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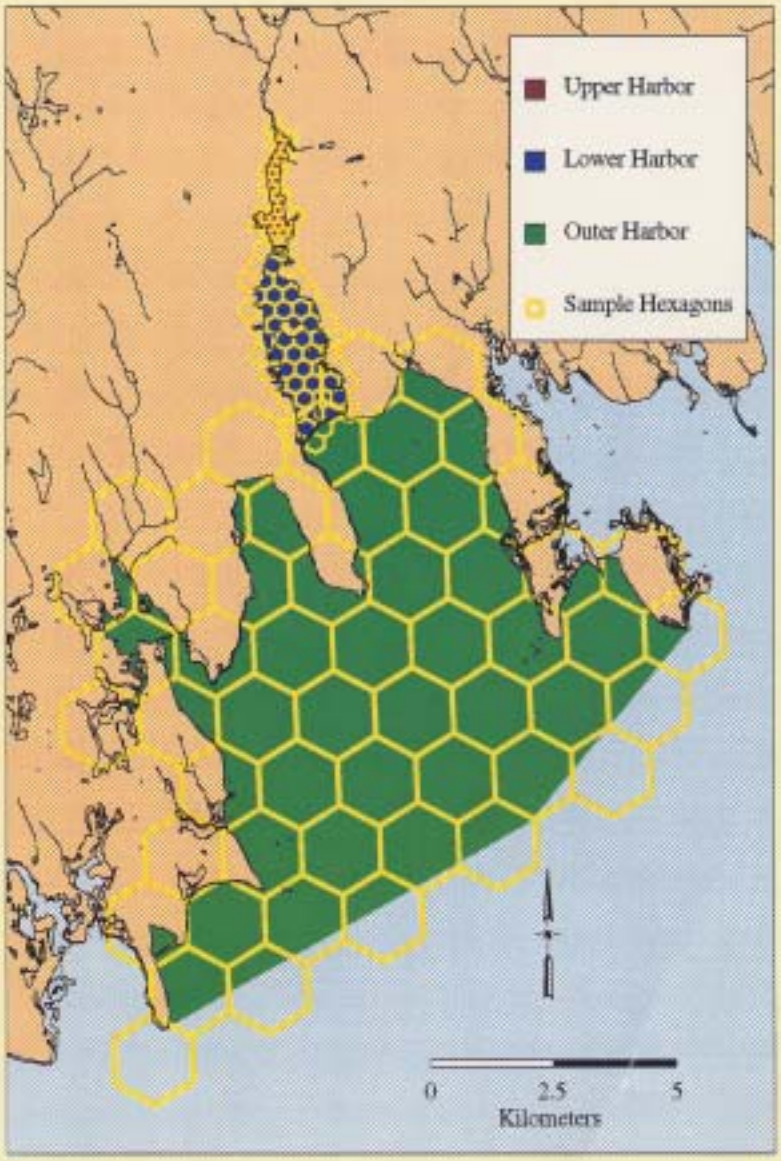
# New Bedford Harbor Long-Term Monitoring Assessment Report: Baseline Sampling



# Abstract

This report describes the Long-Term Monitoring (LTM) Plan designed to assess the effectiveness of remedial activities at the New Bedford Harbor (NBH) Superfund site in New Bedford, MA. Included in this report are an historical overview detailing man's impacts on the harbor, the long-term plan for monitoring the remediation of the harbor, and the initial data set collected prior to remediation to establish the current harbor conditions. This baseline data set includes measurements of sediment physical characteristics, chemical concentrations, and biological responses, such as benthic community analysis and sediment toxicity. In addition, data are presented describing PCB bioaccumulation in blue mussels (*Mytilus edulis*) and mummichogs (*Fundulus heteroclitus*).



**KEY WORDS:** New Bedford Harbor, Superfund, Monitoring, PCBs, Bioaccumulation, Estuarine pollution.

# Preface

This report describes the Long-Term Monitoring (LTM) Plan developed for the New Bedford Harbor (NBH) Superfund site in New Bedford, MA, and the baseline data collected as part of this program. The plan was developed by the Atlantic Ecology Division (AED), Narragansett, RI, of EPA's National Health and Environmental Effects Research Laboratory (NHEERL). This project was initiated as a request for technical support by the U.S. Army Corps of Engineers, New England Division (COE-NED), Waltham, MA, and EPA's Region I, Boston, MA. Because of AED's experience in marine monitoring programs, ecological assessments, and specific research efforts in NBH, the COE-NED and Region I requested support to design and implement a state-of-the-art long-term monitoring program to assess the effectiveness of remediation at this marine Superfund site.

The report is organized as follows: Section I provides a brief background of the New Bedford site, including an historical perspective to show how the area arrived at its present condition as well as the planned remedial activities to clean it up; Section II is an overview of the long-term monitoring plan designed to assess how effective the clean-up is; Sections III and IV provide the results and a discussion of the 1993 baseline sampling effort which established the ecological condition before remediation. Section V provides information on the electronic data. This report describes how and why specific measurements were made, as well as interprets the data in an understandable format. To that end, most data are displayed in a geographical information system (GIS) format which is easy to visualize. Also, a glossary of technical terms, shown in bold letters in the text, is included at the end of the report. References are provided for those interested in more detail concerning the information provided. Finally, for those more technically oriented, a diskette is available that includes both the actual data and documentation on the procedures used in the NBH-LTM. The diskette is PC-compatible and uses an interactive Microsoft Windows® format.

This report reflects the efforts of numerous individuals. The project leader and point-of-contact at AED is Dr. William Nelson. Other significant contributors at AED include Barbara Bergen, Sandra Benyi, Steven Rego, George Morrison, Charles Strobel, Dr. Glen Thursby, Darryl Keith, Richard Voyer, Carol Pesch and Dr. Daniel Campbell. Contract support for GIS and data management at AED were provided by Jane Copeland, Harry Buffum, and Randy Comeleo of Signal Corporation. The points-of-contact for the COE-NED are Joseph Mackay, Mark Otis, and William Hubbard. The major contractor for the COE-NED was Normandeau Associates, with significant contributions by their sub-contractors, Inchcape Testing Services and SAIC. The EPA Region I remedial project manager (RPM) responsible for the New Bedford Superfund Project was Gayle Garman at the initiation of this project. This role currently is filled by David Dickerson.

The appropriate citation for this report is:

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# Section I: Background

## Superfund Remedial Activities

The introduction of **anthropogenic** contaminants into the environment has produced numerous hazardous waste sites throughout the United States. These sites are located on land and in both freshwater and marine locations, and pose varying degrees of risk to both human health and the environment. The worst of these areas are listed on the Environmental Protection Agency's (EPA) National Priorities List (NPL) for cleanup under **CERCLA** and **SARA** (Superfund) legislation. Currently, there are more than 1,200 Superfund sites; slightly over 200 of which have completed remediation.

New Bedford Harbor (NBH), located in southeastern Massachusetts, is a Superfund site currently on the NPL primarily due to sediment contamination by polychlorinated biphenyls (**PCBs**). In order to most effectively monitor remedial activities in NBH, it was separated into three segments: the upper, lower and outer harbors (Figure 1). Sediment concentrations as high as 100,000 parts per million (**ppm**) have been measured in some parts of upper NBH. These **organic compounds** were manufactured for over 40 years and used in transformers and other electronics applications in New Bedford because of their advantageous physical and chemical properties. While useful in the electronics industry, subsequent human health and ecological studies have demonstrated that PCBs have adverse effects on plants and animals (Connolly, 1991; Miller et al., 1991). Approximately 18,000 acres of NBH and adjacent Buzzards Bay have been closed to commercial and recreational fishing because PCBs have accumulated in the food chain. Based on human health concerns and **ecological risk assessments**, the decision was made to remove PCB-contaminated sediments from the harbor.

A pilot study was initiated in 1987 to examine dredging and disposal options for NBH contaminated sediments. The results indicated that dredging was feasible both from an engineering perspective (i.e., sediments could be removed with minimal resuspension) and an environmental perspective (i.e., remediation did not cause unacceptable ecological damage; Nelson and Hansen, 1991). Based on this pilot study, a Record of Decision (**ROD**) was signed in 1990 to remove approximately 10,000 $yd^3$ of the most PCB-contaminated sediment (greater than 4,000 ppm) in the upper harbor, termed the "Hot Spot". This activity was completed in the fall of 1995. Subsequent RODs will describe the removal of additional PCB-contaminated sediments from other areas of the harbor and Buzzards Bay.

The remediation of Superfund sites can be very expensive. Therefore, it is important to assess the effectiveness of the remediation process and to document the environmental benefit gained for the money spent. One method for accomplishing this is to monitor the site before and after remediation. Because Superfund sites can be quite different, both with respect to types of contaminants (e.g., PCBs, metals, dioxins) and physical characteristics (e.g., land, streams, estuaries), there is no all-encompassing monitoring blueprint. However, certain elements are characteristic of any well-designed monitoring effort. First, specific environmental goals must be clearly articulated and understood prior to designing an effective monitoring program. Second, the monitoring program should provide the information necessary for managers and/or scientists to make site-specific assessments of whether or not the goals were attained. Finally, the experimental design should be both statistically rigorous to allow for quantitative assessments and flexible enough to accommodate changes over time. Each of these elements were incorporated into the long-term monitoring program to assess the effectiveness of the NBH Superfund site remediation.

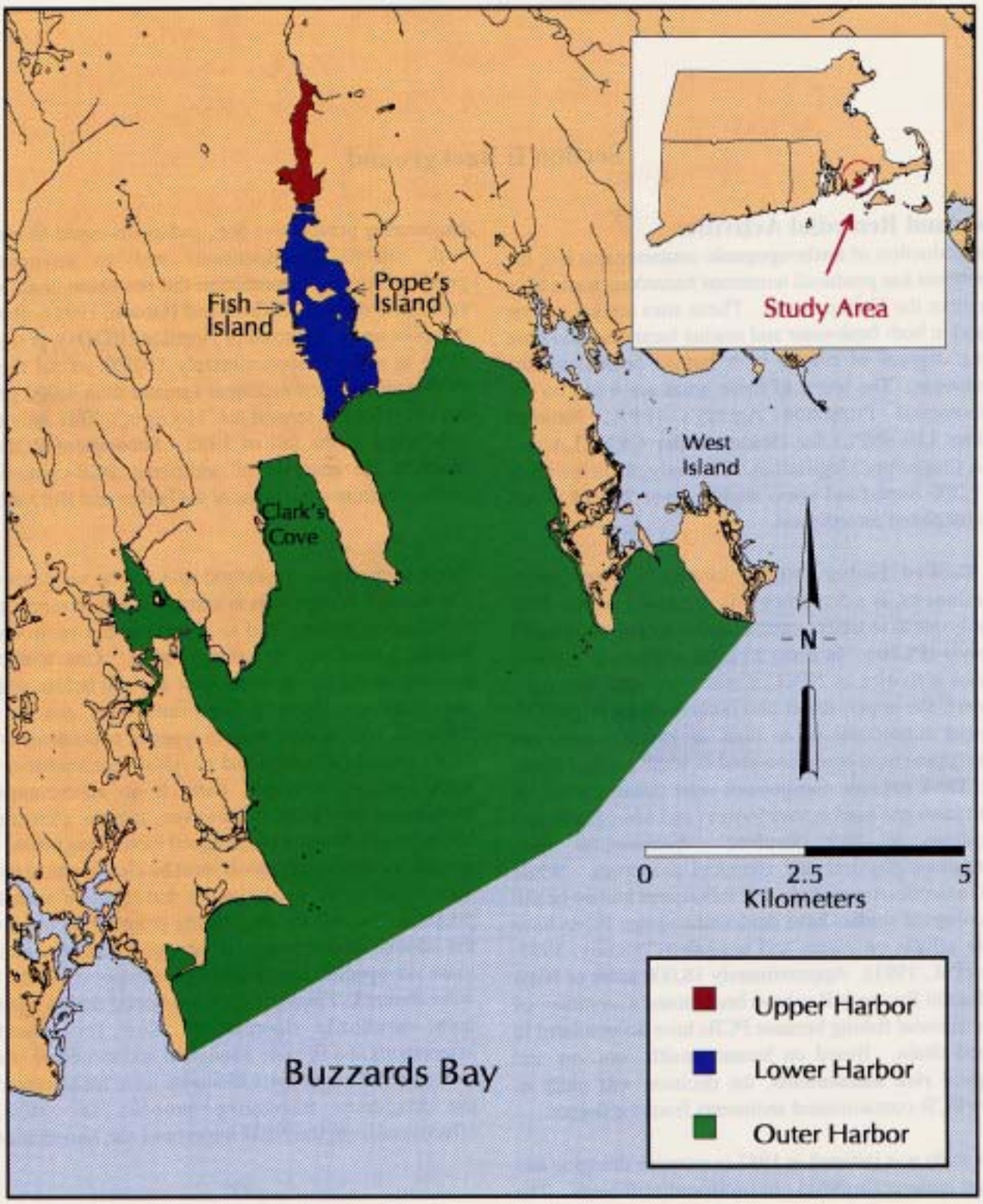


**Figure 1.** Upper, lower and outer harbor delineations for New Bedford Harbor and Buzzards Bay, MA. The hurricane barrier is the boundary between NBH and Buzzards Bay.

## New Bedford - Historical Analysis of Urbanization and Ecological Effects

The current ecological condition of New Bedford Harbor, or any other estuary, reflects the cumulative effects of natural and **anthropogenic** impacts. This historical assessment of the development and urbanization of the New Bedford area offers insights into some factors which influenced ecological changes in NBH. It is included in this report to provide a perspective on how the area became a Superfund site. Sources of information used in this analysis include property surveys, U.S. Geological Survey (USGS) maps, written historical accounts of the New Bedford area, personal interviews, census records, and information from fishing, industrial, public health and economic reports.

Review of the available information reveals four sequential developmental periods, each of which exerted a distinctive effect on estuarine conditions. During the early settlement period (ca. 1676 to 1750), agriculture was the basis of inhabitant employment and livelihood. Settlers in the New Bedford area employed farming practices typically used by Europeans throughout New England; they cleared, fenced, and cultivated the land (Cronon, 1983). In New Bedford, by the time of the American Revolution, a portion of the once "noble" forest had been replaced by cornfields, meadows and pastures (Ricketson, 1858). Timbering probably resulted in an increase in water runoff and erosion, with a concomitant loss of soil and nutrients. Livestock were important to early Europeans in New England as a food source, as work animals, and as a marketable commodity. Records show that by 1771 settlers along the Acushnet River owned sheep, swine, horses, oxen and cows (Hegarthy, 1959). The close cropping feeding behavior of these animals presumably contributed to the erosion of soil and its nutrients.

The population in the area during this time period was low. Results of a land survey indicated 11 families owned 23 parcels of land in 1690. The population has been estimated at 500 persons in 1790 and 700 in 1795 (Ricketson, 1858). The latter population figure, in terms of the total area of New Bedford (ca. 19 sq. mi.), suggests that the population density during the agricultural period probably did not exceed 36 persons per sq. mi. Although early settlers altered the New Bedford landscape, neither the degree nor the significance of their impact is clear. Certainly, the low population density ameliorated consequences due to farming practices.

The second developmental period began with the advent of the whaling industry in New Bedford. The number of vessels using the harbor progressively increased from two or three vessels committed to near-shore whale hunting around 1750 to 329 involved in the international whale trade in 1857 (Figure 2). By 1830, New Bedford had become the world's leading whaling port and by 1845 it was the fourth leading tonnage (vessels) district in the U.S. behind New York, Boston and New Orleans.

