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NCCOSC/ERLN CASE STUDY OF ESTUARINE ECOLOGICAL RISK ASSESSMENT AT NAVAL SHIPYARD PORTSMOUTH KITTERY, MAINE

PHASE I DRAFT INTERIM REPORT

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ABBREVIATIONS AND ACRONYMS[1]

cfu	colony-forming units
CLP	Contract Laboratory Program
CRM	Certified Reference Material
EMAP	Environmental Monitoring and Assessment Program
ERLN	Environmental Research Laboratory, Narragansett, Rhode Island
EPA	U.S. Environmental Protection Agency
HSWA	Hazardous and Solid Waste Amendments
MDL	method detection limit
MF	membrane filtration
MPN	Most Probable Number
NAI	Normandeau Associates, Incorporated, Bedford, New Hampshire
NCBC	Naval Construction Battalion Center Davisville, Rhode Island
NCCOSC	Naval Command Control and Ocean Surveillance Center (formerly Naval Ocean Systems Center), San Diego, California
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
NOSC	Naval Ocean Systems Center (now Naval Command Control and Ocean Surveillance Center)
NPDES	National Pollution Discharge Elimination System
NRC	National Research Council of Canada
PAH	polycyclic aromatic hydrocarbon
PBS	phosphate buffered saline
PCB	polychlorinated biphenyl
PE	performance-based evaluation
ppb	parts per billion
ppt	parts per thousand

[1] See Table 2 for abbreviations used for chemical analytes.

QA	quality assurance
QC	quality control
RCRA	Resource Conservation and Recovery Act
RFI	RCRA Facility Investigation
ROV	remotely operated vehicle
SAIC	Science Applications International Corporation
SHIPYARD	Naval Shipyard Portsmouth, Kittery, Maine
SDS	sodium dodecyl sulfate
SFG	Scope for Growth
SOP	standard operating procedure
SRM	Standard Reference Material
SWMU	solid waste management unit
UNH-JEL	University of New Hampshire, Jackson Estuarine Laboratory, Durham, New Hampshire
VOC	volatile organic compound

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EXECUTIVE SUMMARY

A research and monitoring project is being sponsored by the Navy to provide a framework for assessing the ecological risk of Naval Shipyard Portsmouth (SHIPYARD) operations to the Great Bay Estuary. The ecological risk assessment framework consists of quantitatively estimating the likelihood of adverse ecological effects resulting from exposure to hazardous waste releases at the SHIPYARD. The project, initiated in August 1991, involves a detailed assessment of the existing environmental quality in lower Piscataqua River to determine if contamination from the SHIPYARD can be linked to measurable environmental impacts. The effect of SHIPYARD contaminants on the estuary is being determined by comparing measures of contamination and biological impact made at sites in the immediate vicinity of the SHIPYARD with similar measures made at reference sites in the estuary. The information developed from the study will provide a context for evaluating ecological risks from SHIPYARD operations.

A network of 34 stations has been established to develop information on the distribution and effects of contaminants from the SHIPYARD. The main emphasis is on sampling in depositional areas of the estuary, where fine grain sediments accumulate, and where the likelihood of measuring contamination is maximized. An extensive sampling grid, circumscribing Seavey Island and extending into the Clark Island embayment, was located to provide samples for measuring sediment chemistry and toxicity, and collections of mussels, eelgrass, and benthic organisms. Other stations, located upstream, downstream, and across-stream from the SHIPYARD, in Spruce Creek, and in the York River were established to provide information on the possible extent of contamination from the SHIPYARD, other sources of contamination in the Estuary, and background reference levels of contamination. In addition to these stations, fishing net trawls were conducted in the Piscataqua River and in the York River to obtain fish and lobster samples for analysis of contaminant burdens.

The study is being conducted as a cooperative research project between the Naval Command Control and Ocean Surveillance Center and the U.S. Environmental Protection Agency Environmental Research Laboratory at Narragansett, with assistance from the University of New Hampshire Jackson Estuarine Laboratory. Field sampling for the first phase of the project has been completed and the compilation and analysis of the results obtained from the physical, geological, chemical, biological, and toxicological tests is underway. This document provides an interim status report of the activities being conducted for the study and an evaluation of the ability of the selected methods and procedures to accomplish the tasks identified in the statement of work.

INTRODUCTION

BACKGROUND

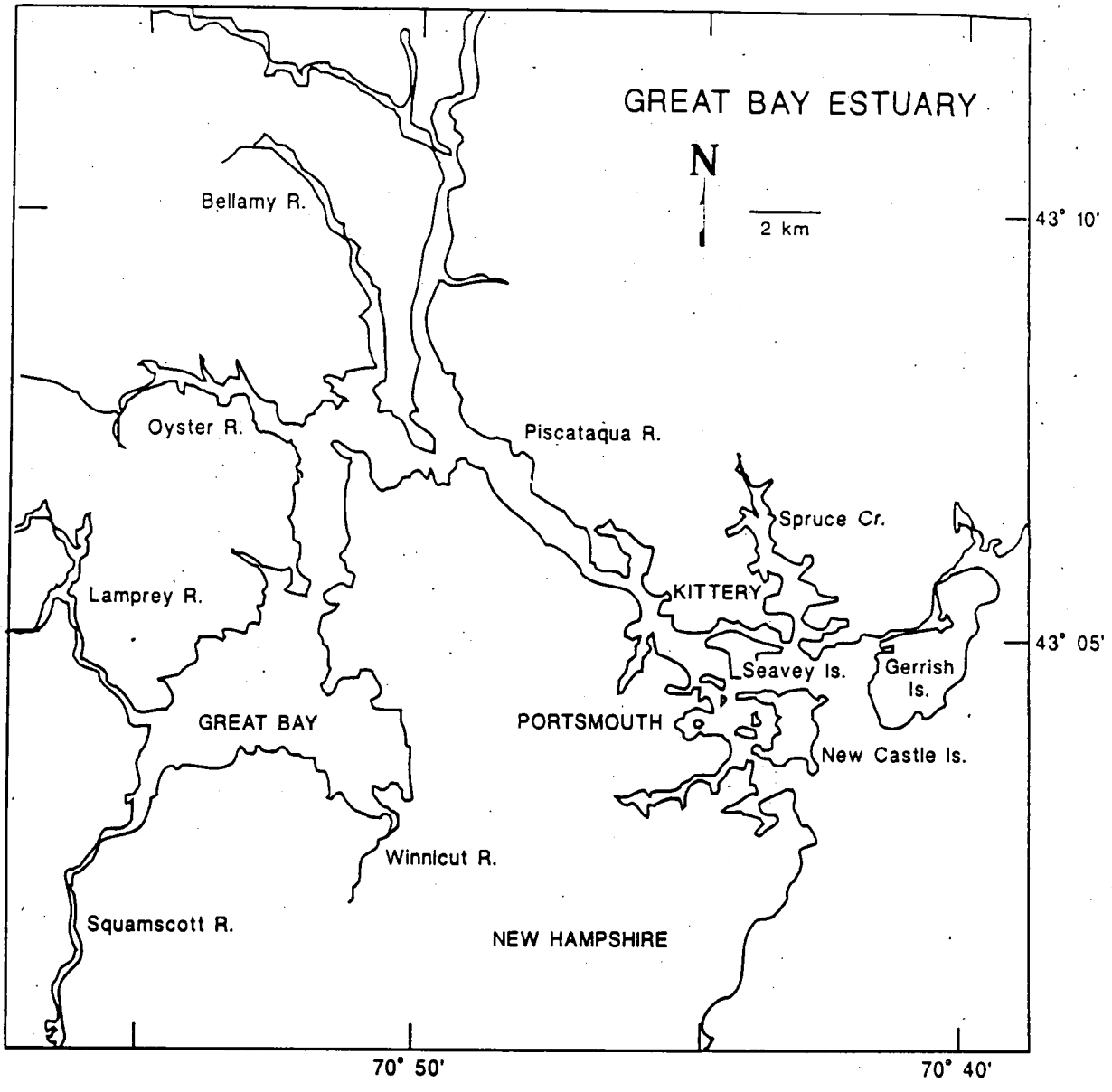
The Naval Shipyard Portsmouth (SHIPYARD) in Kittery, Maine has a requirement to assess the ecological impact of SHIPYARD past and current operations on the surrounding Piscataqua River Estuary. The SHIPYARD is located on 278-acre Seavey Island situated in the Piscataqua River between the states of Maine and New Hampshire (Figure 1). The mission of the SHIPYARD is to: "Provide quality repair, overhaul, modernization, and refueling of nuclear submarines in a safe, timely and cost effective manner"[2]. To fulfill this mission the SHIPYARD must comply with the provisions of the Hazardous and Solid Waste Amendments (HSWA) permit for storage, treatment, and disposal of hazardous materials used at the SHIPYARD. Special conditions of the HSWA permit requires the Navy to characterize the potential impact of hazardous materials on surface water, sediment, and biota within the estuary and to evaluate exposures and associated risks to the environment from hazardous materials used at the SHIPYARD[3]. About two-thirds of the SHIPYARD is involved with heavy industrial operations. There are three operating drydocks on the south and west sides of the island, numerous storm water outfalls are located around the SHIPYARD, and industrial waste is collected for pretreatment before it is discharged for disposal at the municipal waste treatment plant in Kittery, Maine. There are thirteen solid waste management units (SWMU) that are being studied for the Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI) required by the HSWA permit (Figure 2). These include disposal areas, underground storage tanks, industrial waste outfalls, storage areas, and a 25-acre landfill where hazardous wastes were disposed (Fred C. Hart Associates 1989).

The area surrounding the SHIPYARD and Portsmouth Harbor is very scenic and includes Kittery Point and Gerrish Island in Maine and New Castle and Pierces Islands in New Hampshire. Portsmouth Harbor is the only deep water harbor in New Hampshire and is very busy with traffic composed of oil barges and submarines operating at the SHIPYARD as well as tugs and ships operating out of the New Hampshire Port Authority Cargo Terminal. Fishing trawlers, lobster boats, and recreational vessels are also frequently present in the estuary. Parts of the shoreline are heavily developed and the SHIPYARD, commercial docks, and marinas dominate the landscape. However, numerous parks and historic areas impart a scenic beauty and charm on the area. Most ships wait for favorable tides before moving up the river because of strong currents which can reach up to 6 knots at Henderson Point, located a few miles upstream from the SHIPYARD. The Great Bay and Piscataqua River estuary system extends about 20-25 miles into New Hampshire. The estuary is fed by seven rivers. Much of the estuary shoreline is undeveloped, but industrial activities in southeast New Hampshire, such as tanneries, have discharged wastes into the estuary. The recently

PROVIDE REFERENCE

[2] Sign located near the main entrance to Portsmouth Naval Shipyard.

[3] RCRA Facility Investigation Proposal with Conditions, EPA Region I (15 January 1991).



SHOULD BE TYPED

Figure 1. Location of the Naval Shipyard Portsmouth.

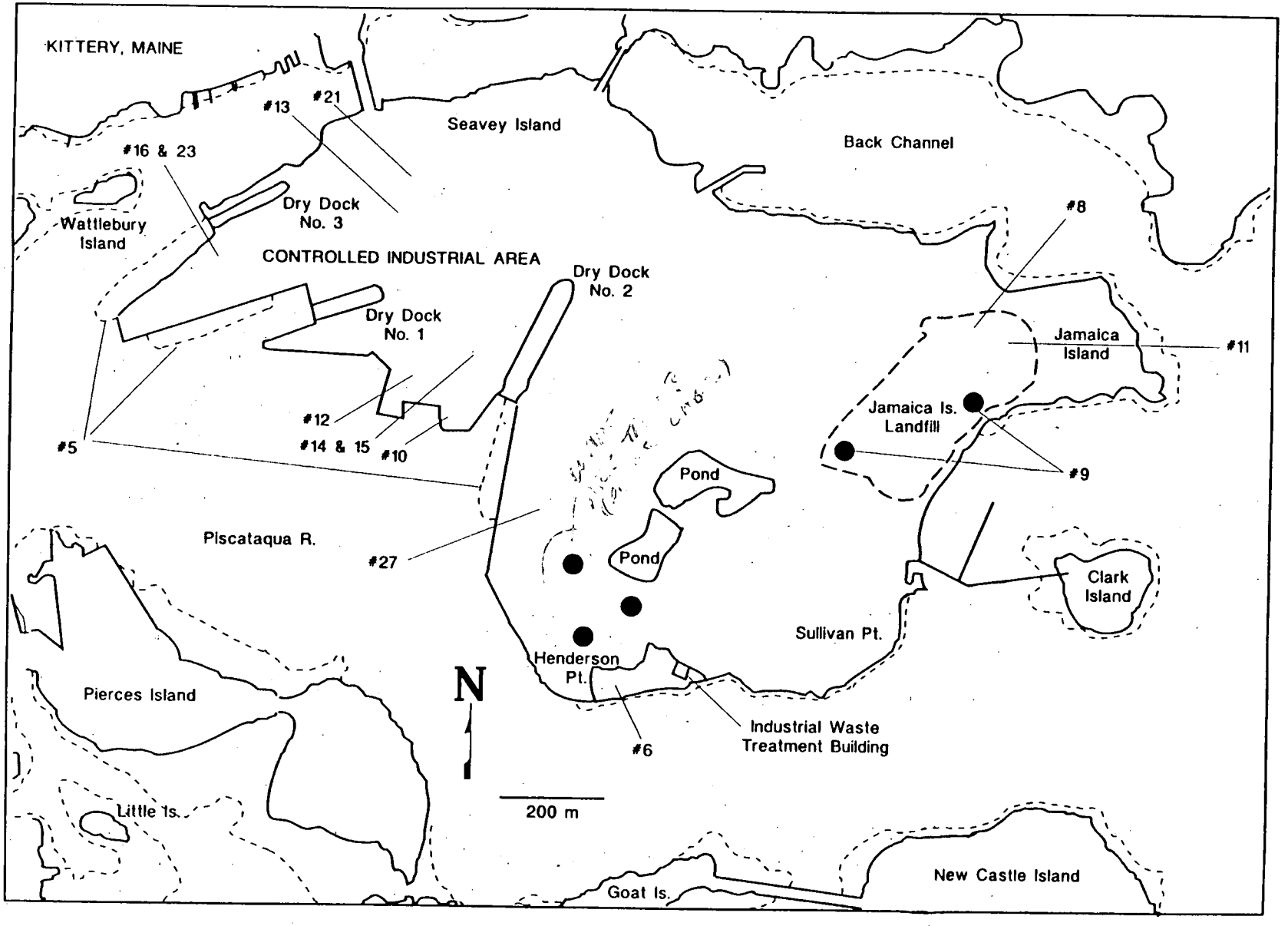


Figure 2. Solid waste management units at the Naval Shipyard Portsmouth.

closed Pease Air Force Base is located on the east side of Great Bay. There are about 30 permitted discharges of waste into the estuary with the majority being municipal sewage discharge. The estuary is generally well-mixed with a salinity gradient from the mouth of the harbor to the tributary rivers. Fresh water is found upstream of the old mill dams on the tributary rivers.

The research and monitoring activities reported here provide a framework for assessing the ecological risk of past and present SHIPYARD operations to the estuary. While a focus of the research and monitoring program is to satisfy the special conditions of the RCRA permit, the project is aimed at developing a comprehensive assessment framework for the estuary that will provide the SHIPYARD with an effective management tool to identify potential risks and select appropriate corrective actions. The integrated ecological risk assessment framework will provide a scientifically sound basis for determining the presence and extent of adverse impact on the estuary and will support the development of a strategic risk management plan which will allow SHIPYARD operations to comply with current as well as future environmental requirements.

The Naval Command Control and Ocean Surveillance Center (NCCOSC; formerly the Naval Ocean Systems Center) and the U.S. EPA Environmental Research Laboratory Narragansett (ERLN) have developed a cooperative research and monitoring project to conduct an estuarine ecological risk assessment for the SHIPYARD in accordance with an existing Memorandum of Agreement between NCCOSC and ERLN. Under this agreement case studies are developed to characterize the risks of hazardous waste disposal at Navy sites which could potentially impact aquatic ecosystems. The agreement provides the opportunity to develop and refine methodologies for examining ecological risks associated with anthropogenic wastes in the marine environment through their application in specific case studies.

The ecological risk assessment framework consists of quantitative estimation of the likelihood of adverse ecological effects resulting from exposure to toxic substances from hazardous waste releases. This strategy involves collection of information concerning: the physical and chemical attributes of the waste material (Waste Site Characterization); the ecological systems potentially impacted by contaminants in the waste material (Ecosystem Characterization); the distribution of contaminants within the marine environment (Exposure Assessment); and the effects of these contaminants on marine ecological systems (Effects Assessment). The information is then synthesized into a characterization of ecological risks associated with the waste material (Figure 3).

The first application of this approach to ecological risk assessment was a pilot study developed to assess the marine ecological risks of hazardous waste disposal sites located at the Naval Construction Battalion Center (NCBC) Davisville, Rhode Island on Allen Harbor and Narragansett Bay. In 1984 Allen Harbor, a small embayment in Narragansett Bay, was closed to shellfishing by the Rhode Island Department of Environmental Management due to concern of contamination from disposal sites--particularly a 15-acre landfill--located at NCBC

ECOLOGICAL RISK ASSESSMENT

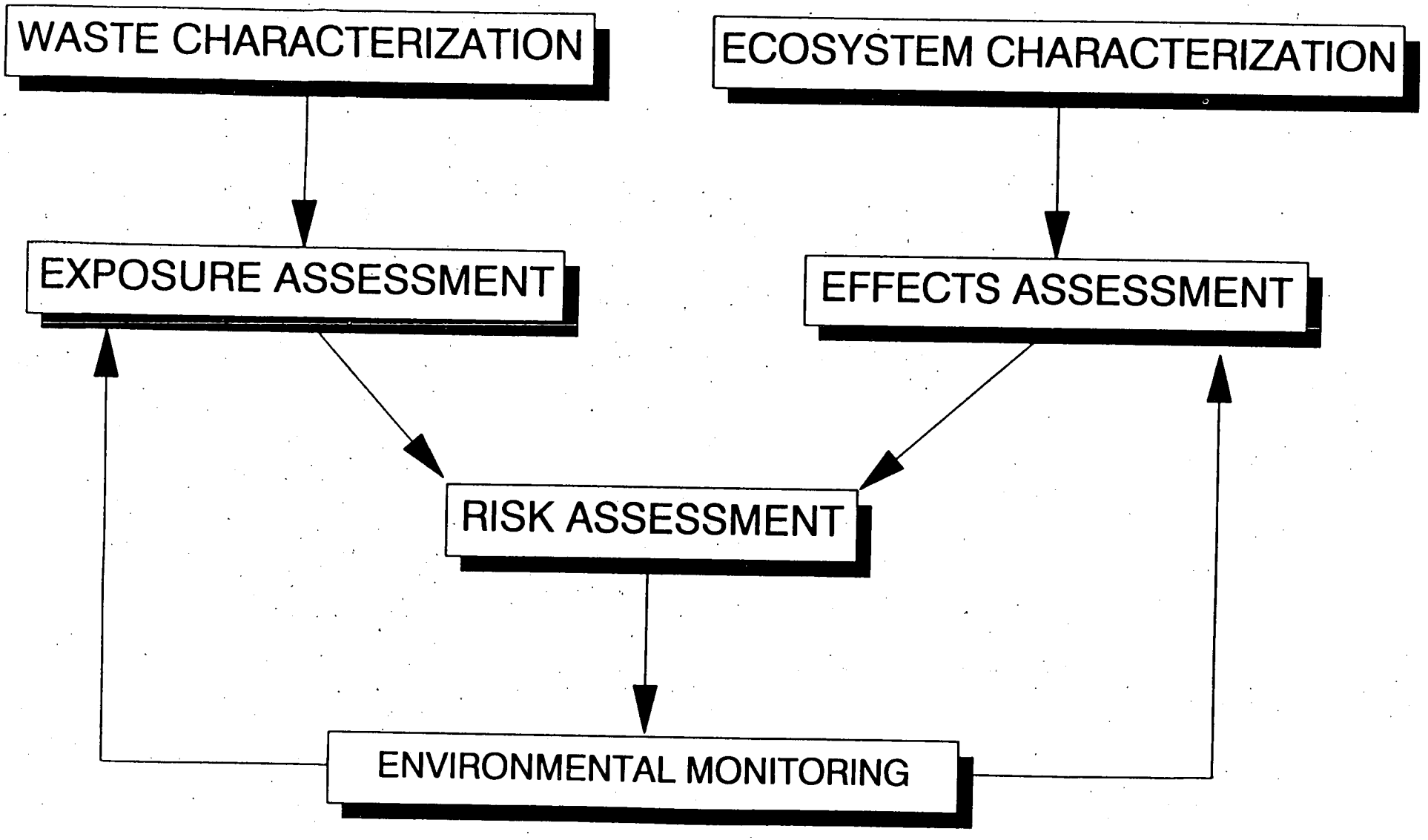


Figure 3. Ecological Risk Assessment framework.

