SOUTHEAST HARBOR	1700	2500	630	170 - 9200	15

In 1982, Shiaris and Jambard-Sweet (1986) analyzed triplicate surficial sediment samples from 23 sites in Boston Harbor and 1 site (The Graves) in Massachusetts Bay for levels of nine individual PAHs (Table 14.1). The mean $tPAH^9$ concentration for Boston Harbor was 52,000±150,000 ppb with a range of 592 to 720,000 ppb. The mean $tPAH^6$ concentration was 49,000±150,000 ppb with a range of 394 to 670,000 ppb. When the two samples with concentrations greater than 100,000 ppb were excluded from the calculations, the mean $tPAH^9$ concentration became 12,000±21,000 ppb with a range of 592 to 94,000 ppb. The mean $tPAH^6$ concentration became 11,000±20,000 ppb with a range of 394 to 93,000 ppb (Table 14.3). The median concentrations, excluding the two high samples, were 5700 and 5500 ppb (Table 14.3) for $tPAH^9$ and $tPAH^6$, respectively. Approximately 65 percent of the Boston Harbor sites had $tPAH^6$ concentrations between 1000 and 10,000 ppb and approximately 17 percent had concentrations between 10,000 and 100,000 ppb. The remaining 18 percent were evenly divided (two each) between less than 1000 ppb and greater than 100,000 ppb. The single site outside the Harbor, The Graves, had a $tPAH^9$ concentration of 740 ppb and a $tPAH^6$ concentration of 550 ppb.

Table 14.3. Mean/median $tPAH^6$ concentrations in the surficial sediments of Boston Harbor and the four divisions of the Harbor, in ppb dw, based on the data of Shiaris and Jambard-Sweet (1983), Boehm *et al.*, 1984; MA DEQE, 1986 and 1987; EPA, 1988; and NOAA's NS&T Program (unpublished). The numbers in parentheses are the number of data points used to calculate the means (*excludes the samples over 200,000 ppb, see text).

	Shiaris & Jambard-Sweet*	Boehm *et al.**	Mass. DEQE	EPA	NOAA NS&T
	82	83	85-86	87	84-87
OVERALL	11,000 (21) /5500	2100 (4) /2000	6100 (25) /610	5100 (34) /2800	3800 (25) /3500
INNER HARBOR	15,000 (4) /23,000	N/A	20,000 (7) /20,000	N/A	N/A
NORTHWEST HARBOR	16,000 (8) /5500	1200 (1)	1100 (12) /700	N/A	4800 (19) /3600
CENTRAL HARBOR	7400 (3) /2200	2900 (2)	<600 (4)	5100 (34) /2800	N/A
SOUTHEAST HARBOR	3200 (6) /1700	1400 (1)	<600 (2)	N/A	560 (6) /510

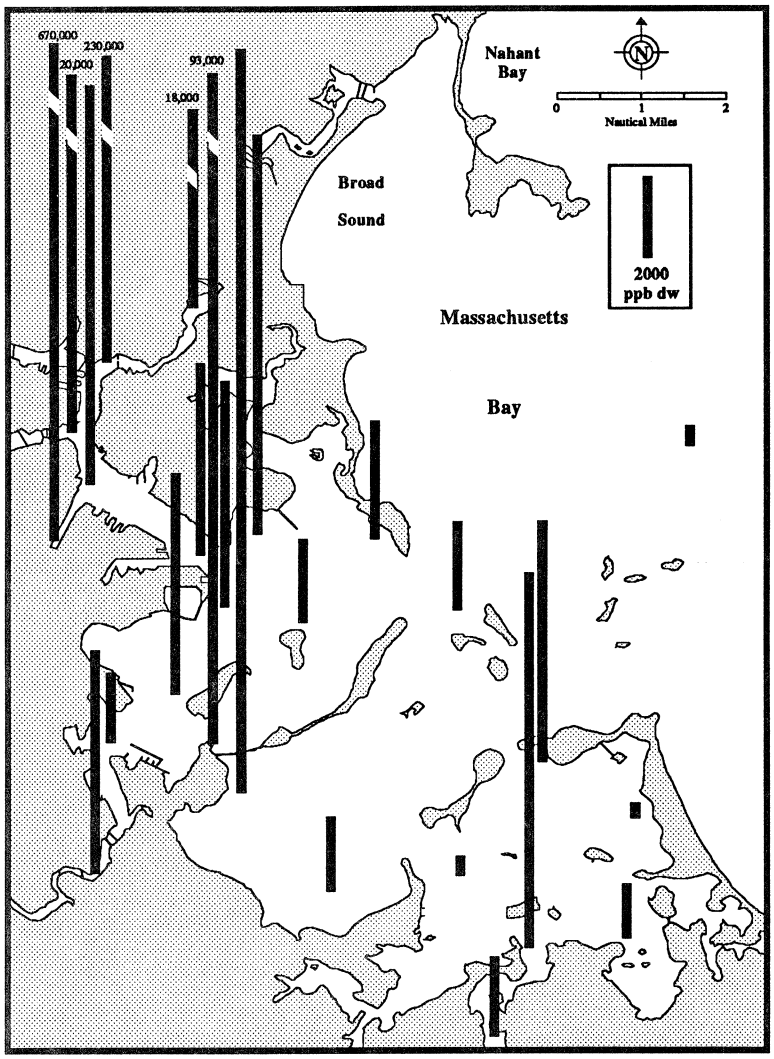


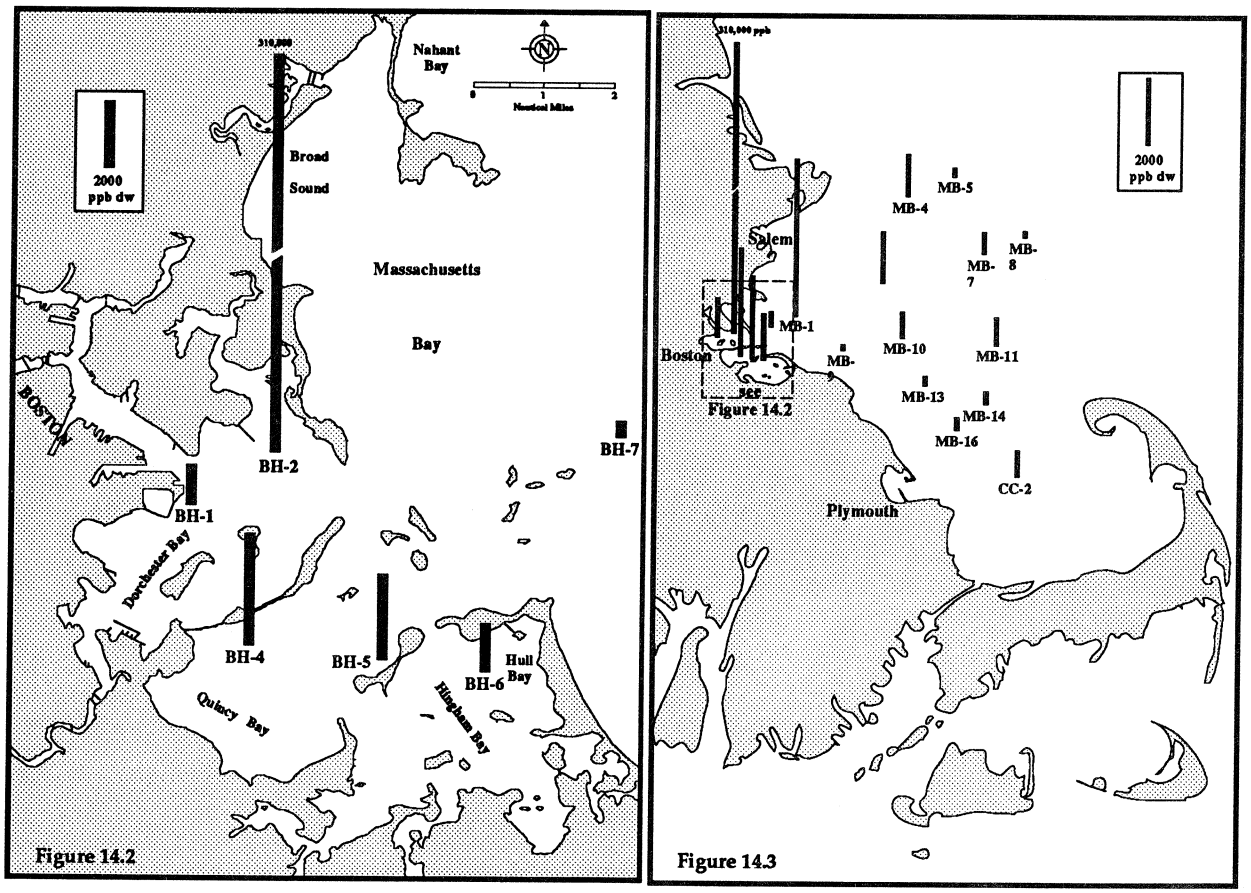
Figure 14.1. tPAH6 concentrations (ppb dw) in the surficial sediments of Boston Harbor in 1982 (Shiaris and Jambard-Sweet, 1986).

When the data from the Harbor were broken down by harbor division, the inner harbor had the highest mean $tPAH^6$ concentration, 160,000±270,000 ppb with the northwest harbor second, 16,000±31,000 ppb. However, when the two sites with concentrations in excess of 100,000 ppb were excluded from the calculations, the inner harbor became second, 15,000±9700 ppb (Table 14.3). The central harbor had the third highest mean, 7400±9400 ppb while the southeast harbor had the lowest, 3200±3600 ppb. The means, excluding the two high sites, suggest that the inner and northwest harbors had approximately equivalent concentrations, followed by the central, and then the southeast harbor, the medians clearly suggest a trend of decreasing $tPAH^6$ concentrations from the inner harbor (23,000 ppb) to the northwest harbor (5500 ppb) to the central harbor (2200 ppb and finally to the southeast harbor (1700 ppb) (Table 14.3). When the northwest harbor was further subdivided, the Dorchester Bay area had the highest mean $tPAH^6$ concentration (19,000±36,000 ppb) while the Winthrop Bay area had the second lowest mean (6400±4900 ppb). However, based on the medians, the Winthrop Bay area (6400 ppb) ranked second and the Dorchester Bay area (5500 ppb) ranked third. The large standard deviations and the large differences between the means and medians suggest that PAHs are heterogenously distributed throughout Boston Harbor. This heterogenous distribution of PAHs is displayed graphically in Figure 14.1.

In 1983, NOAA sponsored a study of organic pollution in Boston Harbor, Massachusetts Bay, and Cape Cod Bay (Boehm *et al.*, 1984). Five replicate surficial sediment samples from 5 sites in Boston Harbor and 14 sites outside the Harbor were analyzed for levels of 27 individual PAHs (Table 14.1). The mean $tPAH^{27}$ concentration for Boston Harbor was 180,000±390,000 ppb with a range of 2400 to 870,000 ppb. The mean $tPAH^6$ concentration for the Harbor was 64,000±140,000 ppb with a range of 1200 to 310,000. When the single site with tPAH concentration greater than 100,000 ppb was excluded from the calculations, the mean $tPAH^{27}$ concentration became 4500±2300 ppb with a range of 2400 to 6900 ppb. The mean $tPAH^6$ concentration became 2100±990 ppb with a range of 1200 to 3300 ppb. The medians, excluding the high value, were 2500 and 2000 ppb for $tPAH^{27}$ and $tPAH^6$,

respectively. When the data was analyzed by harbor division, there appeared to be a trend of decreasing PAH^6 concentrations going from the northwest (160,000 ppb) to the southeast harbor (1400 ppb) (Figure 14.2). However, when the 310,000 ppb site (Figure 14.2) was excluded from the calculations the northwest harbor had the lowest PAH^6 concentration (1200 ppb) and the central harbor had the highest (2900 ppb) (Table 14.3). The 310,000 ppb site was located in the Winthrop Bay area of the northwest harbor. The 1200 ppb northwest harbor site was located in the Dorchester Bay area (Figure 14.2). This difference between the two northwest harbor sites might have been due to differences in contamination levels between the two areas or to a heterogenous distribution of PAHs among sites throughout the Harbor.

When the data for Massachusetts and Cape Cod bays were compared to the Boston Harbor data, there was more than a twofold reduction in mean $tPAH^6$ concentrations going from the Harbor to the bays, even when the 310,000 ppb site was excluded from consideration. The combined bays mean was 940±1200 ppb as compared to the Boston Harbor mean of 2100±990 ppb. The $tPAH^6$ concentrations at the individual sites ranged from 190 ppb (MB-8) to 4812 ppb (MB-1) (Figure 14.3). Only three bay sites had $tPAH^6$ concentrations in excess of 1000 ppb, while none of the Harbor sites had concentrations below 1000 ppb. MB-1 is a depositional site a short way outside of Boston Harbor which receives materials from the Harbor (Boehm *et al.*, 1984); when this site was excluded from the calculations, the mean for the bays became 640±430 ppb.



Figures 14.2 & 14.3. Mean tPAH6 concentrations (ppb dw) in the surficial sediments of Boston Harbor and Massachusetts and Cape Cod bays in 1983 (Boehm *et al.*, 1984).

Between 1985 and 1986, the Massachusetts DEQE, as part of their annual Boston Harbor Water Quality and Wastewater Discharge Survey, analyzed 25 surficial sediment samples for PAHs (MA DEQE, 1986; 1987). The results of the 1985 analyses were reported as

concentrations of 10 individual PAHs while those for 1986 were reported as concentrations of 14 individual PAHs. Based on the 9 common PAHs for all 25 samples (Table 14.1), the overall mean $tPAH^9$ concentration for Boston Harbor was 7700±16,000 ppb with a range of from 450 to 68,000 ppb and a median concentration of 1000 ppb. The overall mean $tPAH^6$ concentration was 6100±13,000 ppb with a range of from 300 to 59,000 ppb and a median of 610 ppb. The majority of the samples (approximately 56 percent) had $tPAH^6$ concentrations less than 1000 ppb (eight samples had concentrations below the detection limits of 600 ppb). Approximately 28 percent of the samples had $tPAH^6$ concentrations of between 1000 and 6000 ppb and 16 percent of the samples had concentrations in excess of 10,000 ppb. Figure 14.4 graphically displays the DEQE data by station and year.

