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FINAL REPORT

for

MODELING OF THE TRANSPORT, DISTRIBUTION, AND FATE OF PCBs AND HEAVY METALS IN THE ACUSHNET RIVER/ NEW BEDFORD HARBOR/BUZZARDS BAY SYSTEM

VOLUME I

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EXECUTIVE SUMMARY

This report provides information on a modeling program begun for NUS Corporation by Battelle Ocean Sciences in 1984 under the REM-FIT program. Field and laboratory studies provided data for input to a physical/chemical model, developed by Battelle, which was interfaced with a food chain model developed by HydroQual, Inc. for simulating various activities in connection with the remediation of PCB effects in the New Bedford Harbor system.

The overall objective of the sampling and modeling program was to develop, validate, calibrate, and apply mathematical models which would:

- predict the movements, distribution and fate of PCBs and heavy metals in the Acushnet River, New Bedford Harbor, and adjacent Buzzards Bay;
- predict the bioaccumulation, transfer, and possible biomagnification of PCBs and metals within key biological components of the local marine food chain, including lobsters, clams, and winter flounder;
- assess the potential effects of dredging, other remedial actions, or storm events on the physical movements and food-chain transfer of PCBs and metals in the harbor and adjacent bay;
- determine possible wast sources of PCBs and metals in different regions and biological components of the Acushnet River/New Bedford Harbor/Buzzards Bay system.

Existing background data for the models prior to the start of the modeling program, including physical, chemical, and biological information, were obtained from a variety of sources including the open literature and a database of information about PCBs in the Acushnet River/New Bedford Harbor/Buzzards Bay system developed by Metcalf and Eddy for EPA, Region I. Other useful data for the models were found in reports of studies conducted by the U.S. Coast Guard, U.S. EPA, the Commonwealth of Massachusetts, Woods Hole Oceanographic Institution (WHOI), U.S. National Weather Service, National Ocean Survey, the U.S. Army Corps of Engineers, and other state and federal agencies.

The existing background data demonstrated that, for considerations of sediment transport and mixing, the major response of the Bay and outer harbor regions is to storm systems. Under all conditions, the outer harbor is forced by conditions in Buzzards Bay, and that the inner harbor is forced by the outer harbor/Buzzards Bay. The available data indicate that the Bay and outer harbor forcing can be reasonably well-characterized from local measurements.

Hydrodynamic field studies were performed to determine the normal and storm-induced patterns of water currents in Buzzards Bay and the inner and outer New Bedford Harbor. An array of current meters was deployed at the entrance to Buzzards Bay for approximately five months in order to establish conditions of water, sediment, and contaminant flux across the boundary of the physical/chemical model. Additional shorter-term current meter and drogue studies were performed in the vicinity of New Bedford Harbor to establish patterns of current flow in this region during summer and winter conditions.

Three drifter experiments were conducted, each yielding increasing amounts of data. The first experiment, designed to test the equipment and determine logistics of the tracking process, was conducted from November 28 through 30, 1984. The second experiment, to yield more data in the vicinity of New Bedford Harbor by increasing the number of buoys deployed and by eliminating the reference buoy interference problem, was conducted from December 17 through 21, 1984. The third drifter experiment was conducted from April 9 through April 13, 1985.

Profiles of velocity and temperature were measured at two locations in Buzzards Bay in December 1984 and January 1985. The first location was in the proximity of Cleveland Ledge and the second was adjacent to Buoy 11 in New Bedford outer harbor. Woods Hole Oceanographic Institution (WHOI) characterized seasonal hydrographic conditions by means of drifters and moored arrays of current meters and temperature/depth sensors. Two hydrographic surveys were carried out during September and October 1984. Current meters providing data on current speed and duration were deployed by Ocean Surveys in shallow, mid-water, and deep locations at three stations in Buzzards Bay over the period from February 6 through March 16, 1986.

During the summer of 1986, a study was conducted by WHOI to provide ground truth for numerical simulations of the circulation of New Bedford Harbor. Information was collected from fixed instruments deployed at five sites throughout the inner and outer harbors, from drifters deployed in the inner harbor, and from two conductivity, temperature, depth (CTD) surveys, one in the inner harbor and one in the outer harbor.

Field sampling was undertaken to provide chemical data for input to the physical/chemical model, and information on biota for the food-chain model. The primary objective of the analytical chemistry program was the analysis of field samples of sediment, water, and biota for PCB, copper, lead, and cadmium. The majority of the anlytical chemistry activities conducted in support of the New Bedford Harbor modeling program were not part of the technical scope of work for the program, but were included in a separate scope of work awarded by NUS Corporation under the REM-FIT Contract. Analytical chemistry included in the modeling program consisted of the analysis of field samples collected during four surveys, and bioconcentration, adsorption/desorption (K_d), and partitioning studies conducted in the laboratory to determine the rates at which selected species of marine animals indigenous to the New Bedford Harbor take up and excrete PCBs, copper, cadmium, and lead from waterborne exposure.

Sampling took place during four seasons in 1984 and 1985 at up to 25 stations in the Acushnet River, New Bedford Harbor and Buzzards Bay. Samples included surficial sediment, surface and bottom water, and biota. Biota samples consisted of hard clams, mussels, polychaete worms, spider crabs, winter flounder, and lobsters. Animals used in the laboratory studies included lobsters and winter flounder fed polychaete worms and clams exposed to the contaminants. All analytical chemistry data used in the modeling program were from the analyses conducted by Battelle Ocean Sciences, Energy and Environmental Engineering, Inc., and Aquatec, Inc.

Data management for the modeling program included two different types of activities. The original prupose of the data management task under the REM-FIT program was to compile field data collected for model calibration and

validation, implement a central database, and disseminate data to modelers in formats that would facilitate calibration and validation of the models. Under the REM III program, Battelle assumed responsibility from Alliance Technologies Corporation for management of a wider variety of historical data sources from the site.

For the physical/chemical model, a three-dimensional hydrodynamic and sediment/contaminant transport model, the TEMPEST/FLESCOT code, was applied to New Bedford Harbor to analyze the transport and fate of PCBs within the system. The marine version of the TEMPEST computer code, based on the Navier-Stokes equations, was designed as a three-dimensional computer code to model large-scale marine hydrodynamic simulations such as three-dimensional, time-dependent flows in bays, estuaries, coastal zones, lakes, and oceans. The FLESCOT constituent transport routines are operationally embedded in the marine version of TEMPEST, and account for sediment transport, contaminant transport, and sediment-contaminant geochemistry in the water column and bed. The model is a tool that can be used to comparatively evaluate the no-action and remedial-action alternatives of a future period. The model developed for New Bedford Harbor estimates water column and bed sediment total PCB concentrations, which in turn can be used in risk assessment studies and in modeling total PCBs in the food chain.

Various field data were collected and used to establish initial and boundary conditions for the TEMPEST/FLESCOT model, and to develop a conceptual description of circulation and contaminant transport in New Bedford Harbor. Bathymetric data and shoreline location information were obtained from National Ocean Survey charts, surveys performed for the U.S. Army Corps of Engineers, and unpublished surveys performed by Tibbetts Engineering Company. These data were used to establish the initial depth conditions in the model. Information on grain size and distribution of PCBs in bottom sediments, used as initial conditions, was obtained from the Battelle, Alliance, and GCA databases. The Alliance and GCA databases were later incorporated into the overall Battelle database. The PCB data represented many depth intervals. Only the surface samples, representing the upper 20 cm of a sediment core, or

results from surface grab samples were used in generating the initial conditions for the model.

The time-varying distribution of PCBs in New Bedford Harbor depends on a number of factors, including the source of the PCBs, physical-chemical properties of PCBs--especially their affinity to bind to sediments--resuspension of PCB-contaminated bottom sediments, and circulation patterns and intensity for transporting dissolved and sediment-bound PCBs within the harbor. Conceptually, the migration of PCB contamination from the source area in the upper harbor to Buzzards Bay and the atmosphere was modeled as follows:

- PCBs migrate from the highly contaminated bottom sediments into the overlying water column as a result of 1) desorption from fine-grained sediment particles and upward diffusion in interstitial (pore) water, 2) erosion and resuspension by boundary layer currents, and 3) benthic organisms. The latter two processes are responsible for most of the PCB transport from the sediments.

- Dissolved PCBs in the water column readsorb to "clean" fine-grained sediment particles exported to the harbor from Buzzards Bay and upland sources.

- Gains and losses of particle-bound PCBs from the Harbor represent a sediment transport problem involving erosion and deposition and advective and diffusive transport of suspended particles.

- Transport and losses of dissolved PCB from the water column depend on the balance between the rates at which the chemical evolves diffusively from contaminated bottom sediments, advects to and from the system, and evaporates to the atmosphere.

The most important PCB transport processes occurring in the calibration simulations is the tranfer of PCBs from the bed to the overlying water through direct desorption. Once in the water column, PCBs are volatilized in significant amounts in the shallow areas of the upper estuary. PCBs are also transported toward Buzzards Bay through the action of tidally driven flow. Although these observations are in general agreement with field measurements, the estimated concentrations computed by the model should be used as a

baseline to compare the relative effectiveness of the modeled remedial actions.

The food chain model used to compute PCB concentrations in the New Bedford Harbor lobster and flounder food chains is formulated from equations that describe the uptake and loss of chemical by species representative of the major predator-prey links from the base of the food chain to the animals of interest. Development and application of the model involves:

- determination of the species that form the food chain of the animals of interest (i.e., lobster and flounder) and the predator-prey relationships between these species,
- quantification of the growth and respiration rates of each species, and the dependence of these rates on temperature and animal size or age,
- estimation of the efficiency of food assimilation for each predator,
- determination of the average concentrations to which animals within a defined region are exposed and determination of the average concentration in each animal within the defined region,
- determination of appropriate ranges for the rates of chemical uptake and excretion for bounding these parameters during model calibration,
- calibration of the model by determining the uptake and excretion rate values that result in computed chemical concentrations that quantitatively agree with measured values and are consistent with laboratory and field measurements of these parameters,
- projection of the response of the animals to changes in water and sediment chemical concentrations that the physical/chemical model projects will result from various remedial alternatives.

The PCB and heavy metals measurements determined in the analytical chemistry portion of the program form the calibration data set for the food chain model. The water column and sediment measurements provide estimates of the contaminant concentrations to which the biota were exposed. The biota measurements provide body estimates against which the food chain model was

calibrated. Historical data were compared to the Battelle cruise data to assess temporal trends in biota contamination and evaluate the validity of assuming that the exposure concentrations were constant over each animal's life span. The calibration of the model for PCBs and metals is presented, but because the physical/chemical model only evaluated PCB fate and transport, the food chain model did not evaluate metals past the calibration phase.

Food chains are considered for each of the closure areas. Initially, a fourth area representative of the Buzzards Bay region south of Area 3 was planned to be modeled. However, since the physical/chemical model did not extend this far into Buzzards Bay, this region was not modeled past the calibration phase

In the model, the lobster food chain is represented by crabs, mussels, polychaetes, phytoplankton, and sediment detrital organic material. Young-of-the-year winter flouder are assumed to consume equal percentages of phytoplankton and polychaetes. Older flounder are assumed to consume polychaetes only. In the model, polychaetes are viewed as representatives of the variety of benthic animals that are prey for the flounder.

The food chain model was calibrated for homologs 3 through 6 and for total PCB. There is generally good agreement between the observed data and the calculated concentrations for the homologs and for total PCB. The model successfully reproduces the variation in body burdens across the homologs and over the entire food chain. Computed and observed whole body concentrations in flounder are higher than in the lobster. The model indicates that this is due to the higher whole body lipid content of the flounder and to differences in the food chain structures of these species.

The final chapter of the report presents estimates of the long-term fate and transport of PCBs in the New Bedford Harbor system over a 10-year future period for a No-Action and various Remedial-Action scenarios. The physical/chemical model was interfaced with the food chain model for simulation of the various scenarios.

The results of the remedial action scenarios in the physical/chemical model can be put into perspective by comparing the computed net flux and area averaged water column and bed sediment concentrations at the end of the 10-year simulations. The Hot Spot and 500-ppm scenarios can be seen to produce comparable results because of the similarity of their initial distributions of PCBs within the bed sediments. In addition, the results of the remaining scenarios show much reduced fluxes through the Coggeshall Street Bridge and the Hurricane Barrier as well as lower water column and bed sediment concentrations compared to the No-Action scenario. The Remedial-Action and No-Action scenarios yield similar concentrations in the outer harbor region, suggesting that the effects of a cleanup action will be localized. For example, removal of the Hot Spot will not lead to dramatically reduced water column and bed sediment concentrations in the lower harbor and outer harbor.

The results of the food chain model generally follow the same pattern as the physical/chemical model projections. Little change is seen in biota PCB concentrations relative to No-Action south of the Hurricane Barrier with the exception of the 1-ppm remedial scenario. Results of the Upper-Estuary and Lower-Harbor remedial scenarios are similar to those of the 50-ppm scenario. Similarity also exists between the results of the Hot Spot and 500-ppm scenarios. Between the Hurricane Barrier and the Coggeshall Steet Bridge, there are reductions in biota concentrations resulting from the Upper-Estuary, Lower-Harbor, and 50-ppm scenarios, flounder from the lower portions of Area 1 experiencing an average decline in concentrations of 50 to 60% in response to these scenarios. North of the Coggeshall Street Bridge the greatest decline in steady-state biota levels is associated with the 1-ppm scenario, and significant reductions are projected for the 50-ppm scenario. the 50-ppm scenario exposure conditions are generally similar in magnitude to those of the Upper- and Lower-Estuary scenarios within this region.

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1.0 INTRODUCTION

1.1 OVERVIEW AND REVIEW OF THE NEW BEDFORD SITUATION

The Acushnet River estuary, which in its middle and lower reaches forms New Bedford Harbor, Massachusetts (Figure 1.1), is heavily contaminated with polychlorinated biphenyls (PCBs) and several heavy metals. The cities of New Bedford and Fairhaven, with a combined population in excess of 100,000 occupy the west and east banks of the estuary, respectively.

New Bedford has been a major East Coast shipping and fishing port since colonial times. Although commercial fishing continues to be an important local industry, light manufacturing and processing industries sprang up in the area following the decline of the whaling industry in the mid-1800s. Current and past local industries include textiles, dying, electroplating, metal finishing, and electrical component manufacture.

Two New Bedford electrical component manufacturing facilities, Cornell-Dublier and Aerovox, have used PCBs in the manufacture of electrical capacitors since the 1940s. Wastewater contaminated with PCBs was discharged by these and possibly other industries to the harbor and the municipal sewage system for at least thirty years. In addition, discharges of metal-contaminated wastewater to the harbor and sewer system have occurred for at least as long or perhaps much longer.

Until 1971, the electrical component manufacturers used primarily Aroclor 1242 and lesser amounts of Aroclor 1252 and 1254 in the manufacture of their capacitors. In 1971, Monsanto replaced the more highly chlorinated mixtures with Aroclor 1016 which contained less heavily chlorinated biphenyls and was considered less environmentally damaging. Aroclor manufacture in the U.S. was banned altogether in 1976, but users were allowed to use up the Aroclor in stock. Aroclor use in the Cornell-Dublier and Aerovox facilities probably continued until 1977 or 1978.

Elevated concentrations of PCBs, usually measured as Aroclor 1254, were first reported in sediments of New Bedford Harbor in 1975. Since then, a large number of investigations have documented the widespread contamination of sediments and marine biota of the Acushnet River, New Bedford Harbor, and adjacent Buzzards Bay with PCBs. PCB concentrations in sediments of the upper Acushnet estuary near Aerovox frequently exceed 500 mg/kg (ppm) dry weight and occasional samples contain in excess of 10,000 to 100,000 ppm (1 to 10 percent). Of the local estuarine biota, eels (Anguilla rostrata) appear to be the most heavily contaminated, with body burdens occasionally in excess of 500 ppm. The Food and Drug Administration (FDA) tolerance level for the edible portion of fish and shellfish is 2 ppm. PCB concentrations in lobster (Homarus americanus) and winter flounder (*Pseudopleuronectes americanus*) frequently exceed this level.

Because of the high level of PCB contamination of some commercially important fin- and shellfish, the Massachusetts Department of Public Health (DPH) issued a warning in March 1977 that demersal finfish from the New Bedford Harbor area should not be consumed. In June 1977, a second warning was issued relative to consumption of lobsters from the area. New Bedford Harbor was formally closed to fishing for human consumption on September 25, 1979. The closed area was divided into three sections (Figure 1.2). Area 1 is closed to the taking of all finfish, shellfish, and lobsters; Area 2 is closed to the taking of lobster and demersal finfish (e.g., flounder, scup, tautog, and eels); Area 3 is closed to the taking of lobsters.

In 1980, the Massachusetts Department of Environmental Protection (DEP) formerly known as the Department of Environmental Quality Engineering (DEQE) designated the New Bedford Harbor PCB problem as a priority in the State-EPA agreement drawn up that year. In 1982, the Acushnet River estuary, New Bedford Harbor and adjacent Buzzards Bay were designated a U.S. Superfund hazardous waste site, and remedial action planning was initiated. More recently, the U.S. Justice Department filed a law suite on behalf of NOAA against the capacitor manufacturers seeking damages for the loss of natural resources in the region because of PCB contamination of fishery products and habitat.

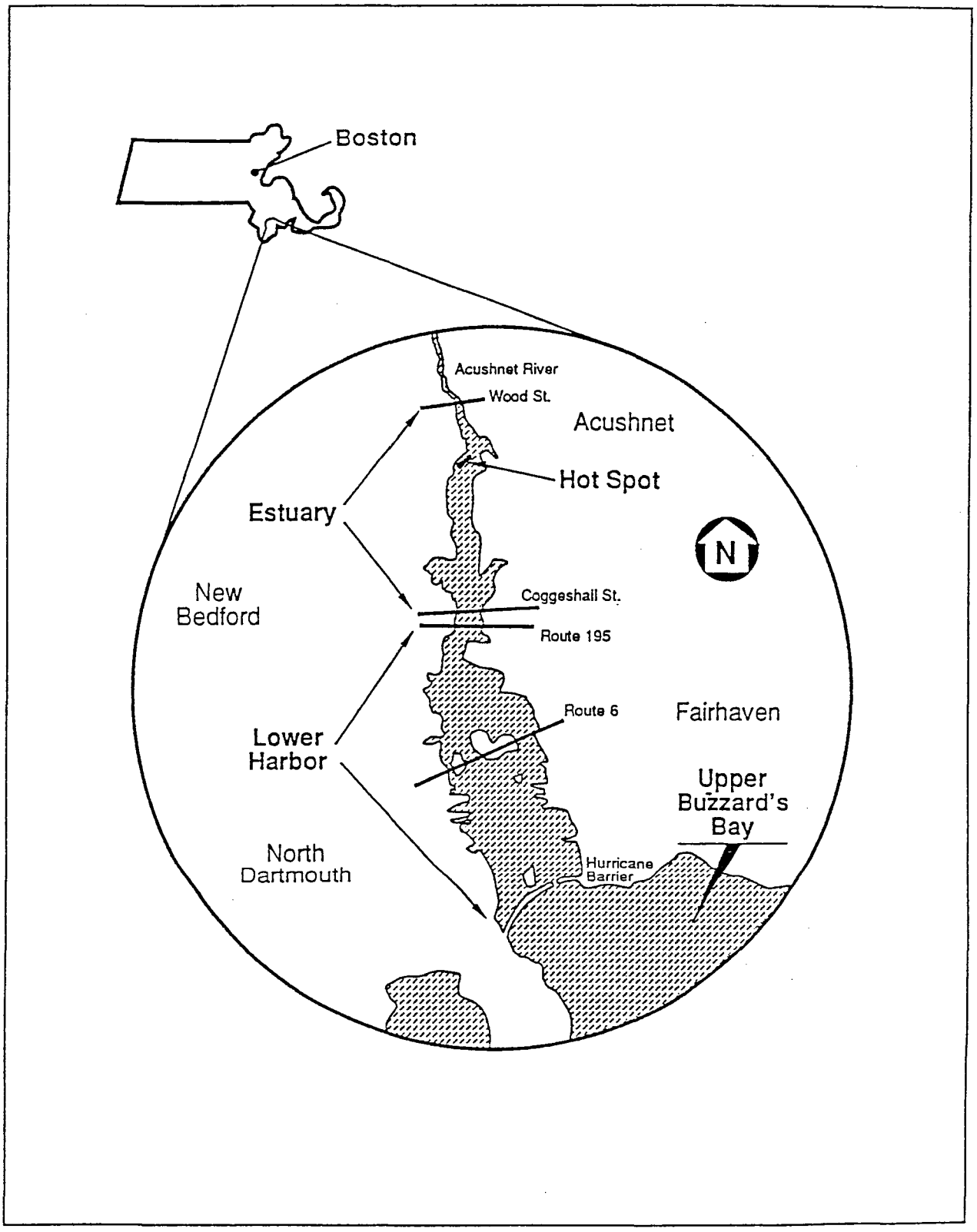

FIGURE 1.1. SITE LOCATION MAP

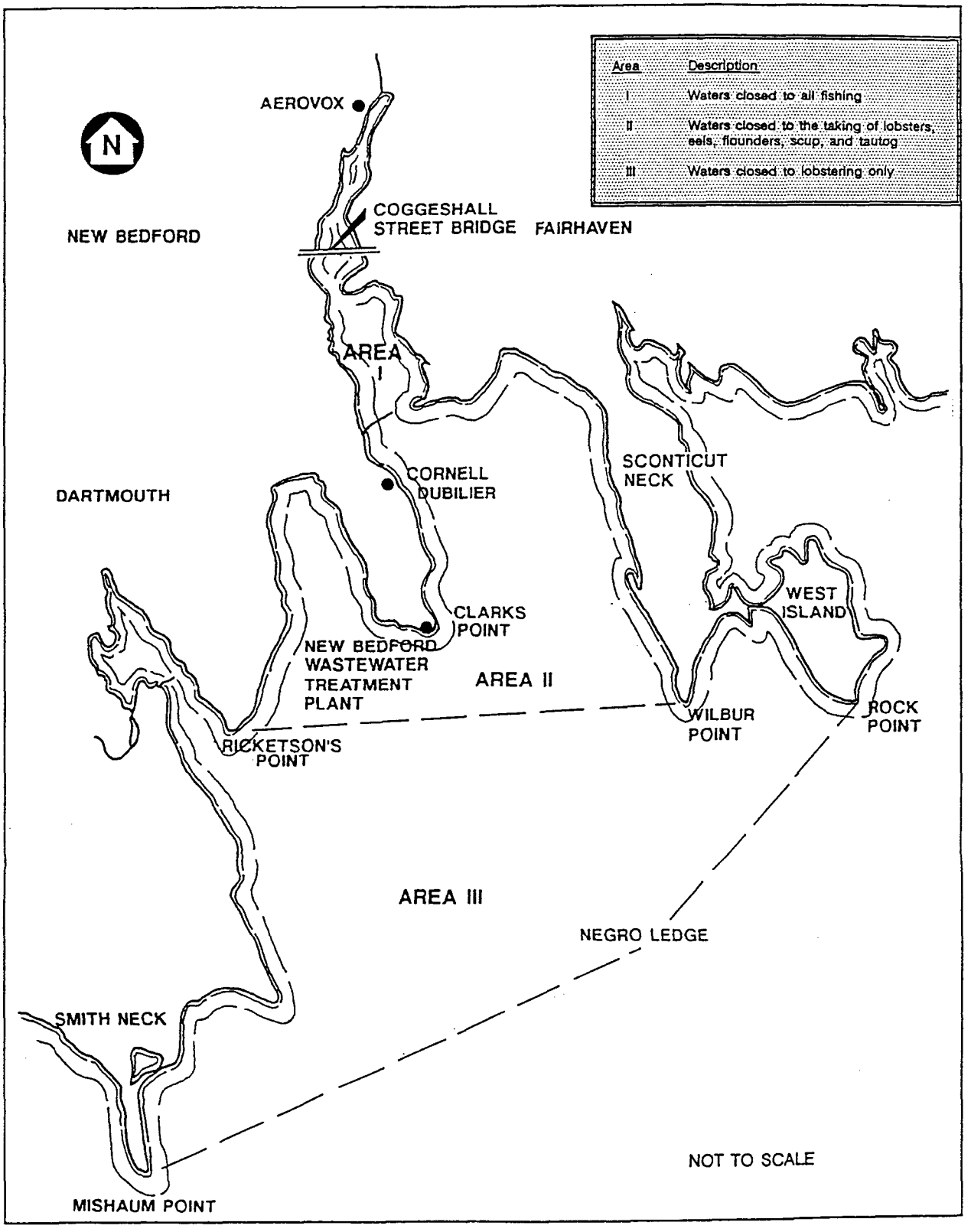

FIGURE 1.2. NEW BEDFORD HARBOR FISHING CLOSURE AREAS

In 1977, sediments from the harbor were reported to contain substantially elevated concentrations of several heavy metals, including arsenic, cadmium, chromium, copper, lead, mercury, silver, and zinc. The most abundant metals were copper, chromium, and zinc. Some sediment samples contained in excess of one percent of these three metals combined.