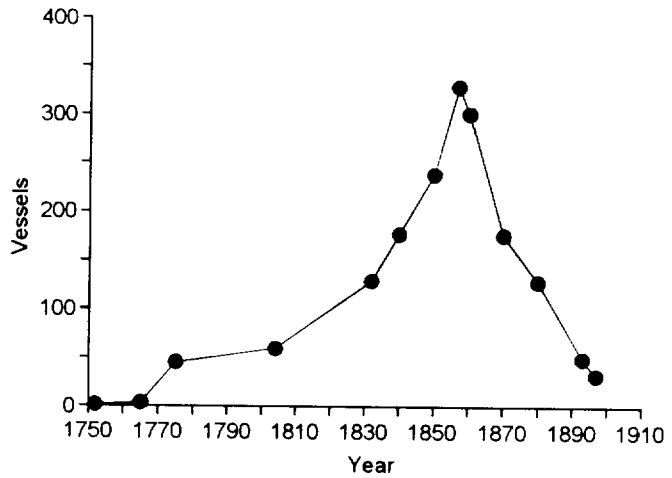


**Figure 2.** Number of ships in NBH based on clearance records (pre-1840) and registrations (1840 and later) (Ricketson, 1858; Tower, 1907).

As a result of this increased maritime commerce in New Bedford, wharfs were constructed to accommodate expanded harbor usage. An early map (Leonard), together with a verbal description of the area (Ellis, 1892), suggest the location of the original, pre-1800 shoreline (Figure 3a). The number of wharfs built increased from 7 in 1807 to 19 in 1851 and significantly changed the shape of the shoreline (Figure 3b).

Wharf construction had a direct and immediate destructive impact on near-shore habitats. A harbor survey conducted by Army engineers indicated that the presence of wharfs, along with a bridge connecting New Bedford and Fairhaven, constricted the river channel between the mainland and Fish Island (Dutton, 1853). This survey revealed that a portion of the ebb flow previously passing through this channel was diverted through a second channel east of Fish Island. This diversion resulted in increased sedimentation in the mainland-Fish Island channel and along the north shore of Fish Island (Figure 3b). Water that continued to flow past the mainland was deflected to the southeast by the presence of wharfs. As it mixed with water passing through the channel east of Fish Island, eddies formed and sedimentation increased on the south shore of Fish Island. Therefore, changing water

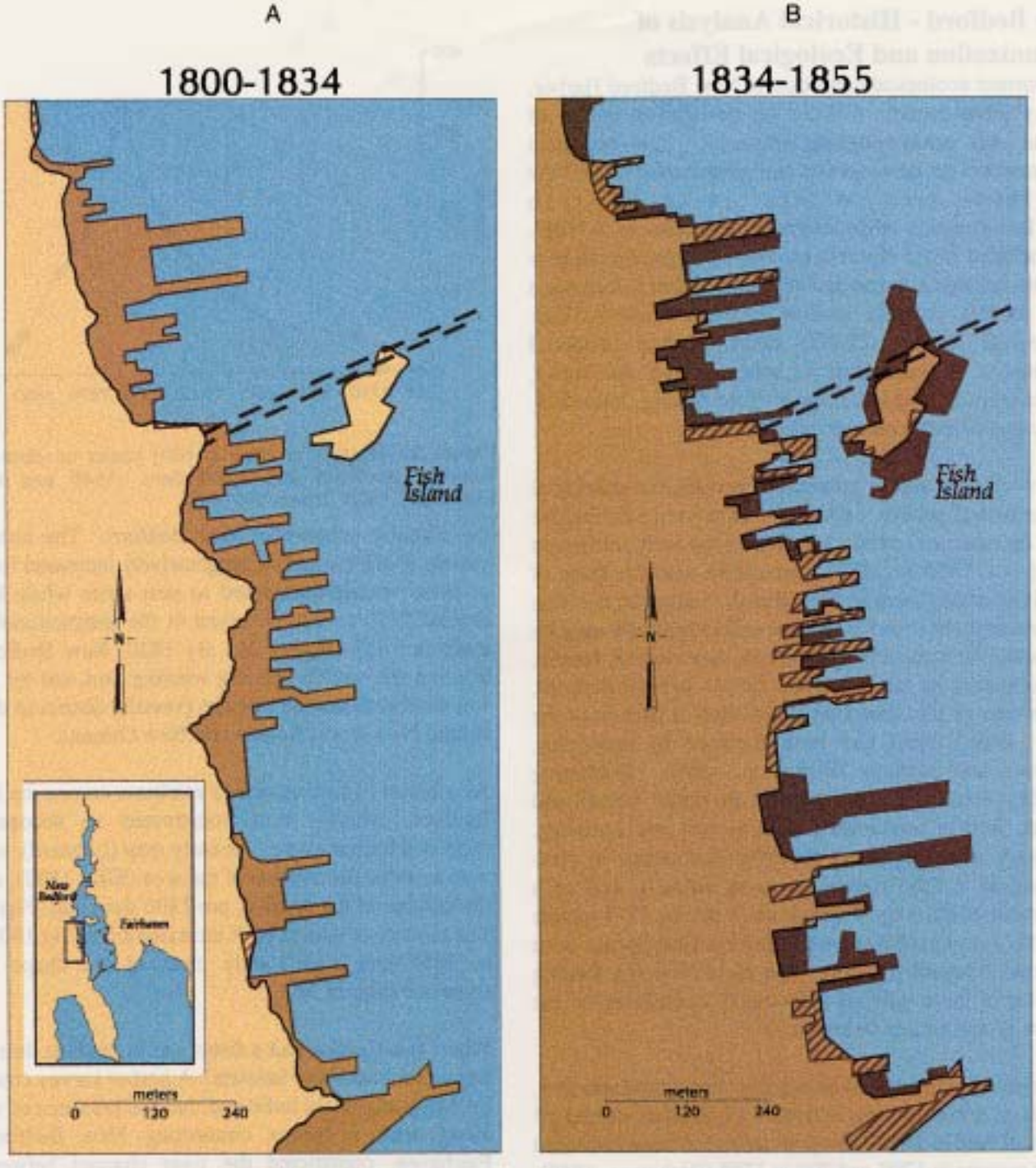


**Figure 3.** Changes in the New Bedford coastline during the whaling boom from a) 1800 to 1834 and b) 1834 to 1855.

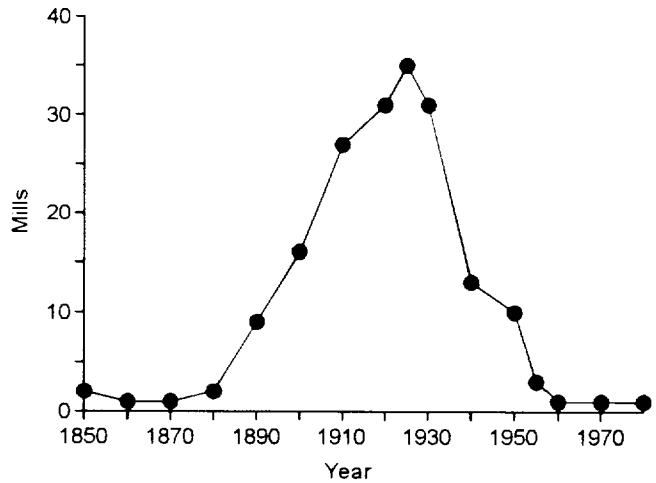


**Figure 4.** Number of textile mills operating in New Bedford from 1850 to 1980.

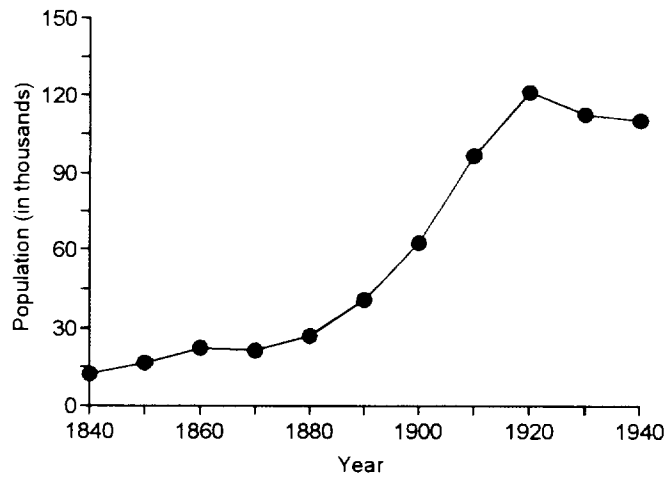


**Figure 5.** Population growth in New Bedford from 1840 to 1940.

movements and sedimentation patterns due to whaling-related construction projects also affected benthic habitats. The third developmental period began with the initial success of the Wamsutta Mill (ca. 1850). The number of textile mills in New Bedford increased dramatically after 1870 (Figure 4). Mills were constructed along the shore north and south of the city center in areas of wetlands, impacting virtually all of the wetland habitats on the west shore of the Acushnet River and in Clark's Cove (Figure 6a). As the textile business expanded, the city's population increased also, from about 20,000 in 1870 to 120,000 in 1920 (Figure 5). At the time, human wastes typically were discharged directly into estuarine waters; therefore, the release of sewer sludge, pathogens and nutrients to the Acushnet River, and eventually Clark's Cove, increased commensurate with population expansion. Because New Bedford is situated on an ascending slope, virtually all sewage-associated nutrients flowed into surrounding estuarine waters. The increase in the volume of wastes generated was sufficiently large that dredging equipment was required to remove sludge from points of discharge (1880 Census, 1881). Thus, in addition to the loss of habitat and related natural resources due to the intentional filling of wetlands, benthic habitats also were affected by discharged sewer sludge. Also, the consumption of contaminated shellfish led to outbreaks of typhoid fever and the closure of shellfish beds in 1904 (Figure 6b). The loss of this shellfishing resource is estimated to represent a total economic activity of about $13 million (Hauge, 1988).

In the 1920s and 1930s, the collapse of the local cotton textile industry due to mill closures and the impact of the general economic depression of that time, affected 50% of New Bedford's population (Wolfbein, 1968). This represented the beginning of a fourth developmental period: fishing and industrial development. Expansion of the fishing industry became possible with the installation of dock-side refrigeration, and New Bedford residents returned to the sea for their livelihood. Over time, the size of the fishing fleet increased. Protection of this fishing fleet was the primary factor for constructing the hurricane barrier in 1964. This further restricted flushing rates and altered flow patterns within the harbor. Also during this fourth developmental period, significant economic inducements, including relocation expenses, favorable tax policies, and low rental fees, were offered by the city of New Bedford to encourage businesses to move there (Wolfbein, 1968). Additional manufacturing benefits included a large semi-skilled and unskilled female labor force, a comparatively low hourly wage scale, and ample space in vacant mills. Perhaps more importantly, the Industrial Development Division of the Board of Commerce exhibited a favorable community attitude, encouraging manufacturers to relocate to New Bedford. For these reasons New Bedford was well-suited as a site for the manufacture of "static" (e.g., capacitors, resistors, transformers) electronic components (Estall, 1966).

Aerovox Corporation and Cornell-Dubilier were two electronic component manufacturers persuaded by the Industrial Development Legion, successor to the Industrial Development Division, to open factories in New Bedford. Aerovox moved to New Bedford in 1938 (Standard Times, June 7, 1939), followed by Cornell-Dubilier in 1941 (Standard Times, March 3, 1941). Both companies produced capacitors and were significant contributors to the war effort. PCBs were used by these manufacturers in the production of electronic capacitors. PCB usage in New

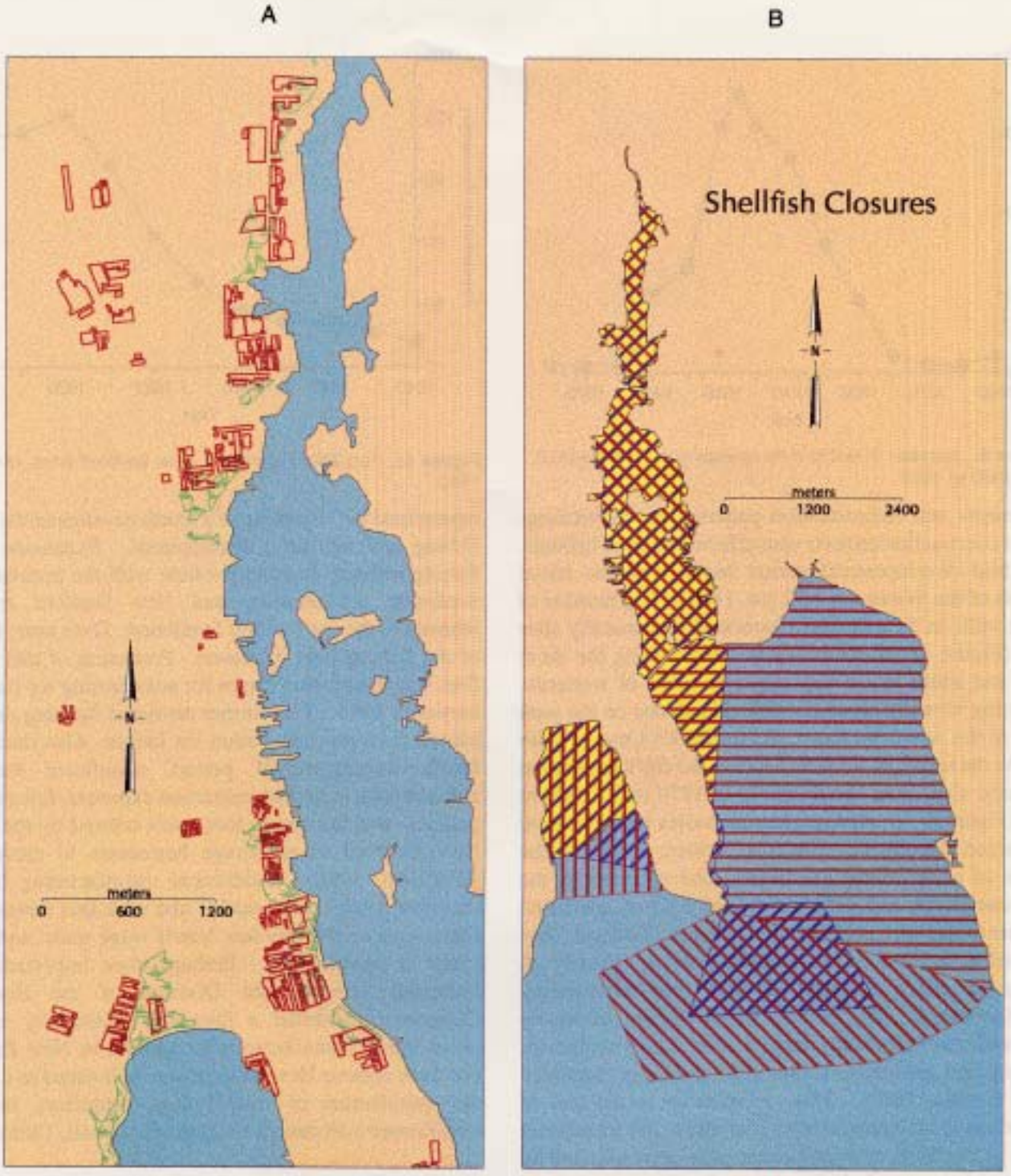


**Figure 6.** Impacts of industrial development and population growth on NBH including a) textile mills and their proximity to wetlands and b) the expansion of shellfishing closures.

Bedford peaked at about 2 million pounds per year during the years of 1973, 1974 and 1975 (Weaver, 1982). The same properties (e.g., chemical stability and low solubility) that make PCBs ideal for industrial use also allow them to persist in the environment. The extensive PCB contamination in NBH, detected in the mid 1970s, has controlled planning, development and economic restoration of the New Bedford area ever since.

In summary, this historical perspective documents the conscious decisions directing the economic activities of the New Bedford area that have had dramatic effects on its ecological condition. One consequence of PCB use during the fourth developmental period is severe sediment contamination in NBH. Activities are underway currently to remediate these sediments. The remainder of this report describes the program designed to document how effective remedial activities will be over time, as well as to define baseline conditions prior to beginning the remediation.

The following section describes the 30-year NBH Long-Term Monitoring (NBH-LTM) program that was designed to quantify spatial (throughout the harbor) and temporal (over time as various phases of the remediation are completed) environmental changes as a result of remedial activities in NBH. Specifically, it contains the goals for the NBH monitoring program, a summary of the data necessary to address these goals, and the experimental design used to collect, synthesize, and present the results. Section III provides specific examples of the baseline monitoring results collected prior to the initiation of remedial dredging. This is the data set against which future spatial and temporal changes will be compared.