When the DEQE data was broken down by harbor division, the surficial sediments in the inner harbor had the highest mean $tPAH^6$ concentration, 20,000±20,000 ppb. Those of the northwest harbor followed with 1100±980 ppb. The central and southeastern harbor divisions had $tPAH^6$ concentrations in all six samples below the detection limits (Table 14.3). When the northwest harbor was further subdivided, the Dorchester Bay area had the second highest mean $tPAH^6$ concentration in its surficial sediments, 1600±1200 ppb and the Winthrop Bay area had the third highest, 670±320 ppb. These means, along with Figure 14.4, suggest a trend of decreasing levels of PAHs from the inner harbor to the southeast harbor.

In 1987, a study of Quincy Bay, essentially restricted to the central harbor area, was conducted under the auspices of the U. S. EPA (EPA, 1988) (Figure 14.5). The study measured the concentrations of 22 individual PAHs (Table 14.1) in 34 samples of surficial sediments. The overall mean $tPAH^{22}$ concentration in the surficial sediments for the study was 13,000±23,000 ppb with a range of 61 to 130,000 ppb and a median of 6700 ppb. The overall

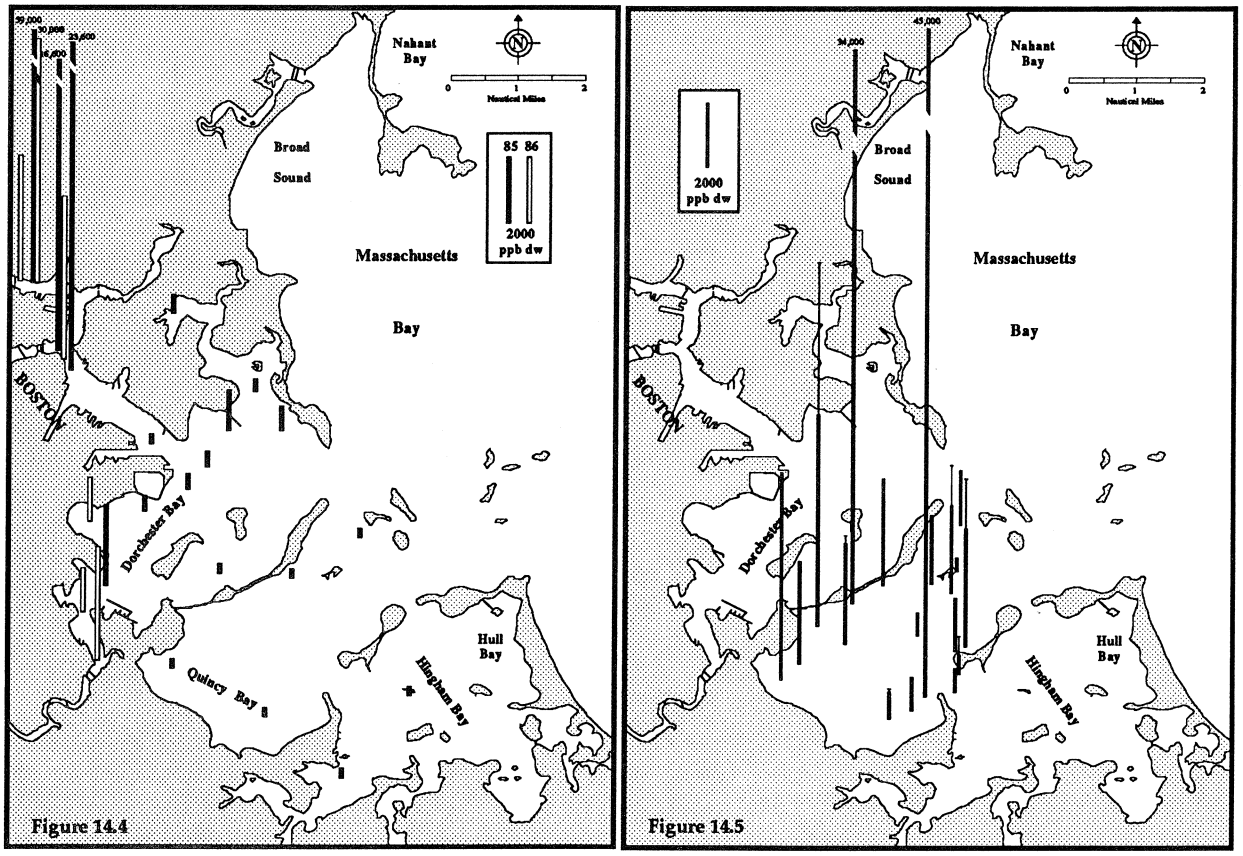


Figure 14.4 & 14.5. tPAH6 concentrations (ppb dw) in surficial sediments of Boston Harbor in 1985 and 1986 (MA DEQE, 1986, 1987) (Fig. 14.4) and in 1987 (US EPA, 1988) (Fig. 14.5) (bars represent one standard deviation).

mean tPAH^6 concentration in the surficial sediments for the study was 5100±9200 ppb with a range of 16 to 45,000 ppb and a median of 2800 ppb (Table 14.3). Only three (9%) of the samples had tPAH^6 concentrations in excess of 10,000 ppb. As Figure 14.5 clearly shows that there is no trend in tPAH^6 concentration within Quincy Bay and the PAHs appear to have been heterogenously distributed there.

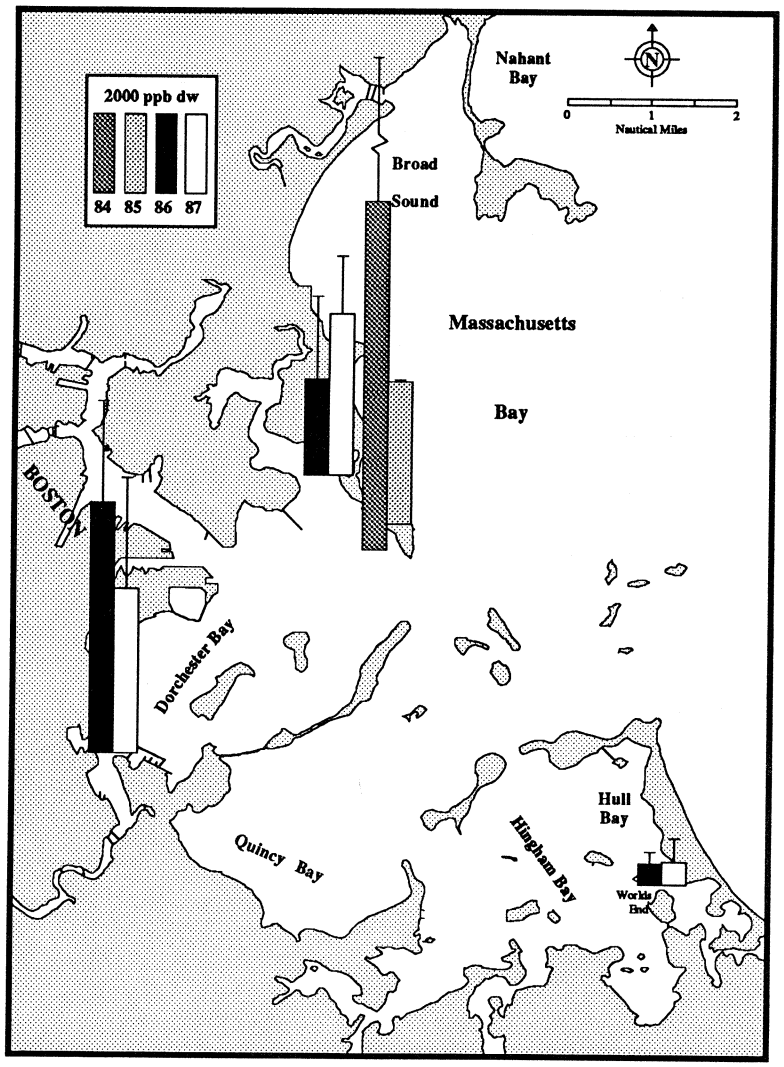


Figure 14.6. tPAH6 concentrations (ppb dw) in the surficial sediments of Boston Harbor for 1984-87 (NOAA, unpublished) (bars represent one standard deviation).

Since 1984, NOAA's NS&T Program has sampled and analyzed surficial sediments from sites around Boston Harbor for several analytes, including PAHs. PAH concentrations were reported as values for 18 individual PAHs by the Benthic Surveillance Program and 19 individual PAHs by the Mussel Watch Program (Table 14.1). The overall mean tPAH^{18} concentration in surficial sediments of the harbor was 12,000±18,000 ppb. Individual sample values ranged from 78 to 65,000 ppb and the median was 5500 ppb. The overall mean tPAH^6 concentration in surficial sediments of the harbor was 3800±3800 ppb. Individual sample values ranged from 56 to 18,000 ppb and the median was 3500 ppb. Only one sample (4%) had a concentration of 10,000 ppb or higher while 24 percent of the samples had concentrations of less than 1000 ppb. Figure 14.6 portrays mean tPAH^6 concentrations graphically by year and site. The individual site means, based on all 4 years of available data, were: 560±380 ppb off the northern tip of Worlds End, 3200±1800 ppb northwest of Deer Island, 5200±2600 ppb in southwestern Dorchester Bay, and 5800±5500 ppb southwest of Deer Island. When the data were grouped by harbor divisions, the means suggested that the northwest harbor (4800±3800 ppb) had higher tPAH^6 concentrations than did the southeast harbor (560±380 ppb). When the northwest harbor division was subdivided, the Winthrop Bay area mean was 4600±4300 ppb and the Dorchester Bay area mean was 5200±2600 ppb.

On a broader scale, between 1984 and 1987, the NOAA NS&T Program analyzed surficial sediment samples from 23 sites from 11 areas, along the outer New England Coast. Figure 14.7 displays the means and standard deviations for the 11 coastal areas, and clearly shows that the mean tPAH^6 concentration of the NS&T Program sites in Boston Harbor was higher than all other areas sampled, except for Salem Harbor. However, it should be noted

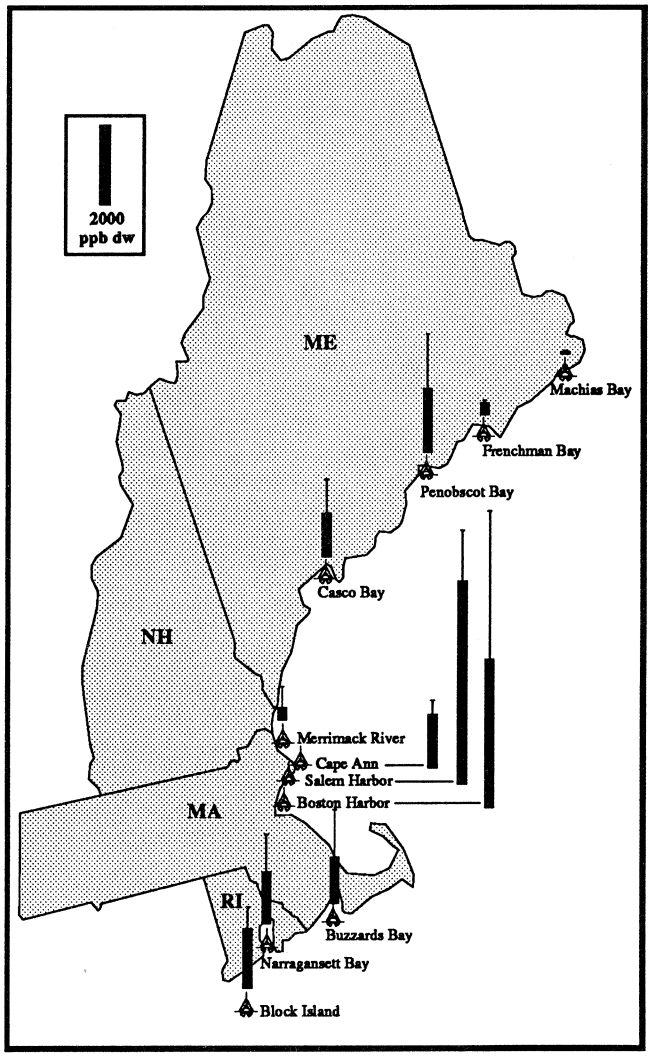


Figure 14.7. tPAH6 concentrations (ppb dw) in the surficial sediments of the outer New England coast for 1984-87 (NOAA, unpublished) (bars representone standard deviation).

that only one site was sampled in Salem Harbor while four sites were sampled in Boston Harbor. When the individual sites were compared, Boston Harbor sites had the first, second, and fourth highest tPAH^6 concentrations; while Salem Harbor had the third highest site (Table 14.4). Only two other areas had mean concentrations in excess of 100 ppb, Buzzards Bay (240±220 ppb) and Narragansett Bay (110±110 ppb).

In an attempt to determine a regional background reference concentration for tPAH^6 in coastal sediments, the overall mean for the five New England sites with the lowest means was calculated; it was 320±330 ppb. Since much of the anthropogenically produced PAHs present in the marine environment were origionally airborne as the result of the combustion of fossil fuels for transportation, heating, and power generation, this mean does not represent natural background levels, *i.e.* nonanthropogenically produced PAHs. The overall mean for Boston Harbor concentration of tPAH^6 (3800 ppb) was more than an order of magnitude greater than the calculated regional background concentration.

Temporal Trends

Because the data is scarce, little can be said with confidence about temporal trends of PAH contamination in Boston Harbor

Table 14.4 The five outer New England coast NOAA NS&T Program sites with the lowest and highest mean tPAH^6 concentrations (ppb dw) based on data from 1984 through 1987.

Site	Mean	Standard Deviation	Count
MACHIAS BAY, MAINE	63	26	4
FRENCHMAN BAY, MAINE	280	76	4
MERRICMACK, RIVER	300	540	5
CENTRAL BUZZARDS BAY	360	320	9
GOOSEBURY NECK, BUZZARDS BAY	450	330	6
PICKERING ISLAND, PENOBSCOT BAY	3000	2400	3
NORTHWESTERN DEER ISLAND	3200	1800	6
SALEM HARBOR	5100	1300	7
DORCHESTER BAY	5200	2600	6
SOUTHWESTERN DEER ISLAND	5800	5500	7

sediments. Figure 14.8A gives the yearly means of $tPAH^6$ in the surficial sediments of Boston Harbor based on all the available data sets, excluding the three samples in which $tPAH^6$ exceeded 100,000 (two from 1982 and one from 1983). The yearly means fluctuate from a low of 2100 ppb in 1983 (excluding the 310,000 ppb sample) to a high of 11,000 ppb in 1982 (excluding the 230,000 and 670,000 ppb samples). The last 3 years of available data, 1985-87, gave relatively consistent yearly means going from a high of 5400 ppb in 1985 to a low of 4700 ppb in 1987. While the means for all the years suggest a decrease in $tPAH^6$ between the early and mid 1980s and continuing from 1985 through 1987, the extremely large standard deviations preclude any such conclusion. The differences in yearly means and the large standard deviations can be largely explained by the inclusion of inner harbor data for three of the years (1982, 1985, and 1986) which had $tPAH^6$ concentrations generally an order of magnitude higher than the outer harbor, and the inclusion of a few scattered samples (six) in the outer harbor with concentrations exceeding 10,000 ppb. When the inner harbor data and the outer harbor data exceeding 10,000 ppb were excluded from the calculations, the standard deviations were greatly reduced; and, with the exception of 1985, the yearly means were all between 2000 and 4000 ppb (Figure 14.8B). The inner harbor means for the 3 years for which data were available, fluctuated from 15,000 ppb in 1982, to 25,000 ppb in 1985, and to 13,000 ppb in 1986.