Davisville. A phased approach was developed to provide information regarding the ecological risks posed by these waste sites to Allen Harbor and Narragansett Bay. Phase I, initiated in 1988, involved the collection and collation of environmental data characterizing the ecology, natural resources, and sediment and water quality of Allen Harbor relative to Narragansett Bay. This information was used to develop a preliminary ecological risk assessment for the harbor. Based upon the findings of Phase I, activities in Phase II were identified to determine the nature and extent of contaminant impact from various potential sources, including the landfill, surface runoff from the surrounding land, and marina and recreational boating activities. Phase III activities, currently in progress, are directed towards development of exposure-response models to quantify ecological risks associated directly with landfill contaminants. A monitoring program for continuous verification of environmental safety and health will be identified in Phase III (NOSC and ERLN 1990, Johnston *et al.* 1990, Munns *et al.* 1991a, Munns *et al.* 1991b).

The general approach developed for the estuarine ecological risk assessment for the SHIPYARD builds upon techniques and methods applied for the marine ecological risk assessment performed at NCBC Davisville. The data and information developed by the current study will provide the SHIPYARD with scientific data to support the selection of appropriate corrective actions and to evaluate the effectiveness of those actions. A long term monitoring plan also will be developed to provide continuous measurement of the estuary's environmental quality.

PROJECT OBJECTIVES

The specific objective of the Estuarine Ecological Risk Assessment Case Study is to determine the extent and degree of environmental impact in the Piscataqua River which may be attributed to past or current activities at the SHIPYARD.

Two phases have been identified to meet this objective. Phase I involves a detailed assessment of existing environmental quality in the lower Piscataqua River and its relationship to the SHIPYARD. This determination will be based upon comparison of measures of contamination and biological health made at sites in the immediate vicinity of the SHIPYARD with similar measures made at nearby reference sites. Emphasis will be placed upon sampling and analysis of sediments, water column, and natural resources. Whereas several potential sources of environmental contamination exist in this region, chemical markers will be explored for establishment of relative contaminant source strengths. This information and supporting knowledge of marine environmental quality will provide a context within which to evaluate the condition of the lower Piscataqua River, and will aid in the preliminary identification of risks associated with SHIPYARD operations.

Phase II will involve the performance of activities to verify Phase I results and to quantify marine ecological risks associated with hazardous material used and disposed of at the SHIPYARD. Although specific activities to be conducted during the second phase will

depend upon the findings of Phase I, these will focus primarily upon experimental descriptions of the responses of ecological systems to SHIPYARD-associated contaminants, and modeling and experimental determinations of contaminant transport and fate. Additional chemical markers research will be directed towards fingerprinting contaminant sources for description of relative source strengths. Together with Phase I findings, this information will be used to develop the final NCCOSC/ERLN Estuarine Ecological Risk Assessment. Finally, a long-term monitoring strategy will be developed to provide continuous verification of environmental health and to help determine the effectiveness of corrective measures and risk management decisions.

The remainder of this document describes the technical approach taken in addressing the objectives of this study. The status of Phase I sampling and analysis activities are described, and preliminary presentations of data are provided as appropriate.

METHODS

OVERVIEW

The technical activities associated with the Estuarine Ecological Risk Assessment Case Study are being conducted by several parties. NCCOSC and ERLN have an oversight and coordination role for all phases of the project. The University of New Hampshire - Jackson Estuarine Laboratory (UNH-JEL), currently under subcontract to Science Applications International Corporation (SAIC), the support services contractor for ERLN, and UNH-JEL's subcontractor Normandeau Associates, are performing the majority of field sampling and measurement activities. Limited field sampling will be conducted by McLaren/Hart Environmental Engineering Corporation, the Navy's RFI contractor for the SHIPYARD. The majority of chemical analyses are being performed by Ceimic Corporation, under subcontract to McLaren/Hart. ERLN also has conducted specific toxicological assessments and limited chemistry as described below, and NCCOSC performed butyltin analyses on selected samples. NCCOSC and ERLN, with the assistance of UNH-JEL, will develop the preliminary ecological risk characterization.

Activities identified for Phase I are intended to provide an information base with which to address ecological risk in a preliminary fashion. The specific tasks of this phase, as described in the project Work Plan (ERLN and NOSC 1991) include:

1. Identify and collate existing environmental data and information pertaining to the SHIPYARD and the Great Bay Estuary.

2. Characterize sediments in the vicinity of the SHIPYARD.

    a. Develop a sediment sampling plan for collecting appropriate exposure and effects information.
    b. Collect sediment samples for chemical and biological analyses.
    c. Perform chemical analyses of sediments.
    d. Conduct geophysical and microbial characterization of sediments.
    e. Assess toxicity of sediments.
    f. Develop a sediment distribution map for the lower Piscataqua River.
    ALSO MAP CONTAM CONCS IN SED.

3. Characterize water column quality in the vicinity of the SHIPYARD.

    a. Develop a water column sampling plan for collecting appropriate exposure and effects information.
    b. Collect water samples for chemical, physical, and biological analyses.
    c. Conduct chemical, physical, and biological analyses of water samples.
    d. Assess toxicity of water samples.

e. Develop an information base necessary to model hydrodynamics in the vicinity of the SHIPYARD.
f. Determine the presence of contaminant plume or leachate.
g. Initiate chemical markers research.

4. Evaluate biological resources in the vicinity of the SHIPYARD.

a. Determine the distributions, abundances, and tissue chemistry burdens of important marine resources in the vicinity of the SHIPYARD -- collect samples and conduct population and chemical analyses.
b. Determination seasonal variation in tissue chemistry of selected biota.
c. Evaluate potential impact on water column organisms using caged *Mytilus edulis*.
d. Evaluate potential impact on benthic community.
e. Conduct an up-estuary transect survey of eelgrass, mussel, and oyster tissue chemistry.

A field sampling program involving a total of 34 stations was developed to obtain information on the distribution and effects of contaminants associated with the SHIPYARD. Depositional areas were targeted, as these possess fine-grained sediments which maximize the likelihood of observing contaminant signals. The original program included 21 stations in the lower Piscataqua River (Figure 4), two reference stations located in the nearby York River in Maine (see Figure 4), and 9 stations extending from Portsmouth Harbor into the upper reaches of the Great Bay Estuary (Figure 5). Because several potential sources of environmental contamination were suspected to exist in the lower Piscataqua River, stations within the harbor were positioned to enhance the success of detecting contamination originating from the SHIPYARD, as well as to evaluate the extent of transport of released contaminants. Of these 23 stations, nine were located to circumscribe Seavey Island in association with specific sites of possible contaminant release. In addition, a grid of six stations was placed within the Clark Island embayment (see Figure 4). These six sites would provide information on the potential release of contaminants from the Jamaica Island landfill located on Seavey Island. Two other sites near the SHIPYARD (designated 10A and 12A) were added to the original sampling plan based upon field observations of their biotic characteristics and their proximity to suspected contaminant sources. Two stations were located on the west shore of the Piscataqua River adjacent to Seavey Island, one upstream and one downstream of the Pierce Island (Portsmouth) wastewater treatment plant. To identify upriver transport of contaminants, two stations were located upstream from the SHIPYARD on opposite sides of the river. These sites were co-located with the southern-most eelgrass monitoring station associated with the National Oceanic and Atmospheric Administration's (NOAA) Coastal Ocean Program and the Great Bay Estuarine Research Reserve. Two stations were also positioned downstream of the SHIPYARD (on opposite sides of the river) to establish if contaminants are being transported down the estuary. Finally, two sets of reference stations were identified. First, two stations were selected in Spruce Creek, Maine,

	Stations
Sediment	1-23
Water column (synoptic)	1-23
Water column (monthly)	1, 8, 10, 15, 16, 23
Mussel	1-23, 10A
Lobster and flounder trawls	T1-T9
Eelgrass	1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 14, 15, 16, 17, 18, 19, 22, 23, 12A
Rockweed	3, 8, 9, 10, 17, 19, 22, 10A
Benthic community	1-23
Mussel and eelgrass (quarterly)	1, 3, 9, 15, 16, 17, 18, 19, 23, 12A
Mussel deployment	2, 8, 10, 15, 19, 22
Current meter deployment	⊗

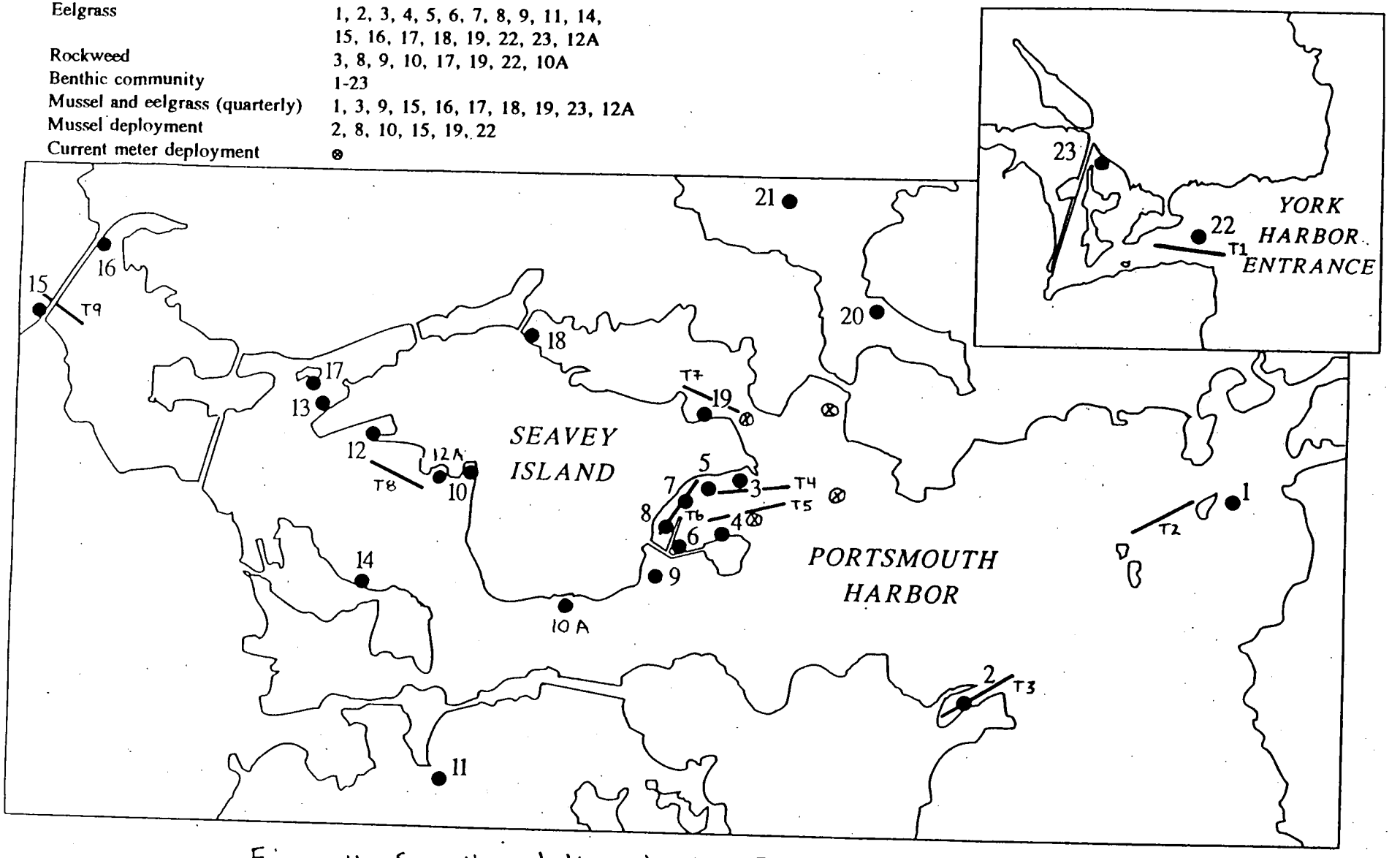


Figure 4. Sampling stations in the Piscataqua and York Rivers

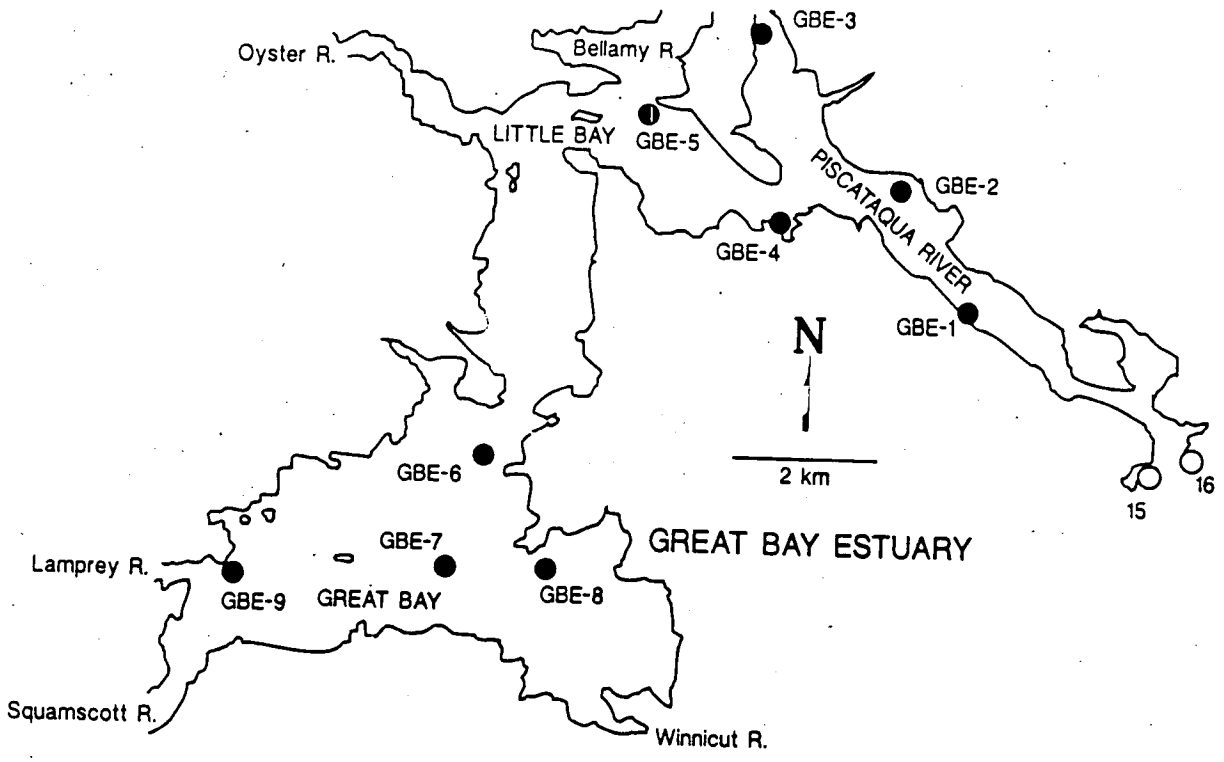


Figure 5. Transect sampling stations in the Great Bay Estuary.

north of the SHIPYARD. This creek has a possible contaminant source far upstream; water from Portsmouth Harbor near the SHIPYARD originally was thought to be the only major source of contamination. These sites also serve to evaluate impacts of other contaminants sources on the Piscataqua River. The second two reference stations, representing background conditions away from known pollution sources, were located in the York River in Maine. This riverine-dominated system is similar in general characteristics to the Piscataqua River, but is much smaller in size. Data obtained at these 25 stations were used to address Tasks 2, 3, and 4 above.

The nine Great Bay Estuary stations (Figure 5) were positioned along an up-estuary transect to provide information on potential far-field transport of SHIPYARD contaminants. Additionally, they could be used to identify potential contaminant sources upstream from the facility. These stations, sampled synoptically to evaluate biological resources, were co-located with stations visited by NOAA's Coastal Ocean Program and New Hampshire Water Resources studies.

Sampling activities conducted at these stations and the analysis methods used to effect project tasks are described below. Analytical chemistry methods are described at the conclusion of this section. The status of project activities is described under Status, Preliminary Results, and Discussion below.

GREAT BAY ESTUARY HISTORIC OVERVIEW

The historical overview of environmental conditions in the Great Bay Estuary was conducted simultaneously with the major portion of the field sampling program. For the past year, information was compiled on Great Bay for NOAA's Great Bay National Estuarine Research Reserve Program. This information provided the basis for the bay-wide overview. Initial efforts were directed towards data that were available for the Piscataqua River and Great Bay Estuary, with a focus on the parameters to be sampled in the field program. Following assembly of literature and data reports, information and data were summarized to provide an overall description of environmental conditions. In addition to including existing information on the Estuary, this document provides a complete bibliography of research and projects done within the Estuary, and identifies information gaps relevant to the risk assessment. Specific topics addressed included the hydrology, geology, chemistry, biology, ecology, and pollution of the estuary.

CHARACTERIZATION OF SEDIMENT CONDITIONS

Field Sampling

Assessment of sediment exposure and effects was accomplished through implementation of a coordinated, synoptic sampling protocol, followed by detailed analyses of

the chemical, geophysical, microbiological, and toxicological characteristics of each sample. The approach to sediment sampling and analysis for this project was to over-sample initially, to composite portions of the material for subsequent analysis, and to archive the remainder. Since all samples originated from a single collection, comparability of data will be high. Over-sampling also guarantees available material for other measurements which may be identified in the future (Munns *et al.* 1991b).

In August 1991, four surficial Shipek grab samples were collected from each of the 23 original stations (excluding Stations 10A and 12A) in lower Piscataqua River and in nearby York River from the R/V MARITIME, a 27' research vessel owned and operated by Normandeau Associates, Incorporated (NAI). Station locations were occupied using detailed station descriptions supplied by UNH. Each grab sample was divided into quarters. The surficial sediment from one quarter of each sample was combined to form a composite for subsequent chemical analysis. The remaining three quarters were handled in like fashion to produce samples for geophysical and microbial determinations, for toxicity evaluation, and for archiving. The grab sampler was decontaminated between replicates using ERLN SOP 2.02.002 (see ERLN and NOSC 1991). Samples were stored on ice following collection and initial handling. Chemistry samples were frozen immediately upon return to NAI, and remained so until analyzed by Ceimic Corporation. All other samples were stored under refrigeration prior to analysis.

In addition to the grab samples, single vertical gravity cores (1-2 m depth) were collected from each station from the R/V JERE A. CHASE, a 45' research vessel owned and operated by UNH, to assess historic impacts. Cores were collected using a Benthos gravity corer with a 1.5 meter long barrel. Usually, three to five horizons in each core were sampled for chemical, grain size, and microbial determinations. These horizons corresponded to the surface, the bottom of the bioturbated layer, and the bottom of the core. Additional horizons, corresponding with sediment discontinuities, were sampled in some cores as appropriate.

Sediment Mapping Activities

A sediment distribution map for the lower Piscataqua River will be developed using data obtained from subbottom seismology, side scan-sonar, or remotely operated vehicle (ROV) to survey bottom conditions between the upriver and downriver sampling sites within Portsmouth Harbor. Sediment samples will be collected by gravity core as appropriate within a grid that will provide quantitative results for mapping sediment distribution and determining the depth of sediments within the Portsmouth Harbor area. At least 10 additional vertical core samples for chemical analysis and up to 90 additional grab samples for sediment analysis will be taken. Information derived from these analyses will be used to establish contaminant distributions in the sediments of the estuary.

Sample Analyses

Geophysical characterization -- Information regarding the geophysical characteristics of sediments will be used to understand contaminant movement, normalize contaminant levels, and identify potential contaminant sources. Surficial sediment samples from replicate grabs, and from three sediment horizons from each core, were analyzed by UNH-JEL for grain size, moisture content, organic carbon content, and particulate carbon and nitrogen content.

Grain size analyses were conducted using the methods outlined in Folk (1980) to determine standard statistics (gravel/sand/mud ratios, mean size, sorting, skewness and kurtosis). Moisture content and combustible content (to approximate total organics) were determined by weight loss with drying (24 hr at 50°C) and ashing (4 hr at 450°C), respectively. REF/METHOD # Selected samples were analyzed for particulate carbon and particulate nitrogen content using a Carlo Erba Nitrogen Analyzer 1500. ARE THERE SD EPA SOP'S FOR THESE METHODS?

Microbial analysis -- The degree of fecal contamination was used to evaluate the contribution of sewage to impact to the estuary. The Most Probable Number (MPN) method was used to estimate densities of the anaerobic, spore-forming gram positive bacterium *Clostridium perfringens*, as described in ERLN SOP 1.03.017. Replicate sediment subsamples were collected aseptically from sediment composites, weighed, diluted 1:1 in sterile phosphate buffered saline (PBS), and blended in a Waring blender for 1 min. Iron milk medium tubes (5 tubes per dilution) were inoculated with appropriate dilutions of the sediment samples, vortexed thoroughly, and incubated in a water bath at 45± 0.2°C for 18 hr. Tubes with stormy fermentation, resulting from acid production that curdled the milk and gas production from lactose fermentation that violently broke up the clots, were scored as positive. This combination of stormy fermentation and rapid growth at 45°C has been shown in numerous studies to give positive results for *C. perfringens* nearly exclusively, thus eliminating the need for further confirmation.