# Section II: Long-Term Monitoring Program

## Goals

The key to a successful monitoring program is the clear and concise statement of the goals. This is especially important because of the 30-year duration of this program. Once the goals are clearly stated, the appropriate data can be identified to address those goals.

In the case of NBH, the primary goal is to: *"assess the effectiveness of the remediation by quantifying spatial and temporal biological and chemical changes in different environmental compartments."* A secondary goal is to show compliance with applicable or relevant and appropriate requirements (**ARAR**s), a requirement at all Superfund site remediations. In this case, two of the most important ARARs for measuring remedial success are water quality standards and Food and Drug Administration (FDA) standards for PCB levels in seafood. While the statement of these two goals may seem simplistic, it is necessary for the selection of appropriate endpoints and experimental design.

## Endpoints

With the goals stated explicitly, the next step was to identify the types of information required (ecological endpoints) to address these goals quantitatively. The approach was to first define the broad ecological areas (i.e., compartments) of interest in this monitoring program: the sediment, the water column and the wetlands. Within each compartment, specific physical, chemical, and biological endpoints were selected and quantified. The primary focus of this monitoring program is the sediment because it is the main repository for PCBs and other contaminants. Therefore, sediment concentrations of PCBs and nine metals were quantified. Toxicity tests also were conducted to ascertain the short-term **acute effects** of the sediments on the **biota**. In addition, the **benthic invertebrate community** was characterized to determine the longer-term **chronic effects** of contaminants on the biota. Finally, several other factors such as sediment **grain size**, **total organic carbon (TOC)** and **acid volatile sulfide (AVS)** were measured. These factors can effect chemical availability to the biota and also are important when interpreting the biological effects data.

A second compartment of interest is the overlying water in NBH. While the highest PCB and metal concentrations are in the sediments, these contaminants are present in the water column also. They are transported to other areas of the harbor and Buzzards Bay, and are subsequently accumulated by organisms such as filter-feeding shellfish. Water column concentrations can be measured directly or indirectly. For direct measurement, a water sample is collected and analyzed at a single point in time. However, in NBH, water column concentrations can vary from one day to the next and from one area to another depending on tides and weather conditions, especially wind speed and direction. Therefore, direct measurements are subject to potentially large spatial and temporal variations. In addition, water column concentrations can be very low, requiring large volumes of water to be collected for analysis.

One indirect method to quantify water column concentrations is **biomonitoring**, in which organisms accumulate and integrate contaminant concentrations over time. This method has been employed extensively in other monitoring programs (CEAS, Mussel Watch, NOAA Status & Trends). For the NBH-LTM Program, **bioaccumulation** in the blue mussel, *Mytilus edulis*, was the method selected to quantify PCB water column concentrations. This approach has several advantages over direct water column measurements. First, because mussels filter water almost continuously, they provide an integrated assessment of water column concentrations over time. Second, because they accumulate PCBs in proportion to water column concentrations, it is possible to estimate water column concentrations from tissue residues (Bergen et al., 1993) and compare those values with water quality standards. Finally, mussels accumulate PCBs 100 to 1000 times that of the water column. This improves the accuracy of low-level contaminant quantification. Through several previous monitoring and research efforts in NBH, an extensive data set has been compiled on PCB accumulation in blue mussels (Bergen et al., 1993; Nelson et al., 1995). These

data provide a baseline so that changes in water column concentrations resulting from remedial activities can be assessed. The mummichog, *Fundulus heteroclitus,* was selected as another species to quantify PCB bioaccumulation within NBH. This fish feeds near wetland areas, remains localized instead of migrating throughout the estuary, and has been found to accumulate PCBs to high concentrations within NBH.

A final compartment of concern is the wetlands. Two aspects of the wetlands will be quantified over time: contamination and functionality. Because only a very small section of wetland area is scheduled for remediation, changes are not expected to be dramatic or rapid. Therefore, a comprehensive wetlands assessment will be completed at 10-year intervals and compared to a baseline assessment. This will occur as a separate wetlands survey program and is outside the scope of this report.

## Experimental Design

As stated previously, the goals of a monitoring program should dictate the experimental design used. For this monitoring program, the goal is to quantify spatial and temporal biological and chemical changes in different environmental compartments resulting from remedial activities. Therefore, the experimental design must be flexible enough to quantify both spatial and temporal changes in the endpoints. In order to accomplish this, a **probabilistic** sampling design was utilized. This type of design is characterized by applying a systematic hexagonal grid to an area to select sampling points. The result is a design that is **unbiased** and statistically rigorous, meaning it can be used to make quantitative statements about the spatial and temporal changes within the sampling areas. A biased sampling design, in which sampling points are selected based on preconceived locations of problem areas, cannot be used to make assessments of the entire area. Because the goal of this program is to quantify changes throughout NBH due to remediation, an unbiased sampling design was required.

In NBH, remedial activities will not be the same throughout the entire harbor. For example, in the area north of the Coggeshall St. Bridge (termed the **upper harbor** in this program, Figure 7) two separate remedial activities will be conducted. The "Hot Spot" remediation, to remove PCB-contaminated sediments with concentrations greater than 4,000 ppm, was completed in the fall of 1995. A future remedial operation will occur to remove other contaminated sediments in the upper harbor. The area between the Coggeshall St. Bridge and the hurricane barrier (termed the **lower harbor** in this program, Figure 7) will have a relatively small area of sediment remediated. Likewise, the area from the hurricane barrier to the outer closure line (termed the **outer harbor** in this program, Figure 7) will have a relatively small area remediated. Because different remedial activities are planned within each area of the harbor, spatial and temporal changes within each of these areas, and the entire harbor, needed to be quantified separately. To accomplish this, the hexagon size in the sampling grid was adjusted to include approximately 30 stations per segment (Figure 7). This sample size allows quantification of the areal extent and magnitude of changes in each endpoint within each area. A full suite of endpoints was measured at each station (Table 1).

With this programmatic framework in mind, the rest of the report will focus on the results of the first sampling effort, completed in the fall of 1993. These results are the baseline against which future monitoring results will be compared. Section III is divided into separate parts for each of the major categories of endpoints measured. Each provides an introduction and a brief discussion of methods and results. In-depth analyses of these data are beyond the scope of this report. Detailed analyses of the data will be provided in additional peer-reviewed manuscripts. Future sampling events will be dependent upon the ongoing remedial activities, as well as the endpoint to be measured. Full-scale sampling will occur before and after other major remedial activities, or on a 3 to 5 year time frame when all remedial activities are concluded. For example, dredging of the "Hot Spot" was completed in the fall of 1995, at which point a full sampling of all parameters was conducted. The next full-scale sampling is anticipated to occur in 1999, immediately prior to the start of the next major dredging activity phase (ROD 2). Smaller scale monitoring activities will occur more frequently. Because water column concentrations are expected to change faster than sediment concentrations, due to flushing and tidal exchange, mussel bioaccumulation will be monitored twice each year.

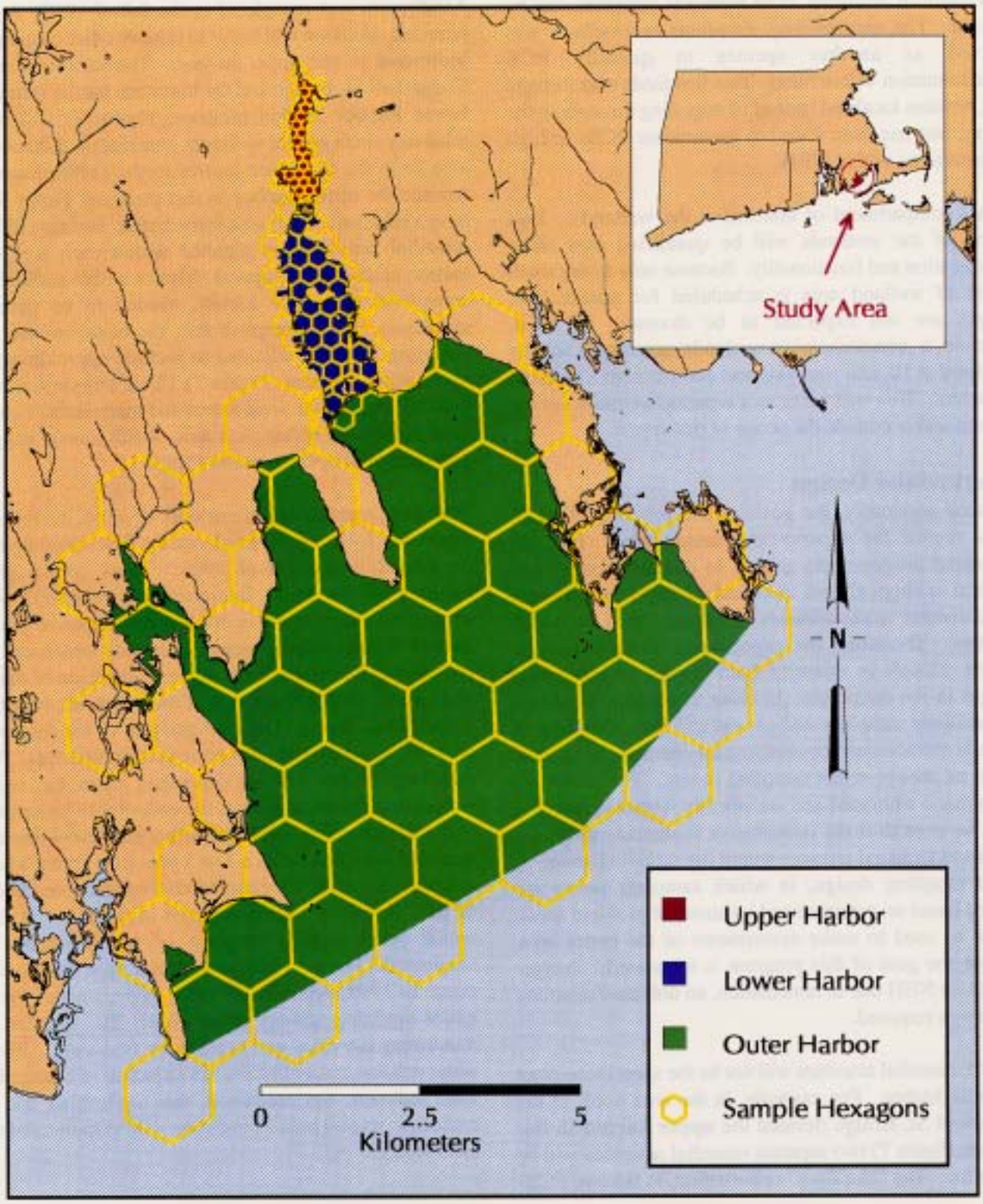


**Figure 7.** Sampling grid for each of the harbor sections. Each section was overlaid with a grid that defined approximately 30 hexagons.

**Table 1.** Endpoints measured in the NBH-LTM program.

| | Endpoint | Measured as: * |
|---|---|---|
| Sediment Chemistry | acid volatile sulfide (AVS) | µmol AVS/ g dry weight sediment |
| | arsenic | µg As/ g dry weight sediment |
| | cadmium | µg Cd/ g dry weight sediment |
| | chromium | µg Cr/ g dry weight sediment |
| | copper | µg Cu/ g dry weight sediment |
| | mercury | µg Hg/ g dry weight sediment |
| | nickel | µg Ni/ g dry weight sediment |
| | lead | µg Pb/ g dry weight sediment |
| | selenium | µg Se/ g dry weight sediment |
| | zinc | µg Zn/ g dry weight sediment |
| | PCBs (18 individual congeners) | µg PCB congener/ g dry weight sediment |
| | Total PCBs | sum of 18 PCB congener concentrations |
| | total organic carbon (TOC) | g C / 100 g dry weight sediment (%) |
| Bioaccumulation | blue mussel (*Mytilus edulis*) | µg Total PCB/ g dry weight tissue |
| | mummichog (*Fundulus heteroclitus*) | µg Total PCB/ g dry weight tissue |
| Sediment Characterization | *A. abdita* sediment toxicity tests (acute toxicity) | survival as a % of control survival |
| | grain size and texture | % silt/clay (< 63 µm) |
| | | % sand (≥ 63 µm and < 2 mm) |
| | | % gravel (≥ 2 mm and < 64 mm) |
| | benthic community (chronic effects) | species richness |
| | | EMAP benthic index |
| | | species dominance |

*µg/g is equivalent to ppm

# Section III: 1993 Baseline Sampling Endpoints and Results

## Sediment Sampling

While the procedures used to quantify individual endpoints were different, sediment collection was identical at each of the study's sampling sites (U.S. EPA, 1995). Sediment was collected using a **Young-modified van Veen grab sampler** (440 $cm^2$ in surface area). At each site, numerous grabs were collected for chemical and toxicological analyses. Only the top 2 cm of these grabs were used in the composite for chemical analysis in this monitoring program, even though greater concentrations of contaminants may have been present deeper in the sediments. The rationale for using just the top 2 cm is that this program is designed to quantify changes over a 30-year time frame, especially changes resulting from remedial activities. Because the upper 2 cm are most reflective of current sediment concentrations, including older, deeper sediments could produce a distorted interpretation of current conditions. Other sediment monitoring activities in NBH, associated with the remedial dredging activities, do quantify concentrations at multiple depths to ensure that all the contaminants are removed.

From each individual grab a 2-cm deep sample was removed for AVS analysis. The remainder of the surficial layer (top 2 cm) from each grab at a given site was composited and homogenized. From this homogenized composite, sub-samples were taken for chemistry (PCBs, TOC, metals), sediment toxicity and grain size analyses. Prior to laboratory analysis, PCB and TOC sediment samples were kept cold (4°C), while the metals and AVS samples were frozen. Sediment for toxicity testing was taken from the same composite, press-sieved through a 2-mm mesh stainless-steel screen, thoroughly homogenized, and stored at 4°C until testing. Finally, approximately 100 ml of the composited sediment were collected and placed in a polyethylene bag for grain size analysis.

Three additional grabs were collected at each site for benthic community description. These grabs were a minimum of 7 cm deep in order to be reflective of the benthic community. Each grab was processed according to the procedures described in Reifsteck *et al.* (1993). A small core (2 cm diameter) was taken from each grab for sediment grain size characterization, independent of the grain size analysis for the chemistry composite described previously. The remaining sample was sieved through a 0.5 mm screen using a backwash technique to minimize damage to soft-bodied animals. Samples were preserved in a buffered 10% formalin and seawater solution with rose bengal added as a vital stain.

## Sediment Chemistry

The primary goal of the remedial activities in NBH is to remove PCBs and other collocated contaminants; therefore, quantification of these contaminants is one of the most important aspects of the NBH-LTM program. PCBs are a class of organic contaminants made up of 209 **congeners**. Each PCB congener has one to ten chlorine atoms attached in a unique molecular arrangement (Figure 8).

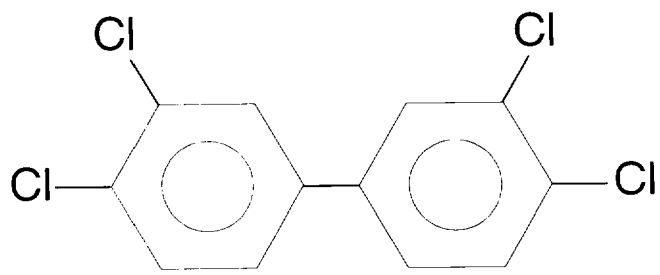


**Figure 8.** Molecular configuration of a selected PCB. This specific congener (CB077) is coplanar. The position of the chlorine atoms around the phenyl rings determines the shape of the molecule. Each ring can have up to five chlorine atoms.

As the level of chlorination increases, the **solubility** of the congener in water decreases and its particle affinity increases. For many years, PCBs were quantified as total **Aroclor®**. The term Aroclor® is a trademark used by the Monsanto company to refer to mixtures of PCB congeners. Depending upon the analytical method used to quantify Aroclors, specifically, which **chromatographic** peaks are selected to represent the Aroclor® mixture, different laboratories could analyze the same sample and get highly

variable concentrations. In contrast, congener-specific analysis is more accurate because standards for single congeners can be made easily and standard reference materials with congener-specific totals are readily available for quality assurance purposes. For this reason, the sediments in the NBH-LTM program were analyzed for 18 of the 209 PCB congeners, rather than Aroclor® content.