New Bedford Harbor is a very busy port. It is utilized by a commercial fishing fleet of approximately 250 to 300 vessels and a recreational fleet of 300 to 400 small boats. Coast Guard cutters up to 315 feet long, cargo ships up to 585 feet long, and cruise ships up to 600 feet long regularly call at the port.

1.2 OBJECTIVES OF THE MODELING PROGRAM

The objectives of this task were to estimate the transport, deposition, and resuspension, as well as the fate of PCBs in the New Bedford Harbor System. The information produced was forwarded to the REM III team conducting a feasibility study to help determine the effectiveness of remedial actions in reducing the concentrations of PCBs in the study area.

1.3 COMPOSITION AND RESPONSIBILITIES OF THE PROGRAM TEAM

Battelle-Northwest modified the three-dimensional TEMPEST/ FLESCOT model to be applicable to the Acushnet River/New Bedford Harbor/Buzzards Bay System case and applied it for a series of cases with and without remedial action scenarios. The model was augmented by physical oceanography data supplied by Woods Hole Oceanographic Institution. These data were derived from a three-component study by WHOI to study the tidal and subtidal circulation and dispersion in Buzzards Bay. The three components included: 1) a study to measure the temporal and spatial structure of Lagrangian currents and particle dispersion near New Bedford Harbor and within Buzzards Bay, 2) a moored array experiment conducted across the mouth of Buzzards Bay to observe currents and inflow into the bay and monitor sea level fluctutions within the bay, and 3) a series of hydrographic surveys to measure water column stratification during the drifter and moored array experiments.

HydroQual, Inc. used data collected by Battelle Ocean Sciences on PCB concentrations in selected fish and shellfish in an existing detailed food web model and applied the model to important sectors of the New Bedford marine ecosystem to evaluate the potential for transfer of PCBs through the food webs as a result of various remediation alternatives. The model was carried through calibration for PCB and metals but only used to model the results of PCB remedial actions.

1.4 NON-TECHNICAL DESCRIPTION OF THE MODELS

PCB migration in the Acushnet River/New Bedford Harbor/ Buzzards Bay system are apparently controlled by several mechanisms including transport resulting from water movement, sediment movement, and bioturbation; intermedia transfer resulting from adsorption/desorption, precipitation/dissolution, and volatilization (for PCBs); and, to a lesser degree, degradation resulting from chemical and biological processes.

In predicting the migration and fate of the PCBs in the study area, as many of these complex and interacting mechanisms as possible were integrated into a single system. Mathematical models, coordinated with field and laboratory measurements are one of the most effective ways to integrate these mechanisms into a single system. The mathematical model chosen for this study included many of these mechanisms explicitly to estimate the transport and fate of PCBs within the, or in some cases, they were modeled implicitly.

A review of the New Bedford Harbor estuary system indicated that the major hydrodynamic characteristics are driven by winds and tide. Because the movement of the water mass is associated primarily with winds and tidal action, the influence of these features was incorporated. For instance, tides were simulated through the daily cycle because, in the absence of winds, tides are the only major causes of water, sediment, and contaminant transport. Winds are expected to induce major circulation patterns in the surface water and, therefore, a variety of wind conditions were considered including storms, which significantly affect the resuspension of sediments. In addition, wind

induced circulation causes three-dimensional velocity distributions, which possibly produce counter flows near the seabed.

Thus, to simulate accurately these flow fields, an unsteady, three-dimensional hydrodynamic model was used. Solar heating during the summer and early fall may lead to a degree of stratification affecting flow patterns in the study area, especially in the shallows of the northern and western regions of the system. Spatial variations of salinity are small, and this effect could probably be eliminated from the standpoint of hydrodynamic analysis.

Transport of sediments in the system is controlled by flows affected by winds and tides, as well as by wind-induced waves that occur under normal and storm conditions. The sediments in the study area vary from coarse sand to fine clay and organic matter. Because sediment migration (transport, deposition, and resuspension) and contaminant adsorption/desorption vary significantly with sediment sizes (e.g., sand, silt,and clay) and types (e.g., inorganic and organic materials), sediments of different sizes and types were evluated separately to determine their migration and adsorption/desorption potential. In addition, because PCBs exist in both dissolved and particulate (sediment-sorbed) phases, the models considered the interactions of PCBs with water and sediments (both suspended and bed sediments).

Therefore, to simulate the hydrodynamics and transport of energy/mass (e.g., water temperature, salinity, sediments, and PCBs) in the New Bedford Harbor system, an unsteady, three-dimensional, numerical model was used to address many of these important physical/chemical/biological phenomena that impact the transport process. The time-dependent, three-dimensional code, TEMPEST/FLESCOT, was used in this study because it has the ability to solve for hydrodynamics, water temperature distribution, salinity distributions, turbulence, sediment transport for three sediment size fractions, dissolved contaminant transport, and particulate (sediment-sorbed) contaminant transport for three size fractions. The code was modified and used to predict the transport, distribution, and fate of the PCBs within the study area. Modeling was coordinated with field and laboratory measurements, which were conducted by Battelle Ocean Sciences and Woods Hole Oceanographic Institution. The

estimated distribution of PCBs in the water column and in the seabed was supplied to HydroQual Inc., as input for their food chain modeling to determine PCB accumulations in selected aquatic biota.

1.5 OVERVIEW OF THE MODELING PROGRAM

1.5.1 Program Components

To achieve the program objectives, the modeling effort was divided into five subtasks:

1. Review and evaluation of existing data
2. Modification of the model
3. Field sampling support and data analysis
4. Application of the model
5. Evaluation and reporting

1.5.1.1 Review and Evaluation of Existing Data

Available information on flows, tides, waves, wind, water temperature, salinity, sediment, PCBs, in the study area were compiled, reviewed, and evaluated for use in the model. In addition, available analytical/empirical formulations of wind-induced waves, wave capacity to suspend the sediment, erosion and deposition of cohesive sediments (i.e., silt and clay), bioturbation, marine turbulence, and bed shear stresses were reviewed to determine their suitability for incorporation into the TEMPEST/FLESCOT code.

1.5.1.2 Modification of the Model

The basic structure of the TEMPEST/FLESCOT code met the program requirements, but certain modifications were made to satisfy the specific requirements of the study. The major modifications to the code were the addition of a free surface calculation scheme and the capability to solve the transport equations using previously computed and stored hydrodynamics. Minor modifications

included expansion of boundary condition tables so that winds could vary spatially in time, improvement of wind stress and bottom drag models affected by waves, and improvement of the turbulence model to handle anisotropic effects. TEMPEST/FLESCOT was modified to include mechanisms of wave mechanics to suspend the sediment. The model code was also streamlined to improve computation efficiency for the Buzzards Bay marine applications.

1.5.1.3 Field Sampling Support and Data Analysis

Woods Hole Oceanographic Institution conducted field studies of the hydrodynamic and fluid characteristics of New Bedford Harbor and Buzzards Bay to be used as open boundary conditions and for calibration and assessment of the TEMPEST/FLESCOT model. These studies included surface drifter deployments in the vicinity of New Bedford Harbor to describe local circulation patterns, continuous current magnitude and direction data at the open boundary, and CTD data elsewhere in Buzzards Bay. Battelle Ocean Sciences collected field data on sediment and sediment/contaminant characteristics at the same time as the hydrodynamic and fluid characteristics data were collected by Woods Hole Oceanographic Institution. These data included bed and suspended sediment characteristics, and PCB/heavy metal concentrations on bed sediment, suspended and dissolved in water. The reduced field data from Woods Hole Oceanographic Institution and Battelle Ocean Sciences was supplied to Battelle-Northwest for incorporation into the model.

1.5.1.4 Application of the Model

The TEMPEST/FLESCOT code was applied to the Acushnet River/New Bedford Harbor/Buzzards Bay system to estimate the transport, distribution, and fate of PCBs. The model included simulations of total PCBs under selected combinations of baseline conditions and potential remedial action conditions to generate 10-year projections. For those cases, the model simulated long-term transport, accumulation, and resuspension of PCBs and heavy metals in the upper esturary, lower harbor, and outer harbor. The results of the simulations were then used in a food chain model to determine the effectiveness of each proposed remedial action on the biota within the system.

1.5.1.5 Evaluation and Reporting

The model results, together with related field and laboratory data were evaluated to determine the effectiveness of selected remedial actions in reducing PCB concentrations in the study area. Monthly and quarterly progress reports, and the final report were prepared under this task.

2.0 DATA COLLECTION PROGRAMS

2.1 DATA OBTAINED FROM OTHER SOURCES

2.1.1 Literature Review

2.1.1.1 Hydrographic Background

Data existing prior to the start of the modeling program demonstrated that for considerations of sediment transport and mixing, the major response of the Bay and outer harbor regions is to storm systems. It is clear that under all conditions the outer harbor is forced by conditions in Buzzards Bay, and that the inner harbor is forced by the outer harbor/Buzzards Bay. The available data indicate that the Bay and outer harbor forcing can be reasonably well-characterized from local measurements. Little is known about the response of the Bay to forcing by the surrounding continental shelf conditions, but for purposes of deriving an empirical forcing function based on data from Buzzards Bay only, lack of knowledge of the response was not a problem.

In spite of a reasonably well-characterized sea level response to tidal and wind forcing, the current response was not well known. Selected near-bottom flow measurements in the outer harbor and in the center of the Bay by W. Grant and B. Butman of Woods Hole Oceanographic Institute (WHOI) and the United States Geological Survey (USGS), respectively, clearly indicated the critical processes and magnitudes of near-bottom flows at these points. These data could be compared in detail to selected events. However, the flow in the inner harbor and the detailed vertical distribution of currents over the water column in the inner or outer harbor or the entire Bay were unknown. This gap was considered important because of the potential onshore bottom flow and offshore surface flow resulting in the seaward transport of contaminants.

The overall circulation in Buzzards Bay outside New Bedford Harbor was also poorly known. This flow determines the transport of pollutants from the system to the surrounding New England coastal waters. There are many indications that the flow out of New Bedford Harbor hugs the coast along the

northwest shore of Buzzards Bay and flows southerly out of the bay. This concept has some support from patterns of density-driven circulation inferred from hydrography and from known tidal currents. This picture is also consistent with as yet unpublished Mussel Watch data of J. Farrington of WHOI. In addition, the overall role of storms in this system and of local wind-driven circulation was unknown.

Data clearly show that sediment resuspension occurs around the Bay and in the outer harbor from the action of surface waves, and that tidal, low frequency, and mean flows cannot generate sufficient stress to resuspend much sediment by themselves. While wave action sufficient to resuspend sediment in shallow water can be generated by local sea breezes in the summer and early fall, only storm waves can resuspend the sediment over most of the outer harbor and Buzzards Bay.

The available data also defined clearly the basic physics which had to be resolved in any circulation and mass transport modeling of parts of the Bay and outer harbor. First, at different times of the year, vertical and horizontal gradients in the density field are pronounced. The effect of local topography on the current is evident. Thus, the model had to include advection, and the influence of stratification on any modeling of vertical stress divergences. In addition, the mean friction was shown to be influenced by surface gravity waves through wave-current interaction and therefore this effect had to be included in models of stress divergence. Finally, both wind-driven and tidal-driven flows had to be included in modeling.

From existing data on tidal currents, hydrography, bathymetry, and satellite imagery, the following very simplified picture of circulations and exchanges exist in the Bay. There is a relatively well-mixed region in the center of the Bay from near Cleveland Ledge to south of New Bedford Harbor. Possibly, there is a net counter-clockwise circulation. The exchange of water into the Bay from the holes along the southeast side is small. The islands act as a block and because of the phase differences between ebb and flood tides in the Vineyard Sound and Buzzards Bay, little tidal-influenced flow comes into the Bay from Vineyard Sound. Bay topography may help a northeastward flow into

the Bay along the southeastward side and a southwestward flow out of the Bay along the northwest side of the Bay.

2.1.1.1 Physical/Chemical Properties of PCBS and Metals

There is a fairly large volume of published data dealing with the physical chemistry (aqueous solubility, partition coefficients, volatility, etc.) of various PCB mixtures (e.g., Arochlors) and several of the metals of concern in New Bedford Harbor. Aqueous solubilities of PCB isomers are difficult to measure empirically, and as a result published values vary widely (e.g., Tulp and Hutzinger, 1978; Lee et al., 1979; Mackay et al., 1980a). Typical solubility values range from 5,900 parts per billion (ppb) for dichlorobiphenyl to 0.016 ppb for decachlorobiphenyl. Adsorption/desorption kinetics and partition (or distribution) coefficients for several PCB isomers and different types of suspended particles have been determined (Dexter and Pavlou, 1975; Karickhoff et al., 1979; DiToro and Horzempa, 1982; DiToro et al., 1982). Evaporation and vapor behavior have been studied (Hague et al., 1974; Mackay et al., 1980b). Relationships between octanol/water partition coefficients and bioaccumulation have also been studied extensively (Leo, 1971; Mackay et al., 1980b; Geyer et al., 1982).

There is also a very substantial published literature dealing with chemical speciation, solubility and adsorption/desportion of metals, including copper, in marine and estuarine environments. Copper speciation in seawater has been studied extensively (e.g., Zirino and Yamamoto, 1972; Battey and Gardner, 1978). Factors affecting the adsorption/desorption of copper and other metals from deposited and suspended sediments have been documented (Payne and Pickering, 1975; Patrick et al., 1977; Luoma and Bryan, 1981; Hunt and Smith, 1983). Earlier literature on copper in the marine environment was reviewed by Schmidt (1978).

Despite the extensive published literature, some site-specific data for adsorption/desorption and partition coefficient parameters for PCB pseudocomponents and copper, using site sediments, were developed for the New Bedford Harbor modeling effort.

2.1.1.2 Local Marine Biota

Although there have been few studies of the marine fauna and flora of the Acushnet River/New Bedford Harbor system *per se*, prior to the development of food-chain model the fauna of Buzzards Bay/Long Island Sound in general, and of several nearby estuaries (e.g., Narragansett Bay), are well-known. The marine fish fauna is similar to that of Massachusetts Bay and Long Island Sound (Bigelow and Schroeder, 1953; Oviatt and Nixon, 1973; Hoff and Ibara, 1977). Dominant demersal fish of the estuary and bay include winter flounder, *Pseudopleuronectes americanus*, American eel *Anguilla rostrata*, scup *Stenotomus chrysops*, summer flounder *Paralichthys dentatus*, windowpane founder *Scopthalmus aquosus*, and tautog *Tautoga onitis*, Important invertebrate demersal and epibenthic fauna include lobsters *Homarus americanus*, mussels *Mytilus edulis*, oysters *Crassostrea virginica* and limpets *Crepidula fornicata*. The benthic infauna have been studied fairly extensively (Sanders, 1958, 1960; McCall, 1977) and sediment-biota interactions have also been studied (Rhoads, 1967; Rhoads and Young, 1970; Driscoll, 1977). Muddy sediments in Buzzards Bay are dominated by the polychaete *Nephthys incisa*, the bivalve mollusc *Nucula proxima* and the snail *Tubonilla* sp. Sandy sedments have different fauna dominated by the polychaetes *Glyceria americana* and *Nephthys bucera*, the amphipods *Ampelisca spinipes* and *Byblis serrata* and the bivalve mollusc, *Cerastoderma pinnulatum*. The hard-shell clam *Mercenaria mercenaria* is extremely abundant in low intertidal and shallow subtidal areas of Buzzards Bay, including New Bedford outer harbor. DeLorenzo reported *M. mercenaria* as the dominant macrofaunal animal collected at most stations in his survey of PCB contamination of New Bedford Harbor marine biota. The soft-shell clam, *Mya arenaria* is abundant in intertidal muddy sand sediments near and in the harbor.

2.1.1.3 Biological and Bioenergetic Database for Species of Concern

The indigenous species of marine animals considered in the food-chain model were winter flounder *Pseudopleuronectes americanus*, lobster *Homarus americanus* and hard-shell clams *Mercenaria mercenaria*. Model prey organisms for the

flounder and lobsters included rock crabs Cancer irroratus, spider crabs Libinia emarginata, mussels Mytilus edulis, and infaunal polychaetes.

The hard-shell clam Mercenaria mercenaria inhabits shallow marine sediments along the eastern Gulf coasts of North America from Nova Scotia to Yucatan and supports important commercial fisheries, particularly in the northern part of its range. Its ecology is well-known (Carriker, 1961). Growth rate and bioenergetics have been studied thoroughly (Tenore et al., 1973; Tenore and Dunstan, 1973; Hibbert, 1977; Epifanio, 1979), and these data were used directly for bioenergetic parameters for the food-chain model.

The American lobster, Homarus americanus is an extremely important commercial species whose range extends form Labrador to North Carolina and from shallow coastal waters to the continental slope and submarine canyons (Galtsoff, 1937). Inshore populations appear to make only small-scale seasonal migrations in response to water temperature changes (Morrissey, 1971). In Buzzards Bay, there may be two populations, a non-migrating inshore populaion, and an inshore-offshore migrating population. Growth rate (Mauchline, 1977; Campbell, 1983) and bioenergetics (Logan and Epifanio, 1978; Capuzzo, 1981) of lobsters have been studied and these studies will provide useful data for use in the food-chain model.

The geographic range of the winter flounder Pseudopleuronectes americanus extends from Labrador to Georgia (Bigelow and Schroeder, 1953). It is particularly abundant in coastal waters of New England and on Georges Bank where it supports large, economically important commercial and sport fisheries. Available evidence reviewed by Klein-MacPhee (1978) and Van Guelpen and Davis (1979) suggests that inshore populations of winter flounder remain in shallow coastal waters as long as water temperatures do not become stressfully high or low. Although winter flounder do migrate, it is to a limited extent and they do not range widely, at least in Massachusetts coastal waters (Howe and Coates, 1975; Pierce and Howe, 1977). Available data on the biology of winter flounder have been summarized by Klein-MacPhee (1978). Feeding habits, growth, and bioenergetics of winter flounder have been studied extensively (Tyler and Dunn, 1976; Klein-MacPhee, 1978; Macdonald, 1983).

Mytilus edulis is probably the most thoroughly studied marine bivalve mollusc. Much of the relevant growth and bioenergetics data is summarized by Bayne (1976). Much less information is avalable on the growth and bioenergetics of spider crabs Libinia emarginata, rock crabs Cancer irroratus and infaunal polychaetes (Chambers and Milne, 1975; Neuhoff, 1979).

2.1.1.4 PCBS And Copper Bioaccumulation Database for Food-Chain Species

There is relatively little published data dealing with the bioaccumulation of PCBs and copper from water and food by the marine species included in our food-chain model. However, there is extensive published information for closely-related marine species. McLeese et al. (1980) studied bioaccumulation of PCBs in lobsters from consumption of contaminated mussels. Efficiencies of uptake of tetrachloro- and hexachlorobiphenyls from food ranged from 40-75 percent. Hard-shell clams were able to accumulate small amounts of PCBs from contaminated sediments (Rubenstein et al., 1983), while infaunal nereid polychaetes were able to accumulate significant amounts of PCBs from contaminated food and sediments (Goerke and Ernst, 1977; Fowler et al., 1978; McLeese et al., 1980). Mussels selectively retain the more highly chlorinated PCBs in their tissues (Calambokidis et al., 1979). Farrington (personal communication) performed bioaccumulation experiments with caged mussels in outer New Bedford Harbor and Buzzards Bay, from which in situ bioaccumulation factors were available. Bioaccumulation factors for several PCB isomers in Mytilus edulis were reported by Geyer et al. (1982). Studies of copper bioaccumulation and dynamics have been performed with winter flounder (Fletcher and King, 1978), mussels (Calabreese et al., 1984) and infaunal polychaetes (Luoma and Bryan, 1982; Windom et al., 1982).

Although PCB-degrading bacteria are associated with PCB-contaminated sediments, their rate of PCB degradation often is nutrient limited (Sayler et al., 1978). The rate of loss of sediment PCBs by this route probably is sufficiently low, particularly in the heavily contaminated sediments of the New Bedford Harbor system. Given the probable magnitude of the biodegradation rates and the lack of specific process kinetics was not parameterized in the physical/chemical model.

2.1.2 Metcalf and Eddy Report/Database

While under contract to EPA, Region I, Metcalf and Eddy, Inc. compiled a PCB database for the Acushnet River/New Bedford Harbor/Buzzards Bay system. The database contained more than 5,000 entries of PCB and metals concentrations in water, sediments, biota, waste water, and air from the estuarine system. The data were compiled from the results of 23 analytical laboratories and 21 different municipal, state, federal, and private agencies and organizations. A total of 158 data references were used to compile the database.

During the development of the modeling program workplan, Battelle requested and received from Metcalf and Eddy a subset of these data from the 90 percent of the total entries that Metcalf and Eddy determined in their quality assurance review to be of sufficient quality and reliability for use. This subset of the total database includes 2,690 records for harbor sediments, 159 records of water column data, 35 records of treatment plant effluent, and 1,180 records of aquatic biota.

The Acushnet Estuary PCBs Data Management Final Report (Metcalf and Eddy, 1983) contains 18 contour and station maps summarizing the distribution of different Aroclors and total PCBs in surficial and subsurface sediments of the Acushnet River and New Bedford Harbor. Highest PCB concentrations are in sediments from the upper part of the estuary, north of the Coggeshall Street bridge adjacent to the Aerovox site. Sediments containing more than 10,000 ppm PCBs have been reported from isolated locations in this area. PCB concentrations in the 50 to 100 ppm range have been reported in sediments from several locations in the inner harbor between the hurricane barrier and the Coggeshall Street bridge, and in the outer harbor adjacent to the Cornell-Dublier site and the outfall of the New Bedford sewage treatment plant at Clark's Point. Well over half of the data entries obtained from Metcalf and Eddy for sediment PCB concentrations show non-detectable (zero) values, probably reflecting inappropriate sample size, sample processing or analytical method more often than low environmental concentration. However, the sediment data were useful to the modeling effort because they provided an overall picture of the distribution of PCBs in sediments of the estuary system.

There are many fewer entries in the data file for PCB concentrations in the water column. In this case, more than 90 percent of the entries report non-detectable levels. The limited available data indicate a trend toward decreasing PCB concentrations in the water as one moves from the upper Acushnet estuary through the inner harbor and into the outer harbor and Buzzards Bay.

2.1.3 Other Data

Extensive data collection programs have been conducted in New Bedford Harbor since the discovery of PCB contamination in the mid-1970s. Studies have been conducted on the distribution of PCBs in bed sediments, in suspended sediments, and dissolved in water in the Acushnet River estuary, inner and outer New Bedford Harbor, and portions of Buzzards Bay. Some studies have included the vertical distribution of PCBs in bed sediments and the flux of contaminated suspended sediments through the inner harbor and estuary. Other studies have dealt with the areal distribution of PCBs, the physical properties of bed and suspended sediments, current circulation patterns and magnitudes, and fluid characteristics in the vicinity of New Bedford Harbor. These studies have been conducted mainly by the U.S. Coast Guard, U.S. Environmental Protection Agency and its contractor, the State of Massachusetts, and Woods Hole Oceanographic Institution.