Sediment chemistry -- An initial analytical screen was performed on replicate sediment samples from Stations 7, 8, 10, 17, and 19. These were analyzed intensively for metals and semi-volatile organic compounds as described below. This information will be used to identify contaminants of potential concern, and will define analytes for quantification in the remaining sediment samples.

Chemical marker development -- Chemical marker research is being conducted by ERLN to identify chemical tags useful in determining unique sources of contaminant input. This work will be a component of ongoing chemical marker research and development at ERLN. The case study for the SHIPYARD will provide an application to examine the use of organic compounds unique to specific sources in description of pollutant transport and fate in the Great Bay Estuary. This description will be valuable in delineating the relative contributions of each source to any observed environmental impact. In conjunction with the spatial nature of the sediment sampling plan, this information will enhance successful determination of the SHIPYARD's potential contribution.

Toxicological assessment -- Composite surficial sediment samples from the original 23 stations were evaluated for toxicity using the *Ampelisca abdita* acute mortality assay (ERLN SOP 1.03.002). This bioassay has been used extensively in EPA sediment testing programs to identify sediment toxicity. It provides an acute mortality endpoint for an invertebrate indigenous to the Great Bay Estuary. These assays were preformed at SAIC's Environmental Testing Center.

CHARACTERIZATION OF WATER COLUMN EXPOSURE CONDITIONS

Field Sampling and Measurement

A synoptic collection of water column samples was obtained from the 23 lower Piscataqua River and York River stations in August 1991. Additionally, a monitoring program was established at five of these stations (Stations 1, 8, 10, 15, and 23; see Figure 4) to generate information on seasonal changes in water column characteristics.

Methods for physical parameter measurements, sample container preparation, and filtration and analysis of water samples for chlorophyll, phaeopigments, pH, and suspended solids analyses were identical to those used in the on-going JEL water quality monitoring program currently funded by NOAA's National Estuarine Research Reserve Program. These are described in ERLN and NOSC (1991). Vertical profiles of temperature, conductivity, salinity, and dissolved oxygen were measured at one meter intervals from bottom to surface using a YSI model 33 S-C-T meter and a YSI model 58 dissolved oxygen meter. Water samples for quantification of chlorophyll *a*, phaeopigments, suspended solids, and pH were collected by subsurface grab using 1-L polyethylene bottles at local low tide. Bottles were prepared prior to sample collection by soaking for 24 hr in a 10% HCl solution, and were drained and rinsed five times with deionized water. Water samples for nutrient and pigment analysis were chilled on ice, stored in the dark, and filtered within one hr of collection. The pH of the water samples was measured prior to filtering using a Fisher Acumet Model 955 field pH meter. Samples for toxicity evaluations were stored under refrigeration prior to and during delivery to ERLN. Separate 250-ml polyethylene bottles were used to collect seawater samples for metal analysis. These bottles were prepared following ERLN SOP 2.01.001, method B. Samples were treated upon collection following ERLN SOP 2.03.008.

Information also was collected for calibration of an existing finite-element hydrodynamic model of the lower Piscataqua River. This model will be used to describe contaminant movement through the harbor, and could be used to identify sediment depositional areas likely to be impacted by potential SHIPYARD discharges. In the previous cooperative UNH-National Ocean Survey project, extensive field measurements were taken of water movement in the harbor (as reported by Swenson *et al.* 1977, Silver and Brown 1979), and the vertically averaged, numerical model CAFE was applied (Reichard and Celikkol 1978). One evident gap in this data base was the absence of information near waste sites on Seavey Island. To fill this gap, vertical and horizontal distributions of currents over 13 hours

were measured at four stations at the east end of Seavey Island (see Figure 4). This information will be correlated with tidal height, which will then be used to calibrate the hydrodynamic submodel.

Direct contaminant input to the Piscataqua River from the SHIPYARD was quantified through sampling and analysis of seepage and leachates from Seavey Island sources. Samples were collected by McLaren/Hart from four sources: SWMU #5, the Jamaica Island landfill, SWMU #6, and from SWMU #10 (see Figure 2). Other collection sites may be added as necessary. These samples will be analyzed intensively for chemical contaminants by Ceimic Corporation. Additional samples will be obtained for assessment of fecal indicators (*C. perfringens*) by UNH-JEL. Quantification of fecal input will help determine if sewage contamination is originating from the SHIPYARD.

Laboratory Analyses

Suspended solids measurements -- Suspended sediment concentrations were determined by filtering a 500-ml sample through pre-dried and pre-weighed glass fiber filters (1.2-μm nominal pore retention). Each filter was then rinsed with deionized water to remove salts, and dried for 24 hr at 80°C. Dry filters were weighed on a Cahn Model 9500 digital microbalance to determine weight of suspended solids by subtraction.

Pigment analysis -- Chlorophyll *a* and phaeopigments were measured by passing 500 ml of sample through a glass fiber filter (1.2-μm nominal pore retention), with 0.2 ml of $MgCO_3$ solution being added to the sample near the end of the process when approximately 25 ml of sample remained. This filter was folded into quarters, placed in a 30-ml centrifuge tube, kept in the dark, and analyzed for pigments immediately, or frozen (-20°C) in the dark and analyzed within seven days. The analytical procedure for chlorophyll *a* and phaeopigments was by acetone extraction according to methods described in Parsons *et al.* (1984). Absorbance was determined on a Beckman Model 35 dual beam spectrophotometer.

Nutrient analysis -- The liquid filtrate obtained during pigment analysis was used for quantification of nutrient concentrations. The filtrate was divided into three equal portions in acid washed polyethylene bottles and analyzed for nutrient concentration on an autoanalyzer (Loder and Gilbert 1977). Samples were analyzed in duplicate for nitrate/nitrite, phosphate, and ammonium immediately after filtration or quick frozen (-80°C) for a period of time less than one week and analyzed by the same procedure.

Microbial analysis - Determinations of *C. perfringens* densities in water samples were made for each station, and will be made for seepage/leachate samples upon their collection. Samples were collected in sterile containers, kept at 5°C, and assayed within 8 hr of collection. The ERLN membrane filtration (MF) method (ERL-N SOP 1.03.014) was used for enumeration of *C. perfringens*. Sample aliquots or appropriate dilutions were filtered onto membrane filters and incubated on mCP agar media anaerobically at 44.5-45°C for 18 hr. The typical large, flat, opaque yellow colonies which formed were counted and then

exposed to ammonium hydroxide vapors. The characteristic acid phosphatase reaction of *C. perfringens* was detected by a magenta color in ammonium hydroxide-exposed colonies. Further confirmation was conducted on presumptive *C. perfringens* colonies by employing an *in situ* gelatin hydrolysis test. Membrane filters were removed from the surfaces of the mCP agar after exposure to ammonium hydroxide, transferred to gelatin agar with sterile forceps, incubated for 1-2 hr at 37°C, and then removed. The gelatin agar was flooded with Frazier's reagent. Gelatinase and acid phosphatase positive colonies were scored as *C. perfringens*.

Water chemistry -- Trace metal analyses were performed on water samples from each of the 23 Piscataqua and York River samples. The analytical methods employed were similar to those described in ERLN SOPs 2.03.008 and 2.04.004 (see ERLN and NOSC 1991).

Chemical analysis of deployed mussels -- Information obtained through trace metal analysis of water samples was supplemented through analysis of tissue residues of mussels deployed in cages at five stations in the estuary (see below). Whereas grab sampling provides a "snap-shot" of current water column conditions, the dynamic nature of tidally-driven systems results in temporal variation in measured parameters. Mussels have been shown to be excellent integrators of water column contamination (*e.g.*, Nelson *et al.* 1987). Deployed *in situ* over reasonably long periods of time (≥28 days), tissue residues reflect temporally averaged water column contaminant levels. This method is more effective for measuring trace levels of water-borne organic contaminants than is analysis of the extremely large volumes of water which must be sampled to obtain a representative measure of these compounds.

Toxicological assessment -- Water column samples from the 23 original Piscataqua and York River stations were tested by ERLN using the *Arbacia* sperm cell assay following ERLN SOP 1.03.006. This sensitive, rapid, and inexpensive test is employed in National Pollution Discharge Elimination System (NPDES) monitoring of effluent and receiving water toxicity. It provides a "reproductive" endpoint for a species representative of lower-trophic level invertebrates indigenous to the Piscataqua Estuary.

EVALUATION OF ESTUARINE BIOLOGICAL RESOURCES

To assess potential impacts of contaminant releases from the SHIPYARD on the living resources of the Great Bay Estuary, quantitative collections of indigenous mussels (*Mytilus edulis*), lobster (*Homarus americanus*), flounder (*Pseudopleuronectes americanus* or *Scophthalmus aquosus*), eelgrass (*Zostera marina*), and fucoid algae (*Ascophyllum nodosum*) were obtained synoptically from sites co-located with sediment and water column stations (Figure 4). These species were selected as being representative of the range of phyla and trophic levels found within the estuary. They also represent ecologically important members of the estuarine community, and have economic and aesthetic value to New Hampshire and Maine. Additionally, these species have been used in a variety of previous ecological studies, and large data bases exist against which study results can be compared. Information regarding tissue contaminant levels will be useful for defining current exposure conditions,

trophic transfer of contaminants, and in human health risk assessment exercises to be conducted by McLaren/Hart.

In addition to the synoptic collections, a one-time survey of selected natural resource species was conducted to describe tissue chemistry throughout the Great Bay Estuary (see Figure 5 for station locations). Eelgrass and bivalves were targeted for this assessment. Two bivalve species of importance in the estuary are blue mussels and oysters (*Crassostrea virginica*). Because their tolerances to salinity differ, neither of these species ranges throughout the entire salinity gradient of the estuary. Mussels were therefore collected in the lower reaches of the estuary, whereas oysters were collected in the upper reaches. Both species were sampled at stations where both were present to evaluate interspecific differences in tissue burdens. Information from this effort will address far-field transport of SHIPYARD contaminants, and will be used to identify additional sources of contamination within the estuary.

Field Activities

Organism collection and sample processing -- Field collection of biotic samples followed the standard protocols described in ERLN and NOSC (1991). Blue mussels were collected at intertidal stations from a known bottom area by hand along a transect, and by benthic grabs using modified oyster tongs to sample a 1/16 m^2 area at subtidal sites. Subsamples of these collections were stored in plastic bags on ice until returned to JEL. Following size and density estimation, a subsamples of animals were frozen prior to delivery for chemical analysis. Collections were made synoptically at all stations in September 1991, and along the Great Bay Estuary transect during September and October 1991.

Oysters were collected along the Great Bay Estuary transect using quantitative oyster tongs. Animals were stored on ice until returned to the laboratory, where they were frozen for subsequent chemical analysis.

Collections of lobster and flounder were made over 9 trawl transects (see Figure 4) using an otter trawl. Species abundances and size distributions were quantified on deck for each station. Determination of gross external pathology of the flounder also was made in the field. Tissue samples (hepatopancreas and tail flesh from lobsters, liver and flesh for flounder) were dissected for chemical analyses, stored on ice, and frozen upon return to the laboratory.

Eelgrass was collected at 19 stations in the lower Piscataqua and York Rivers (see Figure 4), and along the Great Bay Estuary (see Figure 5) using a modified oyster tong to quantitatively sample a 1/16 m^2 area of the bottom. All plant material within replicate grabs was collected. Samples were stored on ice during transport to the laboratory. Six replicate 0.10 m^2 quadrats of fucoid algae was similarly collected from 8 stations.

Caged mussel deployment -- To supplement water column exposure and toxicity

measurements, and to support assessment of living natural resources, *Mytilus edulis* were deployed synoptically at six stations around Seavey Island, at up-river and down-river sites, and in the York River (Stations 2, 8, 10, 15, 19, and 22; see Figure 4) for subsequent evaluation of tissue chemistry and physiological impact.

Mussels were collected by clam rake near Sandwich, MA, and prepared following ERLN SOPs 1.02.001 and 1.02.002. Animals were sized prior to deployment, and subsamples were frozen for subsequent chemical analysis. Caged animals were transported on ice to JEL, and deployed for 28 days at 1 meter above the bottom as described in ERLN SOP 1.02.002. Deployed arrays were retrieved in October 1991, and transported on ice to ERLN for subsequent physiological assessments, or frozen for chemical analysis.

Benthic community analysis -- To supplement sediment toxicity measurements, and to support assessment of living natural resources, benthic community analyses were conducted at each of the 23 original sediment sampling stations. Samples were obtained during sediment collection activities described above, so that benthic community composition could be compared directly with grain size, organic content, and the sediment contaminant concentrations measured in the sediments, as well as with the sediment toxicity. Material from four replicate 23 cm x 23 cm Shipek grab samples from each station were sieved onto 0.5-mm screens. Recovered organisms were relaxed using isotonic magnesium chloride, and preserved with 6% buffered formalin for subsequent enumeration of individuals at the lowest possible taxonomic level.

Laboratory analyses

Mussel condition and population structure -- Density and size structure (measured as shell length) of mussels were characterized following the protocols described in ERLN and NOSC (1991). Soft tissue dry weight and shell volume (measured as displacement volume) were determined to provide information concerning the condition of individual animals. In addition to supporting the assessment of ecological effects associated with potential contaminant release from the SHIPYARD, this information will supplement on-going research of blue mussel recruitment along the Maine/New Hampshire Coast.

Lobster population structure -- Density and size structure of lobster from each trawl transect were characterized following the protocols described in ERLN and NOSC (1991). This information will supplement a current lobster sampling program at the University of New Hampshire to investigate lobster behavior throughout the entire Great Bay Estuary.

Flounder population structure -- Density and size structure of lobster from each trawl transect were characterized following the protocols described in ERLN and NOSC (1991). This information will supplement on-going flounder research funded by the New Hampshire Fish and Game targeting the upper part of the Estuary.

Eelgrass condition and standing stock -- Eelgrass abundance and biomass was quantified

following the protocols described in ERLN and NOSC (1991). Standing stock characteristics measured for *Zostera* included shoot density, leaf number and morphology, and degree of Wasting Disease as described in Table 1 (Short 1987, Short *et al.* 1991). This information will be compared to similar measures made throughout the Great Bay Estuary as part of the ongoing NOAA Coastal Ocean Program Study of *Zostera* condition, and will provide a complete map of eelgrass distribution and biomass for the estuarine system.

TABLE 1. EELGRASS STANDING STOCK CHARACTERISTICS

Characteristic	Measurement method	Measurement units
Biomass	dried for 24 hr at 80°C	g dry weight/m^2
Shoot density	shoots counts per sample	shoots/m^2
Leaf morphology		
length	mean of 10 longest shoots	cm
width	mean of widest leaves of 10 shoots	mm
number	count of leaves of 10 shoots	leaves/shoot
Wasting Disease	Wasting Index (Short *et al.* 1991)	percent leaf area

Rockweed standing stock -- Biomass (wet and dry weight) of *Ascophyllum* was determined as described protocols provided in ERLN and NOSC (1991).

Chemical analysis -- Analyses of tissue burdens were conducted on the five target biological resource species (blue mussel, lobster, flounder, eelgrass, and rock weed) collected synoptically in 1991. An initial analytical screen was performed on a subset of samples of each species as described below. The results of these analyses will be used to identify target analytes for the remaining analyses.

Tissue chemistry of *Mytilus* and *Zostera* also will be monitored at nine stations over three additional seasons to obtain information regarding variability in contaminant exposure and potential effects. Mussels, oysters, and eelgrass collected along the Great Bay Estuary transect will be analyzed for target contaminants to characterize exposure conditions elsewhere in the Estuary.

ANALYTICAL CHEMISTRY METHODS

Currently no procedures have been officially approved, by regulatory agencies, that are capable of analyzing for parts per billion (ppb) concentrations of organic and inorganic contaminants in estuarine sediments and tissues (Valente and Strobel 1991, ERLN and NOSC 1991). Therefore the analytical methods used for this project are those recommended by the NOAA Status and Trends Program (MacLeod *et al.* 1985, Krahn *et al.* 1988), the EPA Environmental Monitoring and Assessment Program (EMAP; Valente and Strobel 1991, Graves *et al.* 1992, Strobel *et al.* 1991), the Puget Sound Estuary Program (Tetra Tech Inc. 1986a, 1986b), and the US Navy Risk Assessment Pilot Study at NCBC Davisville, RI (Gleason and Mueller 1989, Mueller *et al.* 1991). The need to obtain high quality data and to achieve detection levels capable of measuring trace concentrations of contaminants in marine sediments and tissues resulted in the development of a performance-based quality control/quality assurance (QA/QC) protocol for the analytical methods used in this study (see Appendix C of ERLN and NOSC 1991). The performance-based QA/QC protocol does not require that particular analytical methods are always followed, as is done in the Contract Laboratory Program (CLP), but rather, the testing laboratory must demonstrate proficiency through routine analysis of accuracy materials consisting of standard or certified reference materials (SRMs or CRMs)[4].

The performance-based analytical chemistry QA/QC plan requires Ceimic Corporation, the testing laboratory contracted to perform the analyses, to conduct ongoing performance evaluation exercises throughout the study. The first exercise served to demonstrate initial capability through completion of a performance evaluation (PE), which consisted of blind analyses of a set of sediment and tissue samples of known concentrations and documenting method detection limits (MDLs) achievable for the matrices of interest. In addition, performance was documented continuously throughout the project by analyzing SRMs and laboratory control materials, fortified sample matrices, reagent blanks, calibration standards, and laboratory replicates along with each batch of samples. Finally, interlaboratory calibration of a subset of samples was conducted with ERLN (Appendix C of ERLN and NOSC 1991, Ceimic Corporation 1991). The methods and procedures followed for analysis of sediment, tissue, and seep samples are documented in the project work plan (ERLN and NOSC 1991, Mueller *et al.* 1991).

The PE consisted of blind analysis of known sediment and biota samples prepared by ERLN. The samples were analyzed for organic fractions (polycyclic aromatic hydrocarbons [PAHs], polychlorinated biphenyls [PCBs], and pesticides) and inorganic elements (Al, As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Ag, Sn, and Zn), along with the SRM and other quality

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[4] Certified Reference Materials are samples containing precise concentrations of chemicals, accurately determined by a variety of technically valid procedures and accompanied by a certificate or other documentation issued by a certifying body (e.g. agencies such as the National Research Council of Canada (NRC), U.S. EPA, US Geological Survey, etc.). Standard Reference Materials (SRMs) are CRMs issued by the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards.