In addition to measuring PCBs, the TOC in the sediment was quantified because it can affect the availability of organic compounds, such as PCBs, to biota (Connell, 1990). The organic carbon in sediment can bind chemicals, thus making the chemicals inert to organisms. For example, sediment A and sediment B can have exactly the same total PCB concentration. However, if sediment A had high TOC concentrations and sediment B had low TOC concentrations, organisms in sediment B would be exposed to more PCBs. One procedure to determine the amount of PCBs actually available to an organism is to **normalize** them to TOC content.

Although sediment PCB concentrations are the primary source of concern in NBH, metals are present in high concentratrations in some areas of NBH. Because one goal of the remediation is to remove these collocated contaminants, sediments were analyzed for metals also. Nine metals were selected for analysis including: copper, cadmium, lead, zinc, arsenic, selenium, mercury, chromium and nickel. Although not all of these metals are present in high concentrations in NBH, they were quantified because there are existing water quality criteria for each of them.

In addition to these nine metals, sediment samples were analyzed for AVS content. Like TOC for PCBs, the **bioavailability** of **divalent** metals is controlled, in part, by the amount of AVS in the sediment.

### *Methods*

For PCB analysis, approximately 1 g of sediment was **extracted** with acetone and methylene chloride. Extracts were **solvent-exchanged** to hexane and analyzed on a **gas chromatograph**. Extracts were analyzed for 18 individual PCB congeners. Total PCB concentrations were calculated as the sum of these 18 congeners. As part of this analysis, a second gram of sediment was weighed, dried and weighed again to determine moisture content. The analysis of TOC consisted of first removing the inorganic carbon from carbonates and bicarbonates by acid treatment. Organic compounds then were broken down by burning in the presence of oxygen or air and the resultant carbon dioxide measured by direct non-dispersive infrared detection.

Sediments were analyzed for metal concentrations by **sonicating** a mixture of approximately 5 g of sediment and 2M nitric acid. The resultant extract was brought to volume and analyzed on an **inductively coupled plasma spectrophotometer (ICP)** or an **atomic absorption spectrophotometer (AA)** as necessary. Total metals, used for comparison with biological responses, is defined as the **molar sum** of all metals measured (using the 2M nitric acid extraction). A sum of divalent metals was calculated to estimate bioavailable metals. The metals included in this calculation were Ni, Pb, Cd, Cu, Zn and Hg. Because a weaker acid is used for the total metal extraction than for traditional metal extractions, the metal concentrations are more indicative of anthropogenic inputs and exclude metals in the mineral portions of the sediment.

AVS was quantified as the amount of sulfide released upon extraction of the sediment with a cold 1M hydrochloric acid (HCl) solution. The sulfide liberated in this process was trapped and measured with a sulfide-specific electrode.

### *Results and Discussion*

In general, total PCB concentrations decreased along a gradient from the upper to the outer harbor (Figure 9), with sediment concentrations ranging from a high of 431 μg/g in the upper harbor to 0.02 μg/g in the outer harbor. The organic carbon in the sediments ranged from a high of 13% in the upper harbor to a low of 0.16% in the outer harbor.

Metal concentrations generally decreased from the upper to the outer harbor; however, the gradient was not as distinct as the one observed for total PCBs (Table 2). For example, sediment copper concentrations were elevated in the upper harbor near the cove located to the north and west of the Coggeshall St. Bridge, while in the lower harbor, copper was elevated near several industries, Popes Island and several marinas (Figure 10). AVS was variable throughout the harbor, although the highest concentrations were found in the upper and lower harbors (112 μmol/g) and the lowest concentrations (0.1 μmol/g) were observed in the outer harbor.

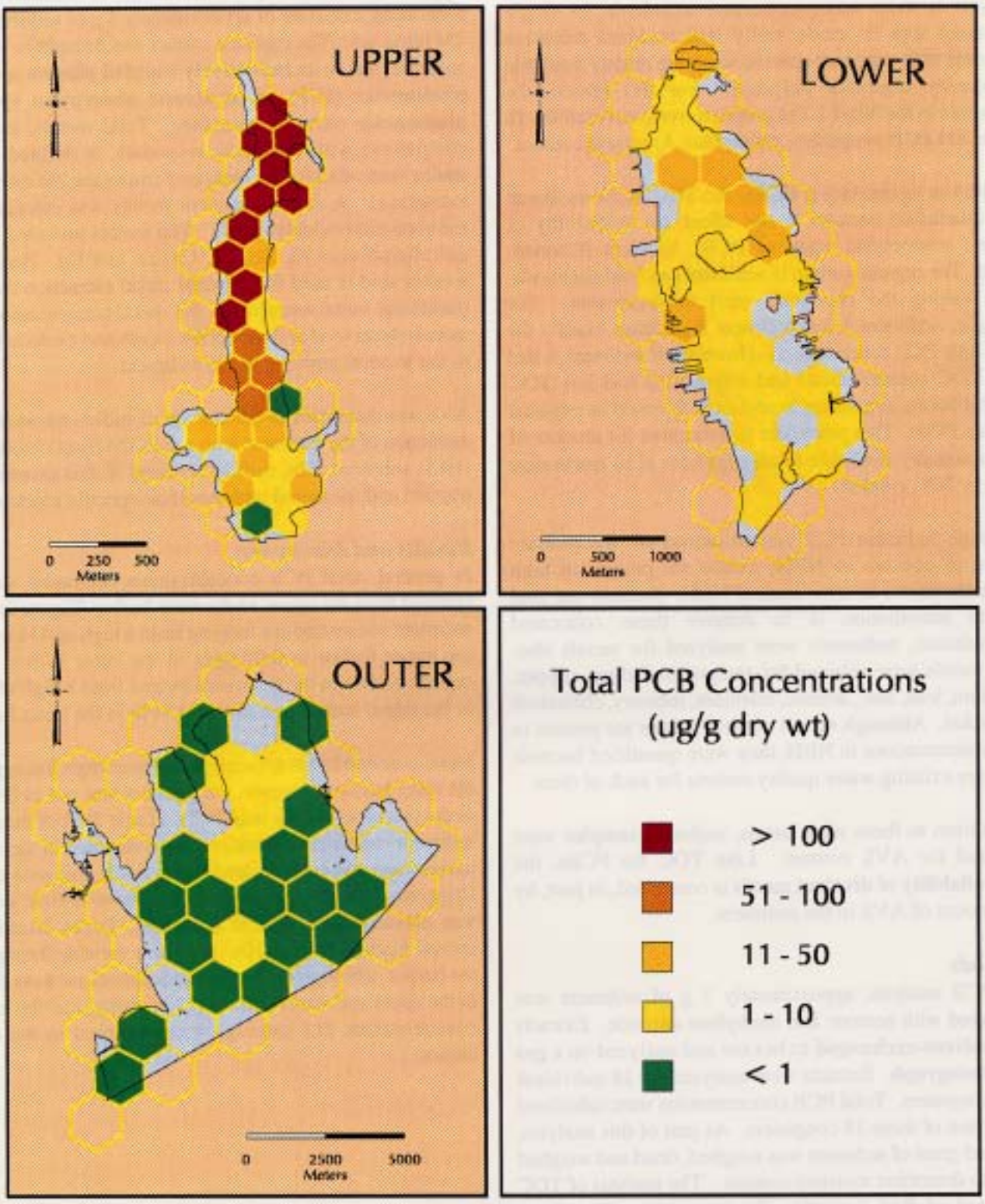


**Figure 9.** Total PCB concentrations (in µg/g dry weight) in NBH sediment. Total PCBs are the sum of the 18 individual congeners analyzed.

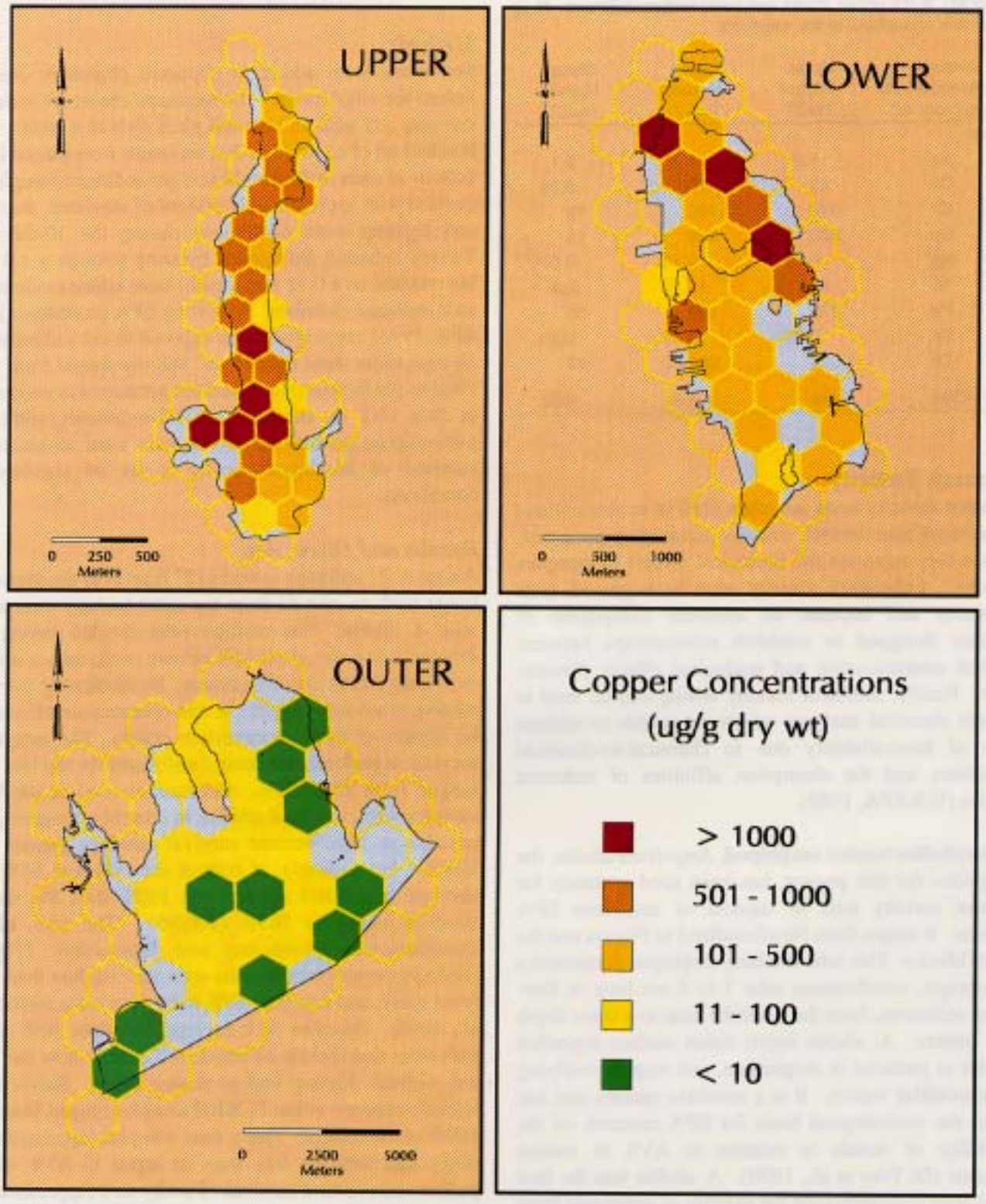


**Figure 10.** Sediment copper concentrations (in µg/g dry wt) in upper, lower and outer harbor.

**Table 2.** Average metal and total PCB concentrations (in µg/gdry wt) in the upper, lower and outer harbor sediment. N is the number of stations in the segment.

| Average Concentrations (µg/g dry wt) | Upper Harbor N=27 | Lower Harbor N=27 | Outer Harbor N=23 |
|---|---|---|---|
| Metals | | | |
| As | 5.2 | 5.3 | 3.1 |
| Cd | 67 | 12 | 0.28 |
| Cr | 310 | 190 | 19 |
| Cu | 630 | 450 | 19 |
| Hg | 0.43 | 0.40 | 0.07 |
| Ni | 34 | 11 | 5.3 |
| Pb | 270 | 130 | 18 |
| Se | 0.32 | 0.42 | 0.23 |
| Zn | 630 | 260 | 42 |
| Total PCBs | 44 | 8.2 | 0.83 |

## Sediment Toxicity

**Sediment toxicity tests** are often used in ecological and contaminant assessments, and in monitoring programs, because they integrate the biological effects of complex mixtures. Laboratory toxicity tests have gained wide acceptance and become an essential component of programs designed to establish relationships between chemical contamination and ecological effects (Swartz, 1987). Finally, sediment toxicity testing can be used to augment chemical analyses which are unable to address issues of bioavailability due to chemical-to-chemical interactions and the absorption affinities of sediment particles (U.S.EPA, 1989).

The **euryhaline** benthic **amphipod**, *Ampelisca abdita*, the test species for this project, has been used routinely for sediment toxicity tests in support of numerous EPA programs. It ranges from Newfoundland to Florida and the Gulf of Mexico. This tube-dwelling amphipod constructs a soft, upright, membranous tube 3 to 4 cm long in fine-grained sediments, from the intertidal zone to a water depth of 60 meters. *A. abdita* ingest either surface-deposited particles or particles in suspension, and respire overlying and **interstitial** waters. It is a sensitive species and has formed the toxicological basis for EPA research on the availability of metals in relation to AVS in marine sediments (Di Toro et al., 1990). *A. abdita* was the first species used to demonstrate the toxicity of sediments from NBH, and subsequently was used to assess the effectiveness of capping procedures as part of the Pilot Dredging Project on-site remediation techniques (Otis and Averett, 1988). Thus, it is appropriate that this species be used during the NBH-LTM as one of the indicators to assess the effectiveness of remedial activities.

### *Methods*

Sediments were added to exposure chambers one day before the amphipods. The exposure chambers were 1-L canning jars with an inverted glass dish as a cover. Two hundred ml of control or NBH sediment were placed in the bottom of each of five replicates per sediment sample and covered with approximately 600 ml of seawater. Aeration and lighting were continuous during the 10-day test. Twenty subadult amphipods (passing through a 1.0 mm, but retained on a 0.71 mm screen) were added randomly to each replicate chamber. Following EPA procedures (U.S. EPA, 1994), amphipods were exposed to test sediments for 10 days under static conditions. Salinity ranged from 30 to 35 parts per thousand (ppt) and temperature was maintained at 20 ± 1°C. In addition to NBH sediments, additional performance control sediments were used to assess the survival of amphipods under a set of standardized conditions.