Other useful data on the physical characteristics of New Bedford Harbor and Buzzards Bay, although not directly related to PCB contamination, were available through the U.S. National Weather Service, National Ocean Survey, U.S. Army Corps of Engineers, Woods Hole Oceanographic Institution, and other federal and state agencies. The data used in the modeling effort are summarized in more detail in the sections of the report dealing with model calibration and application.

2.2 FIELD PROGRAM

Hydrodynamic field studies were performed to determine the normal and storm-induced patterns of water movements in Buzzards Bay and the inner and outer

New Bedford Harbor. An array of current meters was deployed at the entrance to Buzzards Bay for approximately five months in order to establish conditions of water, sediment, and contaminant flux across the boundary of the physical/chemical model. Additional shorter-term current meter and drogue studies were performed in the vicinity of New Bedford Harbor to establish patterns of current flow in this region during summer and winter conditions.

A field sampling was undertaken to provide chemical data for input to the physical/chemical model, and information on biota for the food-chain model. Sampling took place in 1984 and 1985 at up to 25 stations in the Acushnet River, New Bedford Harbor, and Buzzards Bay. Samples included surficial sediment, surface and bottom water collected periodically and through some tidal cycles, and selected marine animals. In addition, selected vertical cores of sediment were collected from New Bedford Harbor.

The physical oceanography studies are briefly described in Section 2.2.1, and the various field sampling efforts in Section 2.2.2. The results of these efforts were used in the models and will be discussed fully in the sections describing the various models.

2.2.1 Physical Oceanography

2.2.2.1 Grant/Beardsley Drifter Studies

Three drifter studies were conducted, each yielding increasing amounts of data. The first study was conducted from November 28 through 30, 1984. This initial study was designed to test the equipment and determine logistics of the tracking process. Five buoys were deployed: two surface type and three sub-surface buoys drogued near the surface. Because there were more sub-surface than surface buoys, a determination was made of how the sub-surface buoys would perform as indicators of surface currents, i.e., whether the shear would be great enough in the top few meters of water to significantly differentiate the trajectories of the two types of floats.

The second drifter study was conducted from December 17 through 21, 1984. This study was designed to yield more data in the vicinity of New Bedford Harbor by increasing the number of buoys deployed and by eliminating the reference buoy interference problem. Seven buoys were tracked over the four-day period. Five of the seven buoys were sub-surface types drogued near the surface. One buoy was drogued at a depth of five meters, and the last buoy was set at the surface.

The third drifter study was conducted from April 9 through April 13, 1985. Because of an increased number of reference buoys and a refinement of the tracking technique, it was possible to obtain seven high quality drifter tracks.

2.2.2.2 Grant/Beardsley Stratification Measurements

Profiles of velocity and temperature were measured at two locations in Buzzards Bay in December 1984 and January 1985. The stations were designated as Stations 1 and 2. Station 1 was in the proximity of Cleveland Ledge in 11.3 meters of water. Station 2 was adjacent to Buoy 11 in New Bedford outer harbor and was 8.2 meters deep.

Station 1 was occupied on December 10, 1984. During this time a drifter study was being carried out at the mouth of the Bay and the Buzzards Bay flux array was in place. In addition, the Cleveland Ledge Station is the location of both U.S.G.S. long-term tripod deployments and of 1983 storm measurements. The duration of the profiling at Station 1 was only 9 hours because of unfavorable weather conditions.

Station 2 was occupied on January 10 and 30, 1985. The station was located near the outer harbor stations where there have been previous storm flow measurements and biological sedimentological studies. The profiles taken on January 10 were considered unsatisfactory because of excessive boat motion due to opposing wind and tide forces. The profiles were repeated on January 30. Only 10 hours of continuous profile data were recorded.

2.2.2.3 Buzzards Bay Boundary Measurements

Woods Hole Oceanographic Institution. Seasonal hydrographic conditions were characterized by Woods Hole Oceanographic Institution. Two hydrographic surveys were carried out during September (summer) and October (winter) 1984. Data were collected by means of drifters and moored arrays of current meters and temperature/depth sensors.

Ocean Surveys, Inc. Ocean Surveys, Inc. was responsible for the deployment of three current meter arrays in Buzzards Bay. Current meters were deployed at shallow, mid-water, and deep locations at each of Stations 23, 24, and 25 over the period from February 6 through March 16, 1986. The arrays provided data on current speed and direction at 30-minute intervals over that time period.

2.2.1.4 Geyer Summer 1986 Study

The principal intent of the study was to provide ground truth for numerical simulations of the circulation of New Bedford Harbor. Information was collected from fixed instruments deployed at five sites, from drifters deployed in the inner harbor, and from two conductivity, temperature, depth (CTD) surveys.

Fixed instrument deployment began on July 9 and was completed September 5, 1986. All of the instruments were in place for a 28-day period between July 24 and August 15, 1986. The five sites instrumented included Clark Point and Butler Flats in the outer harbor, and sites in the lower inner, middle inner, and upper inner harbor. Time-series data for velocity, conductivity, transmission, pressure, and temperature were collected.

Two drifter deployments were carried out in the inner harbor on July 24 and 25, 1986. The first deployment covered most of the lower inner harbor (south of Popes Island) and the second one covered the middle inner harbor (between Popes Island and I-195). The upper inner harbor was not covered due to difficulty in navigating the shallow water. During the July 24 deployment, both shallow and deep drifters were deployed, while during the July 25

deployment only shallow drifters were used. Each drifter consisted of a 20-cm diameter float with a small flag, tethered to a 75-cm diameter, 1-m long "holey sock" drogue. The drifters were tracked visually and their positions fixed with a shipboard microwave navigation system.

One CTD survey was conducted on July 24 and another on August 6, 1986. During the first survey, several transects were made between the middle inner harbor mooring and Butler Flats, at various phases of the tide. During the second survey, measurements were made only in the outer harbor.

2.2.2 Field Sampling Program

2.2.2.1 Overview of Sampling Program Design and Objectives

A field sampling program was undertaken to provide chemical data for input to the physical/chemical and food-chain models. Sampling took place during four seasons in 1984 and 1985 at up to 25 stations in the Acushnet River, New Bedford Harbor and Buzzards Bay. Samples included surficial sediment, surface and bottom water (collected in some cases at intervals during the tidal cycle), and marine animals. Selected vertical cores of sediment were collected from New Bedford Harbor.

Field samples were collected during September/October 1984 (Survey 1), November/December 1984 (Survey 2), June/July 1985 (Survey 3), and February/March 1986 (Storm Event). Sediment and water samples were collected at all 25 stations (Figures 2.1 and 2.2) during Survey 1 in order to establish initial conditions for the physical/chemical model. Water samples were collected at each station during Surveys 2, 3, and 4, while sediment samples were collected at a subset of eight of the 25 stations (Stations 2, 9, 10, 12, 16, 18, 21 and 24) during those sampling periods. Biota samples were collected from four areas, three of which correspond to the fishery closure areas and one of which was immediately adjacent to the closure areas (Figure 2.3), during the September/October and November/December 1984 and the June/July 1985 sampling trips. Biota collections were primarily for the purpose of providing data for

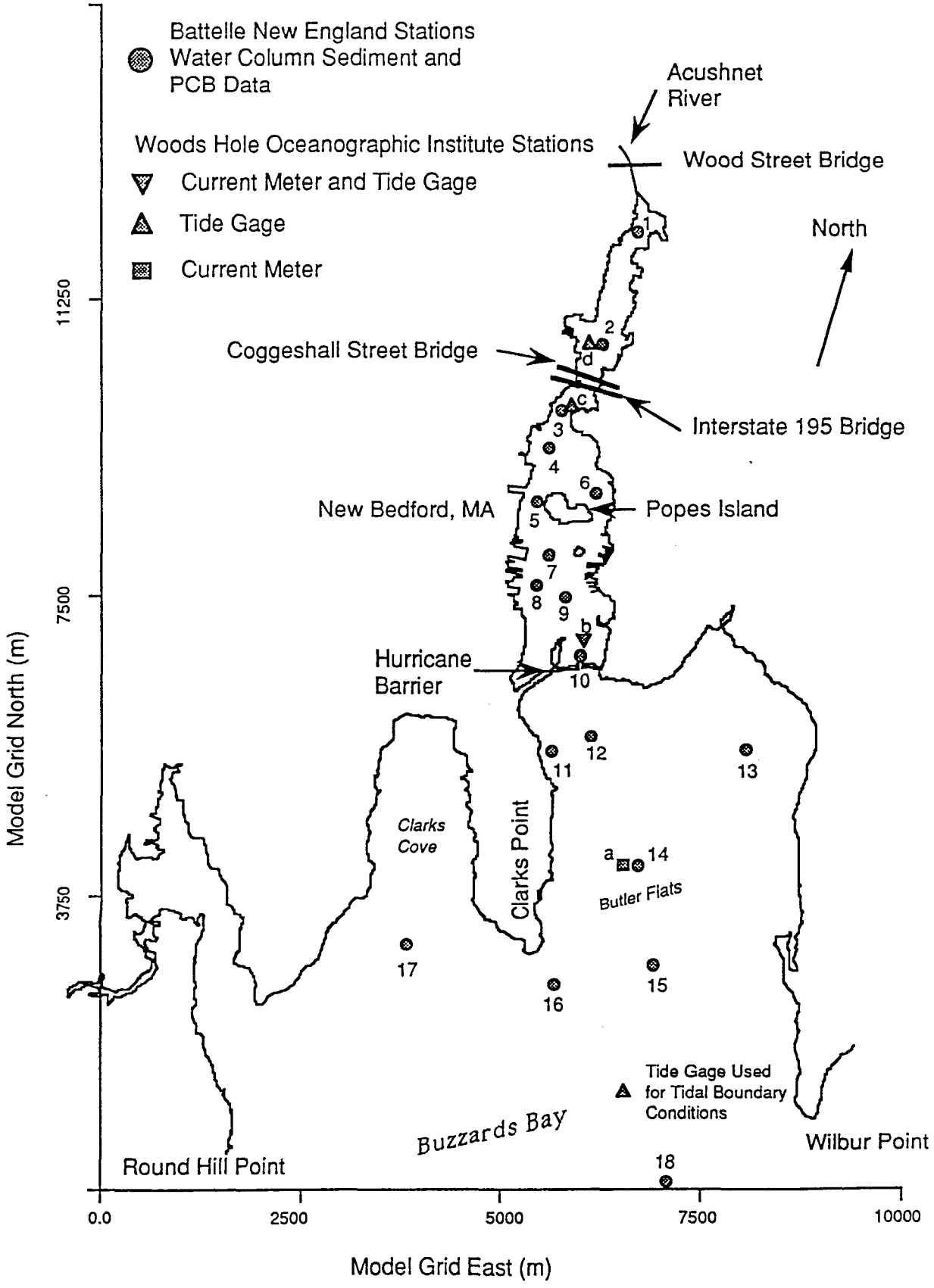

FIGURE 2.1. LOCATIONS OF FIELD MEASUREMENT STATIONS IN UPPER BUZZARDS BAY

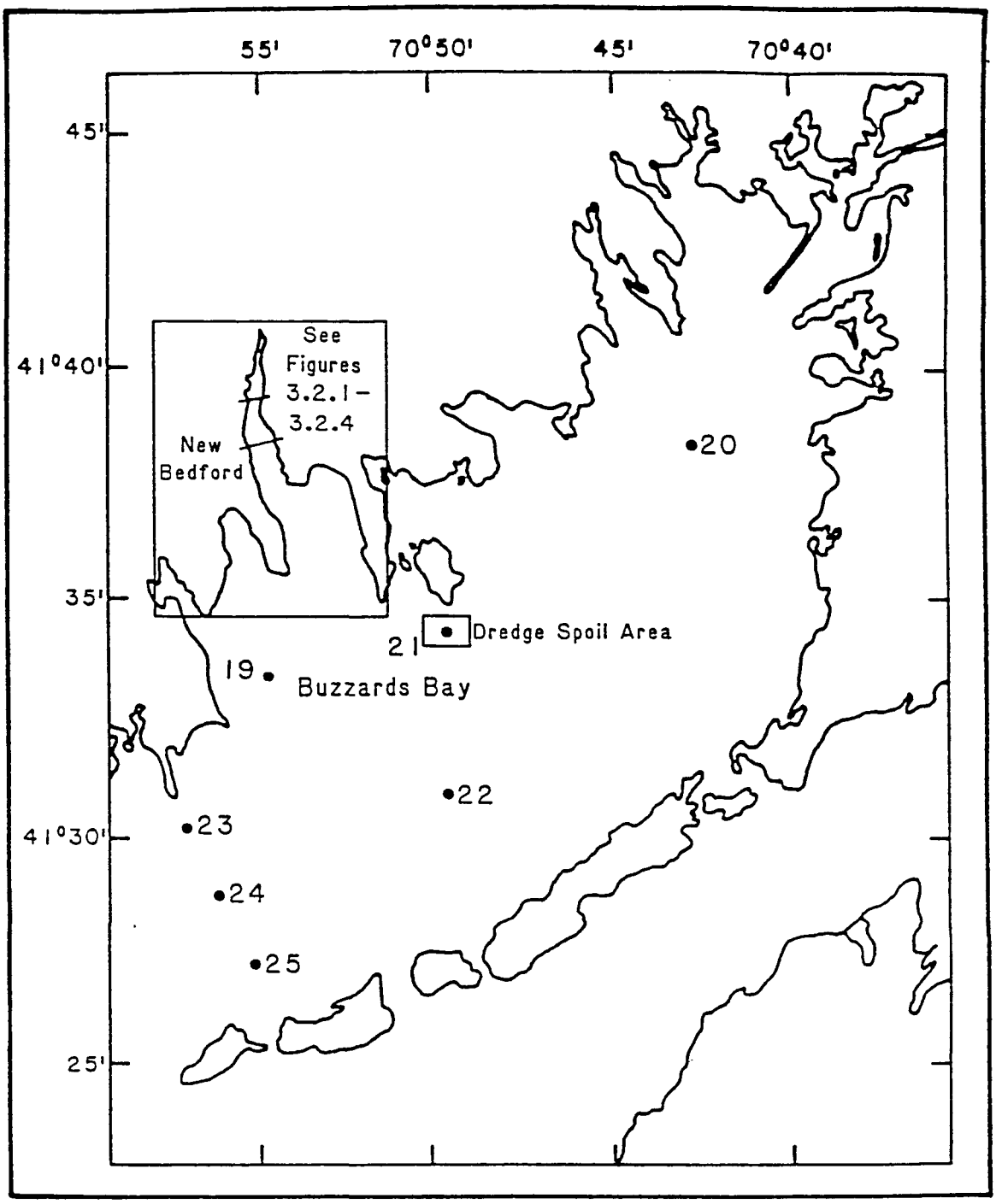

FIGURE 2.2. LOCATIONS OF FIELD MEASUREMENT STATIONS IN BUZZARDS BAY

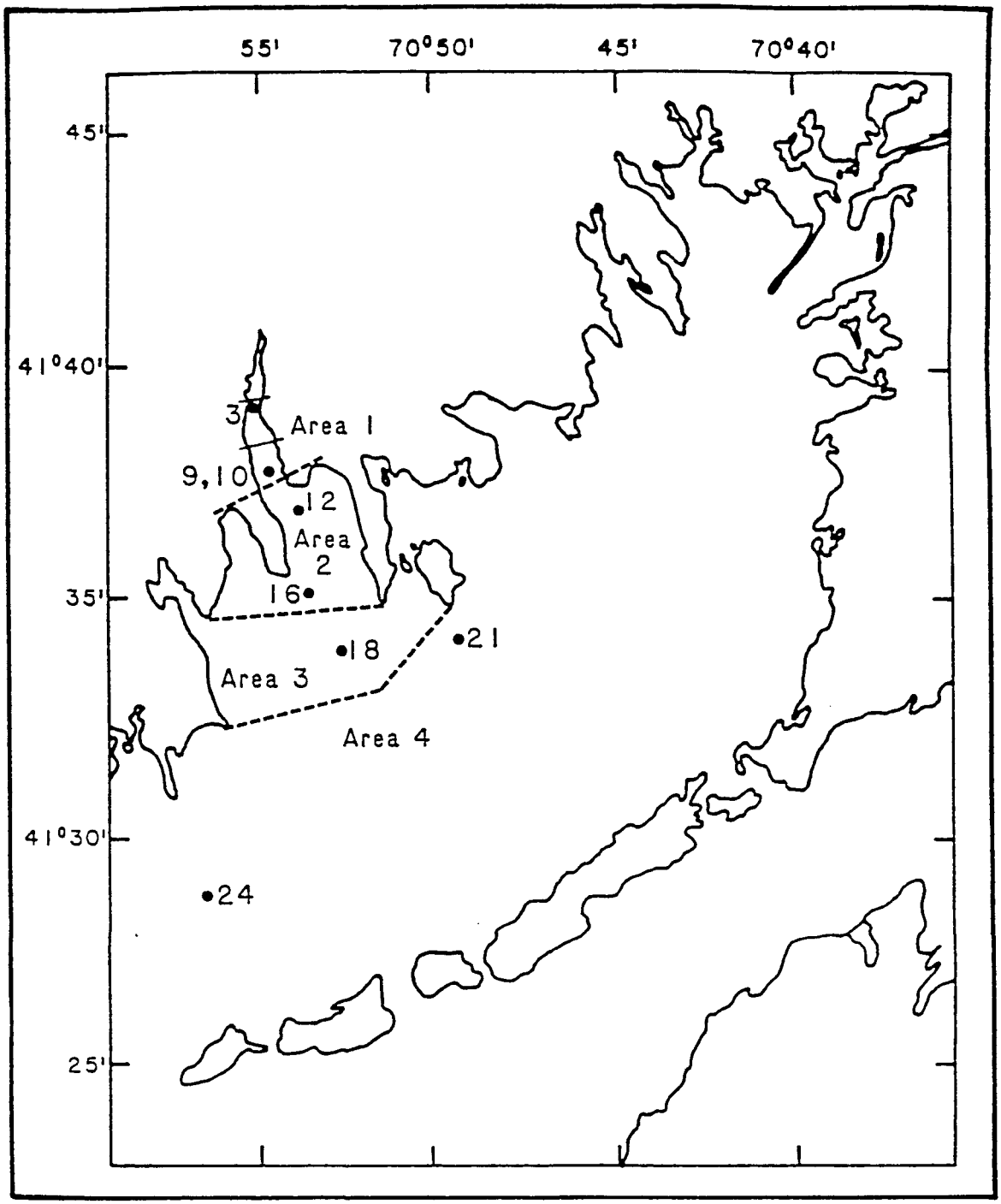

FIGURE 2.3. BIOTA SAMPLING AREAS

the food-chain model. The September/October and November/December sampling trips were scheduled to be concurrent with the moored array current meter study at the bay boundary, and the drogue studies in the outer harbor. Details of the four field sampling surveys are provided in the following sections.

2.2.2.2 Survey 1 - September/October 1984

The first sampling of water, sediment, and biota in New Bedford Harbor was conducted from September 13 to October 10, 1984. Samples collected included collection of three sediment cores at all 25 stations; collection of one additional core for profiling at Stations 1, 6, and 7, respectively; collection of water samples over a tidal cycle (4 collections) at each of eight stations; collection of non-tidal cycle water samples at each of the remaining 17 stations; collection of "high-volume" samples for determination of PCBs by size fraction in suspended materials; and collection of various biota samples.

Sediment Sampling. All sediment field sampling was performed aboard the R/V Mya by Battelle personnel using a 3.3-inch (8.4-cm) diameter hydraulically-damped gravity corer provided by the U.S. Geological Survey, Woods Hole, Massachusetts. The corer had a knife-edge nose-core and narrow (0.094-inch) wall core tubing which allowed the corer to penetrate with little disruption of sediment integrity, thus making it ideal for the collection of both undisturbed surface material and core samples to 50 cm. Because of the weight of the sampler, support bars had to be welded to the Mya's boom to provide lateral support in rough seas. This resulted in some delays, extending the cruise by one day.

The corer was designed for core barrels of a brand of 3-inch diameter fiberglass tubing known as "red-thread." This material was unable to be obtained, and a similar material was substituted which did not form as tight a seal with the valve that prevents loss of the core. Consequently, the cores were not as long as the corer was designed to take, although all were considerably longer than the 5 cm required for a sample.

Corer performance was markedly reduced in sediments which contained large amounts of gravel and shell, and it was necessary to use a stainless-steel Smith-McIntyre grab to take samples at Stations 10, 15, 21, and one sample at Station 13. Because of some confusion due to the continually changing cruise schedule and attempts to obtain high-volume total suspended sediments (TSS) samples, the cores at Station 12 were not collected. Cores at the shallow Stations 1 and 2 were obtained by hand using the fiberglass core barrels alone but were otherwise similar to those taken with the corer.

Tidal Cycle Water Sampling. Tidal cycle water samples were successfully collected at eight stations (3, 9, 10, 12, 16, 18, 21, and 24). In general, this phase of the sampling presented no unusual problems. In some cases, the purging time was reduced somewhat in order to maintain the schedule. It was agreed in the post-cruise meeting that the purging was sufficiently important that when this decision became necessary in future samplings the full 30-minute purging would continue, even at the expense of missing the exact tide. Scheduled sampling times were based only on a small map of tidal currents in the harbor and were probably somewhat inaccurate in any case.

At Station 9, only the surface sample was collected during the maximum ebb tide and the bottom water at maximum ebb was collected four days later. All other samples were collected and all other surface and bottom samples were collected within approximately 30 minutes of each other.

Non-Tidal Water Sampling. Non-tidal (i.e., one-time) water samples were successfully collected at 16 of the 17 proposed stations. The missed station was Station 11, where the samples were collected, but on different tides. At Stations 1, 2, and 6, the water was so shallow that only a single mid-depth sample was collected.

Biota Samples. Less than half of the proposed biota samples were obtained, some only after considerable effort. In general, the success of the biota sampling depended entirely on the species collected. Winter flounder were probably the most available species and quotas were obtained with relatively

little effort. On the other hand, it was not possible to obtain sufficient infauna (e.g., polychaetes) without much more effort than was budgeted for.

2.2.2.3 Survey 2 - November/December 1984

The second New Bedford Harbor field sampling was conducted from November 26 to December 12, 1984, requiring approximately 12 working days. Approximately one day was lost due to boat and equipment malfunctions. The 12 days were two more than was projected. A more intensive effort devoted to collection of biota than had been originally budgeted and the addition of samples for the k_d analyses resulted in the extra days.

Samples collected included sediment cores and tidal cycle water samples at eight stations, non-tidal water samples from the remaining 17 stations, vertical profile cores at three stations, various biota from all four areas, and sediment for k_d analysis from four stations. With the exception of certain classes of biota, nearly all samples were collected successfully. Some minor problems were encountered in the collection of physical data, as detailed in this Section.

Sediment Sampling. The hydraulically-damped corer functioned without incident and all 24 scheduled core samples (3 replicates x 8 stations) were collected. Because of cool air and water temperatures during the sampling, cores were stored on deck rather than in a cooler with ice, as specified by the protocols. This decision was made by the chemist in the field based on his understanding of the analyses to be conducted, ambient temperaures, and the desire to avoid unnecessary disturbance of the cores.

As in the previous cruise, an attempt was made to work from less to more contaminated stations. This was not possible for Station 24 because of sea conditions which prevented sampling until the last day of the cruise.

Sediment cores for vertical profile analysis were collected at Stations 1, 6, and 7 on December 6, December 4, and November 29, 1984 respectively. The hydraulically-damped corer was used at Stations 6 and 7. Because this

instrument requires large amounts of silicone-based grease for proper functioning, and the use of silicone was precluded by the planned analyses, it was not possible to collect 50-cm cores. The best cores collected were approximately 40 cm long.