TABLE 2. TARGET ANALYTES FOR CONTAMINANT SCREEN

Analyte	Text abbreviation	Sample matrix
Volatile organics		seep water
vinyl chloride		
1,1-dichloroethene		
methylene chloride		
trans-1,2-dichloroethene		
chloroform		
1,1,1-trichloroethane		
carbon tetrachloride		
1,2-dichloroethane		
trichloroethene		
1,2-dichloropropane		
bromodichloromethane		
2-chloroethylvinyl ether		
cis-1,3-dichloropropene		
trans-1,3-dichloropropene		
tetrachloroethene		
chlorobenzene		
bromoform		
1,1,2,3-tetrachloroethane		
1,3-dichlorobenzene		
1,2-dichlorobenzene		
methyl-t-butyl ether		
benzene		
toluene		
ethylbenzene		
m,p-xylene		
o-xylene		
Butyltins		sediment biota
monobutyltin	MBT	
dibutyltin	DBT	
tributyltin	TBT	

TABLE 2. Continued

Analyte	Text abbreviation	Sample matrix
PAHs		
anthracene	ANTH	sediment seep water biota
benz(a)anthracene	BAA	
benzo(a)pyrene	BAP	
benzo(e)pyrene	BEP	
chrysene	CHRY	
dibenz(a,h)anthracene	DBAH	
fluoranthene	FLRA	
fluorene	FLRE	
perylene	PRYL	
phenanthrene	PHEN	
C_1 alkyl phenanthrenes + anthracenes	C1	
C_2 alkyl phenanthrenes + anthracenes	C2	
C_3 alkyl phenanthrenes + anthracenes	C3	
C_4 alkyl phenanthrenes + anthracenes	C4	
pyrene	PYRE	
benzo(g,h,i)perylene	BGHI	
indeno(1,2,3-cd)pyrene	I123	
Chlorinated pesticides		
Aldrin		sediment seep water biota
alpha-chlordane		
trans-nonachlor		
Heptachlor		
Heptachlor epoxide		
hexachlorobenzene		
Lindane (gamma-BHC)		
Mirex		
o,p'-DDD		
p,p'-DDD		
o,p'-DDE		
p,p'-DDE		
o,p'-DDT		
p,p'-DDT		

TABLE 2. Continued

Analyte	Text abbreviation	Sample matrix
PCB congeners[a]		
8 (2 4')		sediment
18 (2 2'5)		seep water
28 (2 4 4')		biota
52 (2 2'5 5')		
44 (2 2'3 5')		
66 (2 3'4 4')	PCB66	
101 (2 2'3 5 5')	PCB101	
118 (2 3'4 4'5)	PCB118	
153 (2 2'4 4'5 5')	PCB153	
105 (2 3 3'4 4')	PCB105	
138 (2 2'3 4 4'5')	PCB138	
187 (2 2'3 4'5 5'6)	PCB187	
128 (2 2'3 3'4 4')	PCB128	
180 (2 2'3 4 4'5 5')		
170 (2 2'3 3'4 4'5)		
195 (2 2'3 3'4 4'5 6)		
206 (2 2'3 3'4 4'5 5'6)		
209 (2 2'3 3'4 4'5 5'6 6')		
Major elements		
aluminum	Al	sediemnt
iron	Fe	water
manganese	Mn	seep water
		biota
Trace elements		
copper	Cu	sediment
nickel	Ni	water
chromium	Cr	seep water
lead	Pb	biota
silver	Ag	
cadmium	Cd	
tin	Sn	
zinc	Zn	
arsenic	As	
mercury	Hg	

[a] congener number (position of chlorines)

STATUS, PRELIMINARY RESULTS, AND DISCUSSION

GREAT BAY ESTUARY HISTORIC OVERVIEW

The Great Bay Estuary has been an active site of research for decades. In 1986, a research bibliography was assembled for Great Bay proper (Short and Tracy 1986) and in 1989 it was expanded to include references on the upland watersheds (Penniman *et al.* 1989). In 1991, a site profile for the Great Bay National Estuarine Research Reserve was completed (Short 1991). The draft Historic Overview, released for review in December 1991, updates and expands the bibliography to include information on the Piscataqua River and Little Bay. In combination with the site profile, this material provides a complete historical overview for the entire Great Bay Estuary, including the Piscataqua River and Portsmouth Harbor. Summarization of information from several hundred reports and publications provide a unique and valuable document for use in evaluating the results of this study. Additionally, the overview can be used to identify major gaps in our knowledge of the estuary, and to recommend areas of research that are needed to support the ecological risk assessment for the Naval Shipyard Portsmouth.

CHARACTERIZATION OF SEDIMENT CONDITIONS

Sample Collection

Surficial grab samples were collected from all 23 sediment stations in the lower Piscataqua and York Rivers. No problems were encountered during sample collection, and SOPs were followed without modification. Replicates were composited for subsequent analyses as appropriate.

Nineteen gravity cores ranging in length from 17 to 23 cm were collected from 19 of the 23 Piscataqua and York River sampling stations. No problems were encountered during coring operations at these 17 sites, and SOPs were followed without modification. Sediments were too coarse at the remaining four stations to allow penetration of the gravity corer, although numerous attempts were made. A total of 138 sediment subsamples were obtained for subsequent analyses.

Geophysical Characterization

Analyses for moisture and organic content, and for grain size characteristics of surficial grab sediments have been initiated, but are not yet complete. Analyses are proceeding without difficulty, and SOPs are being followed without modification. Analyses for moisture and organic content of vertical core subsamples have been completed.

Sediments in the cores ranged from mud to gravel. Many of the cores penetrated a

grayish, cohesive clay which is believed at this time to be of the Presumpscott Formation, a glacial marine sediment often composed of cohesive clay deposited in the early Holocene. When encountered, the Presumpscott clay stopped penetration of the gravity corer. The moisture and organic contents of samples taken from cores were within the ranges usually found in estuarine sediments. Moisture content ranged from 18 to 66%, and the combustible organic content ranged from 1 to 11%. Preliminary results have been supplied to ERLN for inclusion in the project data base system.

Microbial Analyses

Surficial sediment and vertical core samples were analyzed according to established SOPs without modification. Samples were adequately preserved to minimize stress to *Clostridium*, and no cross sample contamination occurred. Preliminary results have been supplied to ERLN for inclusion in the project data base system.

MPN estimates were averaged arithmetically across replicates on a sediment wet weight basis. Wide variation in MPN was observed among replicate surficial samples at some sites. For example, densities at Station 10 ranged from 320 to 32,000 MPN/g wet sediment. Only two sites, Stations 20 and 22, displayed mean MPN below 1,000 per g sediment. The majority of Stations fell between 1,000 and 5,000/g. Values exceeded 5,000/g at Stations 9, 10, 12, 15, and 17.

Highest levels of *C. perfringens* in vertical core strata were observed in lower layers at Stations 10 (16,000 MPN/g) and at Station 15 (≥16,000). However, concentrations of *C. perfringens* generally decreased with depth (at 12 of the 19 stations where cores were successfully obtained), indicating fecal contamination to have been of recent origin.

IS THERE A FIGURE CORRESPONDING TO THIS DATA?

Toxicological Evaluations

Evaluation of surficial sediment toxicity was conducted for all 23 stations following the *Ampelisca* amphipod test SOP without modification. Two 96-hr water only reference toxicity tests with sodium dodecyl sulfate (SDS) were preformed at assure the quality and sensitivity of the field-collected amphipods used in this evaluation. Preliminary results have been incorporated into the project data base system.

Samples from seven of the stations (Stations 9, 13, 16, 17, 18, 22, and 23) displayed significantly ($P \leq 0.05$) lower survivorship than the central Long Island Sound control sediment (Figure 6). Survivorship measured for five of these (Stations 9, 13, 18, 22, and 23) also were less than 80% of the control, a difference considered to be toxicologically meaningful. Stations 9, 13 and 18 are located immediately adjacent to Seavey Island, whereas Stations 22 and 23 are situated in the York River (see Figure 4).

ISN'T YORK R. SUPPOSED TO BE A REFERENCE SITE?

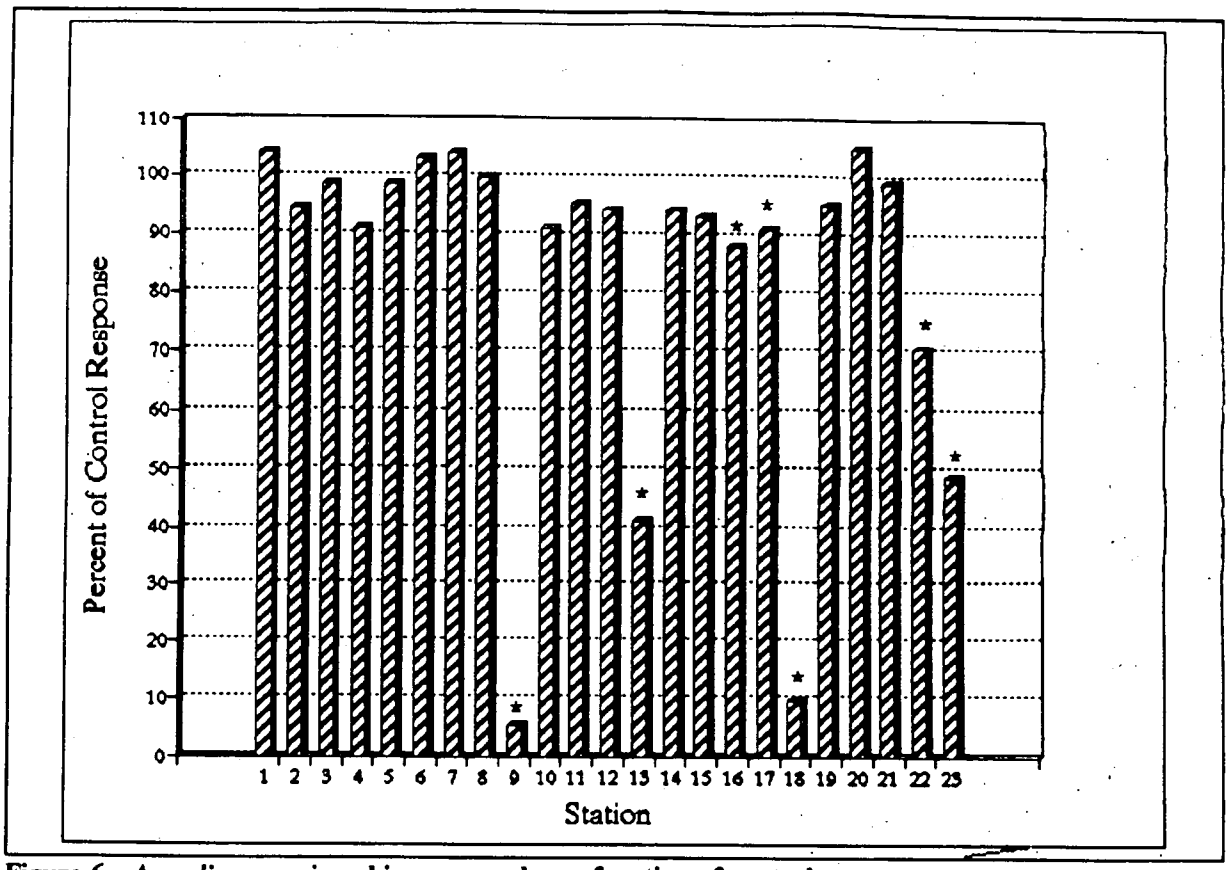


Figure 6. ***Ampelisca*** **survivorship expressed as a function of control response.**

CHARACTERIZATION OF WATER COLUMN CONDITIONS

Sample Collection and Measurement

Synoptic water column measurements and samples for nutrient, pigments, suspended solids, metals, microbial analysis, and toxicological assessment were successfully obtained at all stations in the Piscataqua and York Rivers. SOPs were followed without modification. Temperature, salinity, dissolved oxygen, and pH measurements all were consistent with the seasonal values normally encountered in the lower estuary. Preliminary results have been supplied to ERLN for inclusion in the project data base system.

Time series collection have proceeded on the planned monthly schedule at the five monitoring stations. All samples were successfully transferred for chemical analysis.

Nutrient, Pigment, and Suspended Solids Analyses

Measurements of nutrient, pigment, and suspended solids concentrations have been

completed for the synoptic sampling, following established SOPs without modification. Concentrations of these analytes were within the range observed elsewhere in the estuary. Preliminary results have been supplied to ERLN for inclusion in the project data base system.

Microbial Analyses

Water column samples were analyzed for fecal indicators according to established SOPs without modification. Samples were adequately preserved to minimize stress to *Clostridium perfringens*, and no cross sample contamination occurred. *C. perfringens* densities were expressed as colony-forming units (cfu) per 100 ml sea water. Preliminary results have been supplied to ERLN for inclusion in the project data base system.

Reflecting differences in input source strengths between the riverine systems, *C. perfringens* densities were somewhat higher in the lower Piscataqua River (ranging from 1 to 14 cfu/100 ml) than those measured in the York River (1-4 cfu/100 ml). Highest densities were observed at Stations 2 (11.8 cfu/100 ml) and 16 (12.3 cfu/100 ml).

Toxicological Evaluations

Water samples from the 23 lower Piscataqua and York River stations were evaluated synoptically for toxicity using the sea urchin (*Arbacia punctulata*) sperm cell test. The established SOP was followed with one exception: the holding time between sample collection and assay performance exceeded the recommended limit of 48 hr, potentially resulting in a loss of toxicity. It should be noted that this time limit is a recommendation only; studies have not been conducted to determine general decay rates of the toxicity of receiving waters under standard holding conditions. As the salinity of all samples fell between 28 and 31 ppt, no salinity adjustments were necessary. Filtered Narragansett Bay, RI water was used as the control. Results have been included in the project data base system.

WHOSE?

WHY WERE HOLDING TIMES EXCEEDED?!

Despite violation of the holding time recommendation, toxicity significantly different ($P \leq 0.05$) from the control was observed at Stations 3, 4, and 7 (Figure 7). All three stations are within the Clark Island embayment (see Figure 4).

EVALUATION OF ESTUARINE BIOLOGICAL RESOURCES

Mussel Collections and Analyses

Mussels were collected at all sites except station 8, where a sharp slope of rip-wrap boulders leading into a dredged area rendered collection activities unsafe. Mussels from all sites around Seavey Island, and at stations 17, 20, 22, and 23 were collected from shore. The remaining samples were obtained using modified oyster tongs. The SOP for mussel collection was followed without major modification.

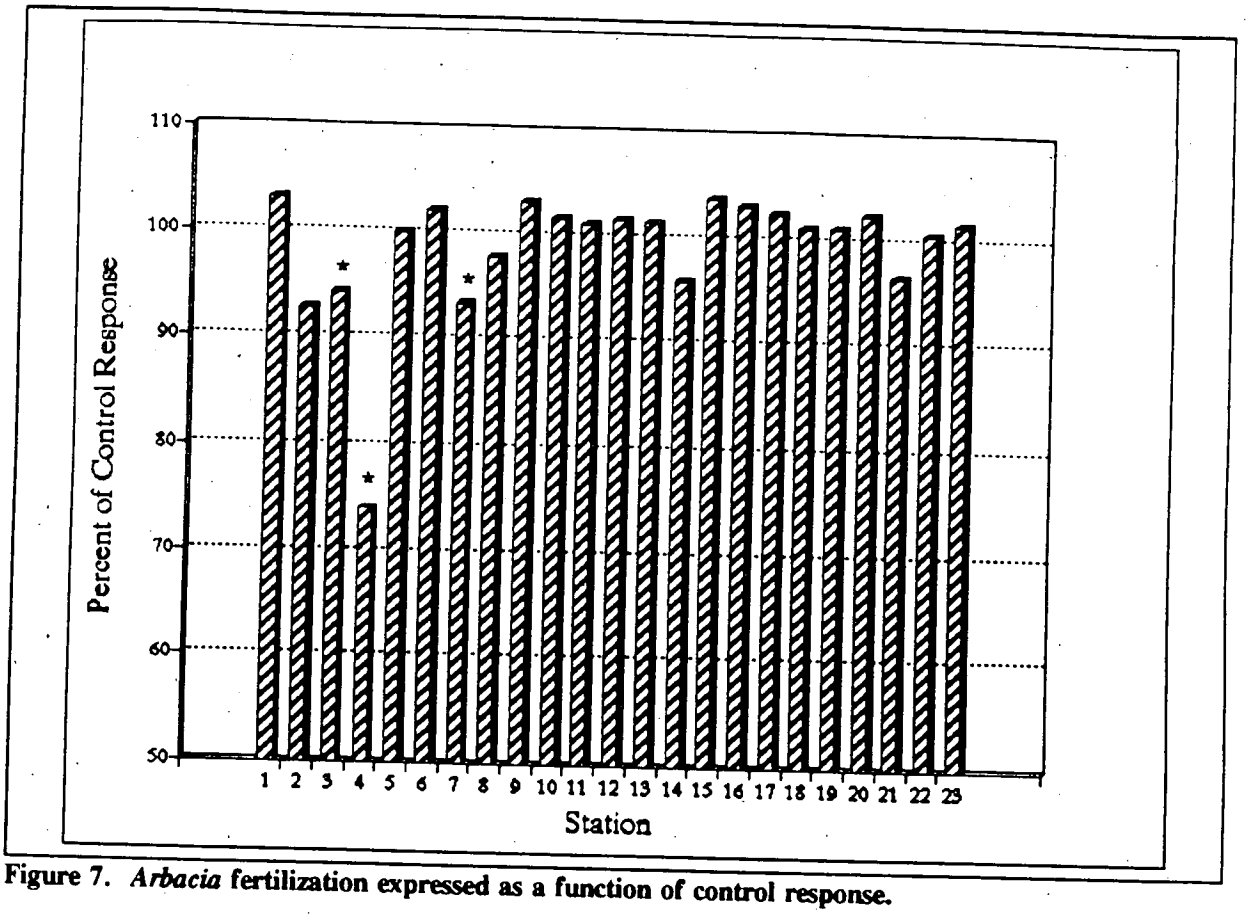


Figure 7. ***Arbacia*** **fertilization expressed as a function of control response.**

Most samples contained more living animals than dead. Length and weight analyses have been initiated, but are not yet complete. Average lengths were comparatively similar. Preliminary results have been supplied to ERLN for inclusion in the project data base system.

Lobster and Flounder Collections and Analyses

Trawl sampling at the nine transect stations were completed following standard protocols. Preliminary data have been supplied to ERLN for inclusion in the project data base.

Some problems were experienced in association with sample collection and assessment activities. First, the sampling interval did not occur during the optimum season to obtain winter flounder, which migrate seasonally through the estuary. Few fish were collected during trawl activities, resulting in insufficient quantities of flesh and liver tissue for subsequent chemical analyses. Secondly, most of the lobsters collected in the trawls were under the legal size limit of 3.25 in, although many adult and juvenile lobster were obtained. Because larger lobster are older, they have experienced longer periods of exposure to contaminants, and would be expected to have higher tissue burdens than do younger lobster. However, unlike younger lobster, older individuals migrate seasonally, and may not remain in

one location for extended periods. Further confounding the tissue residue assessment is the fact that material to be archived was inadvertently omitted from samples transferred for chemical analysis (often because insufficient material was collected to begin with). As a result of these problems, a more detailed analysis of lobster and flounder populations may be required in the next phase of this investigation.

Eelgrass Collections and Analyses

Samples were successfully collected at all stations in the Piscataqua and York Rivers, and the Great Bay Estuary, including the additional station 12A, without modification to SOPs. Modified oyster tongs were used for collection. Use of the tongs significantly reduced collection effort over the diver method, and enhanced personnel safety. Plants at station 15 were rare. Stations 3, 9, 17, 18, and 19 were particularly muddy, and some time was needed to rinse sediment from the shoots. Juvenile lobster were present in grabs from

stations 2, 17, and 19. There were noticeably more worms in the sample from station 17.

Population assessments for all stations are complete. Stations 1, 14, GB-1, and GB-9 had highest densities of eelgrass shoots. Plant morphometrics did not vary greatly among sites, although shoot lengths at stations 1 and 23 were shorter than those at other sites. Shoots were entangled with filamentous algae at stations 8, 16, 19, and GB-6. Preliminary results have been supplied to ERLN for inclusion in the project data base system.

Fucoid Algae Collections and Analyses

Ascophyllum nodosum was collected following the SOP at eight sites in the Piscataqua and York Rivers. Abundance estimations has been initiated but are not yet completed. Preliminary results have been supplied to ERLN for inclusion in the project data base system.

Mussel Deployment and Physiological Analysis

Mussels were successfully collected and deployed following established SOPs without modification. Some mortality was experienced during transport of animals to JEL, although the impact of transit conditions was deemed minimal to the remaining individuals. Deployed *Mytilus* were retrieved from all stations but Station 10; the deployment array at this station was lost presumably due to its interference with activities at that site. Retrieved animals were transported in ice to ERLN, and a subset of mussels from each station were frozen for subsequent chemical analysis.

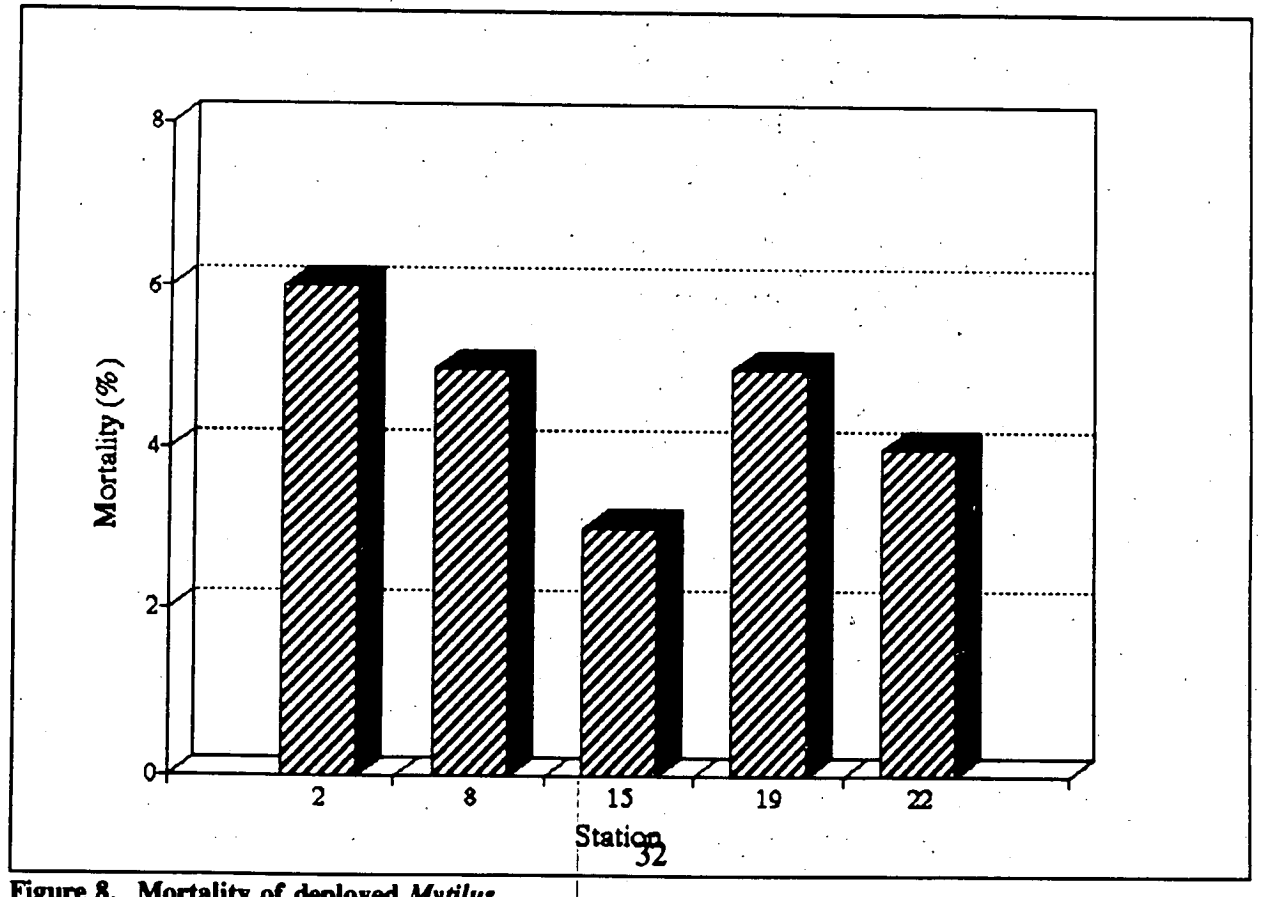


Figure 8. Mortality of deployed *Mytilus*.