### *Results and Discussion*

A total of 77 sediment samples (27 from both the upper and lower harbors, and 23 from the outer harbor) were tested with *A. abdita*. The samples were divided among five different test series, each with its own performance control with Long Island Sound sediment. By measuring survival relative to a control treatment, non-contaminant effects can be separated from contaminant effects. The amphipod survival in performance control sediments for the five tests ranged from 89 to 99%. Because survival in the NBH samples was examined relative to control treatments, it is possible to have percent survival numbers greater than 100%. For example, if control survival was 95% and survival in a NBH sample was 100% then the sample survival would be 105% (100/95). The U.S. EPA's Environmental Monitoring and Assessment Program (EMAP) considers sediments with survival less than 80% to be toxic, and less than 60% to be very toxic (Strobel et al., 1995). Samples with survival less than 10% are so poisonous that there is no way to tell exactly how bad they are without diluting and re-testing them. Survival for animals exposed to the 77 NBH samples ranged from 0 to 109% of the control. Thirty-four samples (approximately 45%) had survival less than or equal to 80% of the performance control survival. Twenty-two (approximately 30%) samples had survival less than or equal to 60% of the performance control. All except one sample considered to be toxic or very toxic were confined to either the upper or lower harbor (Figure 11). Average percentage survival for the upper and lower harbors was similar at 55% and 66%,

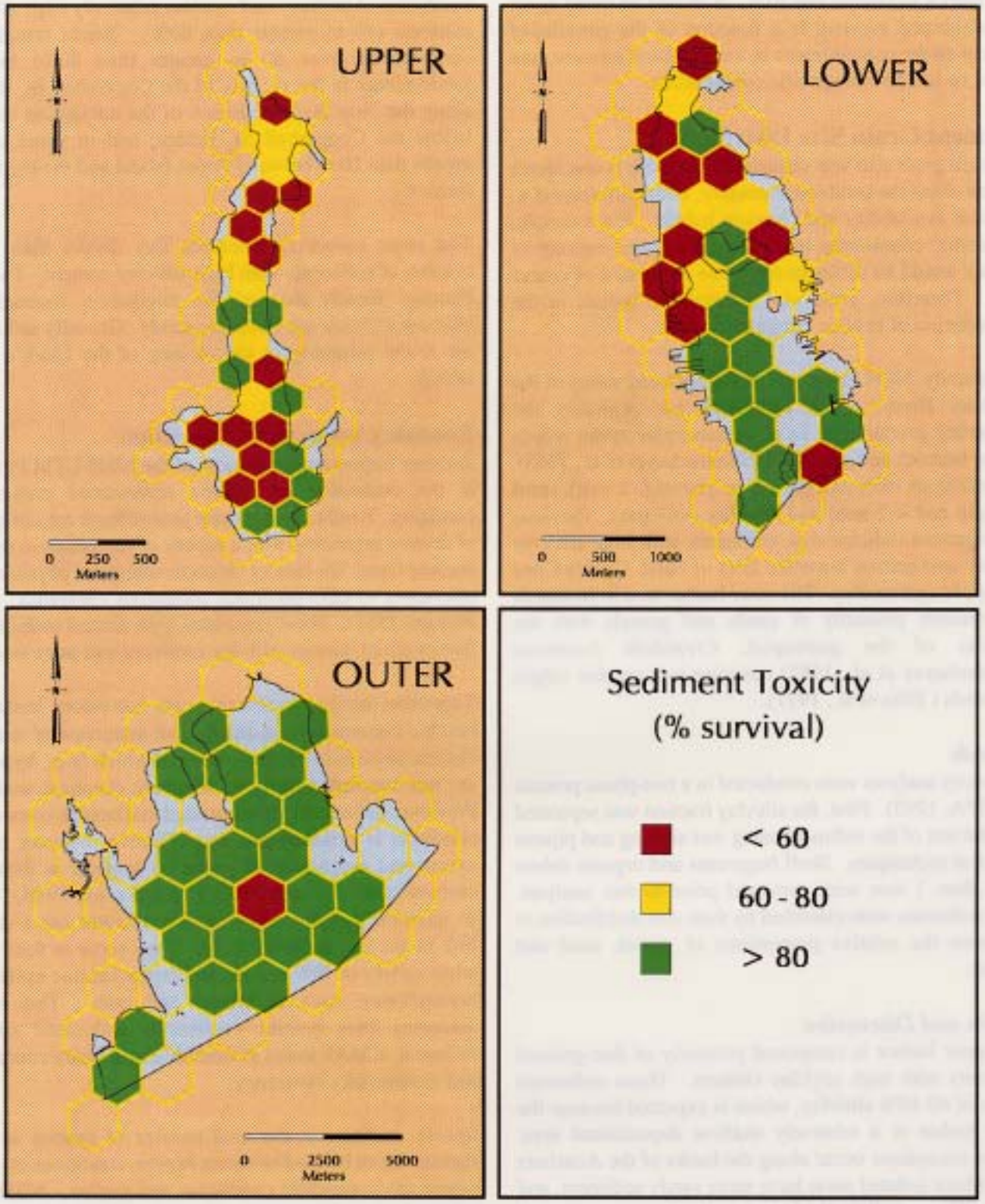


**Figure 11.** Amphipod survival ( in %) in sediment toxicity tests. Survival greater than 80% indicates a non-toxic sediment.

respectively. Overall survival for amphipods exposed to outer harbor sediments was 91%. It should be noted again that amphipod survival is a function of the cumulative effect of all the contaminants in the sediment mixture, and cannot be linked to a specific contaminant.

## Sediment Grain Size Distribution

Sediment grain size was measured because it is one factor that can affect the benthic community, both with respect to chemical availability and physical habitat. For example, the benthic community in an area composed entirely of silt/clay would be different from one composed of coarse sand. Therefore, grain size information assists in the interpretation of benthic community data.

Geologically, NBH forms part of the drowned valley of the Acushnet River. The sediments are primarily the weathering products of local metamorphic rocks which overlay bedrock and glacial till (Summerhayes et al., 1985). The sediments were categorized as **gravel** (>2 mm), **sand** (>63 µm and < 2 mm) and **silt/clay** (<63 µm). Previous investigations indicate that sediments with high silt/clay and low sand content cover the floor of NBH, Clark's Cove and Apponaganset Bay. The outer harbor area in Buzzards Bay consists primarily of sands and gravels with the remains of the gastropod, *Crepidula fornicata* (Summerhayes et al., 1985) covering topographic ridges and shoals ( Ellis et al., 1977).

### *Methods*

Laboratory analyses were conducted in a two-phase process (U.S.EPA, 1995). First, the silt/clay fraction was separated from the rest of the sediment using wet-sieving and pipette analytical techniques. Shell fragments and organic debris larger than 1 mm were removed prior to this analysis. Next, sediments were classified by their size distribution to determine the relative proportions of gravel, sand and silt/clay.

### *Results and Discussion*

The upper harbor is composed primarily of fine-grained sediments with high silt/clay content. These sediments consist of 40-80% silt/clay, which is expected because the upper harbor is a relatively shallow depositional area. Several exceptions occur along the banks of the Acushnet River where isolated areas have more sandy sediment, and near the Coggeshall St. Bridge where fast currents scour the bottom resulting in a gravelly sediment.

The sediment distribution of the lower harbor is more complex. Silt/clay sediments are associated with shallow areas (less than 3 m in water depth) along the northeast and southwest shorelines and contain relatively high silt/clay contents (40 to greater than 80%). Sands (ranging in composition from 60 to greater than 80%) become predominant in the vicinity of the Coggeshall St. Bridge, along the New Bedford Reach of the navigation channel below the Coggeshall St. Bridge, and in water depths greater than 10 m between Popes Island and the Hurricane Barrier.

The outer harbor in Buzzards Bay deeper than 10 m consists of sediments with high silt/clay content. The Fort Phoenix Reach area of the navigation channel and Fairhaven Shoals are generally sandy. Gravelly sediments are found primarily in the vicinity of the Clark's Point outfall.

## Benthic Community Condition

Another important component of the NBH-LTM Program is the evaluation of benthic invertebrate community condition. Benthic invertebrate assemblages are composed of diverse organisms with a variety of reproductive modes, feeding types, life-history characteristics, and physiological tolerances to environmental conditions (Warwick, 1980; Bilyard, 1987). These organisms have limited mobility and live in direct contact with the sediment and **pore water**.

Therefore, unlike short-term acute laboratory bioassays, benthic community condition is an integrator of multiple chronic stresses in the field, some of which (e.g., **hypoxia**) are not coupled directly to sediment chemical analyses. Previous studies have demonstrated that benthic community condition is a reasonable and effective indicator of the extent and magnitude of pollution impacts in estuarine environments (Bilyard, 1987; Holland *et al.*, 1988, 1989). In addition, benthic **infaunal** invertebrates are a critical link in the aquatic food chain. They serve as food for a wide variety of fish species and larger benthic **epifaunal** invertebrates, such as lobster and crab. This report discusses three benthic community endpoints: **species richness**, **EMAP index of benthic community condition**, and **community structure**.

Species richness is the total number of species at each station. It can be used to assess benthic conditions in areas where environmental conditions are similar. NBH is a relatively small estuary with only slight salinity and temperature gradients from the upper to outer harbor. For this reason, species richness can be used to evaluate differences between each section of NBH.

A second endpoint, the EMAP benthic index, integrates several individual measures of the benthic community into a single value which discriminates between good and poor benthic conditions (Strobel *et al.*, 1995). Index values less than zero indicate that the benthic community is poor or degraded, while values greater than zero indicate a good or healthy community structure.

A third endpoint, community structure, uses species composition and **species dominance** to provide insight into environmental conditions. For example, in mature, unimpacted systems **competitive interactions** result in high species diversity and an even distribution of the most abundant species (Odum, 1969). Community structure is determined by interactions among all organisms and, in a healthy community, those interactions are generally **density-dependent**. Stressed ecosystems display relatively low species diversity and few dominant species. In spite of the chemical or physical conditions, those species that are stress-tolerant and can thrive and reproduce quickly will become dominant (Odum, 1969).

The benthic community is also affected by salinity and grain size. NBH has a limited salinity range (28 to 30 ppt). Also, the average percent silt/clay (< 63 μm) for the three segments was not statistically different; 47% in the upper harbor, 39% in the lower harbor, and 42% in the outer harbor. Because salinity and grain size do not vary much, benthic community comparisons are considered valid.

## *Methods*

In the laboratory, **macrobenthos** were sorted, identified to lowest practical taxonomic level (generally species), and counted. **Biomass,** measured as shell-free dry weight after drying at 60°C, was calculated for key taxa; all other taxa were grouped by taxonomic type (*e.g.*, polychaetes, amphipods, decapods). A complete description of the methods can be found in the EMAP Laboratory Methods Manual (U.S. EPA, 1995). All analyses and sample collections were performed in accordance with a strict Quality Assurance/ Quality Control program (Valente and Strobel, 1993).

## *Results and Discussion*

### Species Richness

The number of species per station (*i.e.*, from all grabs collected per station) ranged from 10 in the upper harbor to 116 in the outer harbor. Species richness is presented in Figure 12. Although the groupings are arbitrary and not intended to portray ecological significance, the figure illustrates a clear gradient in species richness in NBH: lowest in the upper harbor (20 ± 7 species per station [average ± standard deviation]), intermediate (31 ± 14) in the lower harbor and highest in the outer harbor (72 ± 21). Using Student's t-test for unequal variances, the values for these areas are statistically different ($p < 0.001$).

### EMAP Benthic Index

One endpoint used to quantitatively assess benthic community health is the EMAP benthic index. A positive benthic index value indicates a healthy community while a negative value indicates a disturbed community, either by natural (e.g., scouring) or anthropogenic stresses. Figure 13 shows the upper harbor to be highly impacted, with an average benthic index value of -5.7 (range of -25.7 to -0.2). The lower harbor is also classified as degraded with an average benthic index value of -1.4 (range of -4.3 to -0.3). Only two stations in the outer harbor are classified as impacted, with an average benthic index value of 1.9 (range of -0.2 to 4.8). For comparative purposes, an evaluation of the EMAP data set for the Virginian Province (*i.e.*, all estuaries, bays and tidal rivers from Cape Cod south to the mouth of Chesapeake Bay) shows the lowest one percentile to have an index value of -2.7. This means that only 1% of the entire Virginian Province area had a benthic index value below -2.7, indicating that the upper harbor, and to a lesser extent the lower, are extremely impacted.

There is generally good agreement between species richness and benthic index values. One exception occurred at a lower harbor station which had a relatively high species richness value (53 species) and a low benthic index value (-3.6). The low benthic index value was due to the high abundance of spionid polychaetes, which are generally indicative of an impacted community. Their presense has the effect of lowering the overall benthic index value. The dominant species at this station was the opportunistic spionid, *Streblospio benedicti,* which was also the dominant species in the upper harbor (Figure 14). This species is frequently associated with eutrophic conditions (Weisberg, et al., 1994); however, the sediment at this station (8% silt/clay, TOC content 1.6%) did not exhibit the characteristics usually present in eutrophic areas (i.e., high silt/clay and TOC).

### Benthic Community Structure

Descriptions of the benthic community include species-level parameters (abundance and biomass), and population-level parameters (species composition and dominance). Total benthic abundance was highly variable in individual grabs for NBH. Total abundance (count of each animal of every species, summed for all grabs) by station ranged from

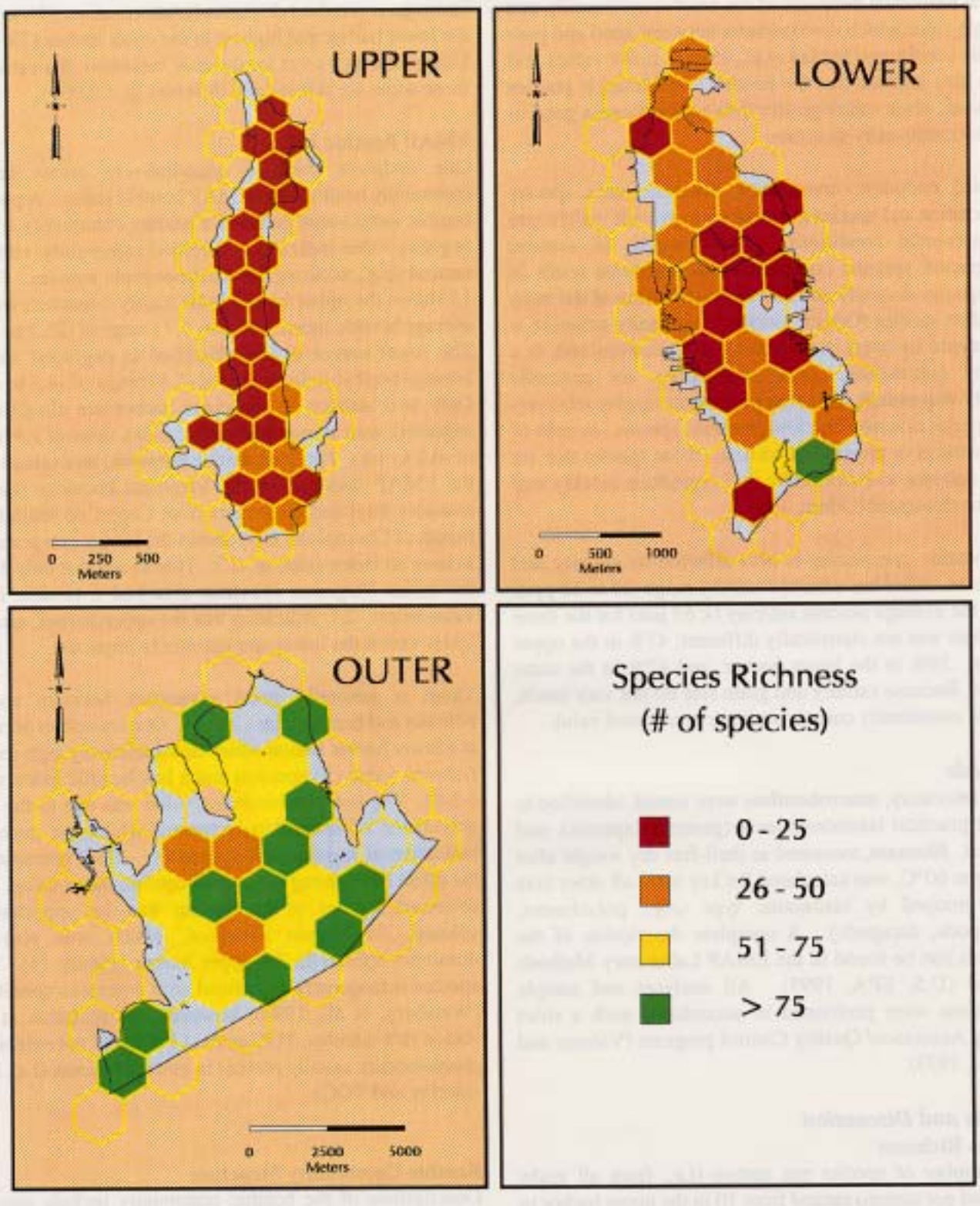


**Figure 12.** Species richness in the benthic community of NBH. Generally, areas with a high species richness, (i.e. that are more diverse) are healthier.