Because Station 1 was located upstream from a low fixed bridge and was extremely shallow, it was not possible to sample this location with the corer. Cores at Station 1 were taken by hand making it possible to obtain cores greater than 50 cm long. As noted above, the cores at Station 1 were taken across the Acushnet River from the previous site of Station 1.

Tidal Water Samples. With the exception of the bottom samples at Station 12 during the ebb tidal stage, all 64 tidal water samples (8 stations x 2 depths x 4 stages) were collected successfully. The inability to collect the single sample was because of the generator running out of fuel. In nearly all cases, purging was conducted for the half-hour specified in the protocols. For a few samples, delays due to other causes were judged to be so severe that conducting purging for the full half-hour would have caused two tidal stages to be taken immediately in succession. For these few instances, purging time was shortened somewhat.

Non-Tidal Water Samples. All 31 (4 stations x 2 depths plus 3 stations x 1 depth) non-tidal water samples were collected without incident or significant deviation from the prototcols, with the exception of a minor relocation of Station 1 due to an oil slick on the suface at the site sampled during Survey 1. Samples from Station 1 were collected approximately 200 meters east of the previous site.

Biota Sampling. In general, biota sampling was much more successful during Survey 2, due in large part to the extra time spent on collections. Two major improvements over the first biota collections are noteworthy. Lobsters were collected in the trawls from Areas 2 through 4, obviating the need to subcontract a local lobsterman to collect these samples. Also, two good locations for mussel collections were located in Areas 3 and 4, respectively, thus providing mussels from all four areas. Howver, catches of polychaete

worms were again minimal, with only several miscellaneous specimens from Areas 3 and 4.

Sediment for k_d Experiments. Raw sediment was collected from Stations 1, 4, and 12 (6 liters each) and Station 24 (1 liter). The sediment was collected with a stainless-steel Smith-McIntyre grab. The central area of each grab sample was carefully removed to a depth of 5 cm and placed in 1-liter polyetheylene jars with minimal disturbance. Because of limitations described previously in reference to the corer, it was not possible to use the Smith-McIntyre grab at Station 1. Samples from Station 1 were collected by hand from approximately mean low water on a sandy mudflat directly across the Acushnet River from the Aerovox plant. This site was inshore of, and approximately 100 meters downstream from, the relocated site of Station 1 described previously.

Physical Data. An ENDECO Model 110 current meter was used to measure current velocity at the surface and bottom during the collection of each water sample. The boat was anchored during collection of these samples but no effort was made to limit the swing of the boat on its anchor line. This movement, plus the unavoidable vertical movement on rough days, undoubtedly contributed some error to these data. On November 26 and 27, temperature was measured using the ENDECO current meter's temperature probe. Thereafter, a VWR electronic digital thermometer placed in the peristaltic pump discharge stream was used for temperature measurements. Based on observations in the field, the readings from the ENDECO instrument were unreliable. Also, the digital thermometer behaved abnormally during the last three days of the sampling, making the data questionable.

2.2.2.4 Survey 3 - June/July 1985

The third New Bedford Harbor field sampling was conducted from June 26 through July 2 and July 23 through August 2, 1985. Samples collected included sediment cores and tidal cycle water samples from 8 stations, non-tidal water samples from the remaining 17 stations, physical data from three stations, and biota from the four biota collecting areas.

Sediment Sampling. The 24 scheduled core samples (3 replicates at 8 stations) were collected with the hydraulically-damped corer without incident. Rinsing and purging of the cores was carried out with no deviations from the protocol.

Tidal Water Samples. All tidal water samples, except the two maximum flood samples at Station 16, were collected, for a total of 62 samples (7 stations x 2 depths x 4 stages plus 1 station x 2 depths x 3 stages). It was not possible to collect the maximum flood sample at Station 16 because the generator supplying power for the water pump did not operate at that time. The generator was subsequently restarted, and the remainder of the tidal water samples were collected without incident.

Non-Tidal Water Sample. All 31 (4 stations x 2 depths plus 3 stations x 1 depth) water samples were collected without incident or significant deviation from the protocol.

Biota Sampling. It was not possible to collect a useful number of lobsters with either the otter trawl or clam dredge. A local lobsterman using commercial traps was therefore used for the collection of lobsters. Catches of lobsters in the traps were unexpectedly low. Also, catches of polychaetes were unexpectedly low (2 specimens) in Area 1, and it was decided that the results were not worth the time spent sieving the sediment and shingle. Collections of polychaetes in Area 1 were therefore suspended.

Physical Data. Salinity samples were collected at the three extra current-depth profile stations. However, because of the inability to collect the tidal water samples at the appropriate stations at the same timeas the extra current-depth measurements, the measurements at Station 14 were taken an hour past the maximum ebb and flood stages.

2.2.2.5 Immediate Processing of Field Samples

Water Column Samples. Upon arrival at a water column sampling station, the pumping system was deployed on the surface water and pumped for at least 30 minutes. The time that purging was initiated was recorded on field station

log forms. Samples for total suspended solids and particulate organic carbon were collected in 1-liter polyethylene bottles during the flushing period and kept in a cooler on ice until processed in the laboratory.

Nineteen liters of water were collected for PCB analysis in a glass carboy with a silicone stopper. There was no shipboard processing of this sample, and the 19-liter carboy was stored on deck until its transfer to the laboratory.

One liter of water was collected for metal analysis. It was placed in a sampling container and labeled. The container was placed in a cooler for transfer to the laboratory.

Sediment Samples. To avoid bringing unnecessary mud onto the deck, the hydraulically-damped corer was hosed off with ship's seawater after the samples were collected and prior to the corer being brought aboard the ship. The core barrel was removed from the corer upon retrieval and placed upright in a cooler. After five minutes, surface water was siphoned from the top of the core, and the core was capped and stored on ice until delivered to the laboratory.

Biota Samples. Prior to retrieval of the various sampling devices, the deck was rinsed with clean seawater from the water sample pump to minimize contamination of the sample. The boat was maneuvered so that exhaust fumes did not blow onto the deck. When the dredges and trawls were brought aboard, the cod ends were placed in clean plastic trays so that they would have minimal contact with the deck. Species of interest were identified and separated out as quickly as possible. Flounder and lobster were cooled in covered fiberglass trays on dry ice to anesthetize the animals for easier handling. As soon as possible, the animals were rinsed with clean seawater and grouped according to size class. Samples were wrapped in solvent-rinsed, acid-soaked aluminum foil, then placed in sealed, acid-washed bags. The samples were frozen prior to transport to the laboratory.

2.2.2.6 Field Quality Assurance Program

Introduction. This section presents an evaluation of the results from the quality assurance/quality control (QA/QC) samples taken during the sampling and processing of field samples from New Bedford Harbor. QC samples were taken for polychlorinated biphenyls (PCBs), metals (cadmium, chromium, and lead), particulate organic carbon (POC), and suspended solids, both silt and clay fractions (the sum of the silt and clay fractions is total suspended solids or TSS). These samples were taken in order to evaluate whether any contamination was being introduced into the samples by the sampling and handling procedures used.

The QC samples were divided into different categories for discussion. Field blanks were blanks prepared during collection and processing of samples in the field. Processing blanks were samples that were extracted and processed at the lab at the same time that the field samples were being processed in preparation for laboratory analysis. Solvent blanks were samples consisting only of the extraction solvent; they were concentrated and analyzed in the same manner as the samples. Re-extraction samples are field samples which were collected and extracted with solvent for quantification of PCBs, and then reextracted with an additional volume of solvent.

A pump was used to collect the actual field samples, so a comparison of QC samples collected using the pump was made to samples collected by hand. PCB, TSS, POC, and metals samples were collected both by scooping water with a container (by hand) and by pumping it through the normal pumping apparatus to see if any contamination or changes in the samples resulted from pumping during collection.

Results

Solvent Blanks. In the extraction of PCBs from the water samples, methylene chloride was used as the extraction solvent. To determine if there was any PCB in the solvent itself, samples of the solvent were concentrated and analyzed in the same way as the solvent extracts from the field samples. The results of this analysis are presented in Table 2.1. The PCB concentration in

nanograms per liter of solvent were unexpectedly high, ranging from 7.36 to 19.60 ng/l. It is difficult to explain how these levels could be so high in an analytical grade reagent, however each solvent sample had a high level of PCB contamination according to these results. In order to examine at these numbers from another perspective, assuming that all of the PCBs in the solvent did contaminate a field sample, the maximum possible contribution on a concentration basis to the field samples was calculated. Using an average sample volume of 17 liters, the maximum contamination which could be associated with these blanks was 0.433 to 1.153 nanograms per liter of sample. These numbers represent a relatively low concentration of PCBs which are not of particular concern relative to the concentration found in the actual field samples. Table 2.2 presents the maximum, minimum, and average concentrations for all measured parameters. The average PCB concentrations were 73.77 and 304.53 μg/l for dissolved and particulate PCB fractions, respectively. Although these numbers were somewhat skewed due to some very large PCB concentrations in samples from the inner harbor area, it was clear that the small amount (less than 1 ng/l) of PCBs which might have been introduced by the solvent contamination, based on the results of the ambient air and filter blanks, should not have had any great impact on the overall results of the study.

PCB Field Blanks. Two types of PCB field blanks were collected: filter blanks and an ambient air blank. The field samples were filtered so that both particulate and dissolved PCB concentrations could be measured.

A filter blank was a filter placed on the filtration apparatus in the same manner as would have been done for a field sample without having had any sample passed through the filter. This would allow a determination of any contamination being introduced into the samples. The ambient air blank was prepared by opening a sample collection container to the air for the same length of time as required to fill the sample container with a field sample. This was done in order to determine if there was any contamination due to exposure of the container to the atmosphere.

TABLE 2.1. METHYLENE CHLORIDE SOLVENT BLANKS

Lab ID	Sample	Concentration (ng/l Solvent)	Concentration (ng/l Sample)[a]
BG10	Solvent Blank	12.90	0.759
BG49	Solvent Blank	7.36	0.433
BG86	Solvent Blank	19.60	1.153
BG88	Solvent Blank	10.80	0.6350

[a]Concentration corrected based on average field sample volume of 17 liters

TABLE 2.2. MAXIMUM, MINIMUM, AND MEAN VALUES OF PARAMETERS FROM THE NEW BEDFORD HARBOR DATABASE

Parameter	Units	Maximum	Minimum	Average
Cadmium, dissolved	µg/l	1.9900	0.0010	0.1069
Copper, dissolved	µg/l	45.2000	0.0150	1.7314
Lead, dissolved	µg/l	29.2090	0.0220	0.5620
Cadmium, partic.	µg/l	1.5193	0.0003	0.0141
Copper, partic.	µg/l	117.4660	0.0300	1.3091
Lead, particulate	µg/l	5.8520	0.0220	0.5228
POC	µg/l	3462.1001	121.6000	552.8219
TSS	mg/l	24002.301	2.000	88.899
Solids, Silt	mg/l	93.8000	1.0000	2.9406
Solids, Clay	mg/l	480.0000	1.0000	84.8034
PCBs, dissolved	ng/l	2433.00	0.26	73.77
PCBs, particulate	ng/l	69312.01	0.39	304.53

Table 2.3 presents the results from these field blanks. For both the ambient air blank and filter blanks, relatively high levels of PCBs, ranging from 3.10 to 9.80 ng, were found. As was done for the methylene chloride solvent samples, these concentrations were adjusted using the average field sample volume of 17 liters in order to determine the level of PCB contamination that might be introduced to the field samples. The values range from 0.182 to 0.576 ng/l of sample. These concentrations are the same range as for the solvent samples. Because solvent was used to extract these field blanks, and these levels were the same as those for the solvent blanks, it appears that the solvent was the source of PCBs, and no further contamination should have been introduced by opening the container and filtering the sample.

Metals Field Blanks. One field blank sample was taken in association with the sampling for metals. This blank was obtained by opening a sample collection container to the atmosphere for the length of time necessary to collect a field sample. The results of this analysis are presented in Table 2.4. The concentrations of metals in this sample were very high, especially in comparison to the maximum, minimum, and average metals values for the field sampling program which are presented in Table 2.2. A possible explanation for the high concentrations is that the sample container was probably filled with laboratory water in order to process the sample in the same manner as the other field metals samples. As will be discussed in depth in the section on metal processing blanks, there was a problem with high metals levels in the laboratory water. It is important to note that no laboratory water was used in the processing of the field samples, so this high level of metals contamination is not of concern in terms of introducing contamination to the field samples.

PCB Processing Blanks

Processing blanks were laboratory water blanks that were extracted with solvent and processed in preparation for analysis in the same way that the field samples were extracted and processed. These samples were taken to evaluate any contamination introduced during the extraction and processing steps. The results for these samples are presented in Table 2.5. The PCB concentrations in these blanks ranged from 0.371 to 1.110 ng/l, which were low

TABLE 2.3. PCB FIELD BLANKS

Lab ID	Sample	PCBs (ng)	Concentration (ng/l Sample)[a]
BH38	Ambient Air Blank	9.80	0.576
BE85	Filter Blank	3.10	0.182
BH05	Filter Blank	4.65	0.273
BJ06	Filter Blank	9.71	0.571
BJ07	Filter Blank	6.38	0.375

[a] Concentration corrected based on average field sample volume of 17 liters.

TABLE 2.4. METALS BLANKS

Lab ID	Sample	Concentration (μg/l)		
		Cd	Cu	Pb
Field Blank				
E1656	Field Blank	0.68	37.8	4.99
Processing Blanks				
E0550	Metals Processing Blank	0.55	20.2	11.8
E0562	Metals Processing Blank	1.06	15.0	11.5
E0564	Metals Processing Blank	0.77	43.7	0.77

TABLE 2.5. PCB PROCESSING BLANKS

Lab ID	Sample	Concentration (ng/l)
AU59	Processing Blank	1.110
AU60	Processing Blank	0.460
AU81	Processing Blank	0.738
AU84	Processing Blank	0.432
AU99	Processing Blank	0.746
BD83	Processing Blank	1.780
BD86	Processing Blank	0.552
BG85	Processing Blank	0.488
BG93	Processing Blank	0.710
BG55	Processing Blank	0.371

values when considered in relation to the actual concentrations found in the field samples (Table 2.2). These concentrations were in the same range as those calculated to have been introduced by contamination of the solvent (Table 2.1), indicating that no contamination is introduced during the processing of the samples.

Metals Processing Blanks. The metals processing blanks were laboratory water samples which were filtered and processed for analysis at the same time and in the same way as the field samples. These samples would indicate any contamination introduced during the filtration and processing of the samples for analysis at the laboratory. Metals concentrations in these samples were found to be quite high (Table 2.4), as was found in the metals field blank. These elevated concentrations are believed to be due to high levels of metals in the water used for preparing these blanks. Laboratory tap water was known to contain high levels of metals, particularly copper and lead. The water used for these blanks was deionized tap water, which may be the reason these samples have such high metals concentrations. The New Bedford Harbor field samples (Table 2.2) hadaverage concentrations of 0.0141, 1.3091, and 0.5228 μg/l of cadmium, copper, and lead respectively. These values are much lower than for the "blanks" created in the laboratory using tap water. It is important to note that no tap water was used in processing the metals field samples. Contamination by tap water would not therefore have been introduced into the field samples during processing. This finding was substantiated by the lower concentrations of metals found in the field samples.

TSS Processing Blank. The total suspended solids processing blanks consisted of laboratory water filtered and processed the same way that the field samples were collected and processed. Only one blank sample was taken, and the TSS concentration was below detection (Table 2.6). Although it was difficult to draw conclusions from only one sample, the results indicate that the filtration and processing of these samples did not introduce any contamination into the field samples.

TABLE 2.6. TOTAL SUSPENDED SOLIDS (TSS) PROCESSING BLANK

Lab ID	Sample	Concentration (mg/l)
E0946	TSS Processing Blank	<d

<d: Below detection.

POC Processing Blanks. Particulate organic carbon processing blanks consisted of laboratory water which was filtered and processed in the same manner as the field samples. The POC concentration in these samples was found to be relatively high, ranging from 81.52 to 164.7 μg/l (Table 2.7), as compared to the average POC value from the New Bedford Harbor samples of 552.82 μg/l (Table 2.2).

Re-Extractions. Samples were extracted with methylene chloride solvent for removal of PCBs. For some samples, a second extraction step was performed following the first step to determine whether the extraction procedure was effective in extracting the PCBs from the sample. The results of the first analysis of the sample and the reextraction of the same sample with an

TABLE 2.7. PARTICULATE ORGANIC CARBON (POC) BLANKS

Lab ID	Sample	Concentration (μg/l)
E0276	POC Processing Blank	164.7
E0436	POC Processing Blank	81.52
E0439	POC Processing Blank	145.8

additional volume of methylene chloride are presented in Table 2.8. The re-extracted concentrations ranged from 0.220 to 1.100 μg/l, which may in several cases appear high in relation to the original sample concentration. On a percent basis, a median value of 3.2 percent of the PCB concentration from the first extraction was obtained during the second extraction. However, the concentration of PCBs in the re-extractions was in the same range as the concentration of PCBs calculated to be introduced by the solvent (Table 2.1). Therefore, the PCBs seen in the re-extractions may actually be contamination introduced by the solvent, indicating that most of the PCBs were effectively removed during the first extraction step, and that the extraction procedure used for preparation of the samples effectively removed the PCBs from the water.

Samples Collected By Pump and By Hand. During collection of samples in the field, a pump was used to pump the harbor water into the sample container. In order to determine whether any contamination was being introduced by the pump or its tubing, samples from Duxbury Bay were taken both by pumping and by scooping samples by hand, and a comparison of the results from these samples was made.

TABLE 2.8. PCB REEXTRACTIONS

First Extraction		Second Extraction		
Sample	Concentration (ng/l)	Lab ID	Concentration (ng/l)	Percent[a]
314B4W/	5.83	BE06	0.564	9.7
316S4WE	4.11	BE07	0.894	21.8
324S4WE	2.07	BE22	0.220	10.6
309B4WH	182.20	BE29	0.788	0.4
319S4W	4.35	BG13	1.050	24.1
303B4WF	126.95	BG32	0.867	0.7
114S4/D	17.45	BG50	0.233	1.3
107S4/D	223.50	BG51	0.557	0.2
113B4/D	9.92	BG52	0.361	3.6
110B4FD	47.12	BG53	0.668	1.4
116B4LD	22.80	BG54	0.645	2.8
321S4WH	13.71	BH71	1.100	8.0

The results of samples analyzed for PCBs obtained by pumping and by hand are presented in Table 2.9. Because of problems which occurred during analysis of the Duxbury Bay water samples taken by pump and by hand, there was a limited amount of data available for this evaluation. The mean PCB concentration in pumped samples which was 4.335 μg/l. For samples obtained by hand the mean PCB concentration was 1.376 μg/l. Statistical analysis using a t-test of the means showed that the differences in these means was not statistically significant (Table 2.10). A sample of laboratory water was also processed by pump and obtained by hand, and, as was the case for the Duxbury Bay water sample, the pumped sample had a higher PCB concentration than the sample that was not pumped. These results seem to indicate that pumping the sample may introduce some contamination into the sample. This conclusion seems questionable, however, because most of the field samples obtained from stations located away from the source of PCBs had concentrations less than the values obtained for the QC pumping samples. If the pump was introducing 3-5 μg/l of contamination into each sample, it is not likely that so many samples would have concentrations below that level. It is possible that the pump introduced some contamination because some of the tubing inside the pump was not made of Teflon. That tubing might have released some contaminants that reacted like PCBs upon analysis. The field sampling protocol required that before any samples were collected, water be run through the pump for 15 to 30 minutes to rinse away any contaminants. It is possible that this procedure was not followed during collection of these samples in order to do a worst-case analysis of possible contamination, or it is possible that new tubing was used which tended to leach higher levels of contaminants. Whatever the explanation, it does not seem likely that the pump actually introduced high levels of contaminants to the field samples, and the lack of a statistically significant difference in the means of the samples obtained by pump and by hand supports this consideration.

Metal Samples Collected By Pump and By Hand. Table 2.11 presents the results of metals analyses in pumped samples versus hand collected samples. Metals concentrations in these samples was very high, concentrations in the Duxbury Bay water being far above those in New Bedford Harbor. The cadmium and copper concentrations were higher in the samples obtained using the pump, while the

TABLE 2.9. PCB SAMPLES TAKEN BY PUMP AND BY HAND

Lab ID	Sample	Concentration (μg/l)	Mean
BF06	Duxbury Bay Water, Pumped	5.200	
BG87	Duxbury Bay Water, Pumped	3.470	4.335
BF40	Duxbury Bay Water, By Hand	1.980	
BG63	Duxbury Bay Water, By Hand	0.772	1.376
BF16	Laboratory Water, Pumped	3.320	
BF32	Laboratory Water, By Hand	0.285	

TABLE 2.10. RESULTS OF t-TEST OF MEANS FOR SAMPLES OBTAINED WITH A PUMP AND BY HAND.

Parameter	Calculated t[a]	Significantly Different
PCBs	0.49	No
Cadmium	0.78	No
Copper	0.50	No
Lead	-0.77	No
POC Cruise 1	0.41	No
POC Cruise 2	4.63	Yes
SS, silt fraction	2.26	No
SS, clay fraction	NC	

[a]Critical region for all samples except PCBs is $t \leq -2.776$ and $t \geq 2.776$.
For PCBs critical region is $t \leq -12.706$, $t \geq 12.706$.
NC Not calculated, all necessary data not available.

TABLE 2.11. METALS SAMPLES TAKEN BY PUMP AND BY HAND

Lab ID	Sample	Concentration (µg/l) Cadmium	Copper	Lead
E0568	Duxbury Bay Water, Pumped, Rep 1	3.56	127	3.56
E0559	Duxbury Bay Water, Pumped, Rep 2	24.39	99.4	137
E0603	Duxbury Bay Water, Pumped, Rep 3	1.93	106	129
	Mean	9.96	111	89.8
E0578	Duxbury Bay Water, By Hand, Rep 1	3.82	82.4	115
E0545	Duxbury Bay Water, By Hand, Rep 2	3.38	87.3	169
E0546	Duxbury Bay Water, By Hand, Rep 3	2.01	81.7	118
	Mean	3.07	83.8	134

lead levels were higher in the samples obtained by hand. However these results are not statistically significant using a t-test of the means.

Suspended Solids Samples Collected By Pump and By Hand. Suspended solids samples taken using the pump had, on average, slightly higher concentrations of silt and clay suspended solids fractions than samples taken by hand (Table 2.12). The mean concentrations for the silt fraction are not significantly different statistically. It was not possible to do statistical analysis for the clay fraction because a number of samples were not analyzed. The concentrations found for the Duxbury Bay water were in the expected range for coastal waters.

POC Samples Collected By Pump and By Hand. Table 2.13 presents the results of the particulate orgnanic carbon analysis for samples which were collected by hand and by pump. These samples were taken during Cruise 1 and Cruise 2, and in both cases the mean POC concentrations in the pumped water were greater than the means of the samples collected by hand. These differences are statistically significant for Cruise 2 but are not statistically significant for Cruise 1. Although the trend appears to indicate that pumping increases the POC concentrations somewhat, the lack of statistical significance in one of the two experiments indicates that this trend would not have any great impact on the values obtained for the POC samples in New Bedford Harbor.

Conclusions

Solvent Blanks. The solvent blanks showed unexpectedly high levels of PCBs (Table 2.1), the average PCB concentration being 12.67 ng/l. In order to determine how much PCB contamination could be introduced to the samples if the elevated concentrations in the solvent were real, the PCB concentration contributed by the extraction of a 17-liter water sample with 1 liter of solvent was calculated. The average PCB concentration was 0.745 ng/l. Compared to the concentrations of PCBs found in the field samples, that value was relatively low, and did not significantly affect the results of the PCB sampling.