Upon their return to ERLN, survivorship, individual growth (measured as changes in shell length) and Scope for Growth (SFG), integrated from physiological parameters, were determined for mussels from each station following ERLN SOP 1.03.013. Mortality was uniformly low across stations (Figure 8), and no station differences ($P \leq 0.05$) were observed. Shell lengths of retrieved animals similarly were statistically indistinguishable (Figure 9), although some differences in dry tissue weights were observed, with animals from Station 15 being the smallest (Figure 10). When adjusted for tissue biomass, mussels at this station displayed statistically higher SFG than those at the remaining five stations (Figure 11). The apparent contradiction between tissue biomass and SFG is unexplained at this time. Animals at Station 10 also exhibited the lowest respiration rate (Figure 12), a potential indication of relatively reduced stress.

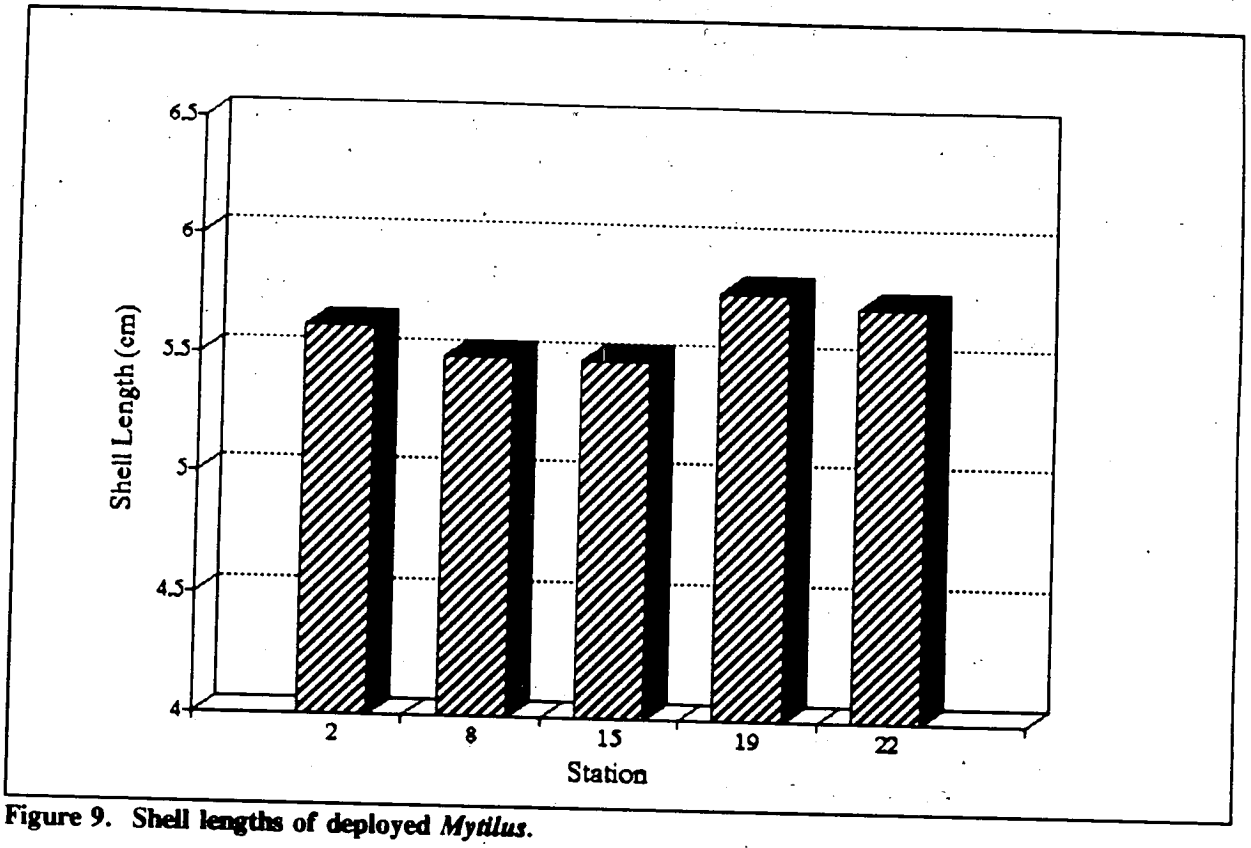


Figure 9. Shell lengths of deployed *Mytilus*.

Benthic Community Collections and Analysis

Analyses of benthic community composition are completed for the 23 lower Piscataqua and York River stations. Four replicates were analyzed per station following established SOPs. Preliminary data have been transferred to ERLN for inclusion to the project data base system.

Although not yet completed, preliminary analyses suggest higher densities of benthic organisms at many stations relative to those observed elsewhere in the estuary. The environmental factors influencing these densities are not clear at this time, but will be explored in subsequent analyses.

ANALYTICAL CHEMISTRY PERFORMANCE EVALUATION

The results of the analytical chemistry PE and the determination of MDLs are provided in Appendix A. Ceimic Corp. was able to meet the PE and MDL requirements identified in the revised analytical chemistry quality assurance and quality control protocols, criteria, and corrective action plan for the project (Appendix B).

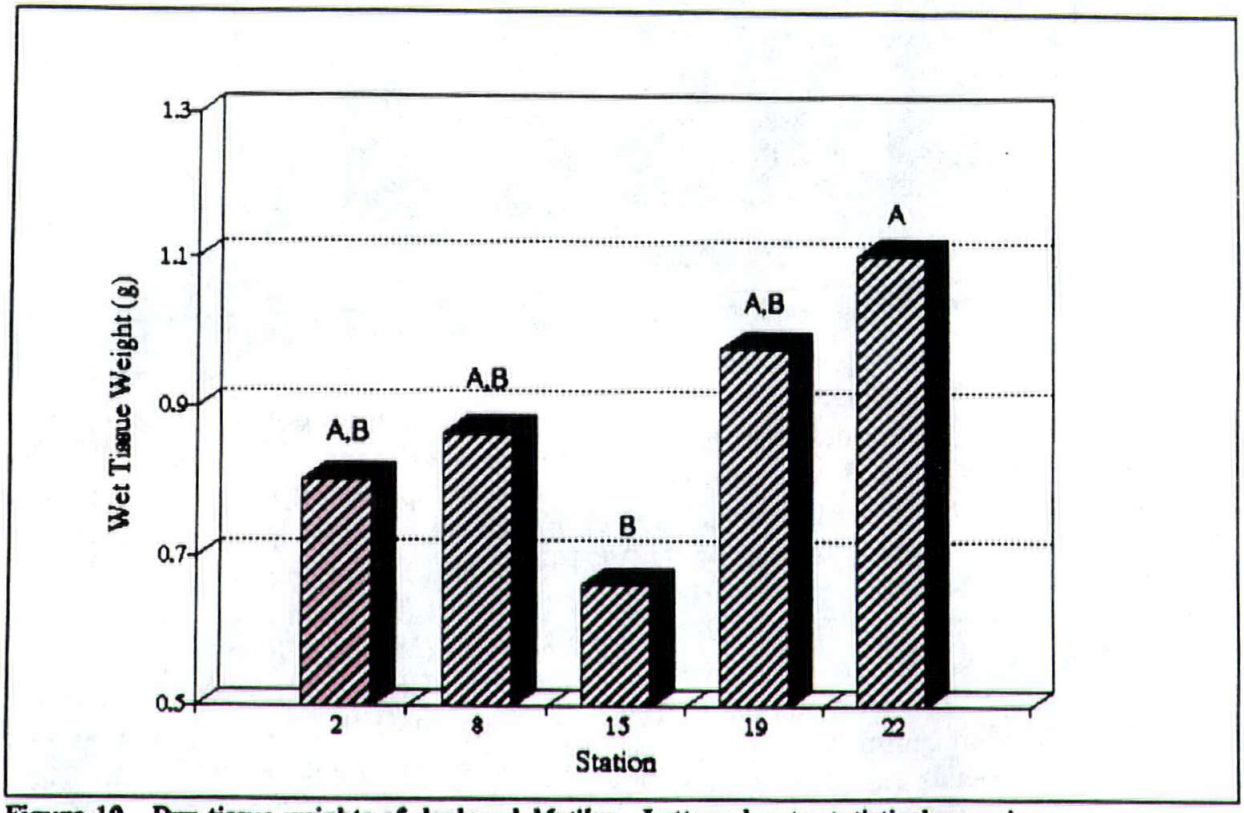


Figure 10. Dry tissue weights of deployed *Mytilus*. Letters denote statistical groupings.

ANALYTICAL SCREEN OF SEDIMENT AND TISSUE SAMPLES

At this time the analysis of the analytical screen samples is nearing completion and therefore, all the analytical screen data are not yet available. Preliminary results are presented to document the capability of the analytical methods selected for this project in attaining the accuracy and precision required to meet the data quality objectives of the study.

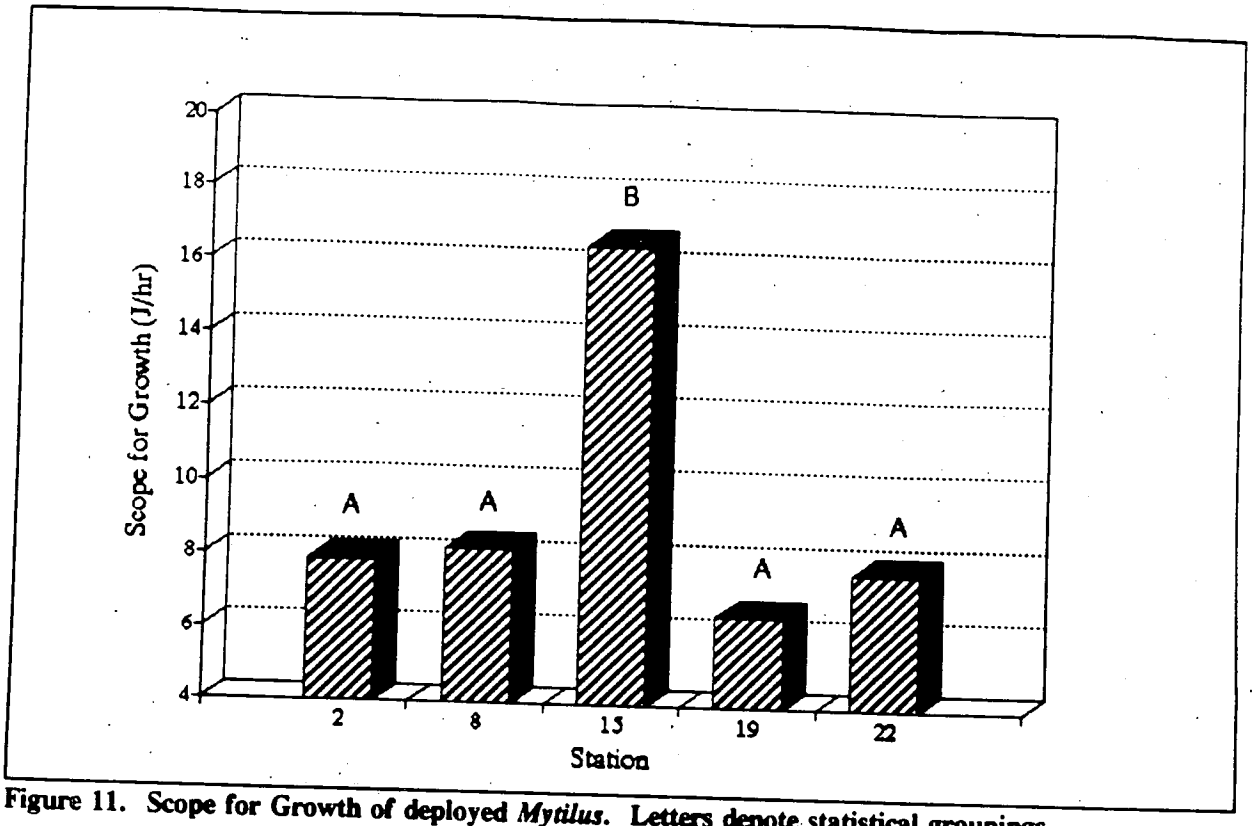


Figure 11. Scope for Growth of deployed *Mytilus*. Letters denote statistical groupings.

Generally, results obtained for the analytical screen of replicate sediment samples showed very good repeatability between stations (Table 3). PAH concentrations were relatively constant between the 5 stations (Figure 13). The compounds SBOF, PYRE, and FLRA were the highest PAHs measured (ca. 600 $\mu g/g$) and were similar in concentration between the stations. The concentrations of BAP (219-423 $\mu g/g$) were comparable to BAP concentrations measured in Allen Harbor, Narragansett Bay, RI (Johnston *et al.* 1991, Munns *et al.* 1991), and in central Long Island Sound (100-500 $\mu g/g$) (Munns *et al.* 1989). Concentrations of PHEN (190-334 $\mu g/g$) were also similar to PHEN levels measured in Allen Harbor and Narragansett Bay (Johnston *et al.* 1991), but were more than twice as high as PHEN levels measured in central Long Island Sound (50-60 $\mu g/g$) (Munns *et al.* 1989). The sum of the PAH compounds quantified (Figure 14) were comparable to those measured at other moderately polluted sites (Munns *et al.* 1991, R. Pruell, ERLN, personal communication).

WHAT DOES THIS MEAN EXACTLY?

Very low concentrations of PCB congeners were measured in the sediment samples used for the analytical screen (Table 4). The hexachlora-PCBs (PCB153 and PCB138) were the highest PCB congeners measured (Figure 15). There was no clear pattern between the distribution of PAHs and PCBs (Figures 13 and 15). PAHs were higher at stations 7, 17 and 19, while the PCBs were highest at stations 7 and 8 (Figure 16).

Concentrations of tributyltin were measured in sediments, indigenous mussels, and

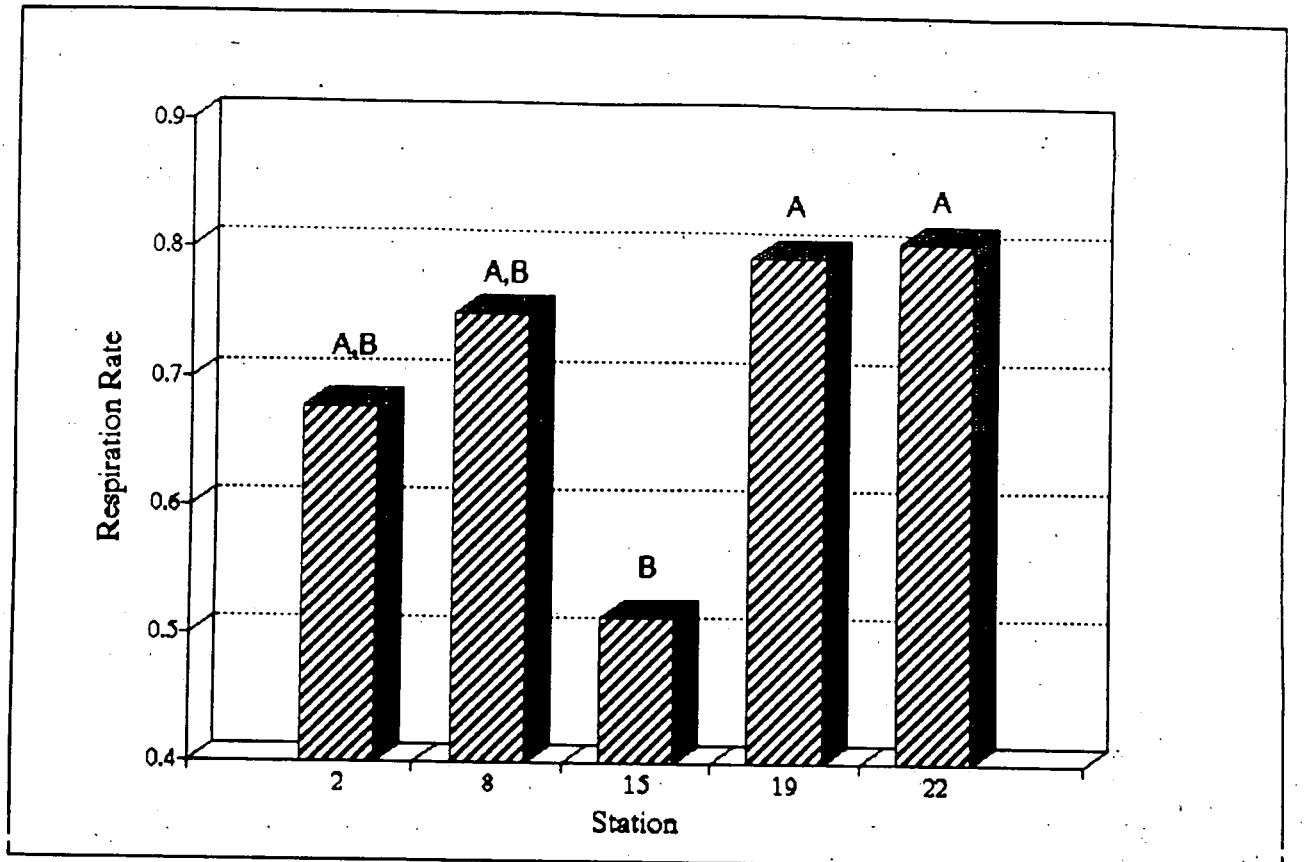


Figure 12. Respiration rates of deployed *Mytilus*. Letters denote statistical groupings.

caged mussels in the Piscataqua Estuary and York River (Figure 17, displayed on a wet weight basis). Tributyltin (TBT) concentrations were more than an order of magnitude lower (on a wet weight basis) than those measured in reference areas of Narragansett Bay for sediments and mussel tissues (Johnston *et al.* 1991, Munns *et al.* 1991).

Comparison between the inorganic contaminants measured in two of the analytical screen sediment samples showed very good repeatability within stations (Figure 18). The metals data from the two stations near the SHIPYARD were very similar to metal concentrations measured in sediment from Allen Harbor (Johnston *et al.* 1991, Munns *et al.* 1991), except that As was slightly elevated in SHIPYARD samples and that Cu and Zn were lower in the SHIPYARD samples.

The results obtained for metals in mussel tissues showed that the concentrations of most of the metals were very near to the MDLs (Figure 19). MDLs for tissue samples were determined by replicate analysis of flounder tissue obtained from a local Narragansett Bay fish market (see Appendix A). Similar metal concentrations were measured in mussel samples from each of the stations screened (Figure 19).