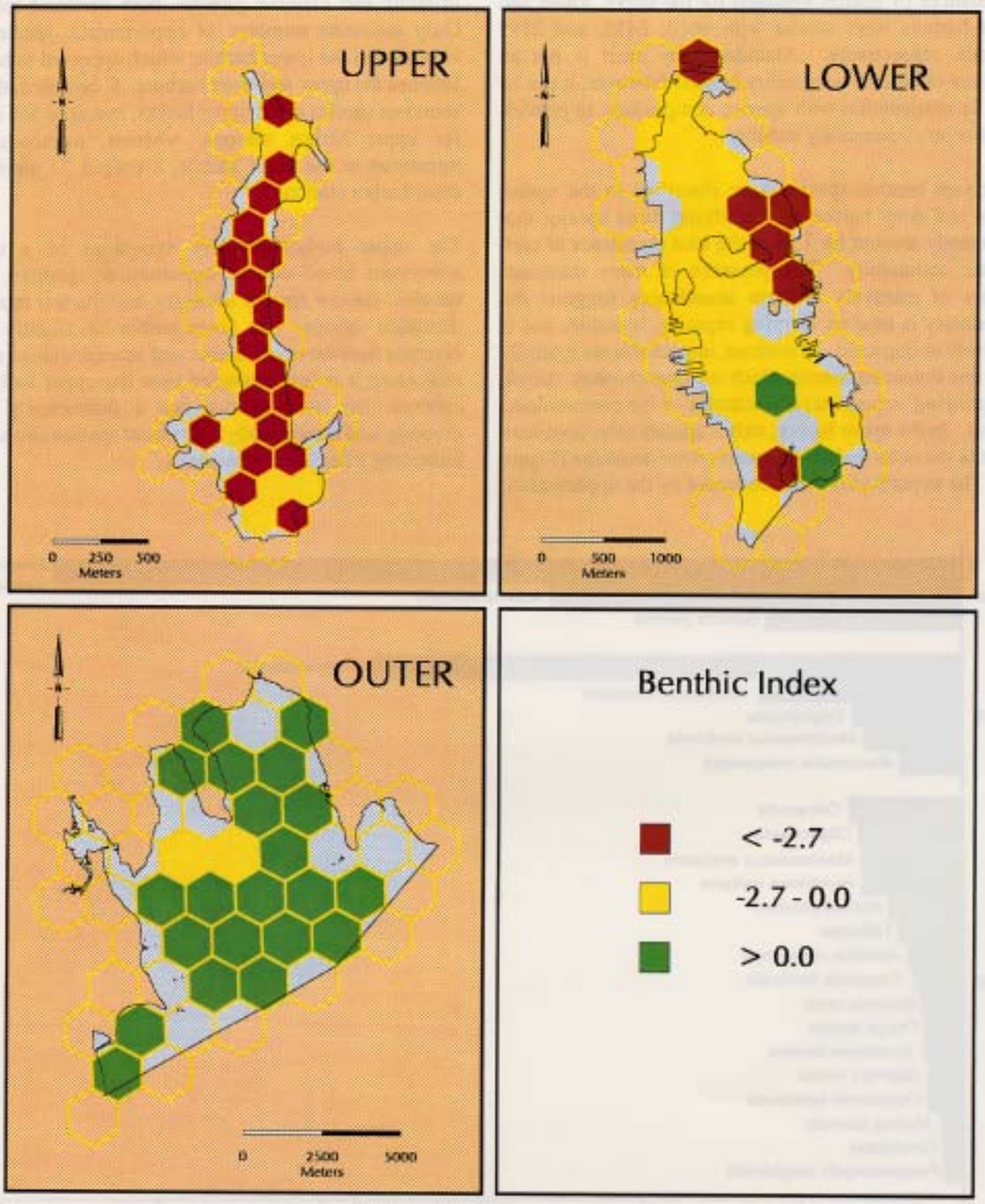


**Figure 13.** EMAP benthic index applied to NBH. A positive benthic index indicates a non-degraded benthic community; a negative benthic index indicates a degraded benthic community.

a low of 154 animals to a high of 18,380 animals. Total abundances by station averaged for the upper, lower and outer harbors were similar with 3612, 2435, and 2295 animals, respectively. Abundance by itself is not an indicator of benthic community health; however, it can be used in conjunction with species composition to provide insights into community stability.

Dominant benthic species were classified in the upper, lower and outer harbor by identifying those species that collectively account for 75% of the total abundance of each benthic community. The presence of many dominant species of relatively uniform abundances suggests the community is near its carrying capacity, is stable, and is relatively unimpacted. In contrast, impacted areas typically have few dominant species which are opportunistic (small, fast-growing organisms) and tolerant of the contaminants present. In the upper harbor, only 3 species were dominant while in the outer harbor, 16 species were dominant (Figure 14). The upper harbor was dominated by the opportunists, *Streblospio benedicti*, a spionid polychaete, and *Mulinia lateralis* and *Gemma gemma*, both veneroid mollusks. Only moderate numbers of opportunistic species were identified in the lower harbor, which appeared to be a mix between the upper and outer harbors. *S. benedicti*, the most abundant species in the upper harbor, averaged 565 animals for upper harbor stations, whereas, ostracods, most numerous in the outer harbor, averaged 71 animals for outer harbor stations.

The upper harbor displays symptoms of a stressed ecosystem based on the opportunistic qualities of the species, the low species diversity, and the low number of dominant species. The lower harbor has slightly greater diversity than the upper harbor and more dominant species, indicating it is less impacted than the upper harbor. In contrast, the outer harbor has a dramatically higher diversity and more evenly distributed species abundances, indicating a healthier ecosystem.

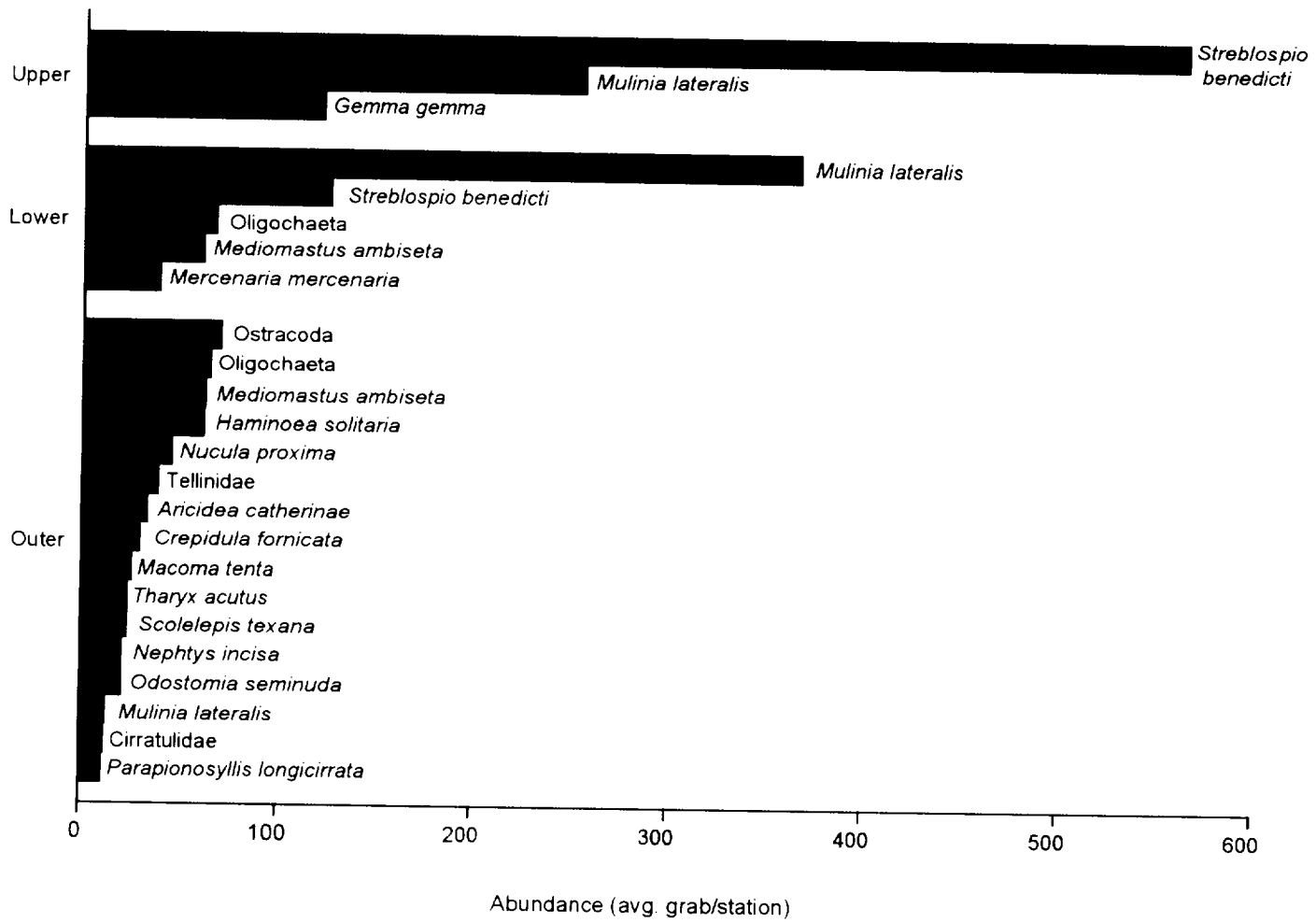


**Figure 14.** Dominant benthic invertebrate species in NBH. Abundances are averaged by grab for each station, then averaged for each harbor segment.



Originals in color.

In summary, all three measures of benthic invertebrate community condition indicate that the benthic community of the highly contaminated upper harbor is degraded. This benthic community had low species richness, a negative EMAP benthic index and was dominated by opportunistic species. The benthic community in the lower harbor, although less degraded than that of the upper harbor, was also significantly impacted. Opportunistic species dominated in the lower harbor; however, in lower numbers than the upper harbor, and species richness was higher. Lastly, with a few exceptions, the outer harbor benthic community can generally be classified as healthy, based on the high species richness, positive EMAP benthic index value, and even distribution of the dominant species.

## Bioaccumulation

### *Blue mussels* (Mytilus edulis)

Quantifying changes in the sediment (i.e., chemical concentrations, toxicity, and benthic community) fulfills one aspect of assessing the effectiveness of remedial activities in NBH. However, contaminants present in the water column can be transported to other areas and also can be incorporated into the food chain. Therefore, a second important objective is to document that reduced PCB sediment concentrations result in reduced water column concentrations. While quantifying PCB water column concentrations throughout NBH is possible, it would require large water volumes and many expensive analyses. Also, one-time sampling events are not always sufficient to encompass all the variability inherent in a dynamic estuarine system like NBH; water PCB concentrations are affected by tides and weather events (e.g., wind, storms). An alternative approach is to use organisms to provide this information.

Filter-feeding bivalves (e.g., mussels, oysters) "sample" the water column almost constantly, thus integrating the effects of tides and weather. Because of this, blue mussels have been used extensively to quantify chemical pollution (Arimoto, 1981; Farrington, 1983; Rice and White, 1987; Tanabe et al., 1987; VanderOost et al., 1988). In addition, a previous study in NBH demonstrated a good correlation between PCB water column concentrations and blue mussel tissue residue concentrations (Bergen et al., 1993). Finally, research conducted with blue mussels in NBH by AED scientists since 1987 shows a relatively constant bioaccumulation rate of PCBs over that time period. This provides an excellent comparative data set to assess future measurements. Based on all these factors, blue mussels were selected to measure PCB concentrations in the water column at several locations in NBH.

### Methods

Detailed methods for collecting and deploying blue mussels are found in Nelson and Gleason (1995). Briefly, uncontaminated mussels were collected from East Sandwich, MA, and placed in polyethylene mesh bags. Four independent replicate bags of mussels were deployed 1 meter above the bottom at three sites: Coggeshall St. Bridge (NBH-2), at the boundary between the upper and lower harbor; Hurricane Barrier (NBH-4), at the boundary between the lower and the outer harbor (Buzzards Bay); and West Island (NBH-5), a reference site in Buzzards Bay (Figure 15). After 28 days, the mussels were retrieved and frozen. Prior to analysis, mussels were thawed, shucked and homogenized. Two grams of the homogenate were extracted with acetonitrile and pentane, solvent-exchanged to hexane and analyzed by gas chromatography for the same 18 PCB congeners quantified in the sediments (Bergen et al., 1993).

### Results and Discussion

Total PCBs in the blue mussel tissue for all three stations are shown in Figure 16. The December 1993 and May 1994 deployments are part of the NBH-LTM program. Mussel deployments at this site for the last four years show no significant difference in mussel PCB tissue residues. Some increases in PCB concentration are seen in the spring and early summer as mussels increase their **gonadal** tissue (and lipid content) prior to **spawning**. However, this same seasonal variability was observed at all three stations, including the West Island reference site.

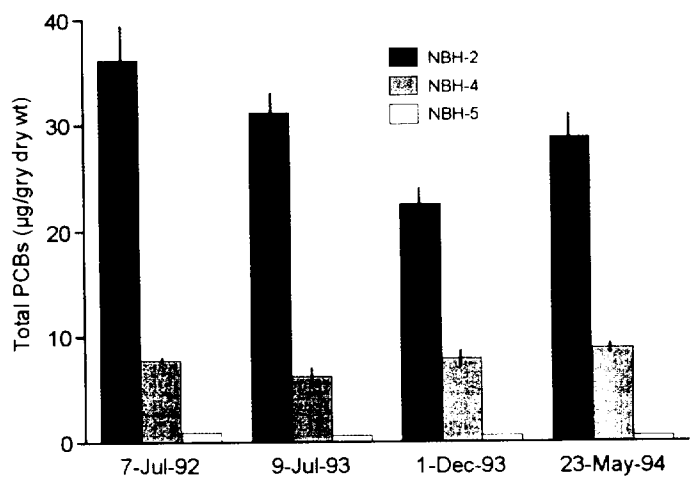


**Figure 16.** Total PCBs (as µg/g dry wt of tissue) in blue mussels at three stations in NBH. The bars represent the average concentration of four replicates; the line represents the standard deviation.

Originals in color.

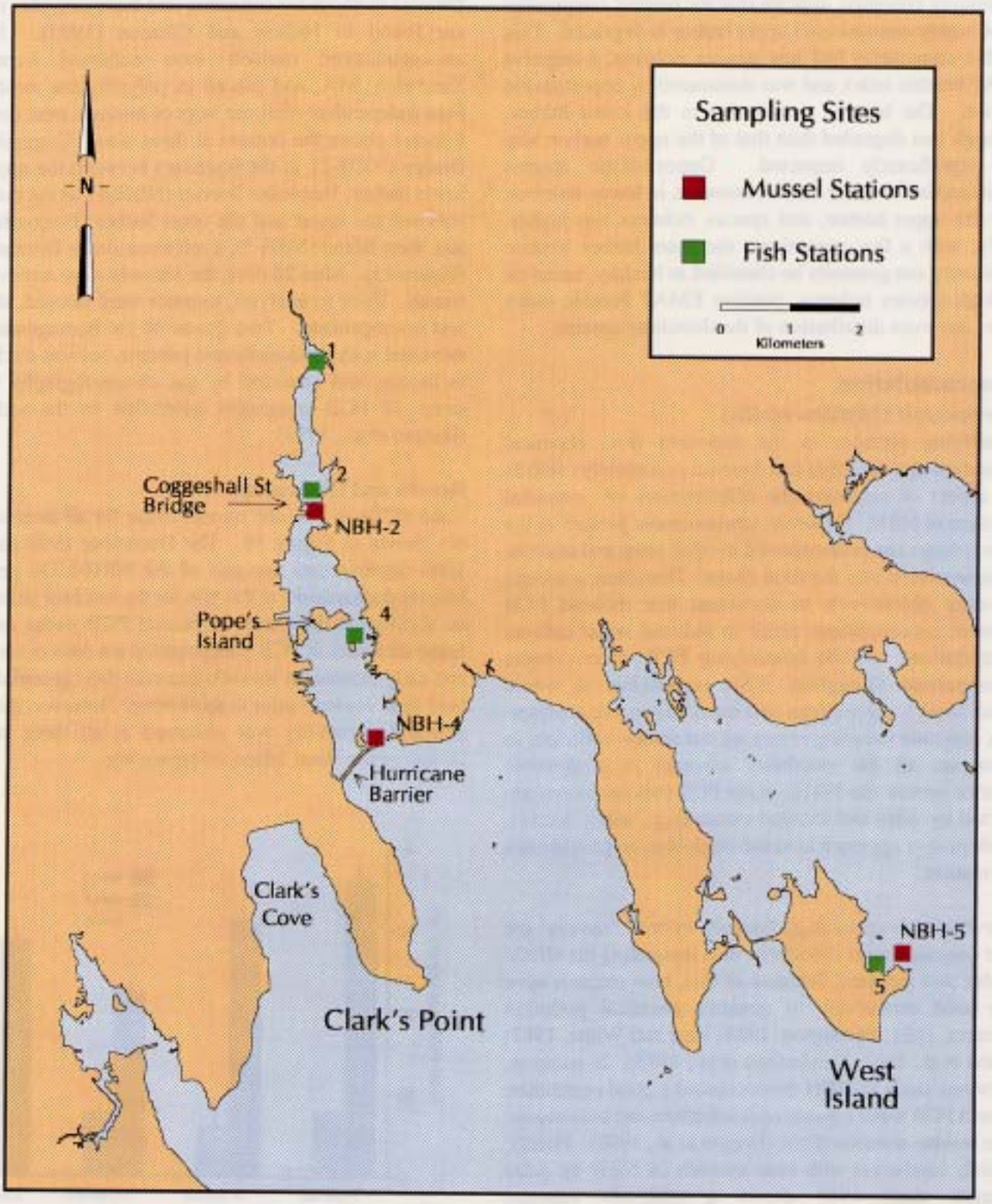


**Figure 15.** Station locations for blue mussel deployments and mummichog collections.

Mussel deployments will continue twice a year (April and October) at all three stations as part of the NBH-LTM program. These data will be used to compare reductions in sediment PCB concentrations due to remediation to corresponding changes in seawater and mussel tissue.