TABLE 2.12. SUSPENDED SOLIDS SAMPLES TAKEN BY PUMP AND BY HAND

Lab ID	Sample	Concentration (mg/l) Silt	Concentration (mg/l) Clay	Mean Silt	Mean Clay
E0922	Duxbury Bay Water, Pumped, Rep 1	4.5	3.2		
E0920	Duxbury Bay Water, Pumped, Rep 2	3.5	2.2	4.3	3.1
E0918	Duxbury Bay Water, Pumped, Rep 3	4.8	3.9		
E0921	Duxbury Bay Water, By Hand, Rep 1	1.9	1.3		
E0919	Duxbury Bay Water, By Hand, Rep 2	1.0	NA	2.1	1.3
E0914	Duxbury Bay Water, By Hand, Rep 3	3.3	NA		

NA: Data for sample not available.

TABLE 2.13. PARTICULATE ORGANIC CARBON (POC) SAMPLES TAKEN BY PUMP AND BY HAND.

Lab ID	Sample	Concentration (µg/l)	Mean
Cruise 1			
E0299	Duxbury Bay Water, Pumped, Rep	1357	.3
E0317	Duxbury Bay Water, Pumped, Rep 2	691	.6834.5
E0303	Duxbury Bay Water, Pumped, Rep 3	1454	.6
E0251	Duxbury Bay Water, By Hand, Rep 1	644	.8
E0296	Duxbury Bay Water, By Hand, Rep 2	662	.7672.2
E0295	Duxbury Bay Water, By Hand, Rep 3	709	.2
Cruise 2			
E0229	Duxbury Bay Water, Pumped, Rep 1	477	.1
E0230	Duxbury Bay Water, Pumped, Rep 2	481	.3499.2
E0233	Duxbury Bay Water, Pumped, Rep 3	539	.3
E0237	Duxbury Bay Water, By Hand, Rep 1	179	.8
E0238	Duxbury Bay Water, By Hand, Rep 2	310	.0253.2
E0235	Duxbury Bay Water, By Hand, Rep 3	269	.7

Field Blanks. PCB sampling field blanks consisted of an ambient air blank and filter blanks. Relatively high concentrations of PCBs were found for these blanks (Table 2.3), the average value for field and ambient air blank combined being 6.73 ng/l. To process the QC samples, the container or filter had to be extracted with a volume of methylene chloride solvent.

The results of the solvent blank analysis showed the solvent to be contaminated with PCBs, and it is likely that the elevated levels of PCBs seen in these samples are due to contamination with the solvent. When the concentrations of PCBs contributed by the solvent on a per liter basis were calculated (assuming that the original volume of 17 liters of sample were extracted), the range in concentrations was similar to that of the solvent blanks, supporting the theory that it was the solvent that was the source of the contamination seen in these samples.

One metals field blank was taken which consisted of a sampling container opened to the air for a period of time equal to the time necessary to obtain a field sample. The metals concentrations for sample were suprisingly high (Table 2.4), which is probably the result of the poor quality laboratory water used to process the field QC sample. This poor quality laboratory water was not used in the processing of field samples, and therefore would not have contaminated the samples, an observation supported by the relatively low concentrations of metals in the New Bedford Harbor field sampling results.

Processing Blanks. The PCB processing blanks had PCB concentrations similar to those contributed by contaminated solvent, indicating that the processing steps do not contribute any contamination to the sample. The metals processsing blanks had very high metals, believed to be due to the poor quality laboratory water used in preparation of the blanks (but not used in preparation of the field samples). The low concentrations of metals in the actual field samples substantiate that the high levels seen in the blanks were not indicative of contamination introduced to the samples in processing.

Only one processing blank was obtained for total suspended solids, with a suspended solids concentration below detection. Although it was difficult to

draw conclusions from only one sample, it appeared that the processing did not introduce any TSS contamination to the samples. The POC blanks had relatively high concentrations of POC.

Re-Extractions. A total of 12 samples were extracted a second time with an additional volume of solvent to determine if the extraction procedure was effectively removing the PCBs from the water sample. An average PCB concentration of 0.662 ng/l was found in the second extraction, and a median value of 3.2 percent of the first extraction concentration was obtained on the second extraction. This percentage was relatively low. In addition, the concentrations of PCBs found in the re-extractions were similar to the contamination levels that may have been introduced by the solvent, indicating that the first extraction was removing the PCBs from the water.

Samples Obtained Using a Pump and By Hand. Samples obtained using a pump and by hand were obtained for PCBs, metals, suspended solids, and POC. Concentrations for all parameters (except lead) appeared higher for the pumped samples than for the samples obtained by hand. However, in all cases but one, There was no statistical difference between samples obtained using the pump and those obtained by hand. The exception was the POC concentrations for Cruise 2. However, the results of the same analysis for Cruise 1 showed that the mean values were not statistically different. Thus while the trend in the data appeared to indicate that pumping increased the levels of all parameters, the differences were not statistically significant.

Chain-of-Custody Procedures

Objective. The objective of the establishement of strict chain-of-custody procedures was to ensure that sample identification and possession was traceable from collection until the samples or data derived from them became available for scientific or legal use. The procedures further ensured that the Program Manager was able, at any time, to quickly identify the status and location of all samples associated with the program.

Procedures. A Field Sample Custodian was designated for each cruise. A sample was considered under custody when it was in the Custodian's possession; if it was in the Custodian's view after being in his/her physical possesion; if it was in his/her physical possession and then locked up by the Custodian to prevent it from being tampered with; or if it was in a designated and identified secure area. It was the Custodian's duty to ensure that all information on sample labels was correct and to sign each label under the space for "Collector" before the labels were permanently affixed to the samples with clear plastic tape. The Custodian also completed duplicate transmittal forms for samples that were transported to the laboratory, and signed the forms under "Collector."

Twice daily, the Custodian relinquished samples to a Battelle courier, and signed the relevant sample transmittal forms under "Relinquished by." The courier signed under "Received by." At that point, the samples were in the custody of the courier. The courier inspected the samples, noted any missing or damaged samples, and wrote "for sample transport" under "Comments." The original transmittal forms accompanied the samples to the laboratory. Copies of the transmittal forms were retained by the Custodian.

Upon arrival at the laboratory, samples were shifted to the custody of the Program Sample Custodian, who also noted any missing or damaged samples and acknowledged in writing that the samples had been received. The Program Sample Custodian was also responsible for entering into the database management system all information contained on field sample labels. Sample custody was retained by the Program Sample Custodian throughout all immediate sample processing. Material not transmitted to other areas for further laboratory processing were labeled and stored under the custody of the Program Sample Custodian.

Records. Lables and forms used in the program include field sample labels, laboratory sample lables, sample transmittal forms, sample storage forms, station log sheets, and water quality data sheets. Field sample labels identified sediment, water column, and biota samples. They were affixed in the field and contained redundant, coded, and descriptive information. Biota

sample labels remained affixed to the samples when they were placed in freezer storage. Sediment and water column sample labels were removed during immediate laboratory processing so as not to damage the lable. They were then turned over to the Qualtity Assurance Officer. Laboratory sample labels identified sediment and water samples that had undergone immediate sample processing at the laboratory. They contained only coded information. Sample transmittal forms accompanied sediment, water column, and biota samples that were sent from the field to the laboratory. The biota sample transfer forms also served as a record of samples in the freezer. Sample storage forms also served as a record of sediment and water column samples put into freezer storage. Station log sheets were numbered sheets, completed at each field station. They included information on date, time, tide, location, current speed and direction, samples taken, and any other information pertinent to a given station. The water quality data sheets were completed at each water sampling station. They included water temperature and salinity (conductivity) measurements associated with the sample.

Audits. Quality assurance audits included regular monitoring and audits by the Quality Assurance Officer. The Quality Assurance Officer was present on selected sampling trips to monitor all field procedures, including monitoring of immediate laboratory processing, and to audit sample documentation and transfer procedures.

2.3 LABORATORY EXPERIMENTS

2.3.1 Assimilation Efficiency

2.3.1.1 Introduction and Objectives

In the development and calibration of the food chain model it was necessary to evaluate the relative importance of different routes of exposure for the contaminants of concern to different species. One route of exposure is the ingestion of contaminated food. Certain contaminants may be ingested and excreted without being absorbed. Some contaminants can be absorbed through the digestive tract and incorporated into various body tissues and fluids.

The degree to which an animal accumulates contaminants from contaminated food is known as the bioassimilation efficiency. The purpose of this portion of the New Bedford Harbor study was to determine the bioassimilation efficiency of adult lobster, Homarus americanus, and winter flounder, Pseudopleuronectes americanus, fed live sand worms contaminated with lead, copper, cadmium, and PCBs.

2.3.1.2 Overview of Experimental Design

Adult lobster and winter flounder were obtained from the Duxbury Bay (Massachusetts) area. During the test each individual flounder and lobster was isolated in a separate compartment in a flowing seawater table. Sand worms, Neanthes virens, were exposed to a soluble mixture of the contaminants for 20 hours in a static exposure system. After the worms were thoroughly rinsed with clean seawater, they were each weighed before they were introduced into the exposure compartments containing the lobsters and flounder. Most individuals began feeding immediately upon introduction of the contaminated worms, and all individuals had fed within two hours, at which time the remaining worms were removed from the compartments. After approximately 20 hours to allow purging of the gut, the lobster and flounder were sacrificed and the whole body concentration of the contaminants determined. A subsample of the contaminated worms was also analyzed in order to provide an estimate of the amount of the contaminants ingested.

2.3.1.3 Methods

Sand worms were obtained from the Maine Bait Co., Newcastle, Maine, and held in flowing seawater. Adult winter flounder (≈0.5 kg) were collected by otter trawl in Duxbury Bay, held in flowing seawater, and fed live sandworms for several weeks before the start of the experiment. Adult lobster (≈0.5 kg) were obtained from a local fish market and had been collected from the Duxbury Bay-Gurnet Point area. They were also held in running seawater and fed live sand worms before the start of the experiment.

The day before the start of the experiment, approximately 50 sand worms were exposed to a mixture of cadmium ($CdCl_2$), copper ($CuSO_4 \cdot 5H_2O$), lead ($Pb(NO_3)_2$), and a 4:10 mixture of Aroclor 1242:Aroclor 1254 in a static system for approximately 20 hours. After this exposure the worms were thoroughly rinsed with fresh seawater before they were used. The lobster and flounder were held without food in a flowing seawater table in individual compartments constructed of perforated acrylic plastic for 1 day before the start of the experiment. Eight lobster and eight flounder were fed contaminated worms; three control animals for each species were fed uncontaminated worms. The worm weights were recorded before they were fed to the animals.

After approximately 20 hours, the animals were removed from the exposure system, wrapped in aluminum foil, placed in a plastic bag and frozen for later chemical analysis. At the time the animals were fed and frozen, three samples of four contaminated worms each were also collected for later chemical analysis. Copper, lead, and cadmium were determined by atomic absorption spectrophotometry and PCBs were determined by GC/MS as described in Section 3.

2.3.1.4. Results

Results of the assimilation efficiency study with winter flounder and lobster are shown in Tables 14 through 17 for copper, lead, cadmium, and PCB congeners Cl_2-Cl_9. The use of these data in the calibration of the food chain model is discussed in Section 6.2 of this report.

2.3.2 Bioaccumulation/Excretion Rate Study

2.3.2.1 Introduction and Objectives

Another important aspect of the food chain model involves the uptake of dissolved contaminants from solution and the release of accumulated contaminants when an animal is returned to a clean environment. The purpose of this study was to evaluate the rates at which selected species of marine animals indigenous to the New Bedford Harbor area take up and excrete PCBs, copper, cadmium, and lead from waterborne exposure.

TABLE 2.14. WHOLE BODY CONCENTRATIONS OF CADMIUM, LEAD, AND COPPER FOR WINTER FLOUNDER (*Pseudopleuronectes americanus*) 24 HOURS AFTER THE INGESTION OF CONTAMINATED WORMS IN THE ASSIMILATION EFFICIENCY STUDY[a]

Treatment	Replicate	Body Weight (g)	Prey Weight (g)	Cadmium (μg/g)	Lead (μg/g)	Copper (μg/g)
Control	1	456	-	0.019	0.093	0.420
Control	2	407	-	0.015	0.145	0.488
Control	3	559	-	0.023	0.085	0.439
Dosed	1	544	7.6	0.080	1.74	0.982
Dosed	2	369	4.8	0.091	1.77	0.662
Dosed	3	359	6.6	0.125	2.42	1.23
Dosed	4	470	5.8	0.089	1.58	0.665
Dosed	5	466	8.8	0.129	2.08	0.903
Dosed	6	504	5.8	0.067	1.61	0.630
Dosed	7	381	5.4	0.115	1.56	0.718
Dosed	8	520	11.4	0.161	2.50	0.848

(a) Mean metal concentrations were 10.9 μg/g cadmium, 139 μg/g lead, and 342.5 μg/g copper for contaminated prey worms.

TABLE 2.15. WHOLE BODY CONCENTRATIONS OF CADMIUM AND LEAD FOR LOBSTER (*Homarus americanus*) 24 HOURS AFTER THE INGESTION OF CONTAMINATED WORMS IN THE ASSIMILATION EFFICIENCY STUDY[a]

Treatment	Body Weight (g)	Prey Weight (g)	Cadmium (μg/g)	Lead (μg/g)
Control	484	-	0.235	0.043
Control	469	-	0.257	0.063
Control	492	-	0.235	0.126
Dosed	456	14.6	0.509	2.10
Dosed	508	11.0	0.509	1.87
Dosed	442	13.6	0.647	3.85
Dosed	551	16.7	0.352	2.05
Dosed	507	18.2	0.475	3.47
Dosed	442	10.4	0.456	1.46
Dosed	479	10.0	0.588	2.98
Dosed	588	10.5	0.410	2.22

(a) Mean metal concentrations were 10.9 μg/g cadmium and 139 μg/g lead for contaminated prey worms.

TABLE 2.16. WHOLE BODY PCB (Cl_2-Cl_9) CONCENTRATIONS (ng/g) FOR WINTER FLOUNDER (*Pseudopleuronectes americanus*) 24 HOURS AFTER THE INGESTION OF CONTAMINATED WORMS IN THE ASSIMILATION EFFICIENCY STUDY.

Treatment	Replicate	Body Weight (g)	Prey Weight[a] (g)	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Total PCBs
Control	1	456	--	0.487	0.537	1.636	5.966	6.867	1.953	0.520	0.143	18.11
Control	2	407	--	0.084	0.404	1.076	4.831	5.998	1.537	0.483	0.229	14.64
Control	3	559	--	0.109	0.986	3.159	11.450	13.913	3.886	1.080	0.248	34.83
Dosed	1	544	7.6	2.064	4.295	6.824	21.338	26.576	5.989	1.598	0.443	69.13
Dosed	2	369	4.8	1.358	4.081	8.308	21.983	19.215	4.965	1.502	0.438	61.85
Dosed	3a	359	6.6	0.860	2.937	3.674	6.602	7.243	1.512	0.388	0.080	23.30
	3b	359	6.6	3.082	9.857	10.459	19.396	21.526	4.578	1.317	0.171	70.39
Dosed	4	470	5.8	0.180	0.572	1.205	2.367	2.798	0.604	0.178	0.040	7.94
Dosed	5	466	8.8	1.275	2.700	3.338	7.397	6.194	1.464	0.334	0.061	22.76
Dosed	6	504	5.8	1.033	3.514	4.793	16.667	21.461	3.958	1.229	0.681	53.34
Dosed	7	381	5.4	0.955	1.520	2.532	4.019	4.180	0.913	0.201	0.032	14.35
Dosed	8	520	11.4	1.001	1.548	2.381	4.335	4.861	1.043	0.357	0.112	15.64

[a] Mean total PCB concentration was 563.7 ng/g for contaminated prey worms.

TABLE 2.17. WHOLE BODY PCB (Cl_2-Cl_9) CONCENTRATIONS (ng/g) FOR LOBSTER (*Homarus americanus*) 24 HOURS AFTER THE INGESTION OF CONTAMINATED WORMS IN THE ASSIMILATION EFFICIENCY STUDY

Treatment	Replicate	Body Weight (g)	Prey Weight[a] (g)	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Total PCBs
Control	1	484	--	0.026	0.583	2.771	9.317	13.679	3.870	1.045	0.199	31.49
Control	2	469	--	0.001	0.149	1.112	2.392	3.580	1.039	0.312	0.048	8.63
Control	3	492	--	0.001	0.478	2.789	11.042	15.529	4.329	1.197	0.197	35.56
Dosed	1a	456	14.6	0.835	6.117	7.732	17.581	16.614	4.348	1.091	0.258	54.58
	1b	456	14.6	2.007	3.828	5.099	11.924	11.247	3.226	0.826	0.209	38.37
	1c	456	14.6	2.520	4.533	5.809	13.499	12.512	3.555	0.901	0.181	43.51
	1d	456	14.6	3.315	6.107	8.159	19.492	17.916	5.140	1.320	0.338	61.79
Dosed	2	508	11.0	2.564	3.784	4.718	6.850	9.014	2.403	0.758	0.068	30.16
Dosed	3	442	13.6	4.641	5.498	7.316	14.055	12.032	3.533	0.832	0.311	48.22
Dosed	4	551	16.7	4.744	7.224	9.821	18.338	14.461	4.052	0.900	0.293	59.83
Dosed	5	507	18.2	5.013	9.910	11.213	18.715	13.924	3.699	0.873	0.296	63.64
Dosed	6	442	10.4	4.464	8.760	10.019	14.622	13.883	4.212	1.259	0.303	57.52
Dosed	7	588	10.5	22.002	43.702	52.895	47.426	34.990	7.937	1.944	0.342	211.24

[a] Mean total PCB concentration was 563.7 ng/g for contaminated prey worms.

2.3.2.2 Overview of Experimental Design

The animals, which included adult and juvenile lobster, *Homarus americanus*, adult and juvenile winter flounder, *Pseudopleuronectes americanus*, hard clam, *Mercenaria mercenaria*, and sand worms, *Neanthes virens*, were exposed in a flow-through dosing system for 42 days and then allowed to depurate in clean flowing seawater for an additional 30 days. Biota samples were taken six times during the uptake phase of the study and four times during the depuration phase. The concentration of the toxicants in the exposure system was monitored during the uptake portion of the study and the whole body burdens of total PCBs, Cu, Cd, and Pb in the animals were determined.

2.3.2.3 Methods

Test Animals. Both adult and juvenile winter flounder were obtained by otter trawl from Duxbury Bay, Massachusetts. Adult lobster were obtained from a local fish market and had been collected from the Duxbury Bay-Gurnet Point area. Juvenile lobster were obtained from Multi Aquaculture System in Long Island, New York. Hard clams were obtained from a local fish market and had been harvested from Duxbury Bay. Sand worms used in the study and also for feeding the lobster and flounder were obtained from Maine Bait Co., Newcastle, Maine. All test animals were held in flowing ambient temperature seawater until they were used in the experiment. During the holding period lobster and winter flounder were fed sand worms; the sand worms were fed chopped clams. Hard clams did not receive any supplemental feeding during this study.

Test System and Procedures. The dosing system consisted of a large polyethylene head tank that supplied a constant flow of filtered seawater to the exposure system. Stock concentrations of reagent grade $CdCl_2$, $CuSO_4 \cdot 5H_2O$, and $Pb(NO_3)_2$ made up in deionized water were pumped into the inflowing seawater line from the constant-pressure head tank.

The Aroclors (1254 and 1242) were dosed into the exposure system with a sand column dosing design. A 1:1 mixture of the two Aroclors was dissolved in hexane and this solution was mixed with clean, washed sand. The hexane was

evaporated by a flow of air and the PCB-laced sand packed into a glass column with a Teflon stopcock and glass wool plugs placed on both ends of the sand bed. Deionized water was pumped through the sand column and the eluant was delivered to the inflow line of the exposure system.

Water quality measurements (dissolved oxygen, salinity) were made at least biweekly. Temperature was monitored continuously with temperature probes and a data logger. The test animals were fed three times per week. Any uneaten food remaining in the exposure tanks during the uptake phase of the study was removed at the time of the next feeding.

Water samples were taken from the exposure system three times per week during the uptake phase of the study and weekly during the depuration phase. Replicate samples were taken for each species and size class (except for juvenile lobster) at 0, 2, 5, 10, 20, 30, 35, 40, 50, and 60 days. The methods used to analyze for metals and PCBs in water and tissues are described in detail in Section 3 of this report.

2.3.2.4 Results

The results of the bioaccumulation and excretion rate study for adult and juvenile lobster, adult and juvenile winter flounder, sand worms, and hard clams for metals are shown in Tables 18 through 23, respectively. The results of the bioaccumulation and excretion rate study for adult and juvenile lobster, adult and juvenile winter flounder, sand worms, and hard clams for PCBs are shown in Tables 24 through 29, respectively. These data in the calibration of the food chain model is discussed in Section 6.2 of this report.

TABLE 2.18. WHOLE BODY CADMIUM AND LEAD CONCENTRATIONS FOR ADULT LOBSTER (*Homarus americanus*) FOR INDIVIDUAL ANIMALS DURING THE BIOACCUMULATION AND EXCRETION RATE STUDY[a]

Treatment	Time (Days)	Replicate	Body Weight (g)	Cadmium (μg/g)	Lead (μg/g)
Control	0	1	464.7	0.152	0.094
Control		2	493.2	0.129	0.090
Uptake	2	1	494.6	0.255	0.28
Uptake		2	519.3	0.290	0.33
Uptake	7	1	520.3	0.315	0.94
Uptake		2	556.9	0.455	1.48
Uptake	15	1	427.4	0.455	1.48
Uptake		2	511.4	0.473	0.71
Uptake	30	1	437.7	0.618	1.93
Uptake		2	518.5	0.560	2.82
Uptake	42	1	444.9	0.600	2.33
Uptake		2	554.3	0.589	2.98
Depuration	02	1	506.9	0.482	1.54
Depuration		2	498.2	0.641	2.33
Depuration	07	1	506.9	0.568	3.63
Depuration		2	547.4	0.452	1.36
Depuration	15	1	414.2	0.587	2.13
Depuration		2	517.2	0.688	1.99
Depuration	30	1	494.9	0.464	1.41
Depuration		2	526.6	0.607	2.21

[a] Mean measured exposure concentrations during the uptake phase were 9.02 μg/L cadmium and 6.9 μg/L lead.

TABLE 2.19. WHOLE BODY CADMIUM AND LEAD CONCENTRATIONS FOR JUVENILE LOBSTER (*Homarus americanus*) FOR INDIVIDUAL ANIMALS DURING THE BIOACCUMULATION AND EXCRETION RATE STUDY[a]

Treatment	Time (Days)	Replicate	Body Weight (g)	Cadmium (μg/g)	Lead (μg/g)
Control	0	1	193.7	0.263	0.067
Uptake	2	1	183.9	0.223	0.26
Uptake	7	1	151.5	0.404	1.46
Uptake	15	1	68.7	0.272	0.63
Uptake		2	132.8	0.392	0.66
Uptake	30	1	116.8	0.430	1.33
Uptake		2	75.5	0.608	1.23
Uptake	42	1	25.8	0.684	3.94
Uptake		2	55.0	0.617	2.45
Depuration	2	1	122.7	0.513	1.64
Depuration	7	1	52.8	0.634	2.31
Depuration		2	89.4	0.470	1.75
Depuration	15	1	153.8	0.611	1.38
Depuration	30	1	124.4	0.493	1.41
Depuration		2	65.8	0.573	1.28

[a] Mean measured exposure concentrations during the uptake phase were 9.02 μg/L cadmium and 6.9 μg/L lead.