The analytical screen of inorganic contaminants in lobster tail flesh (Figure 20) and

Table 3. Results of Analytical Screen for PAH compounds in Sediments.

sample#	Station	FLRE	PHEN	ANTH	C1	C2	C3	C4	FLRA	PYRE	BAA	CHRY	SBOF	BEP	BAP	PRYL	I123	DBAH	BGHI	SumPAH
		PAHs ug/kg (ppb)																		
117424(110210)	19	18	190	72	280	240	100	20	460	550	370	370	600	260	240	120	180	28	210	4308
117427(110210)	19	43	290	120	210	330	120	20	510	590	370	310	810	330	510	130	220	70	250	5233
117430(110210)	19	30	330	120	370	310	110	20	640	640	390	370	590	240	350	100	180	46	200	5036
117434(110210)	19	22	200	100	260	270	100	20	460	460	350	360	710	320	450	95	180	55	230	4642
Averge		28	253	103	280	288	108	20	518	560	370	353	678	288	388	111	190	50	223	4805
Stardard Dev		10	59	20	58	35	8	0	74	66	14	25	90	38	103	14	17	15	19	357
126717(110220)	10	40	340	120	260	180	130	20	750	650	370	380	580	200	240	86	130	54	120	4650
126717(110220)DUP	10	47	380	250	350	220	84	22	1000	860	560	540	740	240	330	100	150	28	150	6051
dup avg		44	360	185	305	200	107	21	875	755	465	460	660	220	285	93	140	41	135	5351
126721(110220)	10	28	160	72	160	140	53	25	310	300	160	140	380	160	200	76	120	47	120	2651
126723(110220)	10	51	300	100	300	150	25	20	530	500	260	270	550	190	250	77	120	22	110	3825
126725(110220)	10	19	160	52	140	110	52	20	330	300	160	160	280	120	140	58	91	26	95	2313
Averge		35	245	102	226	150	59	22	511	464	261	258	468	173	219	76	118	34	115	3535
Stardard Dev		13	88	51	77	32	30	2	227	187	125	127	147	37	55	12	17	10	15	1189
132128(110217)	17	41	350	160	350	240	31	20	660	770	470	400	890	300	410	120	190	60	210	5672
132132(110217)	17	26	210	97	290	160	45	20	420	470	270	280	610	230	330	86	150	26	170	3890
132134(110217)	17	28	220	100	170	140	40	17	550	570	350	320	730	270	400	120	150	76	170	4421
132136(110217)	17	45	320	200	580	310	54	20	700	760	490	440	950	360	550	140	230	91	270	6510
Averge		35	275	139	348	213	43	19	583	643	395	360	795	290	423	117	180	63	205	5123
Stardard Dev		8	61	43	149	68	8	1	109	128	90	63	134	47	80	19	33	24	41	1029
126787(110225)	8	39	280	87	232	206	50	36	530	480	270	340	740	280	390	120	280	390	330	5080
126791(110225)	8	27	210	79	100	61	30	30	390	350	180	180	500	160	230	76	110	56	120	2889
126793(110225)	8	25	230	86	200	120	58	28	470	480	230	250	540	210	270	98	160	25	160	3640
126795(110225)	8	18	117	42	130	93	25	25	200	200	82	82	330	98	130	47	61	29	64	1773
Averge		27	209	74	166	120	41	30	398	378	191	213	528	187	255	85	153	125	169	3346
Stardard Dev		8	59	18	53	54	14	4	124	115	70	95	146	67	93	27	81	153	99	1202
126805(110226)DUP	7	26	190	63	190	130	30	30	390	410	200	190	600	210	270	120	150	35	150	3384
126805(110226)	7	24	220	63	15	140	36	30	470	460	190	230	630	230	290	100	160	33	160	3481
dup avg		25	205	63	103	135	33	30	430	435	195	210	615	220	280	110	155	34	155	3433
126801(110226)	7	69	530	190	200	200	100	30	780	750	360	420	960	330	410	130	260	25	220	5964
126807(110226)	7	29	250	80	190	150	29	28	520	560	260	240	680	260	310	100	170	31	140	4027
126809(110226)	7	41	350	120	340	220	270	27	720	710	380	340	790	280	350	120	160	65	150	5433
Average		41	334	113	208	176	108	29	613	614	299	303	761	273	338	115	186	39	166	4714
Standard Dev		17	125	49	85	35	98	1	143	125	75	83	131	40	49	11	43	15	31	1024

Table 4 . Results of Analytical Screen for selected PCB congeners in sediment.

sample#	Station	pcb66	pcb101	pcb118	pcb153	pcb105	pcb138	pcb187	pcb128
					PCB congeners ug/kg (ppb)				
117424(110210)	19		0.5	0.8	2.3	0.5	1.9	0.5	0.5
117427(110210)	19	0.5	1.8	1.1	6.7	0.5	4.8	2.9	1.2
117430(110210)	19	1.7	0.5	0.8	3.6	0.5	0.5	1.3	0.5
117434(110210)	19	1.7	0.5	0.7	2.0	0.5	1.6	0.8	0.6
Averge		1.3	0.8	0.9	3.7	0.5	2.2	1.4	0.7
Stardard Dev		0.6	0.6	0.2	1.9	0.0	1.6	0.9	0.3
126717(110220)	10	5.4	2.3	1.9	4.4	1.1	3.4	1.4	0.8
126721(110220)	10	3.5	1.7	1.6	3.6	1.7	2.8	2.1	0.9
126723(110220)	10	3.2	1.6	1.2	3.3	0.8	2.6	1.0	0.5
126725(110220)	10	4.0	1.9	1.2	2.6	0.6	2.3	0.9	0.8
Averge		4.0	1.9	1.5	3.5	1.1	2.8	1.4	0.8
Stardard Dev		0.8	0.3	0.3	0.6	0.4	0.4	0.5	0.2
132128(110217)	17	1.4	0.5	0.5	1.9	0.5	1.2	0.5	0.6
132132(110217)	17	1.7	0.5	0.9	2.1	0.5	1.6	0.9	0.5
132134(110217)	17	2.0	0.5	0.8	9.2	2.1	1.8	4.1	1.2
132136(110217)	17	2.5	0.7	0.9	1.6	0.5	1.4	0.5	0.5
Averge		1.9	0.6	0.8	3.7	0.9	1.5	1.5	0.7
Stardard Dev		0.4	0.1	0.2	3.2	0.7	0.2	1.5	0.3
126787(110225)	8	1.8	2.9	3.2	6.0	3.5	4.8	2.8	1.7
126791(110225)	8	3.1	1.4	1.7	3.3	0.6	2.8	1.1	0.6
126793(110225)	8	5.2	2.4	1.8	4.3	0.7	3.7	2.3	0.9
126795(110225)	8	3.6	1.5	1.6	2.5	2.8	18.0	1.3	0.9
Averge		3.4	2.1	2.1	4.0	1.9	7.3	1.9	1.0
Stardard Dev		1.2	0.6	0.7	1.3	1.3	6.2	0.7	0.4
126805(110226)	7	5.7	2.9	3.2	5.1	2.4	3.9	2.5	2.6
126801(110226)	7	0.8	3.4	3.3	13.0	10.0	8.3	15.0	6.1
126807(110226)	7	0.7	2.4	2.9	5.7	0.7	5.0	2.5	1.4
126809(110226)	7	5.3	1.8	2.4	5.4	0.6	4.8	2.0	1.5
Average		1.7	1.9	2.2	6.0	2.8	4.5	4.9	2.3
Standard Dev		2.1	1.2	1.3	4.6	4.2	3.0	5.9	2.3

Figure 13. Sediment PAH Concentration

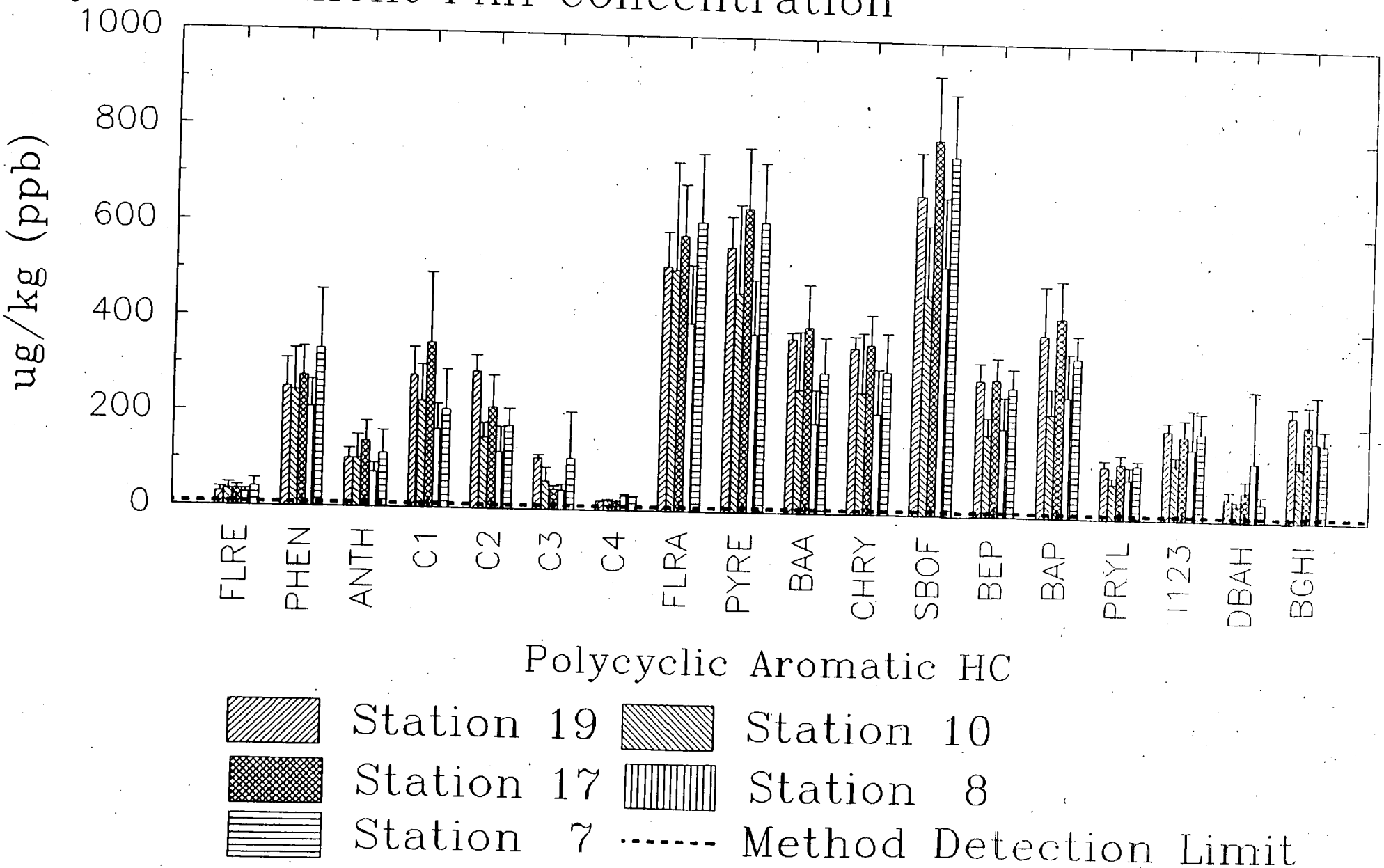


Figure 14. Sediment Sum of PAHs

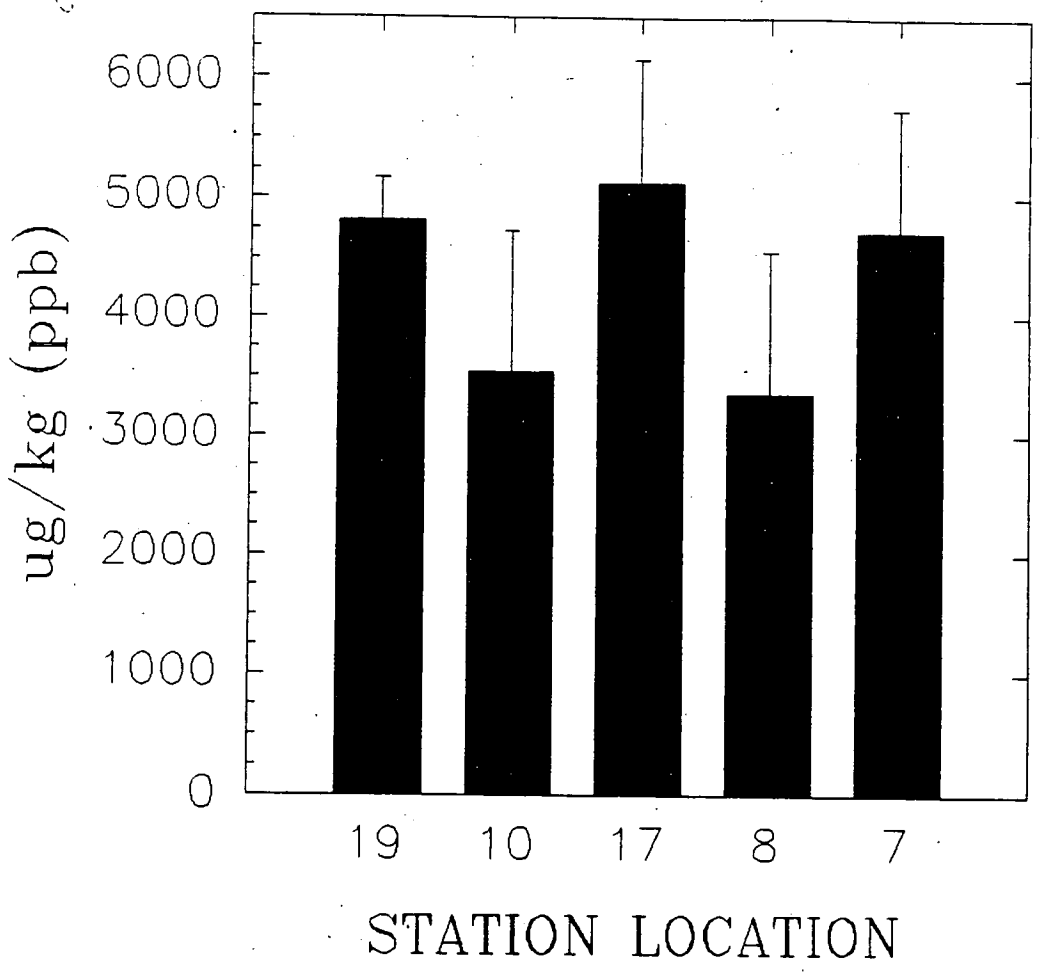


Figure 15. Sediment PCB Concentrations

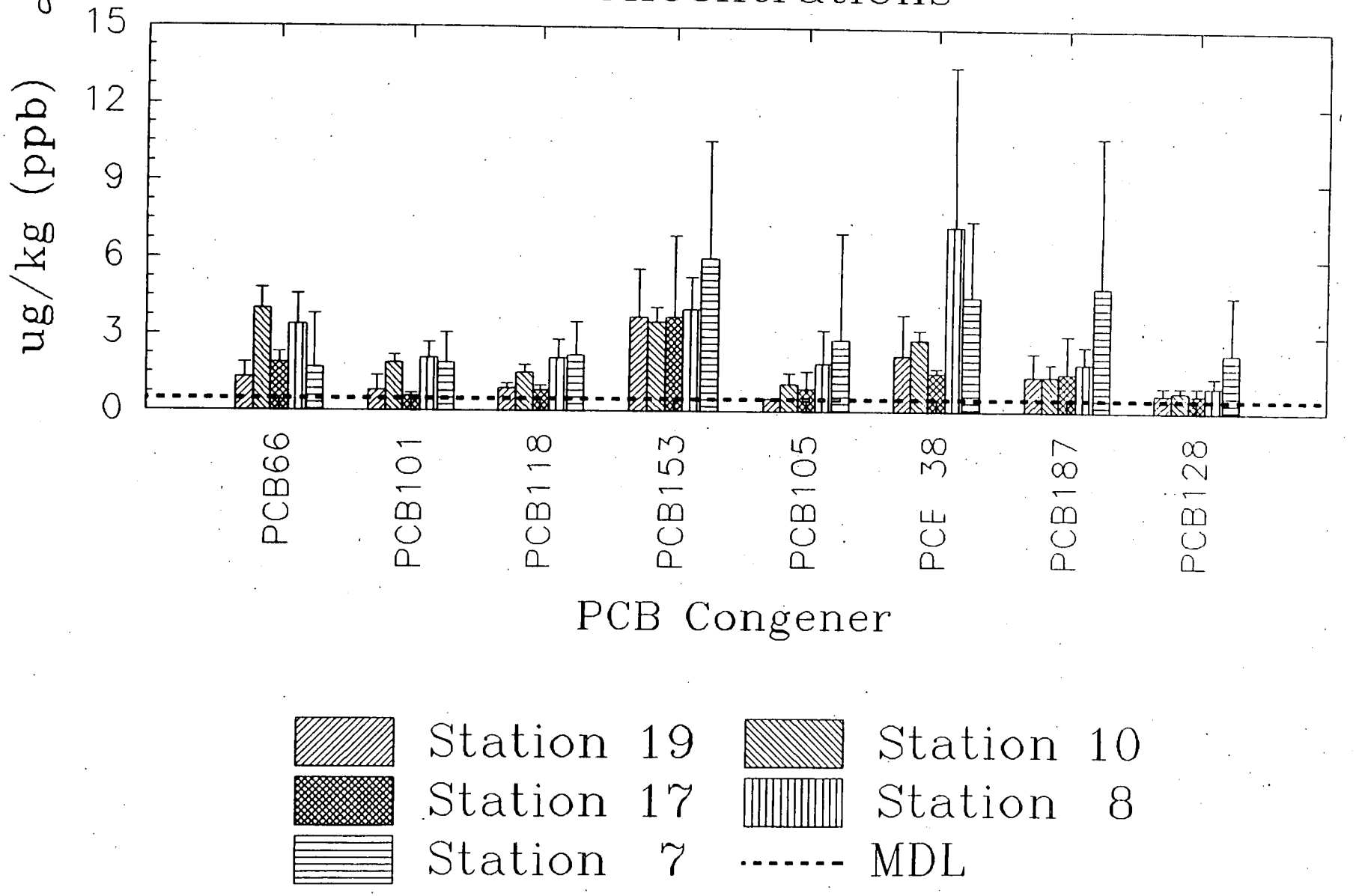


Figure 10. Sum of Selected PCBs

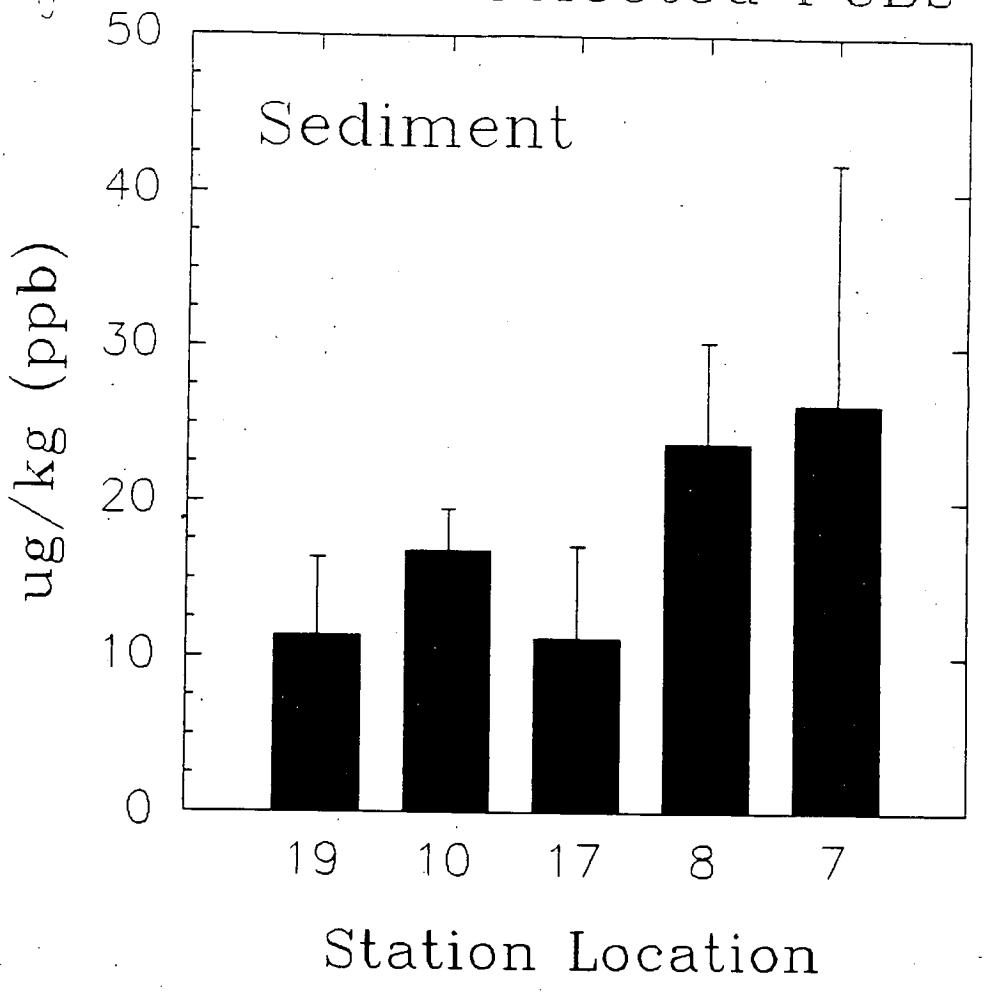


Figure 17.