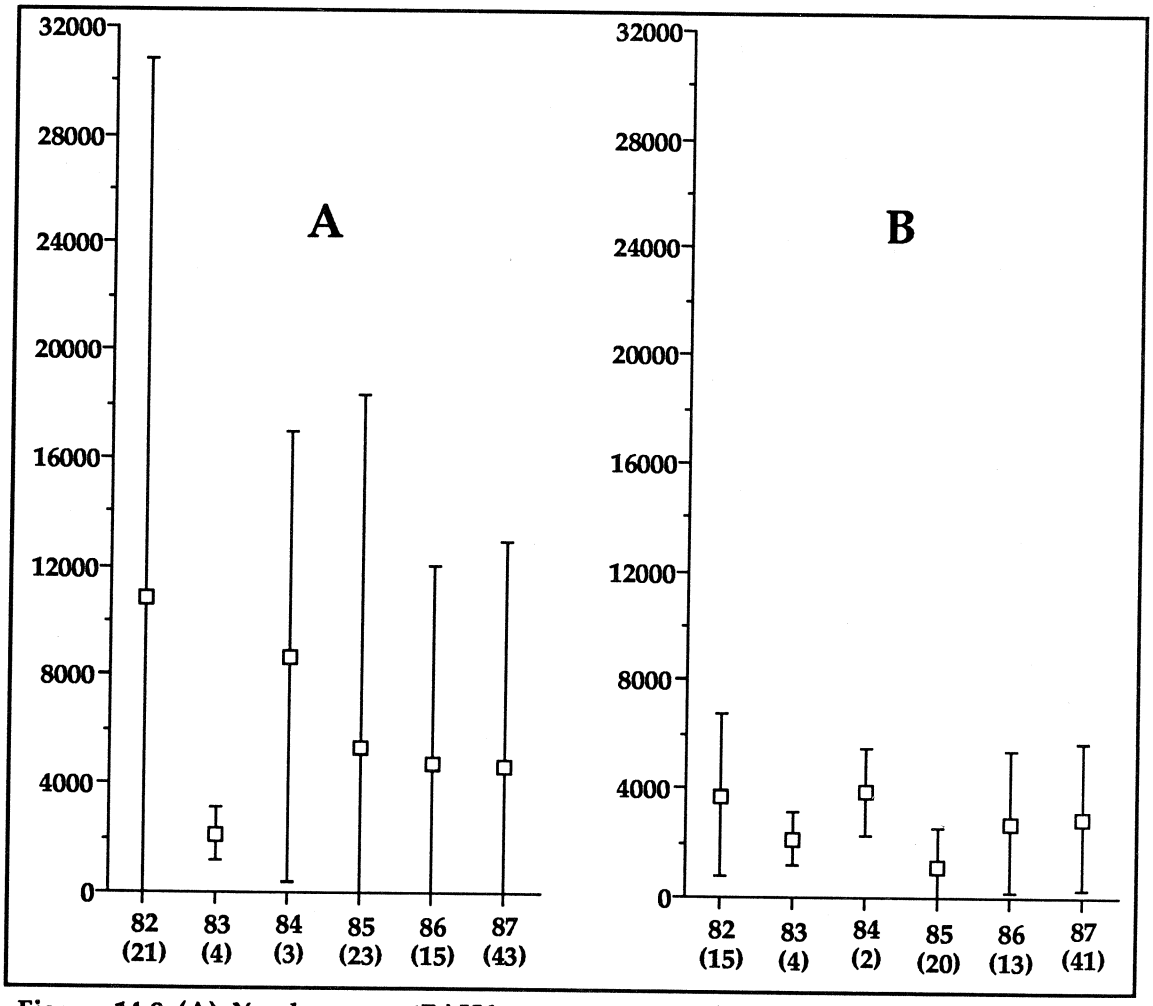


Figure 14.8 (A) Yearly mean tPAH6 concentrations (ppb) in the surficial sediments of Boston Harbor based on all the available data sets excluding the three samples with concentrations in excess of 100,000 ppb; (B) yearly mean tPAH6 concentrations (ppb) in the surficial sediments of outer Boston Harbor based on all the available data sets excluding the six samples with concentrations in excess of 10,000 ppb (bars represent one standard deviation, numbers in () are sample sizes).

The only single data set which spanned more than 1 year was that from NOAA's NS&T Program (NOAA, unpublished). It covered the 4 years from 1984-87, although the same sites were not sampled in each of the 4 years. The yearly mean $tPAH^6$ concentration ranged from a high of 8700 ppb in 1984 to a low of 2900 ppb in 1987. Only the southwest Deer Island site was sampled in 1984 and included the only NS&T Program sample from Boston Harbor which exceeded 10,000 ppb (18,000 ppb). When this sample was excluded from the calculations, the 1984 mean became 3900 ppb, still the highest. The mean for 1985 was 3600 ppb, while that for 1986 was 3000 ppb. The yearly means suggest a steady decrease in $tPAH^6$ concentrations between 1984 and 1987, but the 1984 and 1985 data were only from the southwest Deer Island site while the 1986 and 1987 data were from the northwest Deer Island, Dorchester Bay, and Worlds End sites (Figure 14.6). Therefore, based on this data there was no apparent trend of $tPAH^6$ contamination levels during the 4 years covered by NOAA's data.

Biota

The data used in this report includes the concentrations of PAHs from 74 tissue samples from specimens taken from Boston Harbor between 1976 and 1988. As with the sediment data, PAH concentrations were reported as concentrations of various individual PAHs with different researchers reporting concentrations for different numbers of and different individual PAHs. There were only four PAHs (phenathrene, fluoranthene, pyrene, and chrysene) common to the four different data sets used for this report (Table 14.1). Table 14.5 gives the statistics based on the data for these four PAHs broken down by species and tissue type. In addition to the tissue analysis for PAHs, data are also included from NOAA's NS&T Program Benthic Surveillance Project for PAH equivalents in the bile of winter flounder (*P. americanus*) because fish rapidly metabolize PAHs thus maintaining relatively low levels in their tissues even when exposed to high environmental levels of PAHs (Krahn *et al.*, 1986). Individual samples with the lowest concentrations of $tPAH^4$ were muscle tissue taken from winter flounder (*P. americanus*), less than 2.0 ppb. This would be expected since fish rapidly metabolize PAHs; and, in fact, 8 of the 12 muscle tissue samples analyzed had PAH levels below the detection limits for the individual PAHs.. The highest concentration of $tPAH^4$ reported for a single sample was 5400 ppb from the soft parts of mussels (*M. edulis*), while the highest mean $tPAH^4$ concentration was 2700 ppb in lobster (*H. americanus*) hepatopancreas. The overall data for winter flounder and lobster suggest that PAHs tend to accumulate more in liver or liver-like tissue than in muscle tissue.

Table 14.5 Harborwide means, standard deviations, medians, ranges, and sample sizes (count) for $tPAH^4$ concentrations (ppb dw) in biota by organism and tissues based on all the available data sets (* transplants).

		Mean	SD	Median	Range	Count
P. americanus						
	muscle	2.2	0.33	2.0	<2.0 – 3.0	12
H. americanus						
	hepatopancreas	2700	310	2700	2300 – 3200	8
	muscle	110	22	110	75 – 160	16
Cancer borealis						
	soft parts	31	22	38	6.5 – 48	3
M. arenaria						
	soft parts	96	11	–	88 – 100	2
M. edulis						
	soft parts	1700	1100	1700	280 – 5400	29
*C. virginica**						
	soft parts	200	57	200	130 – 260	4

Geographic Trends

In 1976 and 1977, the U. S. EPA sampled mussels and other bivalves from 107 sites nationwide. The samples were analyzed for a variety of metals and organic analytes, including 12 individual PAHs (Table 14.1) (Farrington *et al.*, 1982). Two composite samples of *M. edulis* from a site on the northwest side of Deer Island were found to have a mean $tPAH^{12}$ concentration in the soft parts of 2900 ppb and a mean $tPAH^{4}$ concentration of 830 ppb. Between Block Island and the Canadian Border, 10 other New England sites were sampled and had mean $tPAH^{12}$ concentrations in the soft parts of *M. edulis* ranging from 30 ppb at the sites at Cape Ann, Massachusetts and Sakonnet Point, Rhode Island, to 180 ppb at the sites at Sears Island and Portland, Maine. The mean $tPAH^{4}$ concentration at these sites ranged from 20 ppb at Cape Ann and Cape Newagen, Maine, to 110 ppb at Portland, Maine.

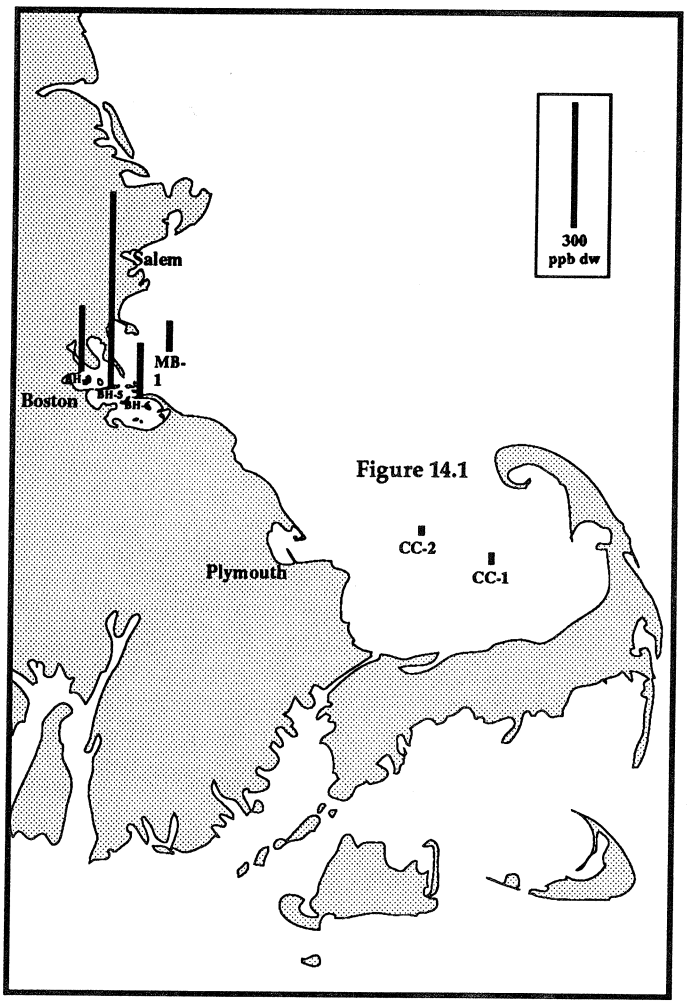


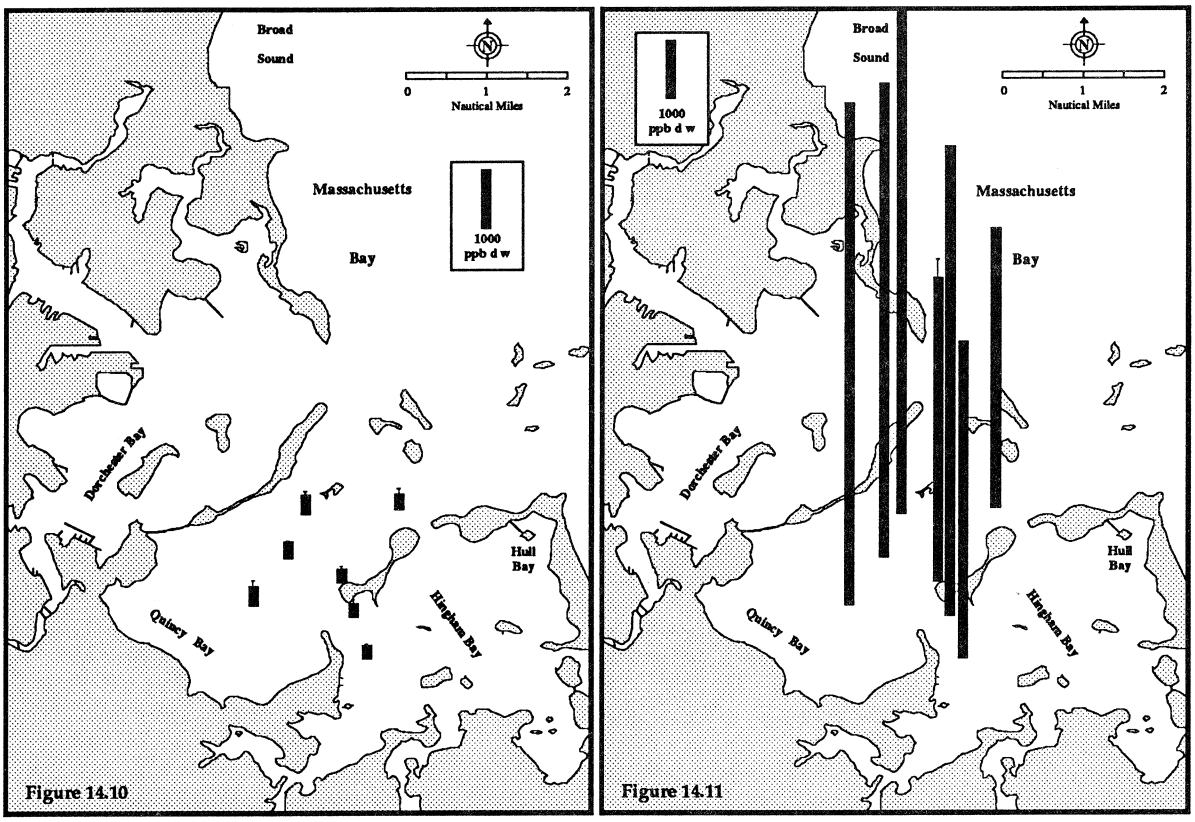
Figure 14.9. tPAH27 concentrations (ppb dw) in *C. borealis* soft parts from Boston Harbor, Massachusetts and Cape Cod bays based on 1983 data (Boehm *et al.*, 1984).