## *Mummichogs* (Fundulus heteroclitus)

Tissue PCB concentrations of indigenous mummichogs (*Fundulus heteroclitus*) were examined because they feed at least partially on material coming from the wetlands and spend their life cycle in a relatively small area. Mummichogs primarily scavenge on the bottom of marsh edges and shoreline and reportedly overwinter in the mud. Gut content examinations have revealed detritus, small crustacea and sand grains in their digestive tract, showing their close ties with the sediment (Bigelow and Schroeder, 1953).

### Methods

In June 1994, four mummichog traps were deployed at each of three sites in NBH and one reference site: Station 1, near the Hot Spot; Station 2, north of Coggeshall St. Bridge; Station 4, near Popes Island; and Station 5, at West Island (Figure 17). Mummichogs were collected and whole fish homogenized for analysis. Approximately 2 g of tissue were extracted with acetonitrile and pentane, solvent-exchanged to hexane and analyzed by gas chromatography for the same 18 congeners quantified in the sediment and mussels. In addition to this suite of 18 PCB congeners, mummichogs were analyzed for **coplanar** congeners CB077, CB126 and CB169. This required an additional split of the extract on a carbon column before analysis on the gas chromatograph.

### Results and Discussion

Mummichog tissue concentrations are shown in Figure 17. Variability was high among replicates within a station; however, there was a dramatic decreasing gradient (two orders of magnitude) in total PCB concentration from the Hot Spot to West Island. Coplanar PCB congeners lack **ortho substitution** on the biphenyl rings. This allows the two rings to move into one plane. While present in low levels, these congeners are particularly toxic (Safe, 1984) and may bioaccumulate in some organisms to higher levels than non-planar congeners (Kannan et al., 1989). All three of the coplanar congeners quantified decreased in concentration by two orders of magnitude from the Hot Spot to West Island. Mummichogs will continue to be collected at these sites every spring to determine whether reduced sediment PCB concentrations result in reduced tissue concentrations of an indigenous fish.

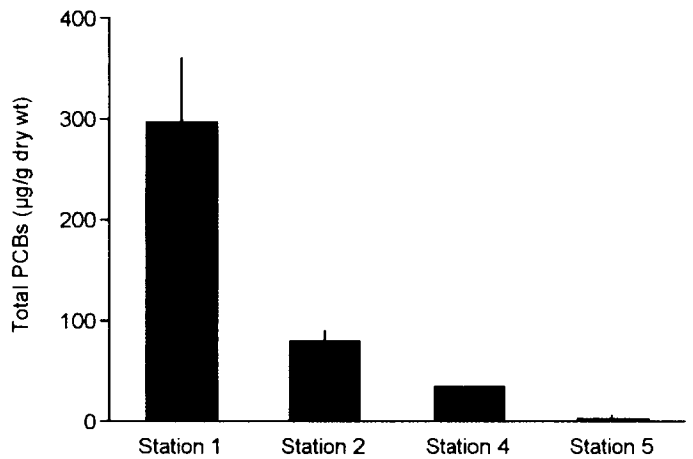


**Figure 17.** Total PCBs (as µg/g dry wt of tissue) in mummichogs collected from NBH. Bars represent an average of four homogenates, with the exception of Station 4. Station 4 is a single homogenate. Vertical lines represent one standard deviation.

# Section IV: Associations Between Biological Indicators and Contaminants

The condition of an estuarine ecosystem is the result of complex interactions between the physical, chemical and biological components of the system. Based on the data from a series of individual measurements, NBH is a highly stressed estuary. This section of the report will examine relationships between these individual measurements in order to better assess the overall ecological condition of NBH. For example, studies referenced in an earlier section suggest that TOC affects PCB availability, which in turn may affect the number of species in the benthic community. However, in NBH, do TOC-normalized PCB concentrations relate better to benthic community indices than total PCB concentrations? If not, what other factors are contributing to the observed effects? Examination of these relationships will provide a better understanding of the current conditions in NBH.

## PCB and Metal Normalization

The interpretation of contaminant data is complicated. Various sediment components, such as the amount of TOC or the presence of AVS, influence the availability of contaminants to benthic biota. As stated previously, PCBs have a high affinity for TOC. Therefore, PCBs in high TOC sediments are less available to cause harm to or accumulate in organisms than PCBs in low TOC sediments. Consequently, PCB concentrations in sediments should be normalized to TOC before comparisons are made between PCB concentrations and biological endpoints. However, in NBH the relationship between biological endpoints and PCBs was equivalent whether or not the PCB concentration was normalized to TOC.

There are two probable reasons for this observation. First, any effect of TOC on the availability of PCBs is overshadowed by the magnitude of PCB contamination in the upper and lower harbors. Second, PCBs and TOC **covary** (Figure 18). In areas where total PCB concentrations are high, TOC is also high, and conversely, where PCB concentrations are low, TOC is low. Because trends between the biological endpoints and PCBs are essentially the same whether or not PCBs are normalized, we chose not to use the TOC-normalized PCBs in the graphical presentation of the biological endpoints.

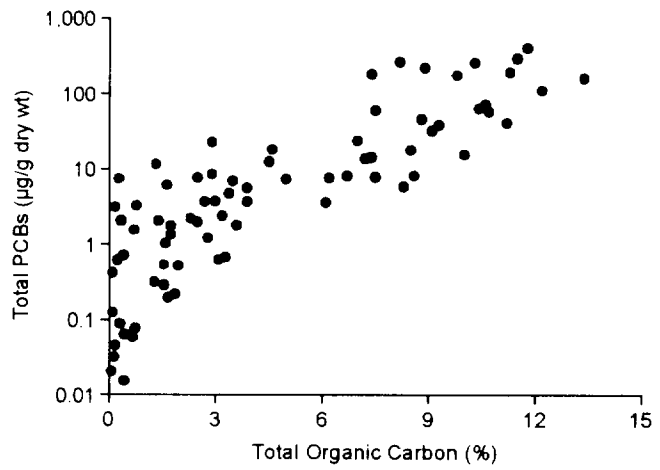


**Figure 18.** Total PCBs plotted against total organic carbon in sediment for all stations in NBH.

The bioavailability of metals in sediment is important to understanding the ecological effects of metals. An organism's response may or may not be related to total metal concentrations. AVS in sediments binds with divalent metals (Cd, Cu, Pb, Ni, Zn and Hg) in a 1:1 molar ratio with the bound metal-AVS complex being biologically unavailable (DiToro, et al. 1990). In this report, normalizing for AVS was done by subtracting the AVS concentration from the sum of divalent metals, both as molar concentrations (Figure 19). Therefore, when the resulting value is negative (i.e., there is more AVS than sum of divalent metals), the sediment should be non-toxic. When metals are in excess, the sediments are potentially toxic. The area with the most stations containing excess metals is the upper harbor.

Importantly, the metal concentrations used in these calculations were the sum of divalent metal concentrations taken from the total metal extraction (2M

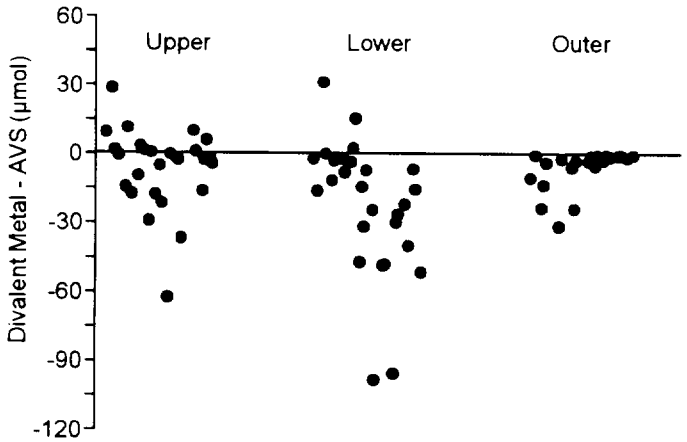


**Figure 19.** AVS normalization (divalent metals - AVS) in µmol/g dry weight for each harbor area. A dot represents a single station. The placement on the horizontal axis is relative to the station's placement in the harbor, but for this purpose it serves only to separate the data.

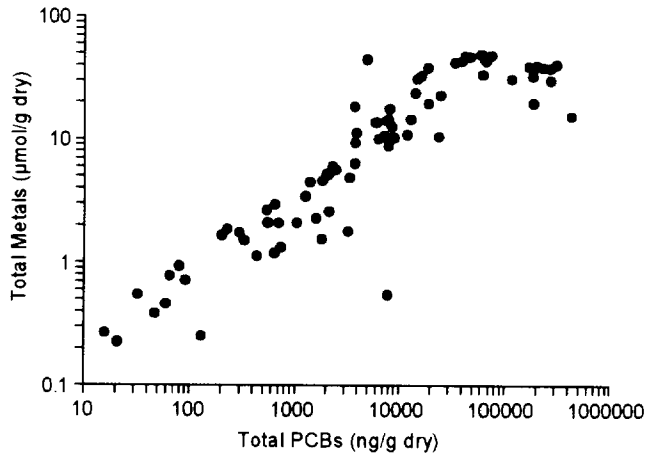


**Figure 20.** Co-location of total PCBs (measured as sum of 18 congeners in ng/g dry wt) and total metals (measured as sum of all metals analyzed in µmol/g dry weight).

nitric acid). Simultaneously extracted metals (SEM) are usually compared with AVS; SEM is the sum of divalent metals from the AVS extraction (1M hydrochloric acid). The concentration of metals from this study should be equal to or greater than SEM because a stronger acid extraction was used than is typical for SEM. Because of this, it is likely that even fewer stations shown in Figure 19 would have available divalent metals.

Normalizing metals with AVS is most often done in conjunction with acute toxicity data (e.g., amphipod survival). Because the data suggest divalent metals may not be biologically available at most stations, only the non-divalent metals (As, Se, Cr) were included in the graphical presentation of the acute toxicity data. However, comparison of the chronic biological endpoint, species richness, was completed using total metals because this is more reflective of what would occur under field conditions.

## Trends Between Biological Endpoints and Contaminants

Comparisons were made between field and laboratory biological effects endpoints and contaminant concentrations. These comparisons used total metals and total PCBs to show the similarity in response to increasing contaminants, regardless of the class (i.e., organic, metal) of contaminant. In general, stations in NBH with high PCB concentrations also had high metals concentrations (Figure 20). Because these contaminants are collocated, it is not possible to attribute causality to a single contaminant. The relationships between species richness and PCBs and metals demonstrate this point. The number of benthic species in NBH decreased as the total PCB concentration increased (Figure 21a). Likewise, the number of benthic species decreased as the total metal concentrations increased (Figure 21b). From these data, it is not possible to determine whether the change in species richness is due to PCBs, metals, or both. More likely, the observed decrease is due to the cumulative effect of both types of contaminants because most sites with high PCB concentrations also had high metals concentrations (Figure 20).

In contrast to species richness, the amphipod sediment toxicity test is a laboratory measure of acute, or short-term, biological effects. Amphipod survival in NBH sediments decreased when the total PCB concentration reached an apparent threshold (Figure 22a). A threshold also was observed as metal concentrations increased (Figure 22b). Because PCBs and metals covary, as shown in Figure 20, it is not possible to demonstrate a clear relationship between individual contaminants and survival. However, sediments from the outer harbor were generally much less toxic than those from the upper or lower harbors.

## Sediment Toxicity and Benthic Community Condition

The amphipod sediment toxicity test and benthic community indices both measure biological responses to multiple stressors. As stated previously, the sediment toxicity test is a short-term assay that responds predominantly to contaminants present at acutely toxic

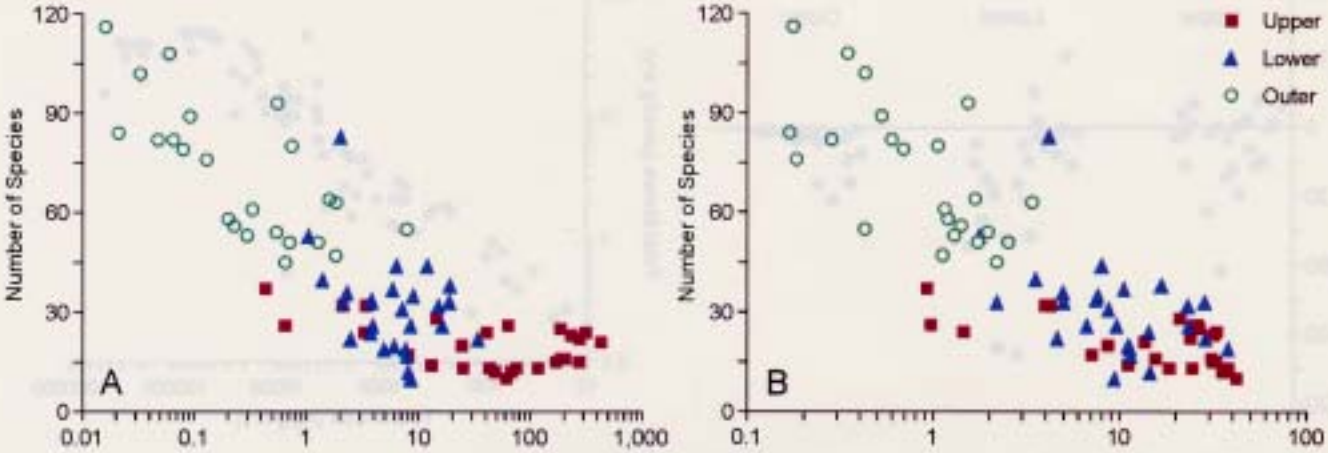


**Figure 21.** Total count of benthic species by station compared to a) total PCB concentrations and b) total metals (as a molar sum of all metals) in the upper, lower and outer harbor sediments.

concentrations. However, benthic community indicators should be more reflective of long-term ecosystem health because they integrate the cumulative effects of all stressors, both chronic and acute. Of the benthic community measures described, the EMAP benthic index assigns a "judgement" of good or bad to a particular community. Benthic index values below zero indicate poor, or degraded, communities. Similarly, in the sediment toxicity test, amphipod survival rates below 80% indicate toxic sediments.