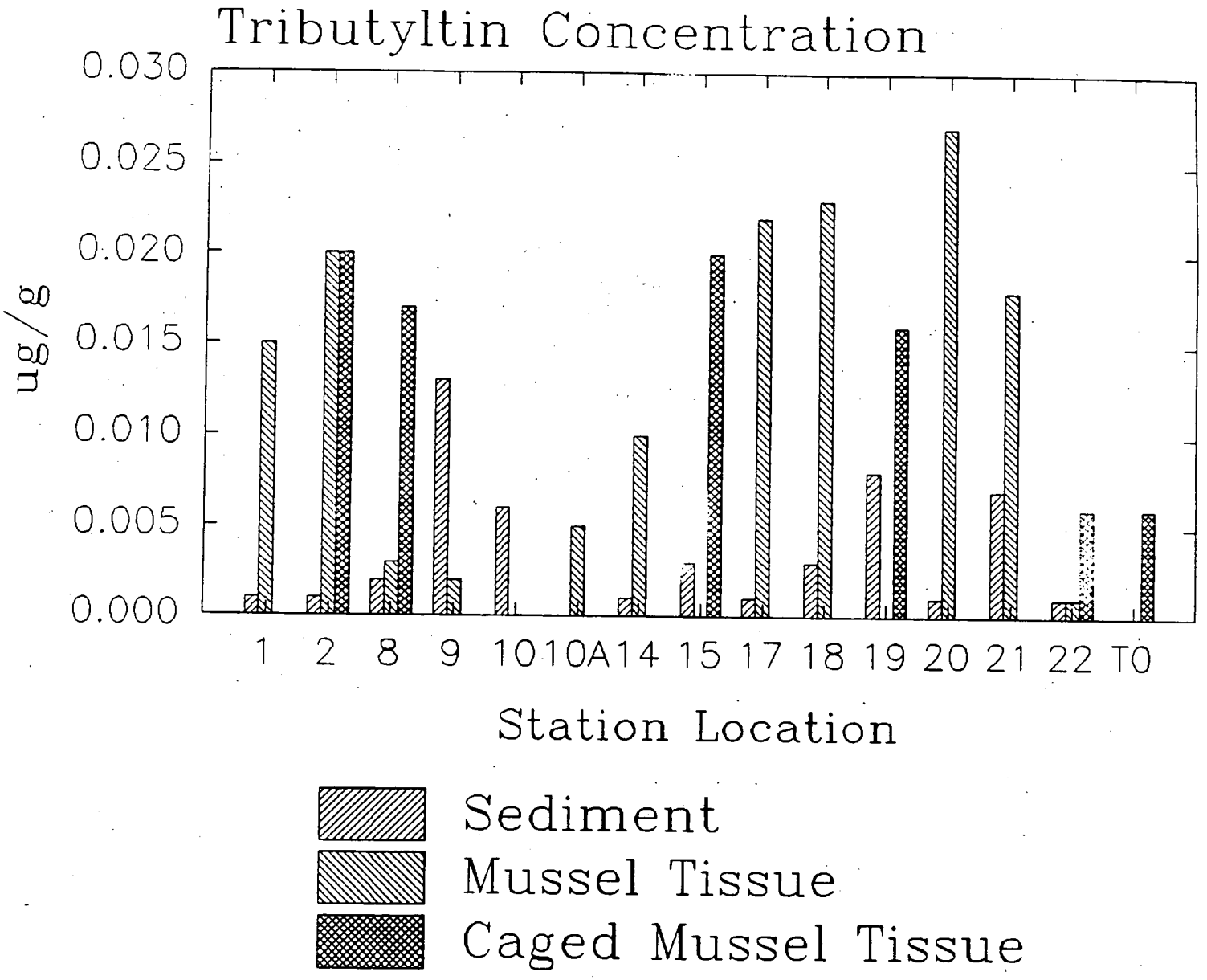

Tributyltin Concentration
0.030
0.025
0.020
0.015
0.010
0.005
0.000
ug/g
1
2
8
9
10
10A
14
15
17
18
19
20
21
22
TO
Station Location
Sediment
Mussel Tissue
Caged Mussel Tissue

Figure 18.

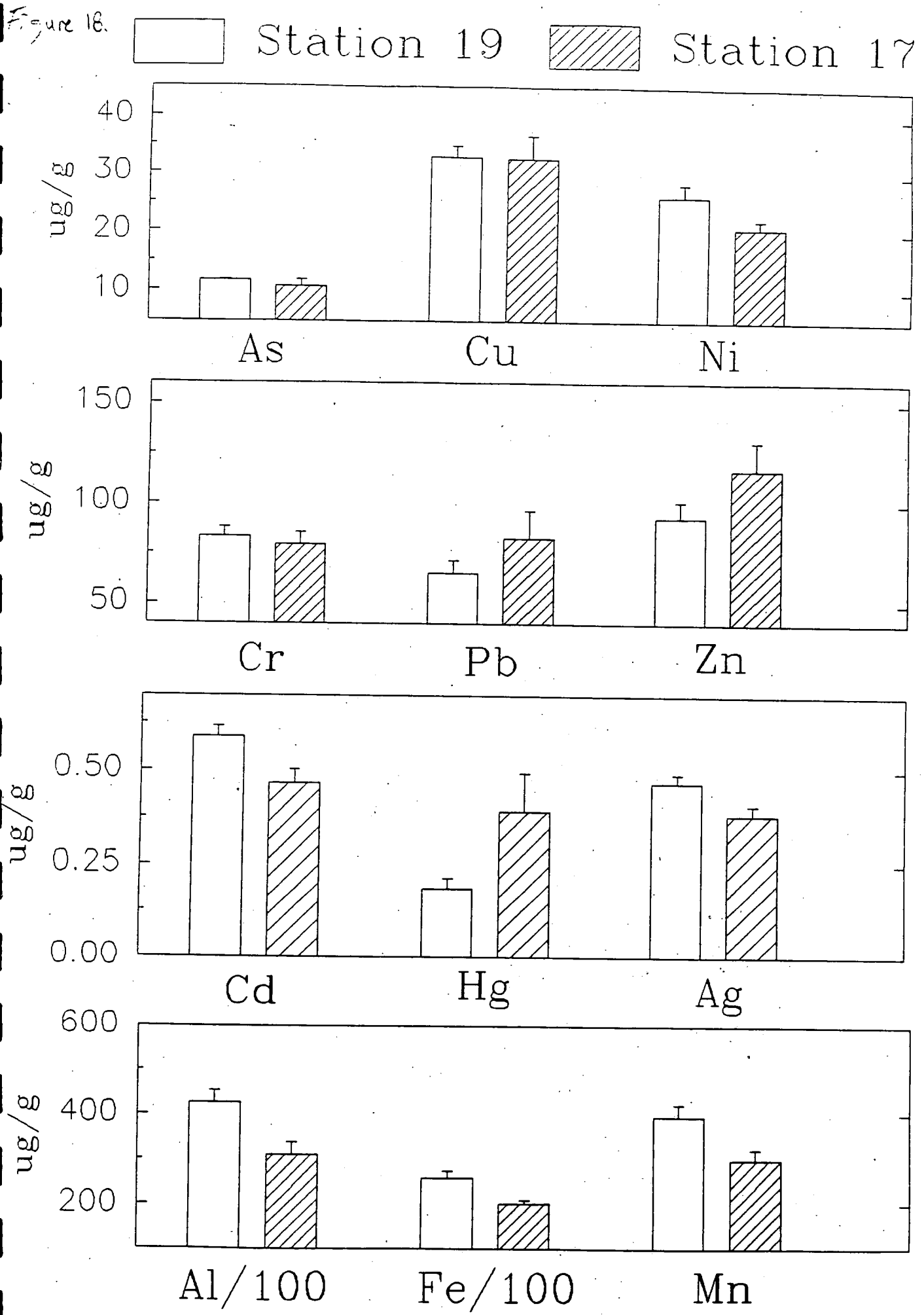

Station 19
Station 17
ug/g
40
30
20
10
As
Cu
Ni
150
100
50
Cr
Pb
Zn
0.50
0.25
0.00
Cd
Hg
Ag
600
400
200
Al/100
Fe/100
Mn

Figure 19

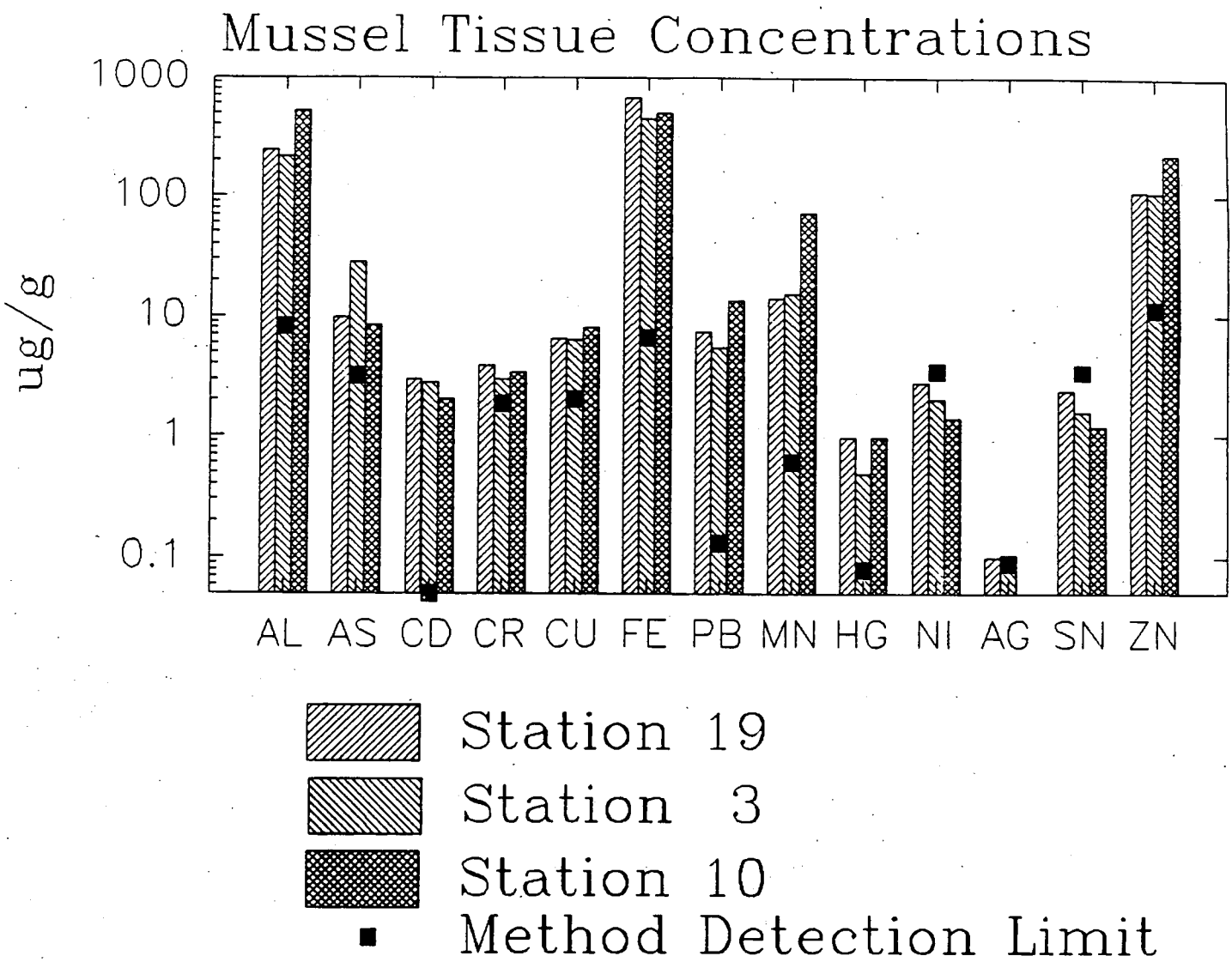

Mussel Tissue Concentrations
1000
100
10
1
0.1
ug/g
AL AS CD CR CU FE PB MN HG NI AG SN ZN
Station 19
Station 3
Station 10
Method Detection Limit

Figure 20

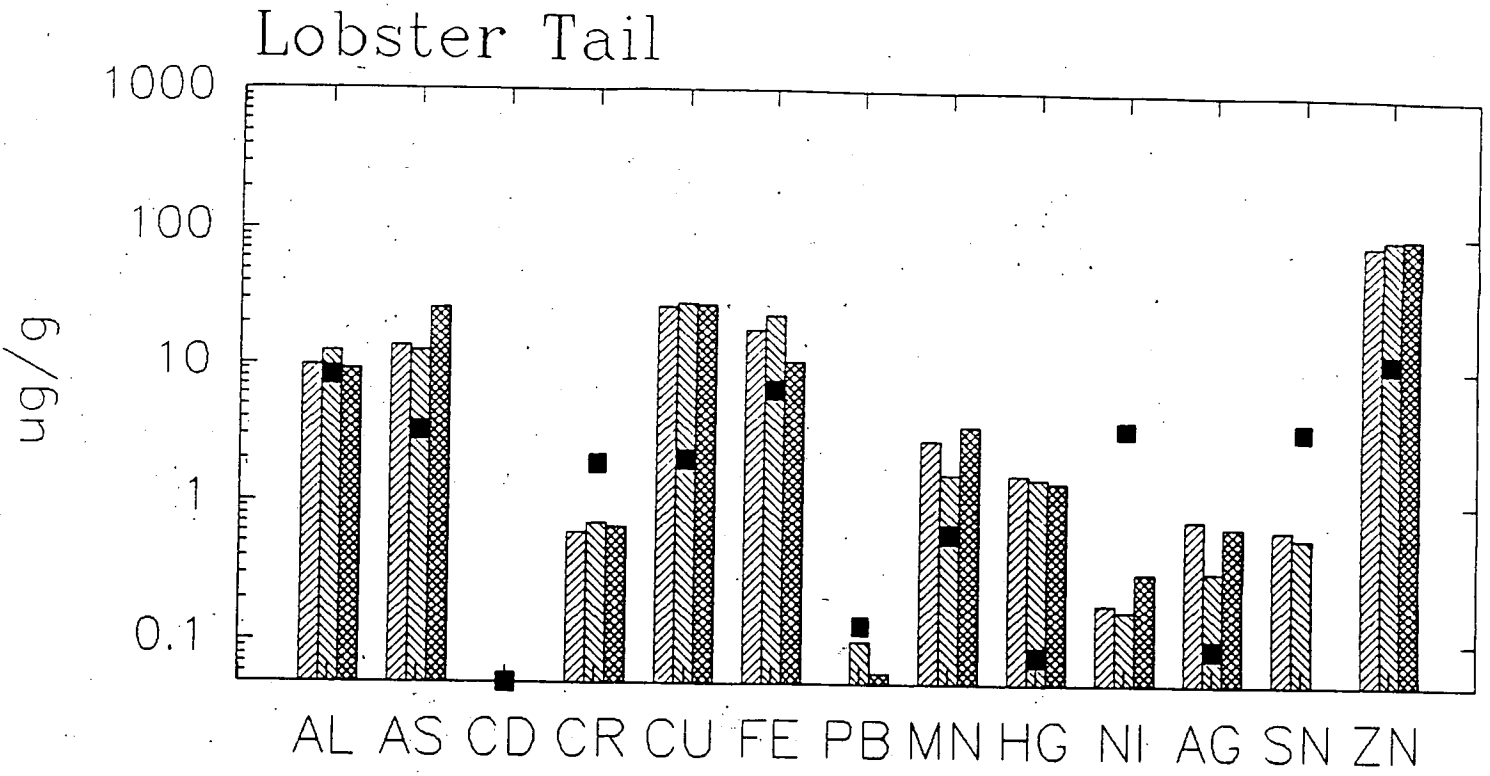
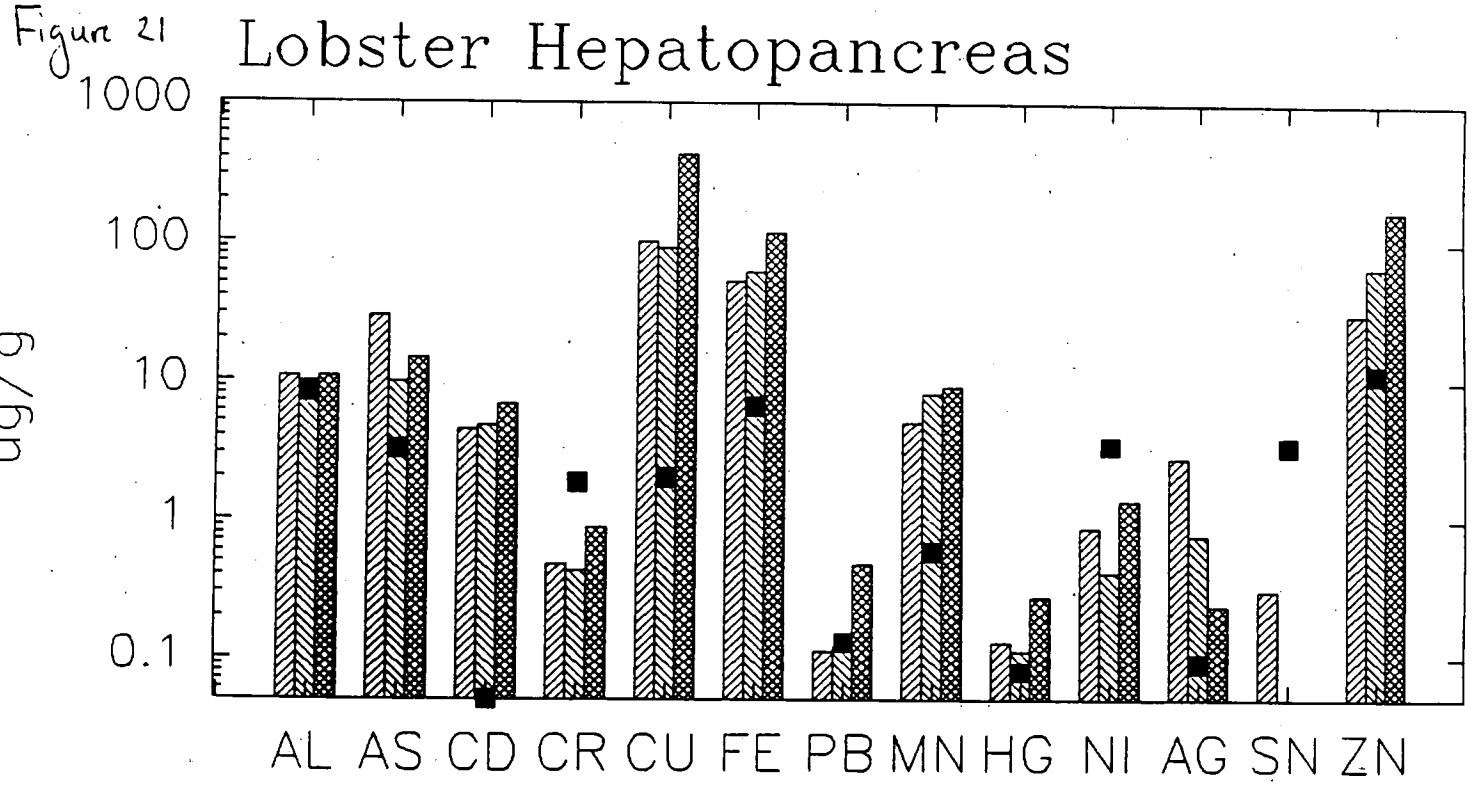


Figure 21



Transect 5

Transect 7

Transect 8

■ Method Detection Limit

hepatopancreas (Figure 21) tissues showed that there were differences in metals concentrations in the two types of tissues. In general the concentrations of most of the metals were at or below the MDLs. Of the metals that were present above the MDLs, Cd, Cu, Fe, and Mn were elevated in the hepatopancreas relative to the tail tissue, while Hg was higher in the tail than hepatopancreas tissue. Hepatopancreas tissue, which is composed of tubules and ducts, which secrete digestive enzymes, and specialized cells which store glycogen, fat and calcium (Barnes 1980), has a higher affinity than tail tissue for some of the metals. Higher levels of Cu measured in the hepatopancreas tissue are most likely due to high concentrations of hemocyanin, a copper-containing blood plasma found only in Malacostracan crustaceans (Barnes 1980). Reduced levels of Hg in the hepatopancreas relative to the lobster tail could be caused by the metabolism of inorganic Hg into organomercury compounds which cannot be detected by the methods used in this study.

Concentrations of metals measured in flounder flesh tissue also were at or below the MDLs, except for Zn (Figure 22). Furthermore, the metal levels (excepting Zn) were all below the matrix concentration of metals measured in the flounder tissue obtained from a local Narragansett Bay fish market during the MDL study (Appendix A).

The results of the inorganic analytical screen of plant tissues sampled at station 19 show the relative concentrations of metals measured in eelgrass leaves, eelgrass roots, and fucoid algae (Figure 23). Metals measured at concentrations above the MDL were Mn, Ag, and Zn. Arsenic was detected at much higher concentrations in the rockweed sample than in the eelgrass samples, while Cr was detected at higher concentrations in the eelgrass samples (Figure 23).