In 1983, as part of a NOAA-sponsored study of organic pollution in Boston Harbor, Massachusetts Bay and Cape Cod Bay (Boehm *et al.*, 1984), composite samples (at least three specimens per composite) of crab (*C. borealis)* soft parts and winter flounder (*P. americanus*) muscle tissue were analyzed for 27 individual PAHs (Table 14.1). Three composite samples of crab soft parts from three sites in Boston Harbor, one each from the three outer harbor divisions, had an overall mean $tPAH^{27}$ concentration of 250±190 ppb with a range of 130 to 470 ppb. The sample with the highest concentration was from the central harbor, northwest of Peddocks Island (BH-5); while the sample with the lowest concentration was from Hull Bay in the southeast harbor (BH-6) (Figure 14.9). Five composite samples of winter flounder muscle tissue from three sites in Boston Harbor were analyzed, three from the northwest harbor (BH-1, -2, and -3) and one each from the central (BH-5) and southeast (BH-6) harbor divisions. The overall mean $tPAH^{27}$ concentration was 14±1.5; however, the vast majority of the individual PAHs were at concentrations below the detection limits. In fact, only four PAHs were above the detection limit in any of the five samples: fluoranthene was detected in one, napthalene and biphenyl were each detected in two, and phenathrene was detected in four samples. In one sample, none of the 27 PAHs were above the detection limits. When the below detection limit values were set at zero instead of 1/2 the detection limit, the mean $tPAH^{27}$ concentration became 2.4±2.1 ppb with a range of from 0.0-5.0 ppb.

In addition to the samples from Boston Harbor, three crab, one winter flounder, and seven American dab (*H. plattesoides*) samples from sites in Massachusetts and Cape Cod bays were also analyzed for PAHs (Figure 14.9). The three crab soft parts samples had a mean $tPAH^{27}$ concentration of 38±28 ppb; less than 1/5 the mean for Boston Harbor crab soft parts, 250±190 ppb. The single winter flounder and seven American dab muscle tissue samples had similar trace concentrations of PAHs as did the Boston Harbor samples. Based on the crab data alone, Boston Harbor biota clearly had higher levels of PAH contamination than did biota outside the Harbor.

An intensive study of Quincy Bay was conducted in 1987 (EPA, 1988) which included the analysis for levels of 23 different PAHs (Table 14.1) in the tissues of native winter flounder (*P. americanus*), lobsters (*H. americanus*), and soft-shelled clams (*M. arenaria*), as well as, transplanted oysters (*C. virginica*) (EPA, 1988). The muscle tissue of from five to seven winter flounder from each of four different trawl transects was analyzed for PAH levels. All samples analyzed had PAH concentrations below the limits of detection.

Both the tail muscle and the hepatopancreas of lobsters from seven sites were analyzed for levels of PAHs. Two replicate samples from the tail muscles of a total of 16 lobsters, 1 to 3 from each of the seven sites, were analyzed. The overall mean $tPAH^{23}$ concentration in the lobster tail muscle was 250 ppb. The $tPAH^{23}$ concentrations in the individual samples ranged from 180 to 380 ppb; while the mean tail muscle concentrations for the seven sites ranged from 220 to 320 ppb. As Figure 14.10 shows, there was little difference in PAH concentrations among the various sites.. Two replicate samples of the hepatopancreas of 8 of the 16 lobsters were also analyzed for PAHs; $tPAH^{23}$ concentrations for the eight hepatopancreases ranged from 4700 to 8300 ppb (Figure 14.11). The overall mean $tPAH^{23}$



Figures 14.10 & 14.11. Mean tPAH23 concentrations (ppb dw) in *H. americanus* muscle tissue (Fig. 14.10) and hepatopancreas tissue (Fig. 14.11) based on 1987 data (US EPA, 1988) (bars represent one standard deviation).

concentration in the lobster hepatopancreases was 6600 ppb. This was more than 25 times the mean tPAH[23] concentration in the muscle tissue of the same eight lobsters indicating that PAHs are preferentially stored in the hepatopancreas of lobsters.

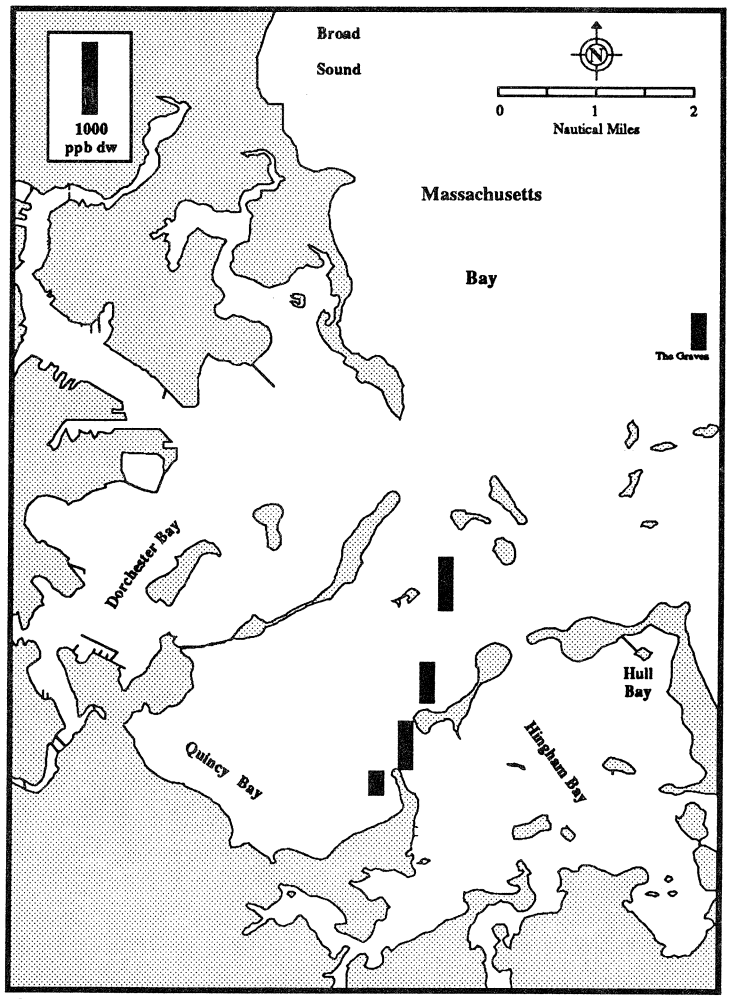


Figure 14.12. Mean tPAH23 concentrations (ppb dw) in the soft parts of transplanted *C. virginica* based on 1987 data (US EPA, 1988).

Oysters (*C. virginica*) were collected from a commercial bed located in Cotuit Bay, Massachusetts and deployed at four sites in Quincy Bay and one site located at The Graves in Massachusetts Bay from June 5 through July 16, 1987. The tPAH[23] concentrations in the oysters at the four sites ranged from 340 to 760 ppb;. The oysters from The Graves had 500 ppb tPAH[23], while those from the source bed in Cotuit Bay had a tPAH[23] concentration of 110 ppb (Figure 14.12). The two samples of soft-shelled clams from around Moon Island, Quincy Bay also were analyzed for PAHs and found to have tPAH[23] concentrations of 280 and 300 ppb.

Since 1986, NOAA's Mussel Watch Project, a part of the NS&T Program, has annually sampled mussels (*M. edulis*) from four sites in and around Boston Harbor. Three whole-body composite samples from each site were analyzed for a variety of analytes including individual PAHs, 18 in 1986, 19 in 1987, and 24 in 1988 (Table 14.1). The overall mean tPAH[18] concentration in mussels for the three sites in Boston Harbor from 1986 through 1988 was 3600 ppb with a range of from 730 to 10,000 ppb. The means for the individual sites were 2600 ppb in Hingham Bay off Worlds End, 4000 ppb in southwestern Dorchester Bay, and 4300 ppb northwest of Deer Island. Mussels from the site just outside the Harbor, Outer Brewster Island, had a mean tPAH[18] concentration of 2100 ppb (Figure 14.13).

On a broader scale, when the Boston Harbor sites were compared to the other New England Mussel Watch sites (Figure 14.14 and Table 14.6), the sites in Boston Harbor had the three highest mean tPAH[18] concentrations. The fourth highest mean was from the site just outside Boston Harbor (Outer Brewster Island). The site at Block Island had the lowest mean tPAH[18] concentration. Table 14.6 and Figure 14.14 suggest that tPAH[18] concentrations in Boston Harbor mussels were significantly higher than in mussels from any other New England site. From this data it appears that tPAH[18] concentrations in mussels varies by more than an order of magnitude throughout New England. In an attempt to determine a regional background reference concentration for tPAH[18] in mussels, the overall mean for the five New England sites with the lowest means was calculated, it was 390±160 ppb. This mean does not represent natural background levels, *i.e.* nonanthropogenically produced PAHs.

The overall mean for Boston Harbor concentration of tPAH[18] (3600 ppb) was approximately an order of magnitude greater than the calculated regional background concentration.

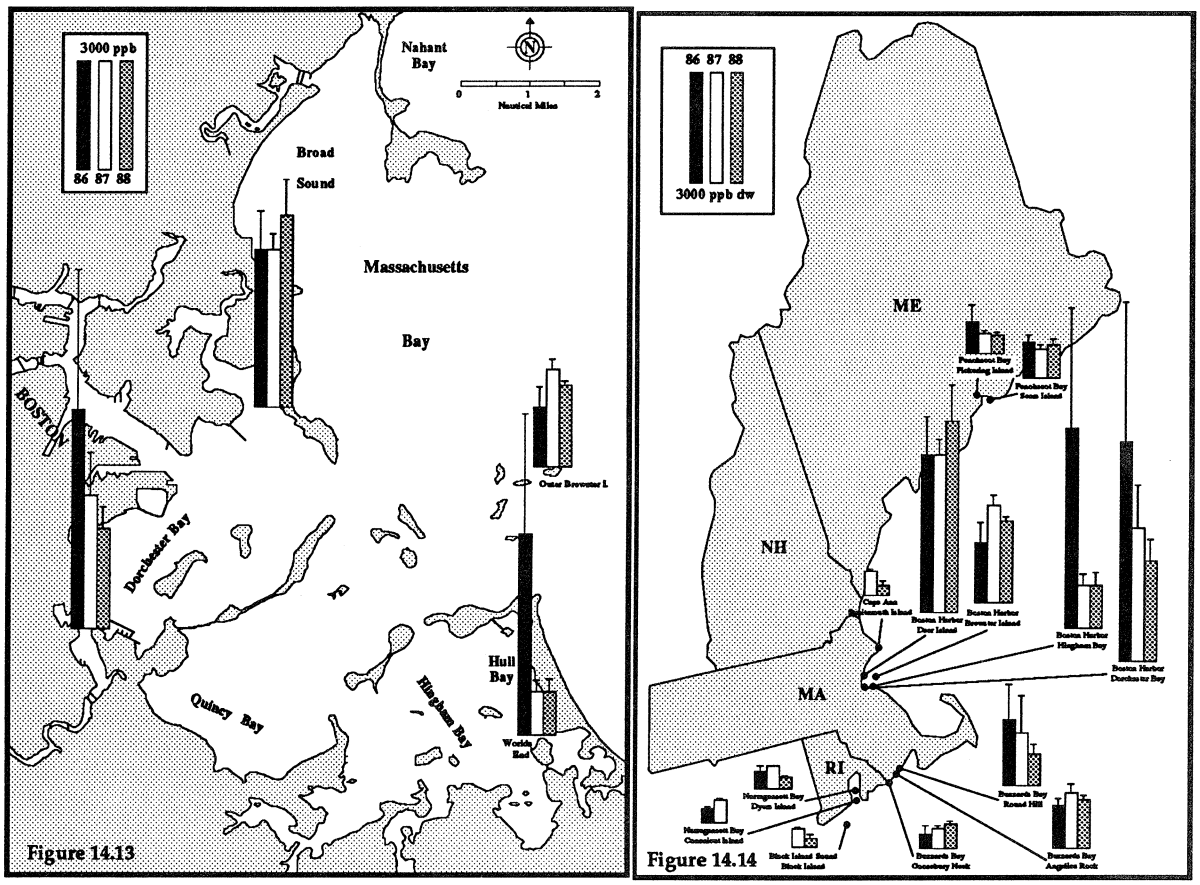


Figure 14.14. Mean tPAH18 concentrations (ppb dw) in the soft parts of *M. edulis* from Boston Harbor (Fig. 14.13) and the outer New England coast (Fig. 14.14) (NOAA, unpublished) (bars represent one standard deviation).

Table 14.6 The mean tPAH[18] concentrations (ppb dw) in *M. edulis* at the 13 outer New England Coast NS&T Program Mussel Watch sites. The outlined means are for Boston Harbor sites.

Site	Mean	Standard Deviation	Count
DEER ISLAND, BOSTON HARBOR	4300	750	9
DORCHESTER BAY, BOSTON HARBOR	4000	2500	9
HINGHAM BAY, BOSTON HARBOR	2600	2700	9
OUTER BREWSTER ISLAND	2100	480	9
ANGELICA ROCK, BUZZARDS BAY	1300	210	9
ROUND HILL, BUZZARDS BAY	1300	830	9
SEARS ISLAND, PENOBSCOT BAY	860	160	9
PICKERING ISLAND, PENOBSCOT BAY	630	300	9
GOOSEBURY NECK, BUZZARDS BAY	510	180	9
CONANICUT ISLAND NARRAGANSETT BAY	480	130	6
DYERS ISLAND, NARRAGANSETT BAY	460	150	9
CAPE ANN, STRAITSMOUTH ISLAND	460	210	6
BLOCK ISLAND, RHODE ISLAND	370	150	6

On a national scale, the Mussel Watch sites where *M. edulis* was sampled had mean $tPAH^{18}$ concentrations ranging from 8.8 to 15,000 ppb (NOAA, 1989); 80 percent of the sites had means lower than the Boston Harbor site with the lowest mean $tPAH^{18}$ concentration (Hingham Bay, 2600 ppb), while 7 percent of the sites had means higher than the Boston Harbor site with the highest mean (Deer Island, 4300 ppb). When the sites where *M. californianus* was sampled were included in the calculations, the range of the individual site means was from below the detection limits to 15,000 ppb, while 86 percent of the sites had means lower than the Boston Harbor site with the lowest mean $tPAH^{18}$ concentration and only 5 percent of the sites had means higher than the Boston Harbor site with the highest mean. Based on this data, Boston Harbor mussels were fairly highly contaminated with PAHs when compared to the nationwide sites.