TABLE 2.20. WHOLE BODY CADMIUM, LEAD AND COPPER CONCENTRATIONS FOR ADULT WINTER FLOUNDER (*Pseudopleuronectes americanus*) FOR INDIVIDUAL ANIMALS DURING THE BIOACCUMULATION AND EXCRETION RATE STUDY[a]

Treatment	Time (Days)	Replicate	Body Weight (g)	Cadmium (μg/g)	Lead (μg/g)	Copper (μg/g)
Control	0	1	418.1	7.22	0.050	0.514
Control		2	320.7	1.61	0.035	0.280
Uptake	2	1	432.3	3.01	0.050	0.274
Uptake		2	457.9	3.01	0.238	0.366
Uptake	7	1	427.4	3.88	0.406	0.361
Uptake		2	445.7	7.66	1.57	0.335
Uptake	15	1	386.0	5.23	0.082	0.144
Uptake		2	410.3	5.54	0.122	0.337
Uptake	30	1	399.4	6.86	0.234	0.389
Uptake		2	353.7	7.14	0.127	0.413
Uptake	42	1	457.5	17.0	0.479	0.512
Uptake		2	373.3	16.0	0.277	0.424
Depuration	2	1	261.5	8.59	0.176	0.397
Depuration		2	407.1	10.6	0.329	0.426
Depuration	7	1	431.7	9.03	0.436	0.462
Depuration		2	518.6	4.27	0.067	0.317
Depuration	15	1	473.1	7.56	0.076	0.238
Depuration		2	421.7	5.98	0.097	0.307
Depuration	30	1	450.6	13.3	0.165	0.305
Depuration		2	383.0	10.5	0.096	0.434

[a] Mean measured exposure concentrations during the uptake phase were 10.8 μg/L copper, 9.4 μg/L cadmium, and 7.5 μg/L lead.

TABLE 2.21. WHOLE BODY CADMIUM, LEAD AND COPPER CONCENTRATIONS FOR JUVENILE WINTER FLOUNDER (*Pseudopleuronectes americanus*) FOR INDIVIDUAL ANIMALS DURING THE BIOACCUMULATION AND EXCRETION RATE STUDY[a]

Treatment	Time (Days)	Replicate	Body Weight (g)	Cadmium (μg/g)	Lead (μg/g)	Copper (μg/g)
Control	0	1	84.2	1.35	0.051	0.245
Control	2	100.5	3.06	0.042	0.338	
Uptake	2	1	97.2	6.20	0.072	0.365
Uptake	2	65.7	3.92	0.089	0.341	
Uptake	7	1	56.0	13.0	0.714	0.413
Uptake	2	60.1	6.82	2.34	0.263	
Uptake	15	1	58.5	7.29	0.083	0.304
Uptake	2	90.8	7.79	0.054	0.399	
Uptake	30	1	58.6	19.4	0.147	0.342
Uptake	2	82.4	11.7	0.165	0.412	
Uptake	42	1	82.5	13.0	0.249	0.513
Uptake	2	60.7	33.4	0.118	0.348	
Depuration	2	1	84.0	15.9	0.145	0.514
Depuration	2	57.1	19.5	0.139	0.557	
Depuration	7	1	58.4	23.1	0.161	0.384
Depuration	2	56.0	20.5	0.075	0.340	
Depuration	15	1	102.8	12.4	0.117	0.516
Depuration	2	82.6	24.7	0.162	0.305	
Depuration	30	1	98.1	9.14	0.051	0.305
	2	80.8	8.73	0.057	0.404	

[a] Mean measured exposure concentrations during the uptake phase were 10.8 μg/L copper, 9.4 μg/L cadmium, and 7.5 μg/L lead.

TABLE 2.22. WHOLE BODY CONCENTRATIONS OF CADMIUM, LEAD, AND COPPER IN POOLED POLYCHAETE (*Neanthes virens*) SAMPLES DURING THE BIOACCUMULATION AND EXCRETION RATE STUDY[a]

Treatment	Time (Days)	Replicate	Pooled Sample Weight (g)	Cadmium (μg/g)	Lead (μg/g)	Copper (μg/g)
Control	0	1	57.8	0.046	0.092	1.04
Control	2	43.6	0.071	0.094	1.25	
Uptake	2	1	33.1	0.046	0.139	1.32
Uptake	2	23.7	0.062	0.165	1.44	
Uptake	7	1	31.6	0.078	1.37	2.93
	2	31.3	0.062	0.694	2.63	
Uptake	15	1	39.9	0.055	0.251	2.80
Uptake	2	25.2	0.056	0.290	3.09	
Uptake	30	1	42.3	0.104	0.604	5.83
Uptake	2	23.6	0.127	0.722	6.83	
Uptake	42	1	48.9	0.185	0.938	10.9
Uptake	2	32.2	0.198	1.00	10.8	
Depuration	2	1	28.9	0.131	0.894	9.58
Depuration	2	44.0	0.115	0.798	10.40	
Depuration	7	1	42.3	0.128	1.00	8.78
Depuration	2	41.5	0.134	0.885	10.0	
Depuration	15	1	41.7	0.153	0.854	9.14
Depuration	2	41.5	0.177	1.03	9.68	
Depuration	30	1	43.1	0.125	0.810	6.26
Depuration	2	43.0	0.147	0.936	5.77	

(a) Mean measured exposure concentrations during the uptake phase were 10.0 μg/L copper, 9.4 μg/L cadmium, and 7.5 μg/L lead.

TABLE 2.23. MEAN TISSUE CONCENTRATIONS OF CADMIUM, LEAD, AND COPPER IN INDIVIDUAL HARD CLAMS (*Mercenaria*) DURING THE BIOACCUMULATION AND EXCRETION RATE STUDY[a]

Treatment	Time (Days)	Replicate	Pooled Sample Weight (g)	Cadmium (μg/g)	Lead (μg/g)	Copper (μg/g)
Control	0	1	59.3	0.049	0.313	0.93
Control		2	57.7	0.046	0.210	0.96
Uptake	2	1	49.8	0.038	0.125	1.11
Uptake		2	54.4	0.051	0.225	0.95
Uptake	7	1	37.7	0.026	0.899	1.17
Uptake		2	36.2	0.036	0.269	1.25
Uptake	15	1	57.4	0.031	0.173	1.88
Uptake		2	41.0	0.040	0.103	1.56
Uptake	30	1	46.8	0.068	0.340	1.64
Uptake		2	46.6	0.131	0.364	1.80
Uptake	42	1	51.4	0.117	0.513	1.78
Uptake		2	43.9	0.100	0.531	1.96
Depuration	02	1	45.2	0.039	0.154	1.61
Depuration		2	47.0	0.131	0.621	2.44
Depuration	7	1	45.5	0.088	0.522	1.35
Depuration		2	43.0	0.101	0.573	1.53
Depuration	15	1	44.2	0.070	0.241	2.19
Depuration		2	45.9	0.122	0.678	2.37
Depuration	30	1	35.6	0.026	0.140	1.15
Depuration		2	40.0	0.147	0.492	2.35

[a] Mean measured exposure concentrations during the uptake phase were 10.8 μg/L copper, 9.4 μg/L cadmium, and 7.5 μg/L lead.

TABLE 2.24. WHOLE BODY PCB (Cl_2-Cl_9) CONCENTRATIONS (ng/g) FOR ADULT LOBSTER (*Homarus americanus*) FOR INDIVIDUAL ANIMALS DURING THE BIOACCUMULATION AND EXCRETION RATE STUDY[a]

Treatment	Time (Days)	Replicate	Body Weight (g)	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Total PCBs
Control	0	1	464.7	0.001	0.179	0.534	1.831	2.683	0.799	0.219	0.073	6.319
Control		2	493.2	0.204	0.417	1.565	7.679	7.703	2.102	0.475	0.103	20.249
Uptake	2	1	494.6	8.087	6.204	4.705	15.359	18.676	5.423	1.707	0.379	60.540
Uptake		2	519.3	4.105	3.954	3.152	10.985	13.158	4.201	1.574	0.233	41.363
Uptake	7	1	520.3	17.713	12.423	8.952	13.008	16.799	4.443	1.209	0.267	74.813
Uptake		2	556.9	20.905	15.254	9.716	11.108	13.140	3.356	1.005	0.275	74.758
Uptake	15	1	427.4	17.402	14.505	8.427	12.720	11.215	2.836	0.601	0.249	67.955
Uptake		2	511.4	48.723	33.432	22.111	19.517	19.750	4.189	1.035	0.161	148.919
Uptake	30	1	437.7	35.960	28.312	14.457	13.909	14.009	4.221	1.089	0.085	112.043
Uptake		2	518.5	38.926	31.083	15.328	10.233	8.184	2.104	0.532	0.092	83.341
Uptake	42	1	444.9	24.368	21.122	11.294	12.097	8.789	2.633	0.710	0.424	81.436
Uptake		2	554.3	26.562	24.515	12.120	10.233	7.182	2.104	0.532	0.092	83.341
Depuration	2	1	506.9	51.484	43.572	21.304	15.658	13.403	3.311	0.805	0.121	149.658
Depuration		2	498.2	14.255	15.366	7.298	6.829	3.750	1.107	0.289	0.069	48.963
Depuration	7	1	510.9	147.228	114.221	61.678	43.580	39.084	9.815	1.981	0.282	417.868
Depuration		2	547.4	41.146	27.635	12.389	9.722	9.333	2.290	0.613	0.119	103.246
Depuration	15	1	414.2	58.031	57.730	28.534	24.598	14.853	4.574	1.035	0.451	189.806
Depuration		2	517.2	30.798	32.918	17.854	20.406	14.835	4.213	1.101	0.327	122.453
Depuration	30	1	494.9	12.951	14.852	11.445	9.538	5.684	1.417	0.392	0.097	56.375
Depuration		2	526.6	11.895	11.392	6.330	6.207	4.773	1.234	0.335	0.065	42.231

[a] Mean total PCB exposure concentration during the uptake phase was 38.5 ng/L.

TABLE 2.25. WHOLE BODY PCB (Cl_2-Cl_9) CONCENTRATIONS (ng/g) FOR JUVENILE LOBSTER (*Homarus americanus*) FOR INDIVIDUAL ANIMALS DURING THE BIOACCUMULATION AND EXCRETION RATE STUDY[a]

Treatment	Time (Days)	Replicate	Body Weight (g)	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Total PCBs
Control	0	1	193.7	0.190	0.359	1.404	4.210	6.182	1.716	0.401	0.149	14.609
Uptake	2	1	183.9	5.056	4.958	3.245	5.082	4.848	1.596	0.480	0.237	25.502
Uptake	7	1	151.5	15.875	13.764	7.938	8.828	7.377	1.877	0.468	0.123	55.862
Uptake	15	1	68.7	33.448	35.535	20.937	9.733	6.886	2.004	0.920	0.208	109.671
Uptake		2	132.8	55.267	54.279	29.983	13.886	9.833	2.742	0.692	0.316	166.998
Uptake	30	1	116.8	16.690	18.379	10.065	6.799	4.571	1.455	0.480	0.146	58.585
Uptake	42	1	25.8	12.945	12.921	7.616	5.537	2.614	0.795	0.198	0.150	42.775
Uptake		2	55.0	14.024	15.617	8.633	5.422	1.831	0.524	0.181	0.117	46.350
Depuration	2	1	122.7	57.596	51.146	23.463	12.108	7.404	2.257	0.855	0.224	155.054
Depuration	7	1	52.8	8.981	9.654	4.795	2.988	1.328	0.361	0.074	0.019	28.202
Depuration		2	89.4	11.266	14.700	10.611	9.379	3.634	0.940	0.238	0.143	50.911
Depuration	15	1	153.8	8.035	15.467	13.855	10.981	7.228	2.033	0.634	0.113	58.346
Depuration	30	1	124.4	38.682	34.518	18.726	12.217	9.243	3.056	1.086	0.000	117.528
Depuration		2	65.8	12.023	19.285	13.718	12.615	4.265	1.168	0.353	0.107	63.535

[a] Mean total PCB exposure concentration during the uptake phase was 38.5 ng/L.

TABLE 2.26. WHOLE BODY PCB (Cl_2-Cl_9) CONCENTRATIONS (ng/g) FOR ADULT WINTER FLOUNDER (*Pseudopleuronectes americanus*) FOR INDIVIDUAL ANIMALS DURING THE BIOACCUMULATION AND EXCRETION RATE STUDY[a]

Treatment	Time (Days)	Replicate	Body Weight (g)	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Total PCBs
Control	0	1	418.1	0.058	0.866	3.085	10.872	13.993	3.187	0.941	0.187	33.190
Control		2	320.7	0.014	0.374	1.235	5.781	8.637	1.615	0.381	0.131	18.168
Uptake	2	1	432.3	5.394	6.868	4.586	8.563	11.469	2.640	0.685	0.260	40.465
Uptake		2	457.9	14.911	12.684	13.831	38.041	52.653	12.675	1.597	0.522	146.916
Uptake	7	1	427.4	24.079	19.596	11.154	17.287	20.777	4.705	1.286	0.133	99.017
Uptake		2	445.7	35.387	29.421	13.751	12.832	14.708	3.125	1.294	0.129	110.646
Uptake	15	1	386.0	50.846	50.562	20.981	12.361	10.146	2.037	0.833	0.138	147.904
Uptake		2	410.3	40.072	43.866	21.969	20.402	19.135	4.328	1.696	0.533	152.000
Uptake	30	1	399.4	105.064	90.871	27.282	23.230	20.622	3.466	2.649	1.476	274.661
Uptake	42	1	457.5	84.307	99.426	52.100	102.812	40.682	4.081	1.392	0.428	385.228
Uptake		2	373.3	79.997	80.816	33.120	26.932	25.368	6.181	1.952	0.891	255.258
Depuration	2	1	261.5	104.156	105.098	33.655	23.878	13.844	2.715	1.636	0.954	285.937
Depuration		2	407.1	65.551	72.277	30.468	17.256	14.641	3.691	1.907	0.472	206.264
Depuration	7	1	431.7	111.397	108.197	42.388	25.414	22.053	3.893	1.488	0.199	315.029
Depuration		2	518.6	243.615	211.690	86.214	47.508	30.216	7.228	1.710	0.000	628.181
Depuration	15	1	473.1	176.746	202.244	92.812	48.883	31.282	5.878	2.763	0.361	560.970
Depuration		2	421.7	112.088	169.584	86.624	42.962	18.111	4.102	1.129	0.259	434.861
Depuration	30	1	450.6	156.662	216.090	103.783	99.456	86.005	20.756	7.467	3.492	693.710
Depuration		2	383.0	32.833	84.579	52.755	28.007	22.633	5.595	2.324	0.382	229.108

[a] Mean total PCB exposure concentration during the uptake phase was 53.6 ng/L.

TABLE 2.27. WHOLE BODY PCB (Cl_2-Cl_9) CONCENTRATIONS (ng/g) FOR JUVENILE WINTER FLOUNDER (*Pseudopleuronectes americanus*) FOR INDIVIDUAL ANIMALS DURING THE BIOACCUMULATION AND EXCRETION RATE STUDY[a]

Treatment	Time (Days)	Replicate	Body Weight (g)	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Total PCBs
Control	0	1	84.2	0.066	0.486	1.073	3.559	5.325	1.104	0.324	0.425	12.362
Control		2	100.5	0.015	0.251	0.557	1.220	2.018	0.433	0.146	0.048	4.689
Uptake	7	1	56.0	27.700	21.234	8.379	9.286	9.436	1.936	0.595	0.149	78.715
Uptake		2	60.1	1.300	19.163	25.059	11.978	6.311	0.901	0.174	0.035	64.922
Uptake	15	1	58.5	75.944	70.902	33.251	18.655	11.902	2.770	0.923	0.266	214.614
Uptake		2	90.8	48.025	41.930	17.230	18.114	12.305	3.256	2.643	2.162	145.665
Uptake	30	1	58.6	88.168	98.810	36.996	18.973	7.319	1.300	0.735	0.760	253.060
Uptake		2	82.4	51.382	50.733	18.440	9.224	3.363	0.632	0.684	0.805	135.262
Uptake	42	1	82.5	53.775	47.284	21.249	12.125	2.440	3.877	3.234	0.702	144.685
Uptake		2	60.7	49.026	43.219	17.180	10.509	3.005	2.578	6.230	0.008	131.754
Depuration	2	1	84.0	115.527	114.450	41.825	18.977	9.434	1.829	0.689	0.273	303.004
Depuration		2	57.1	170.922	186.779	73.117	46.522	24.569	8.413	3.608	2.836	516.766
Depuration	7	1	58.4	30.230	34.184	13.658	7.564	4.203	0.940	1.443	0.000	92.222
Depuration		2	56.0	58.413	95.710	51.458	39.320	26.437	5.479	2.383	0.831	280.032
Depuration	15	1	102.8	23.410	45.844	28.233	15.734	6.002	1.068	0.414	0.365	121.069
Depuration		2	82.6	88.042	112.663	52.005	24.593	11.588	2.057	0.871	0.510	292.330
Depuration	30	1	98.1	19.388	50.912	36.255	20.363	7.575	1.756	0.847	0.315	137.410
Depuration		2	80.8	57.120	80.049	35.474	25.016	10.896	2.463	2.618	0.432	214.071

[a] Mean total PCB exposure concentration during the uptake phase was 53.6 ng/L.

TABLE 2.28. WHOLE BODY PCB (Cl_2-Cl_9) CONCENTRATIONS (ng/g) IN POOLED POLYCHAETE (*Neanthes virens*) SAMPLES DURING THE BIOACCUMULATION AND EXCRETION RATE STUDY[a]

Treatment	Time (Days)	Replicate	Body Weight (g)	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Total PCBs
Control	0	1	57.8	0.045	0.327	0.600	1.079	1.228	0.500	0.194	0.114	4.089
Control		2	43.6	0.003	0.204	0.570	0.825	0.721	0.305	0.086	0.100	2.813
Uptake	2	1	33.1	3.031	4.459	4.686	3.444	3.470	1.086	0.530	0.354	21.060
Uptake		2	23.7	2.973	6.307	3.856	2.959	1.600	0.745	0.240	0.189	18.869
Uptake	7	1	31.6	7.102	19.672	9.981	5.041	2.618	1.097	0.457	0.237	46.206
Uptake		2	31.3	1.421	1.273	0.732	0.338	0.184	0.083	0.075	0.015	4.121
Uptake	15	1	39.9	26.393	27.022	13.338	6.843	1.620	0.660	0.182	0.066	76.123
Uptake		2	25.2	24.309	24.680	15.411	6.670	1.288	0.487	0.417	0.058	73.319
Uptake	30	1	42.3	46.030	49.635	26.939	11.641	2.450	0.766	0.426	0.075	137.963
Uptake		2	23.6	25.669	30.994	17.957	9.841	2.189	0.730	0.355	0.061	87.796
Uptake	42	1	48.9	39.711	49.633	30.529	15.841	2.446	0.583	0.218	0.142	139.105
Uptake		2	32.2	24.178	42.170	25.633	11.275	2.310	0.371	0.410	0.151	106.498
Depuration	2	1	28.9	25.526	39.405	26.885	14.484	3.750	0.722	0.285	0.038	111.096
Depuration		2	44.0	32.614	49.710	27.022	12.658	2.220	0.591	0.232	0.066	125.113
Depuration	7	1	42.3	19.358	26.357	17.433	8.793	1.790	0.489	0.137	0.093	74.450
Depuration		2	41.5	20.836	30.856	19.906	12.255	2.146	0.409	0.230	0.140	86.778
Depuration	15	1	41.7	28.906	58.042	33.970	17.114	3.897	1.264	0.698	0.102	143.992
Depuration		2	41.5	27.878	45.315	32.380	18.165	3.120	0.591	0.280	0.252	127.980
Depuration	30	1	43.1	17.695	19.483	15.681	10.624	2.602	0.640	0.373	0.122	67.221
Depuration		2	43.0	16.079	24.738	19.710	11.556	2.837	0.770	0.294	0.109	76.093

(a) Mean total PCB exposure concentration during the uptake phase was 53.6 ng/L.

TABLE 2.29. MEAN TISSUE PCB (Cl_2-Cl_9) CONCENTRATIONS (ng/g) IN INDIVIDUAL HARD CLAMS (*Mercenaria mercenaria*) DURING THE BIOACCUMULATION AND EXCRETION RATE STUDY[a]

Treatment	Time (Days)	Replicate	Body Weight (g)	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Total PCBs
Control	0	1	59.3	0.000	0.129	0.415	0.590	4.432	0.164	0.069	0.014	5.813
Control		2	57.7	0.000	0.027	0.395	0.863	0.571	0.179	0.038	0.005	2.079
Uptake	2	1	49.8	0.002	0.124	0.295	0.519	0.533	0.213	0.091	0.060	1.838
Uptake		2	54.4	0.031	0.523	0.294	0.643	0.543	0.184	0.029	0.005	2.253
Uptake	7	1	37.7	0.022	0.135	0.472	0.966	0.737	0.221	0.066	0.021	2.639
Uptake		2	36.2	0.023	0.192	0.595	1.237	0.962	0.282	0.086	0.008	3.385
Uptake	15	1	57.4	0.089	0.116	0.327	0.655	0.429	0.149	0.045	0.002	1.814
Uptake		2	41.0	3.103	4.075	2.548	1.913	0.740	0.228	0.056	0.014	12.676
Uptake	30	1	46.8	4.427	5.655	2.395	1.682	0.570	0.183	0.065	0.011	14.990
Uptake		2	46.6	4.730	5.551	2.710	1.618	0.462	0.141	0.039	0.004	15.255
Uptake	42	1	51.4	2.593	3.056	1.807	1.207	0.259	0.107	0.026	0.022	9.078
Uptake		2	43.9	6.954	7.250	3.810	2.065	0.541	0.159	0.065	0.006	20.850
Depuration	2	1	45.2	0.184	0.332	0.423	0.741	0.370	0.156	0.074	0.014	2.295
Depuration		2	47.0	8.792	8.859	4.122	2.245	0.589	0.232	0.067	0.036	24.942
Depuration	7	1	45.5	1.013	2.236	1.371	0.990	0.310	0.061	0.024	0.006	6.010
Depuration		2	43.0	0.964	1.926	0.850	0.609	0.170	0.103	0.038	0.021	4.681
Depuration	15	1	44.2	6.392	5.416	2.311	1.751	0.681	0.217	0.088	0.046	16.903
Depuration		2	45.9	2.959	3.807	1.951	1.125	0.349	0.115	0.053	0.022	10.380
Depuration	30	1	35.6	0.168	0.375	0.634	0.781	0.424	0.170	0.109	0.002	2.664
Depuration		2	40.0	11.326	12.283	5.842	3.690	1.528	0.174	0.056	0.010	34.911

[a] Mean total PCB exposure concentration during the uptake phase was 53.6 ng/L.

3.0 ANALYTICAL CHEMISTRY PROGRAM

3.1 OVERVIEW AND PARTICIPANTS

The majority of the analytical chemistry activities conducted in support of the New Bedford Harbor Modeling Program were not part of the technical scope of work for the program but were included in a separate scope of work that was awarded separately by NUS Corporation under the REM-FIT Contract. Analytical chemistry included in the Modeling Program provided only for analysis of samples generated in the laboratory experiments performed to develop site-specific data for assimilation efficiency, bioaccumulation, and adsorption/desorption (K_d). This section of the report is intended to review briefly the methods used to perform these analyses conducted under both programs, but is not intended to be a detailed summary of the separate analytical chemistry program. Data from the analytical program are summarized in Sections 5 and 6. Details of the analytical results are found in the Battelle Ocean Sciences database.

The primary objective of the analytical chemistry program was the analysis of field samples of sediment, water and biota for PCB and the three trace metals copper (Cu), lead (Pb) and cadmium (Cd). In addition to the analysis of field samples collected during the four surveys described in Section 2.2, chemical analyses funded under the Modeling Program were also performed in conjunction with the bioconcentration, adsorption/desorption (K_d) and partitioning studies conducted in the laboratory and described in Section 2.3. Results of analyses of field samples are presented in this section; results of analyses of samples pertaining to the laboratory experiments are included in Section 2.3.

3.1.1 Review of Samples, Analyses and Laboratories

The initial processing of field samples and their division into various aliquots for analysis has been described in Section 2.2.2.5. The water samples for PCB analyses consisted of approximately 18 liters of filtered seawater for dissolved phase analysis and the corresponding glass fiber filter(s) used to filter each sample for particulate phase analysis. One-

liter filtered seawater samples were used for the dissolved phase metals analyses and the corresponding Nuclepore filter(s) were used for the particulate metals analyses. Particulate organic carbon (POC) and total suspended solid (TSS) seawater samples consisted of separate 1-liter samples which were filtered with glass fiber and Nuclepore filters, respectively.