A comparison between the short-term amphipod survival assay and more integrative EMAP benthic index is shown in Figure 23. This graph is divided into four compartments (I, II, III and IV) based on effect levels (80% of control amphipod survival for sediment toxicity and 0 for benthic index). Stations that have both nontoxic sediments and a healthy benthic community are in I. As might be expected, most of these stations are located in the outer harbor. Stations in II have an impacted benthic community; however, the sediments are not acutely toxic. These stations are found in both the lower and upper harbors. Because the benthic condition is degraded and the sediment is not acutely toxic, it appears that the cumulative impacts of these sediments are chronic. Chronic stressors can include non-

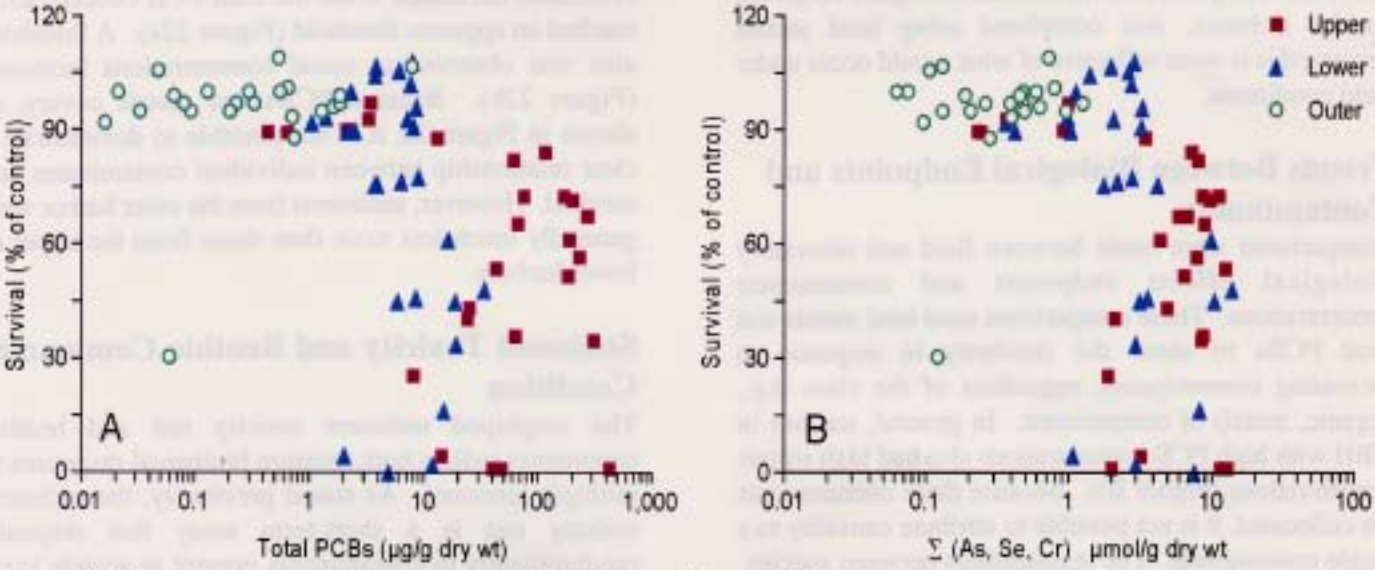


**Figure 22.** Amphipod survival plotted against a) total PCBs and b) non-divalent metals (sum of As, Se, Cr combined as molar equivalents).

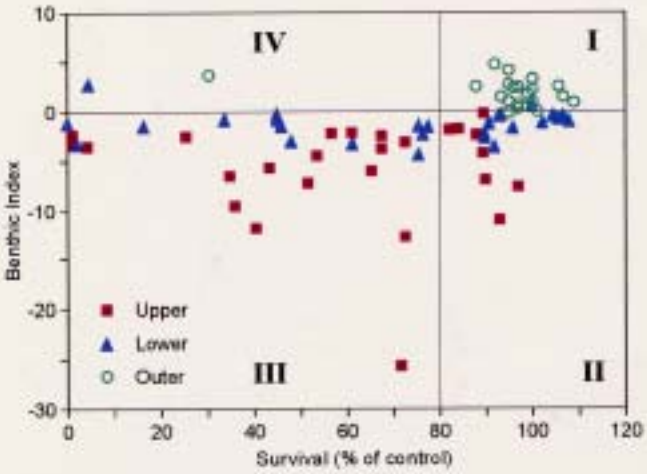


**Figure 23.** The EMAP benthic index plotted against amphipod survival, as a percent of control survival. Negative benthic index values reflect degraded conditions; survival less than 80% reflects sediment toxicity.

contaminant water quality parameters such as low dissolved oxygen concentration. Dissolved oxygen was not measured at each station during the NBH-LTM program. Data collected at the Coggeshall Street Bridge (NBH-2) during the remedial dredging operation indicate intermittent periods when dissolved oxygen concentrations were low. Stations in III have a degraded benthic community and acutely toxic sediments. These stations are distributed primarily among the upper and lower harbors; however, most of the stations are in the upper harbor. At all except two stations, acutely toxic sediments also had a degraded benthic community. These remaining two stations are in IV, where the benthic community is not degraded and the sediment is acutely toxic.

The average total PCBs, selected metals, amphipod survival, and benthic index for I, II and III are summarized in Table 3. Generally, stations in I have low concentrations of PCBs and metals and these stations are not considered impacted. PCB and metal concentrations in II are variable, with many stations having concentrations higher than those in I. Compartment III contains the greatest range and highest concentrations of both metals and PCBs. Only one station in III contained Cu concentrations within the range of concentrations found in I. Overall, these data are consistent with the hypothesis that the biological responses at stations in compartments II and III are due to chronic and acute effects, respectively.

**Table 3.** Health measures and average contaminant concentrations in compartments I, II and III. Metals and PCBs are reported as µg/g dry weight.

| | Compartment | | |
|---|---|---|---|
| | I | II | III |
| Survival (% of control) | 98 | 95 | 45 |
| Benthic index value | 1.9 | -2.3 | -4.5 |
| Total PCBs | 0.93 | 12 | 89 |
| Cd | 0.28 | 24 | 49 |
| Cu | 24 | 240 | 730 |
| Ni | 5.2 | 15 | 27 |
| Pb | 18 | 98 | 270 |

Benthic community analyses, whether species number or a more complex benthic index, are perhaps the ultimate measure of the condition of the sediments at a given station, although such analyses can be costly. Sediment toxicity testing is less costly; however, it does not give as complete a picture of the benthic condition. Figure 23 shows how sediment toxicity and the benthic index can be used together. If sediments are acutely toxic, then there is a high probability that they may also have a degraded benthic community. If resources are limited, benthic community analyses could be concentrated on those samples that are not acutely toxic.

## Future Sampling Recommendations

Future monitoring in NBH should include each indicator used in the baseline monitoring plus several additional indicators. The measurement of these new indicators should improve the ability to define contaminant effects. First, the inclusion of SEM measurements to normalize metals data will improve the estimation of the bioavailable portion of the metals. Six metals are used in the SEM/AVS normalization - copper, nickel, zinc, cadmium, lead and mercury. Those metals could be analyzed from the sediment AVS extract. In addition, interstitial water metals concentrations could be measured.

Second, dissolved oxygen should be monitored in the water column to document potential changes in eutrophication related events, such as algal blooms and low dissolved oxygen. Currently, there is high nutrient input into NBH which can cause eutrophic conditions. Presumably, these conditions are not occurring now because elevated contaminant concentrations are toxic to the algae. However, as the concentration of contaminants

toxic to algae are reduced by remediation, eutrophic conditions may increase. Changes due to eutrophication can be monitored by measuring dissolved oxygen concentrations in the water column. Dissolved oxygen demand increases dramatically as plant and animal materials decompose. This could lead to hypoxia. The most effective way to monitor fluctuations in dissolved oxygen (accounting for temporal changes) is to take measurements over several days. Instruments designed to monitor water quality continuously could be deployed in NBH to document changes in dissolved oxygen. This would help identify eutrophication-related events.

# Section V: Data Documentation

## Data Format and Availability

An electronic copy of the NBH-LTM data and their associated **metadata** are available on PC-formatted 3.5" disks. The data are organized on spreadsheets in Microsoft EXCEL® 4.0 and 5.0 formats. It is the responsibility of the user to read and fully understand the limitations of these data by reading the metadata. In addition, data are stored in hardcopy and electronically at the U.S. EPA, NHEERL, AED. Currently, they are in multiple SAS® data sets that can be combined using unique identifiers such as the station plus sampling date, or sample identification numbers. The data are expected to be converted from SAS® to ORACLE® in the near future at which time all data would be stored in an ORACLE® database using relational tables. Data sets exist with detailed station information (including latitude, longitude, weather conditions and water depth), sampling information, analytical chemistry, sediment grain size, benthic community measures and sediment toxicity tests, quality assurance information, and a dictionary for all data sets available. The name and contents of each data set can be retrieved from the data dictionary. Chemistry and benthic community data sets include all replicates and associated QA codes. Sediment toxicity tests are presented as the average of five replicates, giving a single observation per station.

## Electronic World Wide Web (WWW) Access

It is the intent of this program to make these data easily accessible. Eventually all of the NBH data and associated case studies will reside on the U.S. EPA's WWW service. This service allows users from both the general public and EPA to access this database, browse the data, access GIS maps related to the project, and download data and associated metadata files from within their Web Browser.

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# Glossary

acid volatile sulfide (AVS) - solid phase sulfide in the sediment extracted using cold acid. The ratio of SEM (simultaneously extracted metal) to AVS is used to indicate how available the metals are to the biota.

acute effects - dramatic change in condition of biota, usually mortality, that occurs relatively quickly (hours to days) after exposure.

amphipod - small crustacean, generally scavengers, with an arched 7-segment thorax. Adults range in length from approximately 2 to 40 mm. Some species are tube-dwellers; others are free swimming or burrowers.

anthropogenic - originating from man, does not occur naturally.

ARAR - applicable or relevant and appropriate requirements. ARARs are standards or criteria for cleanup found in federal or state environmental law which are considered pertinent to the Superfund site. Can include water quality criteria or other relevant criteria.

Aroclor® - a trademark used by the Monsanto company to refer to mixtures of PCB congeners.

atomic absorption spectrophotometer (AA) - instrument used to measure metal concentrations. Samples are vaporized and injected into a flame. The light emission of the ignited sample is measured as absorbance at a metal-specific wavelength. Absorbance is related to the sample concentration.

benthic invertebrate community - assemblage of animals without backbones (e.g., worms, shellfish, crustacea) at the sediment-water interface (epifauna) and in the bottom sediments (infauna).

bioaccumulation - the uptake and storage of chemicals from the environment by biota. Uptake can occur through feeding or direct absorption.

bioavailable - the fraction of a compound which is not bound to another material (e.g., AVS, TOC) and which can affect organisms.

biomass - total quantity of organism tissue, generally calculated by drying and weighing a sample.

biomonitoring - analyzing environmental conditions by examing changes in biota (e.g., chemical uptake, survival, etc.).

biota - all organisms, plant and animal, in an ecosystem (collective populations of plants and animals).

CERCLA - Comprehensive Environmental Response, Compensation & Liability Act. Federal law (passed in 1980, modified in 1986) that created a special trust fund (Superfund) to help finance the investigation of hazardous waste sites.

chromatographic - analysis using chromatography. In chromatography, compounds are separated based upon their preference to bind to a stationary or mobile material.

chronic effects - change in condition of biota that occurs over relatively long exposures (months to years). Measures of chronic exposure can include community structure and pathology.

community structure - the assemblage of populations of organisms that interact with each other. The structure is shaped by populations and their geographic range, the types of areas they inhabit, species diversity, species interactions, and the flow of energy and nutrients through the community.

competitive interactions - (competitive exclusion principle) the defining characteristics of a population that are a function of competing with other nearby organisms or populations for limited resources.

congeners - chemical compounds with similar molecular

structures; however, with different molecular weights.

coplanar - lying in the same plane. For PCBs, congeners are coplanar when both biphenyl rings can move into one plane.

covary - things that change in a similar way relative to each other

density-dependent interactions - The defining characteristics of a population that are a function of the number and proximity of its individuals (i.e., in a heavily populated area some organisms do not reproduce). The number and type of relationships between organisms increase as the number of organisms increases in a given area.

divalent - an ion having a double positive charge

ecological risk assessment - a process that defines the magnitude and extent of anthropogenic effects on the ecosystem and estimates the acceptability of those effects.

Environmental Monitoring and Assessment Program (EMAP) - a cross-resource monitoring program designed to statistically evaluate and compare stations across the United States. The Estuaries-Virginian Province team was responsible for monitoring estuaries from the Virginia coast north to Cape Cod, MA.

EMAP index of benthic community condition - a scale indicating degraded or non-degraded bottom sediment communities developed by EMAP. The benthic index is a function of spionid and tubificid abundance, salinity, and Gleason's diversity index.

$$\textbf{Benthic Index} = 0.0489G \quad 0.0545T_{norm} \quad 0.00826\textbf{Spionids} - 2.338$$

$$G = \frac{Gleason}{4.283 \quad 0.498S_{bot} - 0.0542S_{bot}^2 \quad 0.00103S_{bot}^3} \times 100$$

$$T_{norm} = Tubificids - 500 \times e^{-15S_{bot}}$$

$$S_{bot} = bottom\ salinity$$

$$G = \%\ of\ Expected\ Gleason's\ Diversity\ Index$$

euryhaline - organisms able to tolerate a wide variation in salinity.

eutrophic - highly productive ecosystem that generally results from over enrichment of nutrients.

extracted - chemically treated with a solvent to remove a soluble material.

gas chromatograph (GC)- instrument used to separate and identify organic compounds. The volatilized sample is injected into a carrier gas. The carrier gas and sample pass over a stationary material. Compounds pass through the stationary material at different rates, and based on these rates can be separated and identified. The GC can be used for accurate measurements of very small quantities of complex mixtures.

gonadal - relating to the reproductive organs.

grain size - sediment characterization that is a measurement of the average particle diameter. Silt/clay, sand and gravel are the three major classifications used in this report.

gravel - sediment particles greater than or equal to 2 mm diameter and less than 64 mm diameter.

hypoxia - low dissolved oxygen concentration.

ICP - inductively coupled plasma spectrophotometer - analytical instrument used to quantify several metals at the same time.

interstitial - spaces between the sand grains

lower harbor - area between the Coggeshall St. Bridge and the hurricane barrier.

macrobenthos - animals living in the sediment greater than 0.5 mm in length.

metadata - information on quality assurance, quality control, data handling and methods that are associated with research data.

normalize - a technique applied to help evaluate two or more entities on similar scales, mathematically or chemically.

organic compound - generally all carbon compounds (i.e., containing the element carbon) with a few exceptions, such as $CaCO_3$.

ortho substitution - refers to positioning of substituent atoms on adjoining carbon atoms on a biphenyl group ($C_6H_5^+$).

outer harbor - the area from the hurricane barrier to the outer closure line.

ppm - parts per million. Equivalent to μg/g.

polychlorinated biphenyls (PCBs) - two 6-carbon rings (biphenyl - $C_6H_5^+$) with two or more chlorine atoms substituted for hydrogen.

pore water - water in the interstitial space between sediment particles.

probabilistic - designed to be used in statistical manipulations.

ROD - record of decision.

sand - sediment particles greater than or equal to 63 μm and less than 2 mm diameter.

SARA - Superfund Amendments & Reauthorization Act.

sediment toxicity tests - exposure of animals to site-specific sediment for a limited time to determine acute responses (mortality) of the animals to the sediment.

silt/clay - sediment particles less than 63 μm in diameter.

solubility - the ability of one substance to dissolve in another, measured as the amount of solute that will dissolve in a set amount of solvent.

solvent-exchanged - changing the solvent of a solution to one suitable for gas chromatography analysis.

sonicating - disrupting using high frequency sound waves.

spawning - process of fertilization of eggs

species dominance - species or group of species that exert controlling influences over the population by virtue of their population, size, feeding strategy, or mode of reproduction.

species richness - the total number of species in a community.

total organic carbon (TOC) - sum of material in a sample containing carbon compounds. Classically, organic carbon is a result of detritus and decaying organisms.

unbiased - without influence

upper harbor - area north of the Coggeshall St. Bridge in New Bedford Harbor.

Young-modified van Veen grab sampler - a hinged sampling device, resembling a clam shell, for collecting sediment. The device is contained in a frame which helps to keep it flat on the bottom during sample collection. The sediment surface area sampled is 440 $cm^2$.