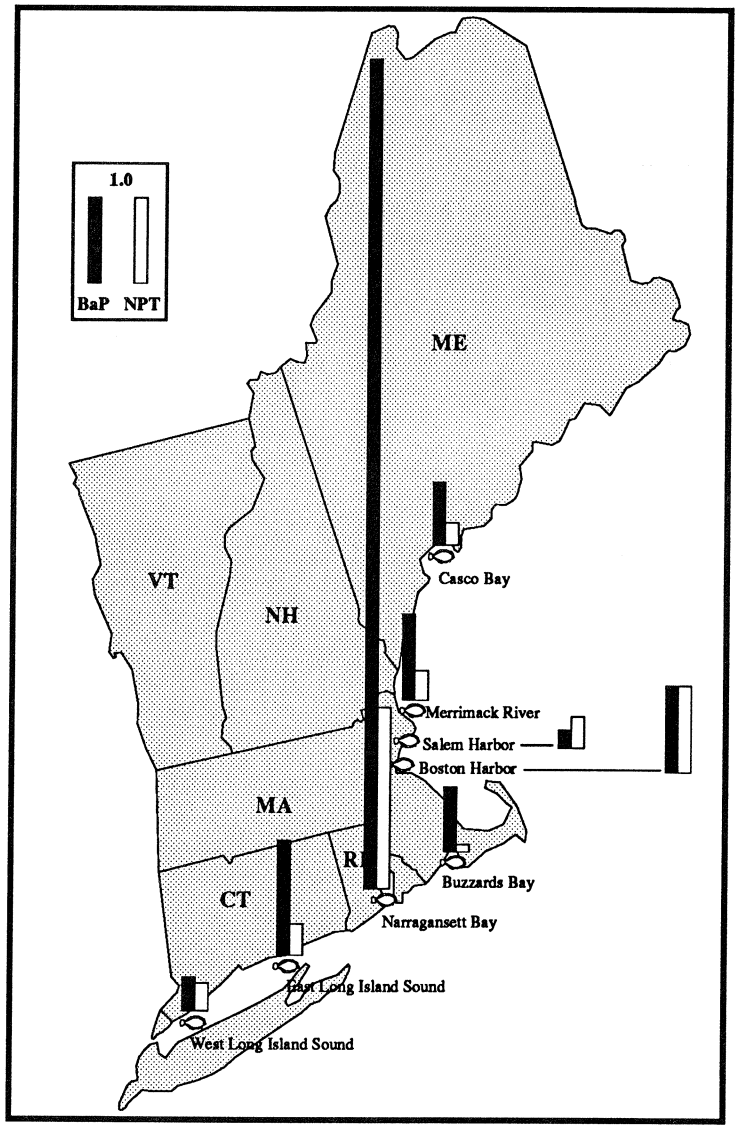


Figure 14.15. Mean ratios of benzo(a)pyrene (BaP) and napthalene (NPT) metabolite equivalents in *P. americanus* bile from the 9 northeast NS & T Program Benthic Surveillance sites in 1984 to the 1984 Boston Harbor site mean (NOAA, unpublished) (bars represent one standard deviation).

Since 1984, NOAA's Benthic Surveillance Project, a part of the NS&T Program, has annually sampled winter flounder (*P. americanus*) from an area just west of Deer Island. Because fish rapidly metabolize PAHs, a high-performance liquid chromotography/ fluorescence detection method was developed to detect PAH metabolites in fish bile (Krahn *et al.*, 1984; 1986). Instead of analyzing the liver for PAHs, NOAA's Benthic Surveillance Project analyzed the bile of the specimens for PAH equivalents, specifically B(a)p and napthalene equivalents. The values reported for the two classes of equivalents are relative values and not absolute values. To simplify the following discussion and to avoid any misinterpretation of the reported values, mean PAH metabolite concentrations will be presented as the ratio of a particular site mean to the Boston Harbor site mean. The B(a)p equivalents are considered to be representative of high molecular weight PAHs (4 or more rings). The mean B(a)p ratios for the eight Benthic Surveillance sites where winter flounder were sampled ranged from 0.22 at Salem Harbor to a high of 9.6 at the Narragansett Bay site (Figure 14.15). Based on the B(a)P equivalents data, Boston Harbor winter flounder appear to be only moderately

contaminated by high molecular PAHs. Napthalene equivalents are considered to be representative of low molecular weight PAHs (less than 4 rings). The mean napthalene ratios for the eight Benthic Surveillance sites where winter flounder were sampled ranged from 0.08 at the Buzzard Bay site to a high of 2.1 at the Narragansett Bay site (Figure 14.15). Six of the sites had mean ratios of 0.36 or less and only the Narragansett Bay site had a ratio greater than 1.0. Based on the napthalene equivalents data, Boston Harbor winter flounder are fairly highly contaminated by low molecular weight PAHs compared to the rest of the Northeast United States except for Narragansett Bay.

Temporal Trends

The only available multiyear data set was the NS&T Program's Mussel Watch Project. The Mussel Watch data also suggested a possible trend of decreasing $tPAH^{18}$ concentrations. The $tPAH^{18}$ concentrations in mussels decreased from 5200 ppb in 1986 to 2800 in 1987 and 1988. However, when the individual sites were examined, the Dorchester Bay site mean decreased each year; the Deer Island remained constant between 1986 and 1987 and then increased slightly in 1988, and the Worlds End site decreased sharply between 1986 and 1987 with no change in 1988 (Figure 14.13). Therefore, there were no clear temporal trends in PAH contamination over the 3 years covered by the study.

The EPA Deer Island site had $tPAH^4$ concentrations in the soft parts of mussels of 670 and 990 ppb in 1976 and 1977, respectively. The NS&T Program Deer Island site (which is about 0.5 miles northwest of the EPA site) had yearly mean $tPAH^4$ concentrations in mussels of 1800, 2100, and 2300 ppb in 1986, 1987, and 1988, respectively. When the two data sets were compared, there appeared to be an increase in $tPAH^4$ levels between the mid 1970s and 1988. However, whether or not this is representative of a long-term trend or simply differences due to site location or methodology, is not clear.

Summary

Boston Harbor sediments were found to contain tPAH at levels which were significantly higher than most other New England sites sampled. In some cases, tPAH levels in Boston Harbor exceeded other sites by one to two orders of magnitude. The only New England sites which approached the most contaminated Boston Harbor sites in levels of $tPAH^6$ in sediments were in Salem Harbor and Pickering Island in Maine (Table 14.4). When the data for Boston Harbor and San Francisco Bay were compared, the Boston Harbor mean, 6000 ppb (excluding the three samples over 200,000 ppb), was 3 times higher than the San Francisco Bay mean, 2000 ppb. When just the NS&T Program data for Boston Harbor and San Francisco Bay were compared, the Boston Harbor mean, 3800 ppb, was more than 2 times higher than the San Francisco Bay mean, 1800 ppb (Long *et al.*, 1988) (Table 14.7).

Table 14.7. Comparison of $tPAH^6$ sediment statistics for Boston Harbor and San Francisco Bay in ppb dw. Statistics for San Francisco Bay derived from Long *et al.*, 1988 (*excludes the three samples over 200,000 ppb, see text).

Area	Mean	Standard Deviation	Median	Range	Count
Boston*	6000	12,000	2700	16 – 93,000	181
NS&T Boston*	3800	3800	3500	56 – 18,000	25
NS&T Reference	320	330	240	29 – 1,300	28
San Francisco Bay	2000	2400	1400	20 – 12,000	61
NS&TP San Francisco Bay	1800	2400	1100	20 – 12,000	42

While the overall combined data set suggested a trend of decreasing PAH levels going from the inner harbor to the southeast harbor based on both the means and medians (Table 14.2), this trend was not clearly supported by the individual data sets (Table 14.3). Because

of the few scattered samples with extremely high reported tPAH concentrations, the means for the individual harbor divisions are unduly affected by one or two samples; therefore, the medians may be more representative of the general contamination levels in the different divisions. In the two cases where the data existed for the inner harbor, it had a median tPAH concentration in the surficial sediments of between one and two orders of magnitude higher than did the entire outer harbor (Table 14.3). There was no clear difference among the northwest and central harbor divisions although the southeast harbor appeared to have the lowest tPAH concentrations. In general, $tPAH^6$ were greater than 10,000 ppb in the inner harbor and between 1000 and 7000 in the northwest and central harbor divisions, with scattered samples exceeding 10,000 ppb. The majority of samples in the southwest harbor had concentrations below 1000 ppb. Only 2 of the 13 samples had concentrations greater than 2000 ppb. No clear temporal trend in sediment contamination was apparent based on the available data.

Based on the available data, Boston Harbor biota appears to be highly contaminated with PAHs. Boston Harbor mussels had the highest mean $tPAH^{18}$ concentrations of all the New England NS&T Program sites sampled with the mean of the most contaminated site, Deer Island, exceeding the mean of the least contaminated site, Block Island, by more than an order of magnitude (Table 14.6). When compared to all NS&T Program mussel sites sampled in the country, the Boston Harbor sites fell into the upper 15 percent with only four sites having higher means than the Deer Island site. The winter flounder bile data also suggested that Boston Harbor had high levels of PAHs, although it was not as definitive as the mussel data. The crab data from Boehm *et al.* (1984) also indicated high levels of PAHs in Boston Harbor biota with the Boston Harbor mean $tPAH^{27}$ concentration (250±190 ppb) exceeding the combined Massachusetts and Cape Cod bays mean (38±28 ppb) by more than a factor of five. Within the Harbor, the data were generally too sparse to determine any geographic trends, although the Mussel Watch data suggested that the southeast harbor had lower concentrations PAHs than did the Dorchester Bay or Winthrop Bay areas. As with the sediment data, the sparsity and variability of the biota data precludes any conclusions regarding temporal trends.

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DISCUSSION AND CONCLUSIONS

The extent of sediment and biota contamination in Boston Harbor have been documented to widely varying degrees. There are considerable data for some chemicals and areas and very little for others. Little data exists for sites sampled on a regular basis. Given this situation, the degree of confidence in which the three objectives of this report can be satisfied varies proportionately.

Geographic Trends

Harborwide

The concentrations of chemical contaminants in selected divisions and areas of the Harbor were compared by examining as much data as possible and identifying trends based upon a preponderance of evidence.

Contaminants were widespread in biota and sediments throughout Boston Harbor. All areas sampled thus far seemed to be at least slightly contaminated, *i.e.*, elevated above coastal reference concentrations or above background levels attributable to natural sources. There was considerable variation and patchiness in contaminant concentrations in the Harbor. Some of the factors that influence this patchiness are discussed later in this chapter. As a result of patchiness and natural variability, it was difficult to piece together an overall picture of trends for many chemicals despite the large number of samples that have been analyzed. In most cases, trends that were apparent in sediments were not supported by data from the biota, thereby precluding the development of a preponderance of evidence.

The geographic patterns in the Harbor varied only slightly from chemical to chemical. There were definite geographic trends for most chemicals, based upon data from the analyses of sediments, but geographic trends based on biota analyses were far less clear. Generally, the highest concentrations of many contaminants occurred in the inner harbor sediments followed by the northwest harbor sediments. No overall trends of biota contamination within the harbor were apparent from the available data.

Figure 15.1 presents the mean (with standard deviation) and median metal concentrations in the sediments for the entire harbor and the four harbor divisions, based on all the available data (see Table 2.1 for sources of data). Among the four harbor divisions, the inner harbor had the highest mean concentrations for all the metals, with the exception of Ag. This trend was generally supported by the median concentrations, except that for Cd and Hg the median concentrations for the inner and northwest harbor divisions were virtually identical and the median concentration for Ag in the inner harbor was higher than the corresponding mean and higher than the median concentrations in the other three harbor divisions. The Ag data needs to be viewed with caution because more than half the inner harbor values used in the calculations were based on half the detection limit with a relatively high detection limit of 8 ppm. When these values were excluded from the calculations both the mean and median Ag concentrations in the inner harbor were lower than the corresponding concentrations for the northwest and central harbor divisions.

The data for Cu and Cr, and to a lesser extent Cd, Zn and Hg, displayed a fairly nice stepwise decrease in concentrations going from the inner harbor to the southeast harbor division (Figure 15.1). Although, in the case of Hg, the trend of decreasing concentrations wasn't really apparent until the central harbor division. Hg, Cd, and Cr concentrations also decreased from the inner harbor to the mouth of the outer harbor. Ag didn't display a clear decrease in concentrations until the southeast harbor, while As concentrations decreased from the inner to the northwest harbor and then displayed a nice stepwise increase from the northwest to the southeast harbor. Pb and Ni display no clear trends between the three divisions of the outer harbor, but Pb concentrations did display a decrease from the inner harbor to the mouth of the outer harbor. When the northwest harbor was subdivided, the overall data indicated that sediment concentrations of Hg and Pb, and to a lesser extent Cd,

Cu, and As, were higher in the Dorchester Bay area than in the Winthrop Bay area. Concentrations of Ag, and to a lesser extent Cr and Zn, were higher in Winthrop Bay area sediments than in those of the Dorchester Bay area.