Sediment samples consisted of gravity cores or (less often) grab samples that were subsampled in the laboratory for PCB, metals, grain size and total organic carbon (TOC) analyses.

Biota samples consisted of hard clams (*Mercenaria mercenaria*), mussels (*Mytilus edulis*), polychaete worms (mixed taxa), spider crabs (*Libinia* sp.), winter flounder (*Pseudopleuronectes americanus*), and lobsters (*Homarus americanus*). The tissue sample extracts were subsampled in the laboratory for separate PCB and metals analyses. Separate fractions were also analyzed for total lipids.

All of the chemical analyses associated with this program were conducted by the following three analytical laboratories: Battelle Ocean Sciences, Duxbury, MA; Energy and Environmental Engineering, Inc. (E^3I), Cambridge, MA; and Aquatec, Inc., Burlington, VT. One additional set of analyses was performed by Gulf South Research Institute using modified EPA GC/MS Method 680 on samples from the bioconcentration experiment. Because nearly all data points were below detection limits, these data were not used further in the program and are not discussed further in this report.

3.1.2 Sample Tracking

Sample tracking through release of samples to the analytical laboratories has been discussed in Section 2.2.2.6; this section describes tracking within the Battelle Ocean Sciences analytical laboratory. All samples received in the laboratory were documented on a Sample Custody and Identification Form (Figure 3.1) and Sample Identification Log (Figure 3.2) and assigned a unique Chemistry Laboratory Identification Number by the sample custodian or laboratory manager. A Sample Preparation Status Log (Figure 3.3) was used to

BATTELLE NEW ENGLAND MARINE RESEARCH LABORATORY
CHEMISTRY LABORATORY
SAMPLE CUSTODY AND IDENTIFICATION FORM

Project Name: _____
Project Number: _____
Number of Samples: _____
Type of Samples: _____
Batch Number: _____

Chemistry Laboratory Identification Number	Sample Description

Relinquished By	Date	Received By	Date	Time	Comments

FIGURE 3.1.

Battelle

SAMPLE PREPARATION STATUS LOG

Page _____

Project no. _____ Project title _____ Batch no. _____

Sample matrix _____ Refer to SOP no. _____

	COMPLETION DATES/INITIALS									
Sample ID no.	Extraction initiated	Extraction completed	Back extraction/ Concentration	Cleanup column/ Concentration	UV/F required?	Lipid weight	Sample split or pooling *	Column chromatography	Fraction weight	Comments

* If samples have been split or pooled, attach new ID info. to this page.

FIGURE 3.3.

BATTELLE NEW ENGLAND MARINE RESEARCH LABORATORY
CHEMISTRY LABORATORY SAMPLE IDENTIFICATION LOG

Project No. _____ Project Title _____
Type of Samples _____
Date logged in _____ Logged in by _____

Chemistry Laboratory Identification Number	Sample Description

Comments

Sample storage location:

FIGURE 3.2.

document the status of the sample through all phases of preparation and analysis. All information pertaining to the splitting and archival of samples was documented on the Sample Preparation Status Log. The transfer of samples from one analytical laboratory to another was documented on the Sample Custody and Identification Form by the sample custodian at each respective laboratory.

3.1.3 Responsibilities

Under the analytical chemistry contract from NUS Corporation to E^3I, E^3I was responsible for overall management of the analytical program, the sample preparation, and metals determinations for the water samples and some of the tissue samples. E^3I also performed all of the TOC, POC, TSS and grain size analyses.

As a subcontractor to E^3I under the analytical chemistry contract, Battelle Ocean Sciences performed all of the water, tissue and sediment sample extractions for PCB analysis, and provided the instrumental analysis for PCBs on the water samples. Battelle also performed the sample preparation and the metals analyses for sediment and tissue field samples and the analysis of tissue for total lipids. Under the technical scope of the Modeling Program, Battelle was initially responsible for analyses associated with the assimilation efficiency, bioaccumulation, K_d and partitioning experiments.

However, due to the extremely low detection limits required for model input, the samples were analyzed by Aquatec Inc., through EPA's Contract Laboratory Program (CLP). The analysis performed by Aquatec Inc. inclused seawater, sediment and biota samples and the samples generated by the bioaccumulation and partitioning (K_d) studies. Aquatec also performed the PCB analyses of the bioaccumulation, K_d and partitioning experiment samples.

3.2 METHODS AND RESULTS

3.2.1 PCB Analyses

Initially, PCBs were analyzed by gas chromatography/mass spectrometry (GC/MS) and quantified as level of chlorination isomer groups (Cl_1 - Cl_{10}) using modified EPA Method 680 and automated data system software. However, the instrumental method detection limit (MDL) using GC/MS techniques of approximately 80 parts per trillion (ppt) was well above the detection limit determined empirically to be necessary for food chain model validation and calibration (approximately 1 ppt).

As a result, it was necessary to analyze or, in many cases, reanalyze, these samples using gas chromatography/electron capture detection (GC/ECD) with a GC column capable of resolving over 90 percent of the 209 PCB isomers. PCBs were quantified as isomer groups versus an added internal standard. The identification of PCB isomers in selected samples, with high concentrations of PCB, was confirmed by GC/MS analyses.

3.2.1.1 Water Column Samples

Each 18-liter filtered water sample was extracted in a 20-liter carboy three times with methylene chloride using a modified vortex stirrer. The methylene chloride extracts were siphoned off and combined and the PCB internal standard mixtures were added. The combined extracts were dried over sodium sulfate (Na_2SO_4) to remove any residual water and concentrated to 10 ml using Kuderna-Danish (K-D) concentration apparatus. The extracts were then transferred to hexane and concentrated to 1 ml under a stream of clean, dry nitrogen gas. If present, elemental sulfur was removed from the hexane extracts by partitioning the hexane versus a TBA sulfite and 2-propanol solution, after which water was added and the hexane drawn off. The hexane extracts were then transferred to a 3 g, 7% deactivated alumina clean-up column to remove any matrix interferences. The alumina column was eluted with 6 ml of 2% ethyl ether in hexane and the eluate concentrated to 1 ml under a stream of nitrogen gas. If further sample clean-up measures were required,

the extracts were treated with concentrated sulfuric acid (H_2SO_4) prior to instrumental analysis.

The analysis of individual PCB isomer by GC/MS followed the selected ion monitoring (SIM) procedures of EPA draft method 680 as described by Gebhart, et al. (1985). The amount of PCB isomer groups were quantified versus the internal standard d_{12}-chrysene and were corrected for differences in instrumental response based on calibration mixtures composed of authentic PCB isomers.

The GC/ECD analyses for PCBs generally followed the priority pollutant/301(h) pesticide instrumental methods outlined in Tetra Tech (1986). However, individual PCBs were summed and reported as level of chlorination isomer classes, not as Aroclor mixtures. Each resolvable PCB isomer was quantified versus the internal standard and corrected for instrumental response based on calibration mixtures composed of all 209 PCB isomers.

The glass fiber filter samples containing the water column particulate material were solvent extracted at ambient temperature and subsequently processed by the same method used for the sediment samples (Section 3.2.1.2). A proportionately smaller amount of solvent was used for the extraction based on the approximately 10 g weight of the filter samples. The PCB instrumental analyses followed the same procedures used for the filtered seawater samples.

3.2.1.2 Sediment Samples

Weighed sediment samples of approximately 50 g were dried with 50 ml methanol after which the internal standards (d_{12}-chrysene and C_{13}-labeled PCB) were added. The samples were then extracted three times with 100 ml of a 9:1 methylene chloride:methanol mixture, at ambient temperature on a shaker table. Each extraction was performed for a period of four hours after which the sample was centrifuged and the solvent decanted. The extracted sediment was dried at 105 °C and weighed to determine the percent moisture content.

The solvent extracts from each sample were combined and partitioned versus distilled water in a separatory funnel to remove the methanol. The methylene chloride phase was drawn off and dried over Na_2SO_4. The dried methylene chloride extracts were concentrated to 1 ml using K-D concentrators and transferred to hexane under a stream of nitrogen gas.

If elemental sulfur crystals were present, the samples were treated with TBA sulfite and 2-propanol. The sample extracts were transferred to a 3 g, 7% deactivated alumina clean-up column and eluted with 6 ml of 2% ethyl ether in hexane. If further sample clean-up was necessary, the extracts were treated with concentrated H_2SO_4. Sample extracts were concentrated to 1 ml under a stream of nitrogen gas prior to instrumental analysis.

Analysis of the sediment sample extracts for PCBs followed the same GC/MS and GC/ECD instrumental analysis procedures used for the water samples (Section 3.2.1.1).

3.2.1.3 Biota Samples

Biota samples comprising whole flounder, lobster, hard clams, polychaetes and crabs were rinsed with distilled water and cut into approximately 1-inch pieces and placed in a Teflon digestion vessel. Clam tissue was removed from the shell prior to digestion. The weight of each tissue sample was recorded and 0.5 ml of concentrated nitric acid was added for each gram (wet weight) of tissue for all taxa except polychaetes and clams; 0.25 ml of acid per gram of tissue was used for the worm and clam samples. The tissue samples were then digested in a shaker table-water bath at 40 °C for a minimum of 12 hours or until a homogeneous digestate was obtained.

After digestion, measured aliquots of the tissue digestate were removed for PCB and metals analyses. Internal standards were added to the PCB tissue aliquot which was then extracted three times with 15 ml of ethyl ether. The ether extract was dried over Na_2SO_4 and concentrated to 1 ml using K-D techniques. The extract was transferred to hexane under a stream of nitrogen gas. The tissue extracts were treated with TBA sulfite if sulfur removal was

required. The samples were then processed through the alumina clean-up column and H_2SO_4 treatment in the same manner as the sediment sample extracts.

Analysis of the tissue sample extracts for PCB followed the same GC/MS and GC/ECD instrumental analysis procedures used for the water samples (Section 3.2.1.1).

3.2.2 Metals Analyses

Three trace metals, cadmium, copper and lead, were analyzed in water, sediment and biota samples. Initially, the trace metals samples were analyzed by flame atomic absorption spectroscopy (FAAS). If the target metals were below the instrument detection limits using FAAS then the samples were reanalyzed by graphite furnace atomic absorption spectroscopy (GFAAS). The GFAAS analysis is more sensitive than the FAAS technique and resulted in a significant reduction in the detection limits for the target metals.

3.2.2.1 Water Column Samples

Measured aliquots of filtered seawater samples ranging from 25 to 250 ml were acidified in Teflon separatory funnels by the addition of 1 μl of concentrated nitric acid (HNO_3) per ml of sample. Samples of less than 100 ml were brought up to a volume of 150 ml with a distilled water:HNO_3 solution (1 ml:1μl) to ensure comparable extraction volumes. The samples were buffered with 2 ml of ammonium hydroxide:acetic acid solution per 100 ml of sample. The samples were then extracted two times with a mixture containing 2 ml of ammonium pyrolidine dithiocarbamate (APDC):diethyl dithiocarbamate (DDC) and 5 ml of freon. The samples were then extracted a third time with 5 ml of freon. The freon extracts were combined and back extracted once with 100 μl of HNO_3 and once with 900 μl of distilled water. The aqueous phase was drawn off and stored refrigerated prior to instrumental analysis.

The Nuclepore filters containing the particulate phase of the water samples for metals analysis were transferred to Teflon digestion vessels. The filters were digested with 500 μl of HNO_3 at 90 °C in an autoclave. After 12 hours

the samples were removed from the autoclave and mixed with 4.5 ml of distilled water. The aqueous phase was decanted and stored until analysis.

The filtered and particulate water extracts were analyzed for cadmium, copper and lead by FAAS. Analyte amounts were calculated by comparison to calibration curves generated from the analysis of standards at three concentration levels. Calibrations were analyzed before and after every ten sample analyses. If the correlation coefficient calculated from any calibration curve was less than 0.99, the samples analyzed using the curve were reanalyzed. Samples with analyte concentrations falling above the linear range of the calibration curve were diluted and reanalyzed. Samples with analyte concentrations below the instrument detection limit (IDL) were reanalyzed by GFAAS following the same calibration guidelines used for the FAAS analyses. Analysis by GFAAS generally resulted in IDL one to two orders of magnitude lower than those attainable by FAAS.

3.2.2.2 Sediment Samples

Sediment samples for metals analysis were freeze dried and approximately 2 g of the dried sediment was weighed into a Teflon digestion vessel. The samples were digested with 10 ml of HNO_3 at 90 °C in an autoclave. After 12 hours the samples were removed from the autoclave and the digestate was decanted and diluted to 100 ml. The sediment extracts were analyzed for cadmium, copper and lead by the same FAAS or GFAAS instrumental procedures described for the water and particulate samples (Section 3.2.2.1).

3.2.2.3 Biota Samples

Weighed amounts (approximately 4 g each) of the metals subsamples of the acid-tissue homogenate generated as part of PCB tissue digestion (Section 3.2.1.3) were transferred to Teflon reaction vessels. The tissue subsamples were digested in 10 ml of HNO_3 at 90 °C in an autoclave. After 12 hours the digestate was removed from the autoclave and diluted to 100 ml in preparation for analysis. The tissue extracts were analyzed for cadmium,

copper and lead by the same FAAS or GFAAS instrumental procedures used for the analysis of the water and particulate sample extracts (Section 3.2.2.1).

3.2.3 Other Analyses

Other analyses of field samples included total organic carbon (TOC) and grain size for sediments, and total suspended solids (TSS), salinity and particulate organic carbon (POC) for water.

3.2.3.1 Total Organic Carbon (TOC)

Sediment samples were prepared for TOC analysis by removing individual 50 mg subsamples from the sediment sample, drying the subsample at 70 °C and recording the dry weight. Inorganic carbon was removed from the subsample by treatment with 10% HCl until no further effervescence was observed.

Samples were analyzed for TOC by high temperature combustion (800 °C) using a Dohrmann-80 Total Organic Carbon analyzer. A calibration blank and three calibration standards were analyzed at the beginning and end of each day analyses were performed. A linear regression generated from the two sets of calibration standards was used to calculate the sample TOC concentrations.

3.2.3.2 Total Suspended Solids (TSS)

Total suspended solids samples of a measured volume (approximately 1 liter each) were filtered through through nested 3.0 μm and 0.4 μm filters to provide separate determination of suspended silt and suspended clay. After filtration, the filters were placed in a desiccator for 24 hours to remove any residual water. The filters were then re-weighed on an electrobalance to determine the total weight of the suspended solids material.

3.2.3.3 Salinity

Salinity measurements during Survey 1 were performed in the field with an Atago S/Mill refractometer. Salinity measurements were recorded directly from

the refractometer. The refractometer was calibrated with distilled water and saline solution standards prior to use.

For Surveys 2 and 3, discrete water samples of approximately 250 ml were collected for salinity determination and returned to the laboratory. Analysis was performed on a Beckmann RS-7B induction salinometer at Woods Hole Oceanographic Institution. Some leakage was apparent when the sample bottles were recovered for analysis and the data appear suspect in some cases.

3.2.3.4 Particulate Organic Carbon (POC)

Water samples of approximately one liter were filtered through pre-weighed glass fiber filters in the laboratory to isolate the particulate organic carbon. The volume of water filtered was recorded to standardize the POC data. The glass fiber filters containing the particulate organic matter from water samples were dried at 70 °C and the dry weight recorded. The dried filters were then treated with 10% HCl to remove inorganic carbon.

The filter samples were analyzed for POC by high temperature combustion (800 °C) using a Dohrmann-80 Total Organic Carbon Analyzer. A calibration blank and three calibration standards were analyzed at the beginning and end of each day that analyses were performed. A linear regression generated from the two sets of calibration standards was used to calculate the sample POC concentrations.

3.2.3.5 Grain Size

Sediment grain size analyses were conducted following the basic procedures described in Folk (1980). Sediment samples of approximately 100 g were treated with 10 percent hydrogen peroxide until no further effervescence was observed. The samples were then heated to remove excess hydrogen peroxide. Gravel and sand size classes were separated from the silt/clay fraction by wet sieving at 2 mm and 62 μm, respectively. The silt/clay fraction was further subdivided into phi classes by pipette analysis in distilled water.

3.2.3.6 Total Lipids

When sufficient tissue was available, aliquots of homogenized tissue were removed from the biota samples prior to digestion. A maximum of 3 g was removed from each sample, after sufficient tissue material had been removed for PCB and metals analysis. The homogenized tissue was extracted three times with a mixture of sodium sulfate and methylene chloride and concentrated on the K-D apparatus. The concentrated extracts were dried to uniform weight and weighed on an analytical balance.

4.0 DATA MANAGEMENT

4.1 DATA PROCESSING

Two different types of activities were conducted under the technical scope of the data management task. The original purpose of this task under the REM-FIT program was to compile field data collected for model calibration and validation, implement a central database, and disseminate data to the modelers in formats that would facilitate calibration and validation of the models. This activity will be described in Section 4.1.1.

Under the REM III program, Battelle was asked to assume responsibility from Alliance Technologies Corporation for management of a wider variety of historical data sources from the site. The activities conducted under this expanded task will be described in Section 4.1.2. The structure and utilization of the New Bedford Harbor Database that was originally developed for the Modeling Program data and subsequently adapted to include the expanded data management responsibilities will be discussed in Section 4.2.

4.1.1 Modeling Program Field Data

Data referred to in this section are considered to be those resulting from the four surveys of New Bedford Harbor and adjacent areas of Buzzards Bay conducted by Battelle Ocean Sciences between September 1984 and March 1986 as described in Section 2.2 of this report. This is also the data set identified as Group 5 in the data tracking system initiated by the REM III team. As discussed in Section 3, analysis of these samples was conducted by a number of different laboratories.

4.1.1.1 Sample Labeling and Data Tracking

Three different field label codes were used during the study, corresponding to the three sample media: water, sediment, and tissue, respectively. All information necessary to uniquely identify a sample was contained in the sample code. The identification code for each sample was based on the

concatenation of pertinent field descriptors (e.g., cruise, station, tide state, sampling depth). These identification codes are shown in Figures 4-1 through 4-3. Upon receipt of the samples by the analytical laboratory, each was assigned a discrete Laboratory Identification Number (see Section 3). The Laboratory Identification Numbers were a 4-digit alphanumeric assigned arbitrarily by the Sample Custodian at the time the laboratory assumed responsibility for the samples.

Samples assigned to the EPA Contract Laboratory Program (CLP) for analysis were assigned consecutive Special Analytical Services (SAS) numbers. The SAS number for each shipment was assigned by the EPA Sample Management Office; individual sample numbers under each SAS number were assigned by Battelle at the time of shipment and recorded on the Sample Custody and Identification Form (Figure 3-1). A separate Sample Transfer Record that listed each SAS number and all other pertinent sample information (e.g. spikes, volume, medium, etc.) was completed and shipped with the samples.

4.1.1.2 Data Receipt and Entry

Data were received from three sources: Battelle's analytical laboratory, E^3I, and Aquatec, Inc., the CLP contractor. Data from Battelle and E^3I were received on data sheets and were entered into computer files as part of this task. Data from Aquatec were received as a series of files on 9-track magnetic tape.

Upon receipt of data on data sheets, the internal sample numbers assigned by the analytical chemistry contract prime contractor E^3I were checked against the E^3I sample log form and the original Battelle Sample Release Form. The Sample Release Form was considered the primary source for regeneration of the original sample code number. All code information, including sample number, cruise, sample type, and analytical parameter was verified. At least 20 percent of the sample labels were randomly selected for verification and all inconsistencies were corrected by manually tracking the history of each sample on the available documentation. The most common errors found were basic

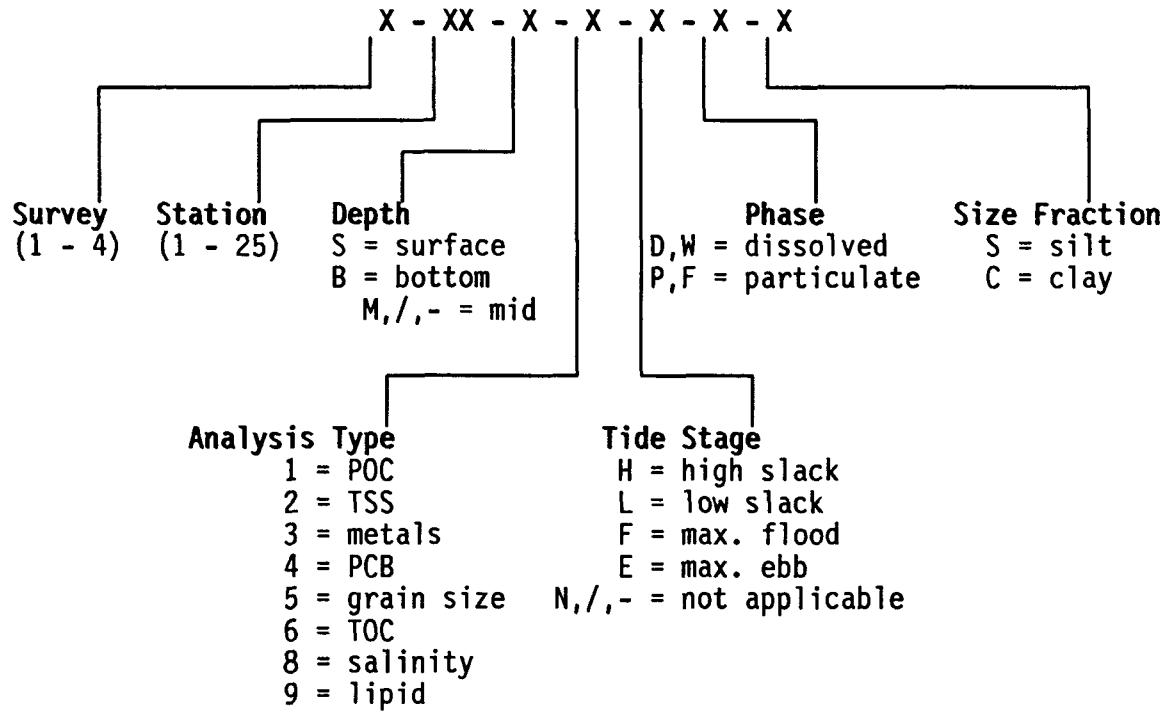

FIGURE 4.1. LABELING KEY FOR WATER SAMPLES

X - XX - X - X - X - XXX - X

Survey
(1 - 4)

Station
(1 - 25)

Core Type
1 = gross
2 = cd*
3 = profile

Size Fraction
(Core Type 3 Only)
SCL = clay
SSI = silt
SSA = sand

Depth
1 = 05cm
2 = 5-10cm
3 = 10-15cm

Replicate
Core Type 1 = Rep 1 or 2
Core Type 2 = N/A
Core Type 3 = Rep 1 or 2

Analysis Type
1 = POC
2 = TSS
3 = metals
4 = PCB
5 = grain size
6 = TOC
8 = salinity
9 = lipid

*compartment differentiation

FIGURE 4.2. LABELING SYSTEM FOR SEDIMENT SAMPLES

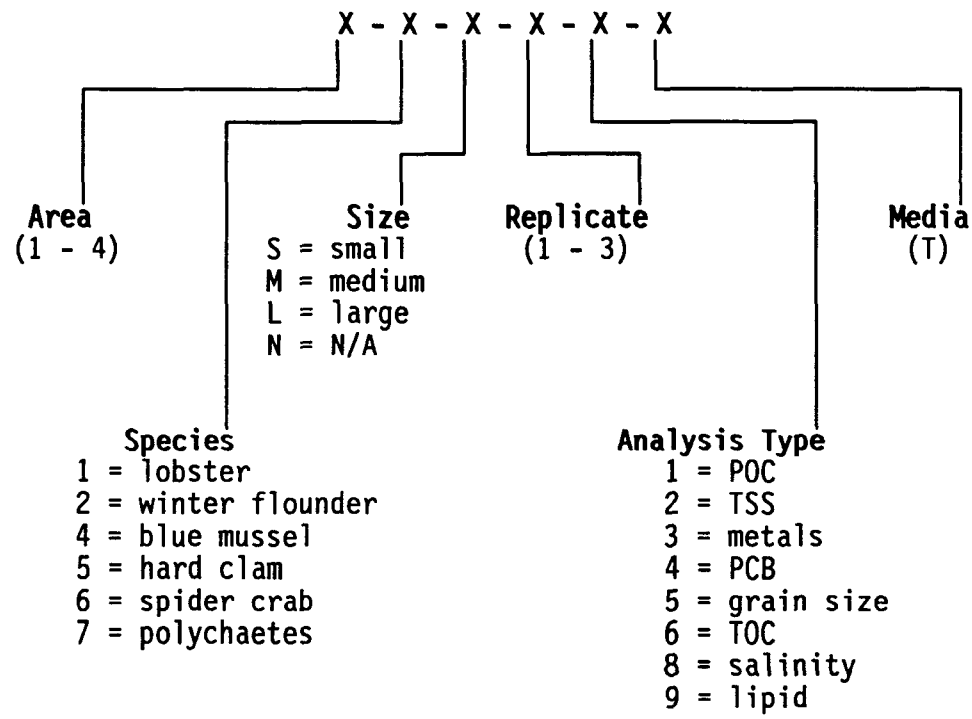

FIGURE 4.3. LABELING SYSTEM FOR BIOTA SAMPLES

transcription errors, duplicate numbering, and reporting of a single mean value for duplicate or triplicate analyses.