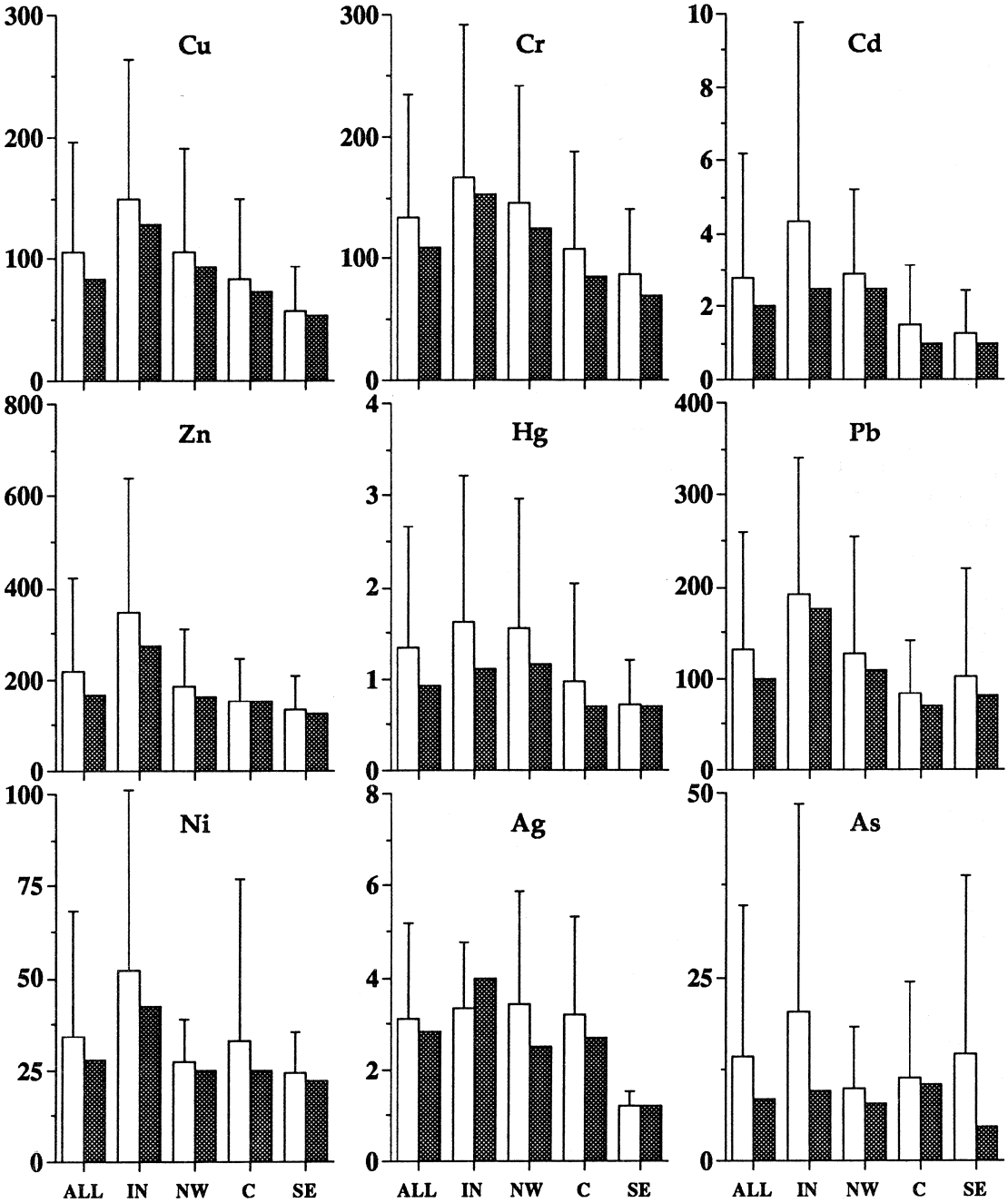

Figure 15.1. The mean (with standard deviation) and median metal concentrations (ppm dw) in the sediments for the entire harbor (ALL) and the four harbor divisions (IN-inner, NW-northwest, C-central and SE-southeast), based on all the available data (see Table 2.1 for sources of data).

These trends, as indicated by the overall data set, were generally supported by analysis of the individual data sets except in the case of As. Each of the individual data sets for As had different relative rankings of As contamina–tion in the different outer harbor divisions. The sed–iment data suggests that, with the exception of Ag, the major sources of metal contamination in Boston Harbor are located within the inner harbor.

Figure 15.2 presents the mean (with standard deviation) and median concentrations in the sedi–ments for tPAH[6] and tPCB for the entire harbor and the four harbor divisions, based on all the available data (see Table 2.1 for sources of data). As Figure 15.2 shows, the overall concentrations of tPAH[6] were 5 to 10 times higher in the inner harbor than the outer harbor with a further slight trend of decreasing concentrations from the northwest to the southeast harbor. This trend was supported by the two individual data sets which analyzed samples from all four harbor divisions (Shiaris and Jambard-Sweet, 1983; and MA DEQE, 1986; 1987). The overall data also suggested a trend of decreasing concentrations of tPCB from the inner harbor to the southeast harbor, however, the overall means for the inner and northwest harbor were only slightly different and the standard deviations were very high for both even though the 50,000 ppb sample was not included in the calculations (Figure 15.2). The median tPCB concentration for the inner harbor was only slightly higher than that for the northwest harbor, which was virtually the same as the central harbor median. This lack of a clear indication of any geographic trend in tPCB contamination in Boston Harbor was also displayed by the individual data sets. The overall data, as well as the individual data sets, indicated tPAH[6] and tPCB concentrations were higher in the sediments of the Dorchester Bay area of the northwest harbor than in those of the Winthrop Bay area.

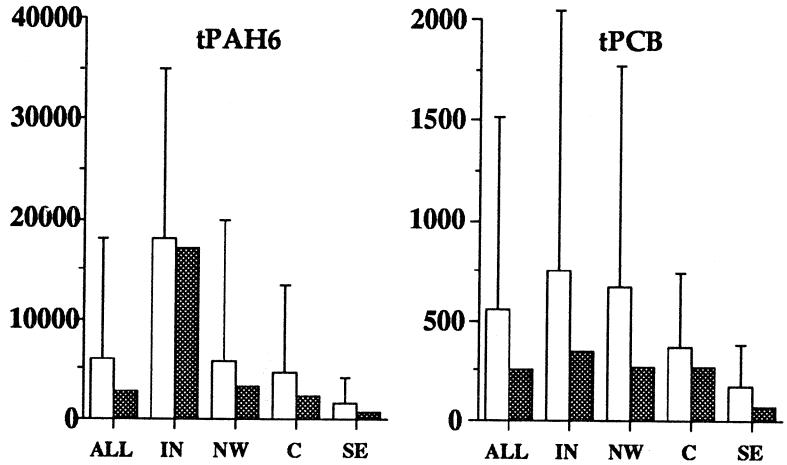

Figure 15.2. The mean (with standard deviation) and median tPAH[6] and tPCB concentrations (ppb dw) in the sediments for the entire harbor (ALL) and the four harbor divisions (IH-inner, NW-northwest, C-central and SE-southeast), based on all the available data (see Table 2.1 for sources of data).

Because of the the sparsity of data, a similar analysis of tDDT concentrations in the sediments of the four harbor divisions could not be done. The NS&T Program data indicated that the northwest harbor sediments had higher concentrations of tDDT than did the sediments of the southeast harbor. However, the southeast harbor site had extremely sandy sediments. How this may have effected the concentration levels will be discussed later in this chapter. The NS&T Program data also indicated that the Dorchester Bay area sediments had higher concentrations of tDDT than did those of the Winthrop Bay area.

There was no clear indication of geographical trends in biota contamination within Boston Harbor. Only data for the soft parts of mussels were available for all four harbor divisions and it was limited to the analysis of six metals (Cd, Cu, Cr, Ag, Ni, and Zn). Only the Cd data for mussels suggested a clear trend of decreasing concentrations from the inner harbor to the southeast harbor. This apparent trend was supported by the statistical analysis of the log transformed data. The Zn mussel data also suggested that the highest levels of contamination were in inner harbor mussels but there were no clear differences in contamination among the outer harbor sites. The highest levels of Ni contamination were found in inner and southeast harbor mussels with little difference among the other harbor divisions. The data also indicated that levels of Ag in outer harbor mussels were higher than those of inner harbor mussels, while there were no harborwide geographic trends apparent in Cu and Cr levels in mussels. However, it should be noted, that the ratio of the overall harbor division low to high means were less than 2 for four of the metals (Cu, Cr, Ni, and Zn), equal to 2 for one (Cd), and greater than 2 (3.25) for only Ag.

Based on the three NS&T Program Mussel Watch sites (two in the northwest harbor and one in the southeast harbor) of the other three metals (Hg, Pb, and As) only Hg showed a significantly different level of mussel contamination among sites. The mussels from the northwest Deer Island site had higher levels of Hg than those from Hingham Bay.

Among the organic contaminants (DDT, PCB, and PAH) there were no clear geographic trends apparent in levels of tDDT and tPCB in biota. However, the two data sets which covered more than one harbor division (Boehm *et al.*, 1984; NOAA, unpublished) suggested that the southeast harbor biota might have slightly lower levels of PAH contamination although the difference between the southeast harbor mean concentrations and the high mean concentrations ranged only from a factor of 2 to less than 4.

Therefore, the only geographic trends in levels of contamination supported by both the sediment data and the biota data were: decreasing levels of Cd going from the inner to the southeast harbor, higher levels of Ag in the outer harbor than in the inner harbor, and relatively low levels of PAHs in the southeast harbor.

Regionally and Nationally

On a regional basis, the sediment data indicated that, with the exception of Ni and As, levels of metal contamination in Boston Harbor ranged from 5 to over 300 times that of background reference levels (based on the five NS&T Program sites with the lowest mean concentration of each analyte) (Figure 15.3). When the 23 NS&T Program sites in New England were ranked based on sediment contamination levels, four of the five Boston Harbor sites ranked in the top 5 for five of the metals (Cd, Cu, Cr, Pb, and Ag) and three ranked in the top 5 for two of the metals (Hg and Zn). A Boston Harbor site ranked number 1 for three of these seven metals (Hg, Ag, and Zn). The Salem Harbor site ranked number 1 for the other four (Table 15-1). Ni and Ag levels were less elevated above reference levels (only about 3 times). While two Boston Harbor sites ranked in the top five for Ni only, one ranked in the top five for As. The lowest level of As was reported for one of the Boston Harbor sites (Table 15-1).

Metal contamination levels in Boston Harbor sediments, with the exception of As, ranged from about 1.5 to 2 times higher than those in San Francisco Bay. Levels of As were less than 1/2 those found in San Francisco Bay. When the NS&T Program sediment data, for 1984 through 1987 were used to compare the mean metal concentrations for Boston Harbor sediments to the means for the Atlantic Coast and the nation, the Boston Harbor mean exceeded the other two means for each of the metals except Ni and As (Figure 15.3). The mean Ni concentration for the Harbor was higher than the Atlantic Coast mean but lower than the national mean, while the Boston Harbor mean for As was virtually identical to the Atlantic Coast and national means.

Table 15.1. Relative ranking of sediment contamination levels for the Boston Harbor sites and the Salem Harbor site among the 23 New England NS&T Program sites for individual analytes and overall.

	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	DDT	PCB	PAH	tRank
southwest Deer Island	1	11	2	2	1	2	4	3	1	4	1	1	1
Dorchester Bay	3	2	3	4	3	4	5	2	5	1	2	2	2
Quincy Bay	2	6	5	3	2	1	7	5	3				4
northwest Deer Island	4	13	4	5	4	6	8	4	6	3	6	4	5
Hingham Bay	8	23	12	17	12	9	18	12	17	7	11	16	14
Salem Harbor	6	3	1	1	7	3	9	1	2	2	4	3	3

Long and Morgan (1990) assembled matching sediment chemistry and biological data from modelling, laboratory, and field studies and determined the ranges in chemical concentrations associated with adverse biological effects. For each chemical, they calculated an Effects Range-Low (ERL) value and an Effects Range-Median (ERM) value.

The ERL value is the concentration equivalent to that at the lower 10 percentile of the data in which effects were predicted or observed for a given compound. As such, it represents the low end of the range of concentrations at which effects were reported in the studies compiled by those authors. The ERM value is the concentration equivalent to that at the 50 percentile of the data in which effects were predicted or observed for a given compound. The ERL represents a sediment concentration above which effects may begin to be observed, the ERM represents a sediment concentration above which effects will probably be observed.

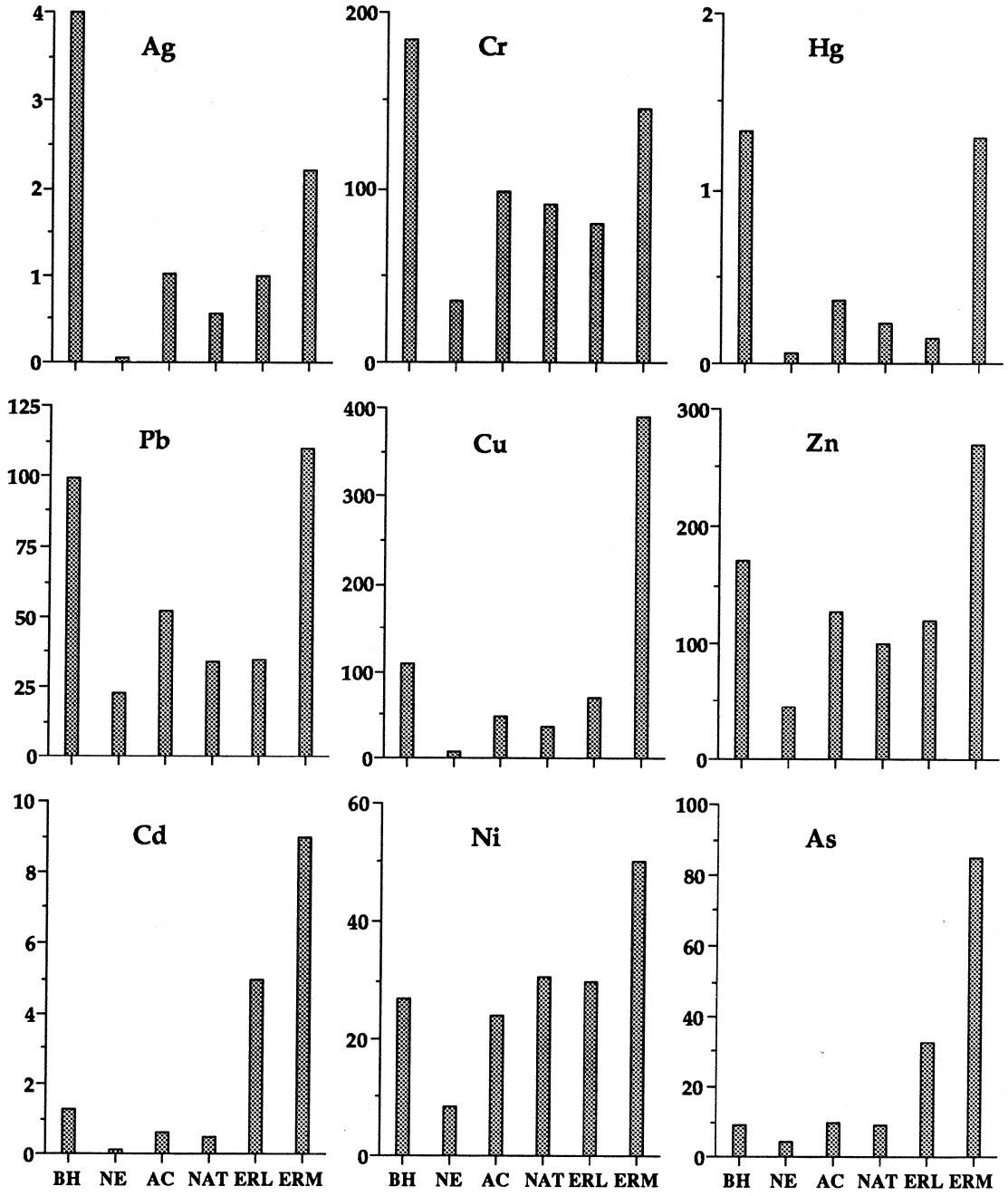

Figure 15.3. Mean metal concentrations (ppm dw) for Boston Harbor (BH), New England reference (NE), Atlantic Coast (AC), and nationally (NAT) based on NS&T Program sediment data for 1984-86, and ERL and ERM values from Long and Morgan, 1990.