Data entry was accomplished using 20/20 spreadsheet software on a VAX 8200 computer located at Battelle Ocean Sciences. Samples were grouped into batches for processing. Each batch of data was entered twice, by different operators. Each operator was assigned a unique identification number that was catalogued with each batch so that the operator could assist in the resolution of any discrepancies.

A quality control template file was used to compare the duplicate entered data for each batch and to identify any inconsistencies between the two data sets. Every data entry in the two files was compared electronically and the comparison results were displayed. Corrections were made manually via comparison with the original data sheets. The quality control program was rerun each time corrections were made. These steps were repeated until no discrepancies were identified between the two files.

After all errors had been resolved, one correct version of each data file was retained and labeled "final"; the quality control template was also retained. Thus, at the completion of data entry, four files of each data batch were retained: each duplicate file, the quality control template, and the final file. The final file was used for loading into the database.

Data received on magnetic tape from Aquatec were subjected to the same sample number validation steps described for data received on data sheets. The sample numbers were checked by generating a hardcopy of the computer file contents and manually comparing it with the Sample Transfer Forms.

Data reformatting programs were written to accept and reformat data from Aquatec magnetic tape files. Before these reformatted data files could be loaded into the database the concentration units were converted from the preinjection volume-based concentrations reported to units per quantity of original sample material. Such conversions were performed for 1406 of the samples analyzed by Aquatec. An additional 236 samples sent to Aquatec as

original media and were extracted by them; these results were reported in terms of the original material and did not require conversion.

4.1.1.3 Unit Conversion Calculations

Most of the data received from Aquatec were reported in terms of concentrations of analyte in the preinjection extract. As part of the data entry process, the data were converted from these relative volume units to units of concentration per original sample volume or weight. This section of the report documents the algorithms used for these conversions.

Water Column PCB Samples. The correction factor for conversion of preinjection volume of extract to volume of the original sample was calculated as

$$F = (Vp/Ve) \times (0.001\ L/mL)$$

where

F = correction factor
Vp = preinjection vol. (mL)
Ve = volume of water extracted (mL)

Final concentration of analyte in nanograms per liter (ng/L or parts per trillion [ppt]) was then calculated as

$$Cf = Co \times F \times (1000\ ng/\mu g)$$

where

Cf = final concentration of PCBs in sample (ng/L)
Co = original concentration of PCBs in sample (μg/L)
F = correction factor

Sediment PCB Samples. The final analyte concentration for sediment samples was calculated as

$$Cf = Co \times (Vp/Ws) \times (0.001\ L/mL)$$

where

Cf = final concentration of PCBs in sample (μg/g)
Co = original concentration of PCBs in sample (μg/L)
Vp = preinjection volume (mL)
Ws = weight of sediment extracted (g)

Tissue PCB Samples. The final concentration for tissue matrix PCB samples was calculated as

$$Cf = Vp \times We \times (0.001\ L/mL) \times Co \times (1000\ g/kg)$$

where

Cf = final concentration of PCBs in sample (μg/kg)
Vp = preinjection volume (mL)
We = weight of tissue extracted (g)
Co = original concentration of PCBs in sample (μg/L)

Additional correction required calculation of the weight of acid (HNO_3) added during extraction; this was calculated as

$$Wa = Va \times Da$$

where

Wa = weight of the acid (g)
va = volume of the acid (mL)
Da = density of the acid (g/L)

The whole animal wet weight correction factor (F) was calculated as

$$F = \frac{Ws}{Ws + Wa}$$

where

F = correction factor
Ws = whole animal wet weight (g)
Wa = weight of the acid (g)

and the corrected aliquot weight as

$$Wc = Wp \times F$$

where

Wc = corrected aliquot weight (g)
Wp = aliquot weight (g)
F = correction factor

The final analyte concentration for tissue samples was then

$$Cf = Co \times (0.001\ L/mL) \times Vp \times (1/Wc) \times (1000\ ng/g)$$

where

Cf = final concentration of PCBs in sample (ng/g)
Co = original concentration of PCBs in sample (μg/L)
Vp = preinjection volume (mL)
Wc = corrected aliquot weight (g)

Water Samples Collected During Bioaccumulation Experiment. During the dosing and depuration stages of the assimilation efficiency and bioaccumulation experiments, a series of water samples was collected and analyzed to monitor the performance of the dosing system and to ensure that the organisms were in fact subjected to the design contaminant concentrations. The final concentration of analyte in these samples was calculated as

$$Cf = Co \times (Vp/Ve) \times (1000\ ng/\mu g)$$

where

Cf = final concentration of PCBs in sample (ng/L)
Co = original concentration of PCBs in sample (μg/L)
Vp = preinjection vol. (mL)
Ve = volume of water extracted (mL)

4.1.2 New Bedford Harbor Project Data

4.1.2.1 Overview and Objectives

In addition for responsibilities for modeling program field data discussed in Section 4.1.1 above, Battelle was also tasked to develop a larger New Bedford Harbor database to allow inclusion of several data sets held previously by Alliance Technologies. The objectives in processing these data were to

organize and quality check the data and to make them available to members of the project team on a computer-based system. To achieve these objectives the data were reviewed, reformatted, keyboard entered, checked for quality, and included in the New Bedford Harbor database management system. In addition, these data were to be distributed to members of the project team for use in risk assessments and modeling.

4.1.2.2 Data Receipt and Entry

Data were received from Alliance Technologies on diskettes and hard-copy data sheets; along with these data sets, Battelle received various documentation describing the data file contents, format, and additional descriptive material concerning the original studies that produced the data.

These data were processed through up to six stages depending on their format upon receipt. A status sheet (Appendix D) was used to track and summarize progress on each data set. The six stages, described below, were executed in the following order:

1. Data Sheet Verification
2. Coding Sheet Validation
3. Keyboard Data Entry
4. Diskette File Validation
5. Error Identification/Correction

Data Sheet Verification. Original data sheets were received in packages separated by study and laboratory. Data sheets were checked for completeness of key fields including sample number, station number, parameter codes, concentrations, and QC codes. It was especially important to verify the parameter codes because of the many conventions that were used to report results. For example, data for PCBs were reported in different studies as total PCB, Aroclor, and PCB homologs. Missing or illegible fields were corrected through discussions with Alliance Technologies personnel or with the cognizant individual from the reporting laboratory. Data sheets were stored according to the batch numbers assigned by Alliance.

Coding Sheet Validation. Coding sheets received from Alliance were validated by visually confirming that all entries on the original data sheets had been correctly transferred to coding sheets and by verifying the chain of sample number assignments, through the documentation provided. Coding sheets that were incomplete were completed to the extent possible by referring to the appropriate documentation. Missing coding sheets and sheets that were illegible due to poor quality reproduction were rewritten by using the available documentation.

Keyboard Data Entry. Much of the data that were received from Alliance existed only as hard copy. These raw data were digitized using commercially available spreadsheet software to ensure accurate entry of data. Data were entered onto spreadsheets twice, by different individuals, and then compared electronically. Any differences between the two files were corrected by inspecting the original coding sheets. Data files were then output in a standard format for loading into the database. Spreadsheet and output files were archived on computer tapes. All hard copy data that were entered were subjected to the same review process described for the diskette files received from Alliance described below.

Diskette File Validation. Data files received on diskette were reviewed for data quality and integrity. The files were output from the dBaseII format and reformatted for entry into the New Bedford Harbor database according to the codes and referencing system used by Alliance. Review of the diskette file contents included tallying the number of samples and stations, plotting the station latitude/longitude locations, listing all codes used, and separating data into reference groups as specified by the REM III team. Any tallies that proved suspect were resolved by comparing the original study description with the data and coding sheets. Station locations were confirmed by reformatting the diskette files of station data into the format used by Battelle's plotting software. Location data were received in latitude/longitude, Universal Transverse Mercator, or Lambert (State Plane); all locations were converted to latitude/longitude prior to entry into the database. Standard conversion programs were obtained from the United States Geological Survey (USGS); these programs were verified with known benchmark points. Following conversion, all

stations were plotted on a digitized coastline of the New Bedford Harbor area; any stations that plotted outside of the area were corrected by examining the original study descriptions.

Diskette files were examined for consistency in codes used. Documentation provided by Alliance defined the codes. Extraneous codes or combined codes were identified and resolved by reviewing the comments on the laboratory record sheets, coding sheets, or in the diskette files "comment" field.

The final step of the diskette contents review stage was the separation of these combined files into smaller subfiles based on reference data set number. The reference data set numbers were defined by the REM III team to differentiate data generated by the different field programs and analytical laboratories. The reference data set number became the primary unit of grouping for all subsequent reviews.

Error Identification/Correction. Preliminary error identification and correction was made based on quality control notes prepared by Alliance that were received with the diskettes. These QC notes documented known errors or discrepancies in the diskette files that had not been addressed as of the date of transfer to Battelle. Corrections to the data were made based on the QC notes, in some cases also with reference to the data sheets, coding sheets, and original study reports. Principal investigators of the studies in question were contacted to resolve problems in some cases.

Final error corrections were made using the New Bedford Harbor database. The database allowed the use of relational checks, legal code lists, valid numeric ranges, and uniqueness constraints for error checking. Relational checks ensured sample integrity by examining, for example, if all samples were related to a station description by a common joining element. The database was used to identify samples that were not logically joined to stations, as well as other relations.

The database management system was used to define the legal code lists and valid ranges for specific elements. Any violations by these elements were

automatically identified and listed in database loading reject reports. Any data that were duplicated were also reported in the reject reports. Reject report errors were resolved by examining data sheets, coding sheets, and original study descriptions. All data that were loaded into the database were subjected to these checks.

4.1.2.3 Quality Control

The procedure used to process the data sets received from Alliance Technologies was audited by the Battelle Ocean Sciences Quality Assurance Unit. The audit included review of the documented steps and random sampling of the entered values. Entered values were audited by comparing the selected samples in the database to their respective original data and coding sheets.

In addition to comparing the entered values to their original data sheets, the database management system was used to compare the entered values to the remainder of the database. Such comparisons enabled checking for logical relations between all samples as described in the previous section. By comparing every sample it was possible to ensure that all values for each numeric parameter were within allowable ranges and all codes were consistent throughout the database.

4.2 NEW BEDFORD HARBOR DATABASE DESIGN AND MANAGEMENT

4.2.1. Overview and Objectives

Two distinct database structures were used to store and manage the data. The first database was designed solely to manage the field data collected by Battelle to support the Modeling Program. The final database was designed to manage both the Modeling Program data and the historical data compiled by Alliance Technologies.

The first objective of this activity was to modify and extend the structure of the original database to incorporate and combine the historical data types with the Modeling Program data. Additionally, the final database was intended

to allow for data security, selective data distribution, and access by data managers. These objectives were achieved through the following steps:

1. Requirements Specification
2. Design Description
3. User Documentation
4. Maintenance and Security Procedures

All requirements, specifications, modifications, maintenance, and documentation needs were determined based on guidance from EPA, the REM III team, and other members of the larger New Bedford Harbor Program team.

4.2.2 Database Design

4.2.2.1 Requirements Specification

Requirements for the database management system were specified through a series of discussions and meetings with various participants in the New Bedford Harbor Superfund Program. These discussions identified the following database design requirements:

- One Central and consistent database structure.
- Capability to receive all historical data types.
- Ability to support output for modeling, risk assessment, litigation, plots, EPA.
- Provision for inclusion of QC qualifiers and auxiliary notes.
- Provision for three spatial referencing systems.
- Security measures to control user access.
- Ability for users to sign on, create files, and download.
- Provision for dial-in access.
- Maintenance of Backup and Recovery whenever database records are added, edited, or deleted.
- Addition of new data.

These design requirements were all considered to be mandatory features. In addition, it was considered desirable to have the capability of producing output in dBaseIII format.

4.2.2.2 Design Description

Functional Design Description. The system design for managing and maintaining the New Bedford Harbor data can be described in terms of four functional components (Figure 4-5). The first and fourth components are collections of programs to preprocess and output the data. The second and third components comprise the database management system for storage, logical organization, and access to the data.

Preprocessing and operating system programs were designed to facilitate data manipulations prior to database loading. Reformatting programs were written to transform any historical type of data into a format that could be loaded into the database. Sorting utilities enabled each data set to be separated by individual reference number. Screening programs were designed to summarize all codes that needed to be stored in the database. Standard programs fulfilled the design requirements of converting between different geographic referencing conventions (i.e. latitude/longitude, Universal Transverse Mercator, State Plane Coordinates). Database loading programs were designed to add any type of reformatted diskette and/or keypunched data to the database. Loading programs included provision for generating reject files to summarize all load-time errors and data. File backups and archival were accomplished as part of routine daily system maintenance. These archival procedures included creation of data files, database definition files, database storage files, programs, and output files.

The database structure and storage design requirements were satisfied by use of the DM Database Management System, a proprietary software product developed and marketed by Battelle. The design allowed the data definition language (DDB) to be independent from the stored data (ODB). Implementation in DM also utilized the journaling utility, a program that automatically records all modifications made to the database structure or contents.

Data Management System Design Components

I Preprocessing and Operating ==>> System Programs	II Actual DB Structure==>> & Storage	III Logical Views & ==>> Relations	IV Data Retrieval, Outputs, and Analysis Progs.
Reformatting	DDB	Stations	Simple Retrievals
Separating	ODB	Samples	Simple Outputs
Screening	Journals	Data	dBase III format
Conversions	User Accts	Keys	Modeling Files
Loadings		Joins	EPA Summary Files
Backup/Archives		Tests	Plotting Routine

FIGURE 4.5. SCHEMATIC DIAGRAM SHOWING THE FUNCTIONAL UNITS OF THE NEW BEDFORD HARBOR DATA MANAGEMENT SYSTEM DESIGN. THE FOUR UNITS WERE EXECUTED IN SEQUENCE, WITH THE EXCEPTION OF CONTINUOUS BACKUP/ARCHIVE AND DATABASE MODIFICATION JOURNALING.

Journaling also satisfied the requirement of recovery from potential system failures. Database user accounts, with private passwords, were designed so that user-specific security could be exercised to allow read-only or read+update+delete privileges at the discretion of the database administrator.

Logical views of the database were designed based on data access and retrieval requirements, and on the types of data being stored. The final database design included three fundamental data views: STATIONS, SAMPLES, and analytical DATA. These views represent the three independent attribute groups. The design allows separate and independent retrieval of station data, sample descriptions, or analytical results. The SAMPLES and DATA views are designed to include a generic code for denoting any of the historical data types. The groups are related to each other by a common sample number element.

A unique key was designed for each view by combining the sample number with additional descriptive elements such as replicate number. Unique keys allow all data to reside in one consistent database, while ensuring that data are not duplicated or intermixed. The design of unique keys that are based on descriptive elements also allows database loading reports to indicate exactly which data might have been duplicated or mixed. For example, a analytical results from sections of a sediment core must be unique based on depth increment in the core; the key ensures that results are only reported once for each section.

The three database views are related to each other by a common sample number element. In many instances one occurrence of a view, for example a STATION, has a sample number that relates to many SAMPLES. This relational database design reduces data duplication and anomalies due to added or deleted data. It is impossible to add new sample descriptions without first adding a station record with the same sample number. Similarly, STATION records cannot be deleted if there are still SAMPLE or DATA records with the same sample number.

The design of unique keys and join elements facilitates testing of logical relations between data view types. For example, it was possible to interactively confirm that every DATA view occurrence had an associated SAMPLE description defining the material analyzed. Similarly, every sample was tested for a relation back to the STATION descriptions.

Detailed Design Description. The detailed design of the final New Bedford Harbor database views is shown in Figure 4-6. Below each of the three view names are the individual elements that describe the view. Each unique key for each view is a concatenation of the elements marked with an asterisk. All non-key elements depend on the unique key to describe an individual view occurrence. A data definition language description of this database structure is included in Appendix C. Brief instructions and examples of how to manipulate these views are provided in the Section 4.2.3.2 of this report.

The analogous detailed design description for Battelle's original monitoring program database can be found in Appendix B. The monitoring program database was designed to relate views based on field sampling descriptor elements such as CRUISE, STATION, SAMPLING DEPTH, and TIDE. These "field keys" were retained when possible, in the COMMENTS element of the SAMPLES view. The second major difference between Battelle's sampling database and the New Bedford Harbor final database design was that the original database used separate views to store each analyte type, versus the more generic final database which accommodates all data types with codes in the one DATA view. Additionally, the original database had separate WATER and BIOTA views to store data about sampling episodes and animals collected.

The code lists and legal value ranges are independent tables that can be modified or extended as new codes become necessary. These tables produce automatic tests designed to restrict element values to only legal codes or reasonable values.

Stations	Samples	Data
*Sample Number	*Sample Number	*Sample Number
Lat/Lon	*Origin	*Parameter
Lambert X/Y	*Material	Concentration
UTM X/Y	*Fraction	Qualifier
Orig Cruise	*Species	Detection Limit
Orig Study	*Top Depth	Units
Orig Station	*Bottom Depth	Analyt. Replicate
Orig Sample No.	*Field Replicate	Lab ID
Date Sampled	Percent Solids	Lab Sample No.
Depth, Temp, Sal	Comments	Date Analyzed
Tide	Alliance Sample No.	Method of Analysis
Time Sampled	Date Entered	Comments
Current Speed		Date Entered
Current Dir.		
Reference No.		
Comments		
Alliance Sample No.		
Date Entered		

FIGURE 4.6. DETAILED DESIGN DESCRIPTION OF THE NEW BEDFORD HARBOR DATABASE STRUCTURE. INDIVIDUAL ELEMENT NAMES ARE LISTED BELOW EACH OF THE 3 VIEWS. THE ELEMENTS WITH ASTERISKS ARE CONCATENATED TO FORM THE VIEWS UNIQUE KEY.

4.2.3 Database Utilization

Implementation of this database design enabled data retrieval, outputs, and analyses to be carried out by many types of users. The independence and relations between the views allowed users to combine view types for customized outputs depending on their intended uses. Simple retrieval and outputs, as described below, were accomplished through interactive queries of the database. More complicated queries, and especially complicated output formats, were accomplished using programs written by the database administrator in DM procedural language. These programs were included in backups so they could be recalled and repeated when similar output formats were needed. Saving the retrieval and output programs also served as documentation of the exact contents of files that were distributed to modelers and risk assessment end users.

Programs were also designed to analyze standard STATIONS output files by producing station location plots. These programs were designed to show each reference study's station locations with respect to the New Bedford Harbor shoreline. These programs were designed to analyze location data originating from the diskette files or keypunching.

4.2.3.1 Maintenance and Security Procedures

The database design specifications required a centralized system that was accessible and secure. These design requirements were satisfied by implementing the database management system on Battelle's VAX minicomputers.

Most database maintenance was performed as part of Battelle's daily system support procedures. These procedures included daily backups of all modified files, and monthly backups of the entire disk storage media. These maintenance procedures provided recovery capability from problems such as system failures, improper data additions, or superseding of custom program files.

Another major database management design consideration was that the database be accessible to several users for outputs, while not allowing any users to change the database. One Battelle scientist was appointed database administrator, with exclusive privileges to add, modify, and delete data. Various other users were given usernames and assigned secure privileges, by the database administrator, for access the database for reading only.

4.2.3.2 User Documentation

Computer-proficient users who required direct access to the database were given written descriptions of the views, elements, and relations between views. These descriptions were sufficient to enable selective retrieval and display of relevant data. In addition, users were given brief descriptions of the pertinent DM commands. Further documentation of DM commands and syntax was made available with on-line help utilities.

The three most important functions that users need are to review database structure definitions, to find pertinent views, and to display the selected views as output. These commands can all be typed into the database management system interactively to provide immediate results. In addition, a HELP command was available to provide descriptions and examples of the needed commands.

Retrieval of Database Structure, View and Element Names. The SHOW/DDB * command is used to review the database structure (i.e. view and element names). DM will respond to this command by showing the Definition Database contents for all (*) views available. More detailed information about a particular view and all of its elements, such as STATIONS, is displayed via the SHOW/DDB STATIONS.* command. This will list names and descriptions of all elements in the STATIONS view.

The most detailed level of this command, for example SHOW/DDB DATA.PARAMETER FULL=YES, allows the user to review details of element design characteristics. The response to this command will provide details (for in this case the PARAMETER element) such as whether the data field is character

or numeric, presence/absence of an index for fast searching, or what legal codes may have been defined for the element.

Retrieval of Database Contents With FIND Command. Finding relevant data in the database is accomplished with the FIND command along with specifications describing which view should be searched and any restrictions. All the STATIONS, for example, can be listed by typing FIND STATIONS. The resultant "set" of views would not necessarily be in any order. Such a general query would be better issued with instruction to sort according to some discriminating element such as the original study name.

A sorted result set is by adding instructions to the previous command, for example FIND STATIONS ORDER BY ORIG_STUDY. A more restricted query such as FIND STATIONS WHERE DEPTH > 10, will return only stations with depths greater than 10 feet. Similar restrictions can be used, for example, to select SAMPLES by species or DATA by parameter code.

Display of Database Contents With TYPE Command. Once a result set has created using the FIND command, its contents may be displayed with the TYPE command. The TYPE command is followed by the names of the elements to be displayed. For example, to display the station number, tide stage, depth, and temperature of the previous STATIONS with depth greater than 10 feet, the command TYPE ORIG_STATION TIDE DEPTH TEMPERATURE is used. Additional elements may be included in this type statement and their display sequence is completely flexible. To create an output file for downloading or storage, the user simply specifies a name for the output file by adding FILE="name".DAT to the end of the TYPE command.

Combining Views with Join Elements. An extension of the basic commands described above is used to join separate views into combined result sets for easier manipulation. Joining is accomplished with the FIND command by specifying which views are to be included and specifying which elements should be use to join the views. In the final New Bedford Harbor database design, the principal join element is sample number (SAMP_NUM). Joining of SAMPLES descriptions and DATA results to create a combined file is

accomplished using the command FIND SAMPLES,DATA WHERE SAMPLES.SAMP_NUM := DATA.SAMP_NUM. In further FIND or TYPE commands operating on the combined file the view name must precede the element name. For example, the previous result set could be displayed by TYPE SAMPLES.MATERIAL DATA.PARAMETER DATA.CONC DATA.QUAL. The database design allows all views to be joined with the FIND command.

Documentation of Output Files. Data output by the database administrator for use on external systems, such as the modeling or risk assessment analyses, were accompanied by detailed documentation of the data file contents, formats, and relationships between data files. This written documentation often included complete definitions of the codes used in key descriptive elements. Complete explanations of the contributing studies were included to document sources of the data included in the output files.