When the Boston Harbor metal concentration means, based on the NS&T Program data, were compared to the corresponding ERL and ERM values, the means for Ag, Cr, and Hg, exceeded both the ERL and ERM values (Figure 15.2). The means for Pb, Cu, and Zn exceeded only the ERL values, while mean Ni,.Cd, and As concentrations exceeded neither.

The regional sediment data clearly indicated elevated levels of organic contaminants in Boston Harbor sediments. The concentrations of organic contaminants (DDTs, PCBs, PAHs) in Boston Harbor sediments were 10 to 400 times higher than reference levels (Figure 15.4). Three of the four Harbor sites where organic contaminants were measured ranked in the top five (Table 15-1) for all three classes when compared to the other New England NS&T Program sites. A Boston Harbor site also ranked number 1 for all three classes of organic contaminants (Table 15-1).

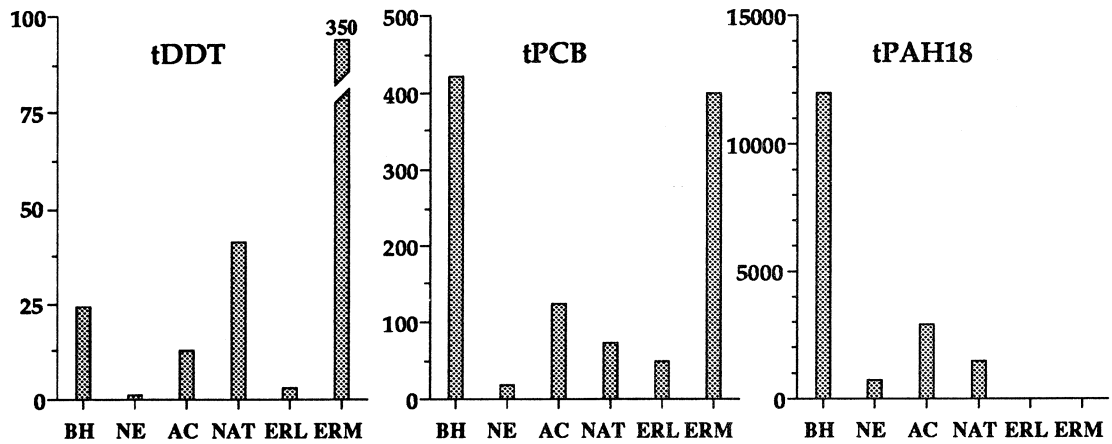

Figure 15.4. Mean organic contaminant concentrations (ppb dw) for Boston Harbor (BH), New England reference (NE), Atlantic Coast (AC), and nationally (NAT) based on NS&T Program sediment data for 1984-1986, and ERL and ERM values from Long and Morgan, 1990.

Levels of tPCB and $tPAH^{18}$ in Boston Harbor sediments were 3 to 4 times higher than San Francisco Bay sediments, while the Boston Harbor DDT levels were about 1/3 those found in San Francisco Bay. The Boston Harbor mean tDDT concentration in sediments was greater than the Atlantic Coast mean but lower than the national mean (Figure 15.4). It was also higher than the ERL value but lower than the ERM value. The Boston Harbor means for both tPCB and $tPAH^{18}$ exceeded the Atlantic Coast and national means (Figure 15.4). The tPCB mean for the Harbor also exceeded the ERL value and slightly exceeded the ERM value. Because the toxicity of tPAH would vary depending on the individual PAHs present, no corresponding ERL and ERM values were available.

Despite the elevated levels of metals in Boston Harbor sediments, the NS&T Program Mussel Watch data indicated that for four of the metals (Cd, Cr, Cu, and Zn) contamination levels in Boston Harbor mussels were only slightly higher (1.3 to 2 times) than the reference levels (based on the five NS&T Program sites with the lowest mean concentration of each analyte) (Figure 15.5). Some of the lowest levels of As and Ni were reported for Boston Harbor mussels; no reference values were calculated for these two metals because all three of the Boston Harbor mussel sites were among the five sites with the lowest mean As concentrations in New England, and two of the sites had the lowest mean Ni concentrations (Table 15.2). However, the other three metals (Ag, Hg, and Pb) had contamination levels 2 to 8 times higher than the reference levels. While contamination levels in Boston Harbor mussels may have been only slightly elevated, a Boston Harbor site ranked number 1 out of the 13 New England sites for five of the metals (Ag, Hg, Cd, Cr, and Pb) (Table 15.2).

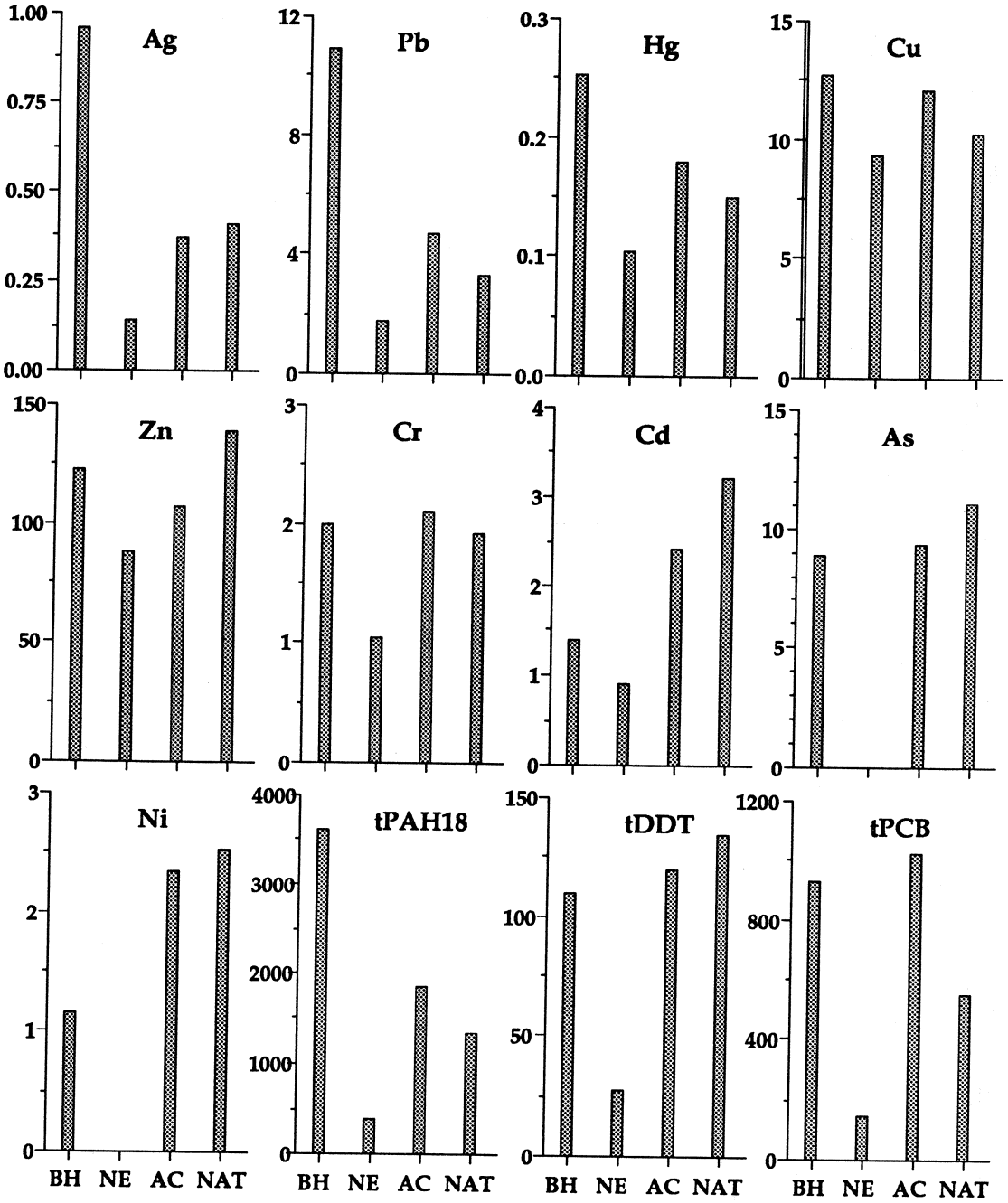

Figure 15.5. Mean concentrations of metals (ppm dw) and organic contaminants (ppb dw) in mussels for Boston Harbor (BH), New England reference (NE), Atlantic Coast (AC), and nationally (NAT) based on NS&T Program Mussel Watch tissue data for 1986-88.

On a national scale, when the three Boston Harbor Mussel Watch sites were compared to the other 78 sites nationwide, at least one Boston Harbor site ranked in the top 20 percent for four of the metals (Ag, Hg, Cu, and Pb). In the case of Ag and Pb, all three sites ranked in the top 20 percent (Table 15.3). The overall mean concentrations in mussels of the same four metals from Boston Harbor exceeded both the Atlantic Coast and national means (Figure 15.5). The mean Zn concentration in Boston Harbor mussels exceeded only the Atlantic Coast mean, while that for Cr was approximately the same as both the Atlantic Coast and

national means. The mean concentrations for Cd, Ni and to a lesser degree As were lower than both the Atlantic Coast and national means (Figure 15.5).

The mussel tissue data supports the sediment data by indicating that the levels of organic contaminants in Harbor biota are 4 to 9 times higher than New England reference values (Figure 15.5). For DDT and PAHs, the three Boston Harbor NS&T Program Mussel Watch sites ranked in the top five and included the number 1 New England site for PAHs. For PCBs, the three Harbor sites ranked in the top six; this lower ranking was a result of the three Buzzards Bay sites, which may be influenced by the PCB problem in New Bedford Harbor, ranking in the top five. Nationally, the Boston Harbor sites ranked in the top 20 percent for PCB and PAH levels in mussels, while for DDT they ranked in the middle third (Table 15.2).

Table 15.2. Relative ranking of mussel contamination levels for the Boston Harbor sites when compared to the other 12 outer New England coast NS&T Program sites where mussels were sampled, for individual analytes and overall.

	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	DDT	PCB	PAH	tRank
Dorchester Bay	3	9	1	1	2	4	12	1	1	2	3	2	1
Deer Island	1	11	3	5	5	1	13	3	2	3	4	1	2
Hingham Bay	2	13	7	4	4	5	4	2	4	4	6	3	3

The NS&T Program Benthic Surveillance winter flounder liver data indicated that the highest levels of Hg, DDTs, and PCBs were in Boston Harbor fish, while at the same time, these fish had some of the lowest levels of As, Cd, Cu, Ni, and Zn. among the 10 sites where winter flounder were sampled between New Jersey and Maine. Boston Harbor fish had only moderate levels of Ag, Cr, Pb, and PAH equivalents. The lack of a clear pattern of overall contamination in winter flounder may be due to the mobility of the organism

When the rankings for the NS&T Program New England sediment sites were summed and the sites given an overall rank based on this sum, the Boston Harbor sites were ranked 1, 2, 4, 5, and 14. The Salem Harbor site ranked number 3 (Table 15-1). Among just the New England Mussel Watch sites, the Boston Harbor sites ranked 1, 2, and 7 (Dorchester Bay, northwest Deer Island, and Hingham Bay, respectively) for overall sediment contamination. When the rankings for mussel contamination levels for the NS&T Program Mussel Watch sites are summed and ranked in the same way, the three Boston sites, Dorchester Bay, northwest Deer Island, and Hingham Bay, are ranked 1, 2 and 3 among the New England sites (Table 15.2) and 8, 12, and 14 out of 81 among the national sites (Table 15.3). The relatively low ranking of the Hingham Bay site for sediment contamination levels while it was ranked only slightly lower than the other two Boston Harbor sites for mussel contamination levels suggests that rates of contaminant loading at all three sites may be comparable and the low levels of sediment contamination at the Hingham Bay site may have been a result of the physical characteristics of the site (*i.e.* low % fines)and not the loading rates. Of the seven national sites with higher rankings than Boston Harbor, four were from the New York metropolitan area and one each was from San Diego, Santa Monica, and San Francisco bays.

Table 15.3. Relative ranking of mussel contamination levels for the Boston Harbor sites when compared to the other seventy-eight national NS&T Program sites where mussels were sampled, for individual analytes and overall.

	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	DDT	PCB	PAH	tRank
Dorchester Bay	12	43	59	17	8	17	79	4	43	25	10	8	8
Deer Island	7	46	63	33	19	4	81	9	44	27	11	5	12
Hingham Bay	10	51	67	29	17	21	58	6	56	31	16	11	14

Temporal Trends

There has been no harborwide, long-term monitoring program for chemical contaminants in Boston Harbor. This has changed in recent years with the advent of NOAA's NS&T Program and the NEA's Mussel Watch Program. However, data from these programs still cover too short a time to draw any conclusions regarding temporal trends in the Harbor. When the overall combined data set was looked at, it suggested a possible decrease in Cr levels in the sediments between the early 1970s and the mid 1980s. Beyond this no temporal trends in sediment contamination could be conjectured based on the available data. The only trend in biota contamination levels suggested by the overall combined data set was a decrease in DDT levels since the late 1960s, early 1970s, and the late 1980s. This decrease agreed with nationwide trends (Mearns *et al.*, 1988).

Representativeness of NS&T Program Sites

All the NS&T Program sites in Boston Harbor are in the outer harbor. The intent of the Program is to track conditions in areas that integrate inputs from multiple sources. The Program was not intended to monitor conditions attributable to single point sources. Table 15.4 presents a comparison of the mean sediment values for the 12 analytes examined in this report from the NS&T Program sites in the Harbor versus the mean values calculated from the historical data from the respective divisions and areas in which the sites were located for the entire outer harbor. In this table, the data from the Hingham Bay NS&T Program site, for example, are compared with those from the overall mean for the southeast harbor division. The "x" indicates the mean NS&T Program values and the historical division mean values were within a factor of 2 of each other, and, therefore, agree relatively well. The designations "low" and "high" indicate the NS&T Program values were less than 1/2 or more than 2 times the division mean values. This comparison is performed despite the fact that the division and area means are largely from historical data that predate the NS&T

Table 15.4. Comparison between NS&T Program means to historical data means for the outer harbor and the various outer harbor divisions and areas.

	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	DDT	PCB	PAH
Outer Harbor	x	lo	x	x	x	x	x	x	x	n/a	x	x
Southeast Harbor	lo	lo	lo	lo	x	x	x	x	lo	n/a	lo	lo
Central Harbor	x	x	x	x	hi	x	x	x	x	n/a	n/a	n/a
Northwest Harbor	x	x	x	x	x	x	x	x	x	n/a	x	x
Winthrop Bay area	x	x	x	x	x	x	x	x	x	n/a	hi	x
Dorchester Bay area	lo	lo	x	x	x	x	x	x	x	n/a	x	x

Program data. The former are calculated based upon data from many sites in each division, including those near combined sewer/storm overflows and discharge point sources, all of which were avoided by the NS&T Program. A comparison was not done for DDT because the historical data were insufficient.

From the sediment data in Table 15.3, it is apparent that only the As values for the overall outer harbor were different. Of the harbor divisions and areas, only the southeast harbor shows a large degree of difference between the historical means and the NS&T Program site means. For 7 of the 12 analytes which were compared, the mean of NS&T Program site in the southeast harbor (Hingham Bay) was lower than the historical data mean. This can possibly be explained by the low percentage of fines composing the Hingham Bay site sediments as will be discussed below in the section on sediment characteristics. In the other divisions and areas, Cu was high in the central harbor division (Quincy Bay), PCBs were high in the Winthrop Bay area (northwest and southeast Deer Island) and As and Ag were low in Dorchester Bay. Despite these few discrepancies, the NS&T Program values are representative of the overall outer harbor and any changes in conditions in the outer harbor would be expected to be reflected in changes in NS&T Program values.

Relationships Between Sediment Physical-Chemical Properties and Contamination

One of the objectives of analyzing sediments is to determine the degree of contamination of a site or area relative to other sites or areas and/or relative to source loading rates. However, many factors, other than patterns in loading rates to a receiving system, may influence or control the degree of contamination of the sediments. Heavy metals and organic compounds initially enter the estuary in the water column either in dissolved form or associated with suspended particulate matter in the water column. Some portion of the contaminant load eventually settles in areas where water velocity is low. The contaminants may enter the sediments by either being sorbed directly by the sediments at the sediment/water interface or by being sorbed to suspended particles before they settle out. Once in the sediments, they may be partitioned among several different phases (sorbed to sediment particles, sorbed to organic matter, sorbed to hydrous iron or manganese oxides, exist as discrete minerals, or occur in crystal lattice positions) depending on the physical and chemical composition and environment of the sediment (de Groot *et al.*, 1976). These physical/chemical characteristics of the sediment can influence concentrations of chemical contaminants in the sediment. Therefore, some of the physical/chemical characteristics that can affect the concentrations of contaminants in estuarine sediments are: the oxidation-reduction state of the sediments, the grain size (texture), the amount of organic matter present, and the concentration of iron and/or manganese in the sediments. In addition, the contaminants can be affected by biological processes and physical disturbance.

Little data was available on the physical/chemical characteristics of the sediments analyzed by the various researchers whose work has been used in the preparation of this report. White (1972) reported percent volatile solids (%VS) as representative of percent total organic carbon (TOC). He found that the inner harbor had a mean %VS (10) slightly less than 2 times as high as the outer harbor (6) with little difference among the outer harbor divisions. Over the years, the USACOE (1981, 1988, and 1972-88) have reported %VS for many of their samples. Based on this data, the inner harbor had a mean %VS (8) 2 times as high as the outer harbor (4). Isaac and Delaney (1975) reported %VS for six sites. The single site at the mouth of the inner harbor had a %VS of 4 while the mean for the five sites in the outer harbor was 7.5 with a range from 12 at a site in Dorchester Bay to 4.1 at a site in Hull Bay. The USACOE (1981, 1988) also reported percent fines (<63μ) for about 30 samples. Based on this data, there was little difference between the inner (mean 65%) and northwest (mean 74%) harbor divisions. NOAA's NS&T Program reported both percent TOC and percent fines. Except for the site in the southeast harbor, the site means ranged from 2.1 to 7.0 percent TOC and 63 to 74 percent fines. The site in the southeast harbor had means of 0.7 percent TOC and 21 percent fines. Based on this limited data set, little can be said about the overall distribution of the physical/chemical characteristics of Boston Harbor sediments; therefore, the rest of this discussion will be based on the findings of the NS&T Program Mussel Watch Project.

When sediments are initially deposited they are generally in an oxidative state that allows for the formation of heavy metal complexes with iron (Fe) and manganese (Mn) oxides. But, as this initial layer of sediment becomes buried by newly deposited layers, it changes to a reduced state. In the reduced state, the heavy metals that were complexed with Fe or Mn oxides will either be released to the interstitial water or form sulfide complexes (de Groot *et al.*, 1976). In oxidized sediments, the Fe and Mn oxides will compete with each other and with the organic matter for the binding of heavy metals (Luoma and Bryan, 1981). Therefore, the higher the concentrations of Fe and Mn oxides and organic matter in oxidized sediments, the more binding sites there are for heavy metals, resulting in higher heavy metal concentrations.

Grain size is generally related to the mineralogic and chemical composition of sediments (de Groot *et al.*, 1976). The minerals composing the finer grained sediments (silts and clays) generally have a greater affinity for adsorbing heavy metals than do the minerals composing the coarser grained sediments (sands) (de Groot *et al.*, 1976). "However, the strength of metal association with clay surfaces is weak relative to metal associations with substrates which would compete for binding in oxidized sediments. Thus, the most likely role of clays in such sediments is that of a carrier for substrates which bind metals

Table 15.5. Raw (top) and normalized concentrations (dw) of the 12 analytes at the three NOAA Mussel Watch sites in Boston Harbor. Normalized values based on the ratio of fines means (middle) or the site fines for all samples with greater than 20 percent fines (bottom) (the latter are from NOAA, 1988a).

Analyte	Units	Dorchester Bay	Deer Island	Hingham Bay
Fines	%	74	66	21
Ag	ppm	3.12 3.12 4.34	3.10 3.47 4.64	1.12 4.02 5.28
As	ppm	13.05 13.05 16.71	8.98 10.06 11.62	3.40 12.14 7.77
Cd	ppm	1.43 1.43 1.87	1.12 1.26 1.68	0.27 0.96 1.29
Cr	ppm	192 192 265	191 214 285	57 203 261
Cu	ppm	118 118 157	103 116 155	25 89 119
Hg	ppm	0.83 0.83 1.09	0.69 0.77 1.05	0.21 0.74 0.92
Ni	ppm	31 31 40	29 33 41	14 52 65
Pb	ppm	132 132 176	110 123 166	36 127 162
Zn	ppm	183 183 242	145 163 213	58 209 265
DDT	ppb	45.2 45.2 62.4	24.4 27.3 36.6	6.7 24.0 34.2
PCB	ppb	642 642 877	231 259 357	66 235 329
PAH	ppb	6990 6990 8900	4340 4860 6550	750 2660 4140

more strongly" (Jenne, 1977 in Luoma and Bryan, 1981). Therefore, as grain size decreases, the surface area for metal-binding substrates (*e.g.*, Fe and Mn oxides) increases and the sediment's capacity for binding heavy metal increases. As indicated above, many interrelated "natural" factors other than loading rates can affect heavy metal concentrations in sediment.

Table 15.5 shows the results of normalizing data to percent fines by two different methods. The first method uses the relative percent fines among a group of sites. In this case, the mean percent fines was calculated for each of the three NOAA Mussel Watch sites in Boston Harbor based on all the samples analyzed (Table 15.5). The mean for each site was then divided by the mean percent fines for the Dorchester Bay site (the site with the highest percent fines). The resulting ratio for each site was then divided into the raw mean concentrations of the individual analytes (top values in the table) for the corresponding site thus producing a normalized mean concentration for each of the analytes (middle values). The second method, used by NOAA (1988a), simply divides the analyte concentration of the individual sample by the percent fines for that sample. The site means are then calculated using the normalized sample concentration for only those samples with greater than 20 percent fines (bottom values). Because the Hingham Bay site has only about 20 percent fines, the normalized concentrations are substantially higher than the raw concentrations. This may indicate that the site is subject to significantly higher loading rates than the raw data would suggest or that percent fines were not the only sediment characteristic influencing contaminant concentration levels.

In the interpretation of data, like those in this report, a question often remains regarding a determination of what percent of differences or changes in heavy metal concentrations is due to differences or changes in loading rates and what percent is due to differences in the physical/chemical characteristics of the sediment. One method used to relate the influence of these factors to contaminant concentrations is a regression analysis. A regression analysis of metal concentration versus a sediment characteristic can be done, but the results must be viewed with caution because "a statistically significant regression may imply a chemical relationship within sediments although such a correlation may also occur if metals and substrates are deposited simultaneously. or if a third variable (*e.g.*, particle size) correlates with both variables" (Luoma and Bryan, 1979).

Table 15.5. Correlation (r^2) between the concentrations of the 12 analytes and 4 normalizers (fines, TOC, Fe, and Mn) based on NS&T Program Mussel Watch data from just Boston Harbor (top value) and all 13 New England sites (bottom value).

Analyte	Fines	TOC	Fe	Mn
Ag	0.58 0.15	0.66 0.26	0.60 0.30	0.81 0.27
As	0.69 0.66	0.76 0.69	0.78 0.60	0.68 0.35
Cd	0.95 0.28	0.70 0.36	0.88 0.35	0.73 0.21
Cr	0.94 0.41	0.73 0.47	0.90 0.59	0.76 0.39
Cu	0.98 0.32	0.84 0.40	0.95 0.50	0.84 0.35
Hg	0.98 0.33	0.75 0.33	0.92 0.54	0.80 0.34
Ni	0.95 0.65	0.82 0.66	0.95 0.86	0.89 0.60
Pb	0.64 0.17	0.42 0.19	0.60 0.28	0.47 0.18
Zn	0.95 0.49	0.77 0.46	0.94 0.76	0.80 0.56
DDT	0.79 0.19	0.68 0.31	0.82 0.28	0.69 0.18
PCB	0.62 0.04	0.41 0.04	0.59 0.02	0.44 0.00
PAH	0.63 0.22	0.32 0.21	0.53 0.20	0.46 0.09

Table 15.5 gives the r^2 values for correlation analyses of the 12 analytes discussed in this report and 4 commonly used normalizers (fines, TOC, Fe, and Mn). Two separate correlation analyses were carried out for each analyte; one based on just NOAA's Mussel Watch data for Boston Harbor (the top values) and one based on the Mussel Watch data for all 13 New England Coast sites (the bottom values). The table shows that r^2 values based on just the Boston Harbor data are always higher than those based on all the New England sites. The r^2 values based on just the Boston Harbor data are higher because the Harbor sites are subject to roughly the same degree of contaminant loading resulting in the differences in contaminant levels among sites being mainly due to the physical/chemical characteristics of the sediments. When all the New England sites are analyzed, contaminant loading overpowers differences in physical/chemical characteristics of the sediments resulting in lower r^2 values. Table 15.6 also shows that the different analytes are influenced by the different normalizers to varying degrees (*e.g.* r^2=0.58 for Ag and 0.98 for Cu based on Boston percent fines data); this fact must be kept in mind when comparing the normalized data.

Conclusions

Elevated levels of inorganic and organic contaminants were found to be present in the sediments and biota of Boston Harbor. While sediment contamination levels for all the analytes discussed in this report exceeded regional reference levels, in some cases by one and two orders of magnitude, mussel contamination levels of only 10 of the 12 analytes exceeded the regional reference levels (As and Ni did not), usually by less than a factor of two. Boston Harbor winter flounder contamination levels, except those for Hg, DDT, and

PCB, were either lower than or just slightly higher than levels from fish sampled elsewhere along the New England and Middle Atlantic Coast.

Within Boston Harbor the highest levels of sediment contamination, except for Ag, were generally found in the inner harbor, while the lowest levels were generally found in the southeast harbor or near the mouth of the Harbor. Biota contamination levels had little variability among the various harbor divisions, suggesting that at least the biologically available contaminants were relatively evenly dispersed throughout the Harbor. The more heterogeneous nature of sediment contamination might also have been the result of differences in the physical characteristics of the sediments sampled.

From an ecological, as opposed to a human health, viewpoint, the contaminants of most concern in Boston Harbor should probably be Ag, Cr, Hg, and PCBs because the means for all four of these contaminants exceeded the ERL and ERM concentrations in sediments, suggesting that they might be effecting the harbor biota. Cu ,Pb, Zn, DDT, and PAHs should also be of concern; the first four because mean sediment levels in the Harbor exceeded the appropriate ER-Ls and PAHs because both sediment and biota levels exceeded regional reference levels by an order of magnitude or more. Cd, except possibly in the inner harbor, does not appear to be of major concern, while As and Ni were barely elevated in the sediments and had some of the lowest levels in biota.

Because of the lack of past synoptic data, the only temporal trend apparent was a reduction in DDT levels. Since 1984, NOAA's NS&T Program has been annually sampling a number of sites in Boston. These sites appear to be representative of Boston Harbor as a whole. Since 1986, the NEA's Mussel Watch Program has been annually sampling mussels at two sites within the Harbor, which compliment NOAA's sites, and two sites outside of the Harbor including one sampled by NOAA's NS&T Program. The analysis of these two data sets should make any future trends in contamination levels readily apparent.

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