Sufficient analytical data is not yet available to draw conclusions about the relative distribution and ecological effects of contaminants in the estuary. However, the initial results do show that the analytical methods are capable of measuring trace concentrations of the contaminants of concern in the estuary. The use of these methods will permit accurate confirmation of the presence or absence of environmental contaminants in the estuary.

Figure 22 - SHOULD BE TYPED

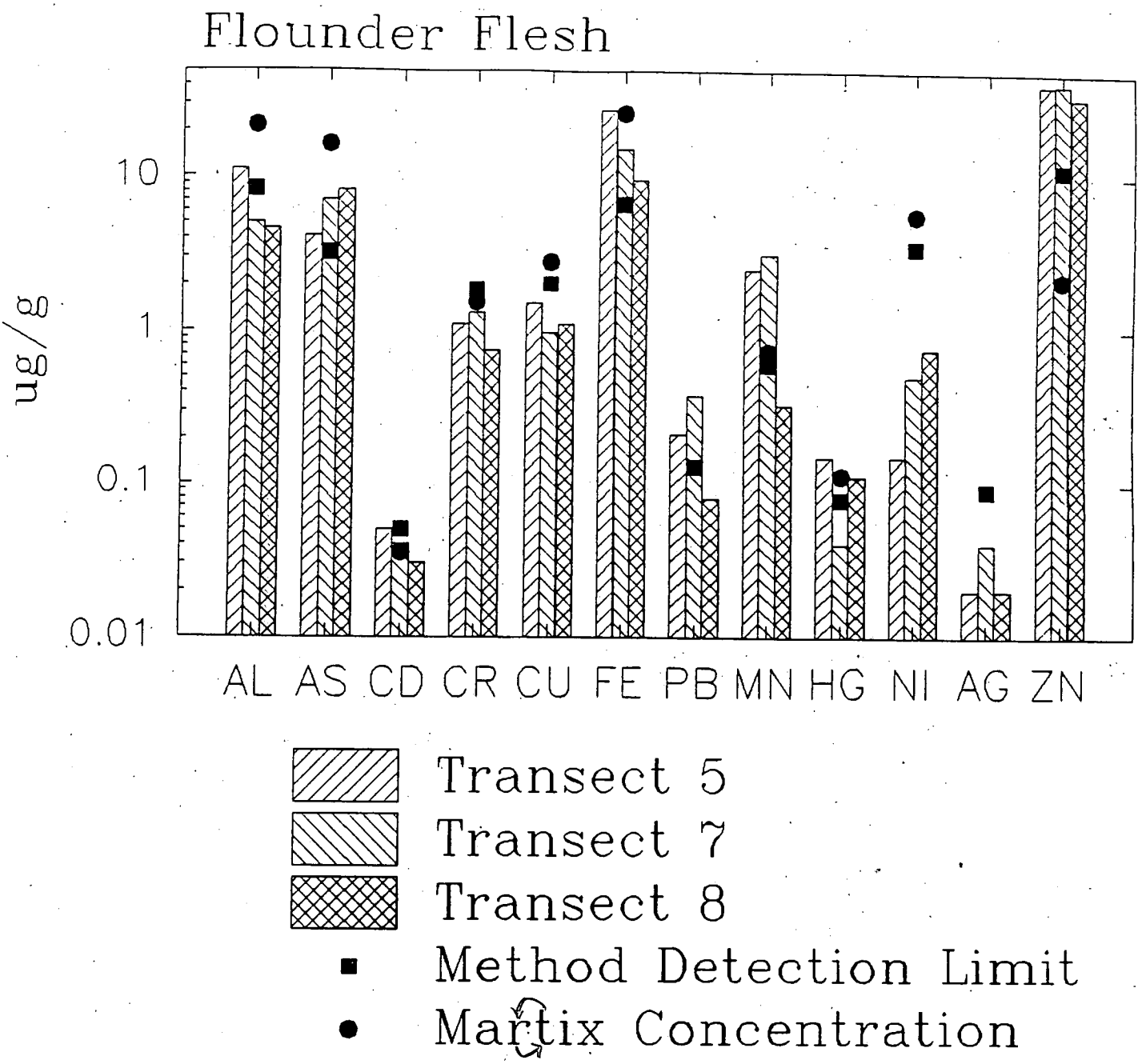
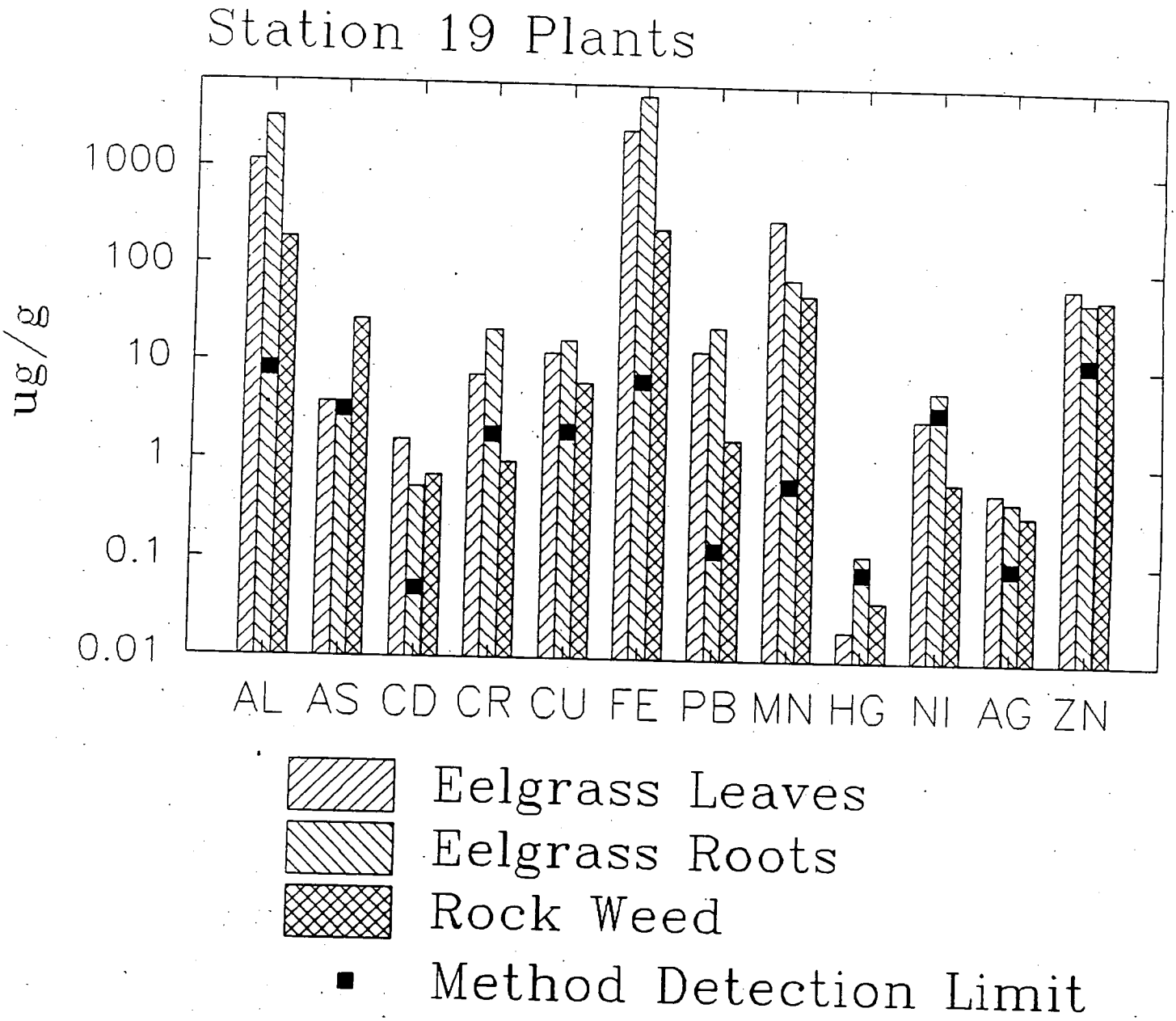


Figure 23


Station 19 Plants
ug/g
1000
100
10
1
0.1
0.01
AL AS CD CR CU FE PB MN HG NI AG ZN
Eelgrass Leaves
Eelgrass Roots
Rock Weed
Method Detection Limit

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APPENDIX A

RESULTS OF ANALYTICAL CHEMISTRY PERFORMANCE EVALUATION AND MDL DETERMINATIONS

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Environmental Research Laboratory
27 Tarzwell Drive
Narragansett, Rhode Island 02882

MEMORANDUM

Date: December 27, 1991

Subject: Review of the Organic Chemistry Performance Evaluation Data related to the Portsmouth Ecological Risk Assessment

From: Richard Pruell, Research Chemist
Environmental Research Laboratory, Narragansett (ERL-N)

To: Robert K. Johnston
Naval Oceans Systems Center, San Diego

As requested by the Navy, ERL-N is providing technical assistance related to the chemical analysis of marine samples for the Portsmouth Ecological Risk Assessment. As part of this effort ERL-N provided eight sediment and tissue samples to Ceimic Corporation. These samples were to be analyzed as a Performance Evaluation exercise to evaluate the capabilities of Ceimic for the analysis of marine samples.

On December 18, 1991 the last of the data for the unknown samples was provided to ERL-N and today (December 27) the MDL r sults for the organic measurements were delivered. This completes the Performance Evaluation work for the organic measurements. The following is our evaluation of the results produced from the analysis of these samples for organic compounds.

Sediments

Overall we were very favorably impressed with the organic analysis results produced for the three sediment samples. With few exceptions the data were very similar to the "certified" values for all three samples. This was especially impressive because the samples represented a wide range of concentrations including levels similar to the Method Detection Limits (MDLs) required in the QA plan.

Some problems were noted, however, with a few of the analyt s. In sample OR-1 three problems were noted with the PAH det rminations. Dibenz[a,h]anthracene was not detected but was present in a significant concentration, the results obtained for chrysene were high as were the C_2 and C_3 alkyl phenanthr nes anthracenes. The PCB and pesticide measurements also showed a f w problems in sampl OR-1. These included elevated values for HCB and some DDT series compounds. W feel that there may have also

been some problem with the separation and peak assignments for PCB congeners 105 and 153 because congener 153 was present in high concentrations but was not reported.

Sample OR-2 was only certified for PCBs. Results from this sample showed only one problem. The concentration listed for congener 170 was very high. We have found that this problem can occur because of a contaminant found in the octachloronaphthalene standard or due to phthalate contamination. The remainder of the results were excellent for this sample.

PAH determinations were requested on sample OR-3. Results for some of the analytes were somewhat low, others were very close to the certified values.

The MDLs for the PCBs and pesticides were generally at or below the Target Detection Limit of 0.5 ng/g. The only value notably higher was that of PCB congener 18. A few PAHs showed MDLs somewhat higher than the range of Target MDLs (1-5 ng/g). A significantly higher value (21 ng/g) was measured for the benzofluoranthenes. All in all, however, the measured MDLs for the sediments were in good agreement with the target values.

Tissues

A low bias was seen for the PCB and pesticide data in both the unknown sample and in the data generated for SRM 1974. This bias was fairly consistent and may be the result of a problem with standards concentrations or may be due to positive interferences with the internal standards. In addition, the benz[a]anthracene and chrysene concentrations reported were high for both the unknown and SRM 1974 samples.

With the exception of HCB and p,p'-DDE (2.41 and 2.01, respectively), all of the MDLs measured for the PCBs and pesticides wer very near or below the Target MDL of 0.5 ng/g. All of the PAH MDLs measured in the tissue samples were very near (less than or equal to 25 ng/g) or below the range of Target MDLs (10-20 ng/g).

Recommendations

Organics in Sediments

Although some problems were identified with a few analytes, overall the sediment analyses were highly successful. We would suggest that with some minor changes, the analysis of sediment samples for organic compounds could begin.

Organics in Tissues

Because of the significant offset seen in the PCB and pesticide results in the tissue samples, we feel that some additional work should be done before the initiation of tissue analyses. This should include a close look at standard solutions

and chromatographic interferences with the internal standards. We suggest that new data be submitted for SRM 1974 and the unknown. Additional samples of an unknown material could be provided if necessary.

A more detailed technical discussion of these results should be conducted. We would be glad to meet with Ceimic and Navy personnel to provide detailed information on the results of this exercise and to provide any technical assistance that may aid in the resolution of the remaining problems. When we receive MDL results for the metals a separate memo describing the findings of the trace metals exercise will be distributed.

c: Jim Sykman, NORTHDIV
Warren Boothman, ERL-N
William Nelson, ERL-N
Norm Rubinstein, ERL-N

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
ENVIRONMENTAL RESEARCH LABORATORY
SOUTH FERRY ROAD
NARRAGANSETT RHODE ISLAND 02882

MEMORANDUM

Date: January 14, 1992

Subject: Review of the Organic Chemistry Performance Evaluation Tissue Data related to the Portsmouth Ecological Risk Assessment

From: Richard Pruell, Research Chemist
Environmental Research Laboratory, Narragansett (ERL-N)

To: Robert K. Johnston
Naval Oceans Systems Center, San Diego

In our memo to you on December 27, 1991 we indicated that a significant bias was seen in the PCB and pesticide data submitted by Ceimic for the tissue samples analyzed as part of the Performance Evaluation exercise for the Portsmouth Study. At that time we suggested that additional tissue samples should be analyzed and new results submitted for review.

Another set of unknown samples were provided to Ceimic on December 30, 1991 and the results from the analyses of these samples were submitted to us on January 10, 1992. The memo that Ceimic provided with the new results also discussed some of the changes that they have made to address a problem previously identified with two of the PAH measurements in the original tissue unknowns and problems with a few other specific analytes in the sediment samples.

The new results indicate that the systematic bias noted in the results from the first series of tissue unknowns has now been eliminated. Results for most analytes are now within an acceptable range of the consensus values. However, the results for four of th PCB congeners (18, 44, 101 and 187) were lower than the consensus values and should be checked. In addition, congen r 8 was not reported although it is present in a detectable amount in the sample.

Recommendations

Except for the few analytes mention d above th newly submitted r sults are significantly bett r than thos produc d for the first tissue exercise. Based on this and th good PAH and MDL

results previously provided, we would recommend that the analysis of the tissue screening samples for organic compounds could proceed. However, some work should be done to investigate the reasons for the low values for the congeners listed above. In addition, and data generated for these compounds in the SRM samples analyzed with the screening samples should be looked at closely. Please call me at (401) 782-3091 if you have any questions.

c: Linda Dietz, NORTHDIV
Warren Boothman, ERL-N
William Nelson, ERL-N
Norm Rubinstein, ERL-N

PERFORMANCE EVALUATION RESULTS

FOR

PAHs, PESTICIDES AND PCBs

IN

MARINE TISSUES

CEIMIC CORPORATION

ORGANIC CHEMISTRY LABORATORY

DECEMBER 11, 1991

Revised: December 12, 1991

PROJECT OVERVIEW

One marine tissue sample was provided to Ceimic Corporation by U.S. EPA Environmental Research Laboratory at Narragansett as part of a performance evaluation effort for marine samples. The results of our organic analysis of the tissue sample OR-1 is included in this report.

ANALYTICAL METHOD

The tissue sample provided by EPA was processed in the same fashion as the Standard Reference Material (SRM) Mussel Tissue 1974, available from the U.S. National Institute of Standards and Technology.

All the results submitted were obtained by using the "Standard Operating Procedures for the Conduct of Marine Environmental Sampling and Analysis", ERL-N Contribution No. 1263, February 1991 with minor modifications.

The Internal Standards used for the analysis of PAH's were d_{10}-Phenanthene and d_{12}-Perylene spiked at about 25 ng/g wet weight. The external standard was d_{10}-Acenapthene spiked at 25 ng/g wet weight.

The Internal Standard used for the analysis of Pesticides was gamma-chlordene spiked at about 1.25 ng/g wet weight. For the analysis of PCB's the internal standards was OCN spiked at about 12.5 ng/g wet weight. The external standard used was DBC spiked at 25 ng/g wet weight.

RESULTS

A. Polycyclic Aromatic Hydrocarbons (PAHs)

Table 1

Concentrations of PAH's measured in SRM Mussel Tissue 1974.

Individual concentrations observed for each of four subsamples of SRM 1974 are reported along with Average, Standard Deviation (STDV), and Relative Standard Deviation (RSD). Average concentrations were compared to expected SRM 1974 values and a percent (%) recovery estimated. All PAH's concentrations are reported in ng/g on a Wet Weight basis.

Recoveries for the Internal Standard used are also reported.

Table 2

Recovery Study of PAHs in Laboratory Control Samples.

In one of the study (replicates I0738, I0739, I0740) the subsamples were spiked with all target PAHs at a concentration of 125 ng/g Wet Weight basis assuming a initial weight of 20 g of tissue. In the other study (replicates I0854, I0855) the subsamples were spiked with all target PAHs at a concentration of 12.5 ng/g (Target MDL level) Wet Weight basis assuming a initial weight of 20 g of tissue.

Individual concentrations observed for each of the subsamples are reported along with Average, Standard Deviation (STDV), and Relative Standard Deviation (RSD) for each of the two studies. Average concentrations were compared to spiked values and a percent (%) recovery estimated.

Recoveries for the Internal Standard used are also reported.

Table 3

A summary of PAHs concentrations measured in subsamples of EPA Marine Tissue OR-1.

Subsamples concentrations are reported along with the Average, Standard Deviation (STDV), and Relative Standard Deviation (RSD) for each analyte.

The results of the analysis of two method blanks are also reported in this table summary assuming that 15 g of wet tissue was extracted.

Recoveries for the Internal Standard used are also reported.

B. Polychlorinated Biphenyls and Chlorinated Pesticides.

Table 4

Concentrations of PCBs/Pesticides measured in SRM Mussel Tissue 1974 using a DB-5 capillary column.

Individual concentrations observed for each of four subsamples of SRM 1974 are reported along with Average, Standard Deviation (STDV), and Relative Standard Deviation (RSD). Average concentrations were compared to expected SRM 1974 values and a percent (%) recovery estimated. All PCBs/Pesticides concentrations are reported in ng/g on a Wet Weight basis.

Recoveries for the Internal Standard used are also reported.

Table 5

Concentrations of PCBs/Pesticides measured in SRM Mussel Tissue 1974 using a DB-17 capillary column.

Individual concentrations observed for each of four subsamples of SRM 1974 are reported along with Average, Standard Deviation (STDV), and Relative Standard Deviation (RSD). Average concentrations were compared to expected SRM 1974 values and a percent (%) recovery estimated. All PCBs/Pesticides concentrations are reported in ng/g on a Wet Weight basis.

Recoveries for the Internal Standard used are also reported.

Table 6

A summary of PCBs/Pesticides concentrations measured in subsamples of EPA Marine Tissue OR-1 using a DB-5 capillary column.

Concentrations are reported along with the Average, Standard Deviation (STDV), Relative Standard Deviation (RSD) and Bias Correction based on the Percent Recovery of SRM 1974 for each analyte. There were no target analytes detected in the method blanks above the target detection limits.

Recoveries for the Internal Standard used are also reported.

Table 7

A summary of PCBs/Pesticides concentrations measured in subsamples of EPA Marine Tissue OR-1 using a DB-17 capillary column.

Concentrations are reported along with the Average, Standard Deviation (STDV), Relative Standard Deviation (RSD) and Bias Correction based on the Percent Recovery of SRM 1974 for each analyte. There were no target analytes detected in the method blanks above the target detection limits.

Recoveries for the Internal Standard used are also reported.

PROBLEM AREAS

On the DB-5 capillary column the response of the internal standard used to quantitate PCB congeners was variable compared to the response of the internal standard used to quantitate pesticides. This observation is reflected by RSD of each PCB congener analyte reported from the DB-5. This was not observed on the DB-17 column.

The evaluation of the internal standard for the PCB congeners from the DB-5 column occurs during the end of the temperature program when the column temperature is approaching 300° C and column bleed is characteristically high. Variability in response may be attributed to difficulty of integration.

TABLE 1 RECOVERY STUDY OF PAHs IN SRM 1974 CEIMIC

SRM 1974 ng/g wet	10734	10735	10857	10856					
PAHs	1125-01	1125-02	1203-01	1203-02	AVERAGE	STDEV	RSD	TRUE VALUE	% RECOVERY
Anthracene+	1.25	1.19	1.67	1.84	1.49	0.32	21	0.75	198
Benz(a)anthracene*	7.85	5.98	9.75	11.1	8.67	2.23	26	4.6	188
Benzo(a)pyrene+	2.39	1.96	1.94	2.09	2.10	0.21	9.9	2.29	91
B nzo(e)pyrene*	13.8	11.1	13	13	12.73	1.15	9	10	127
Chrysene*	28.3	20.5	32.4	32.7	28.48	5.68	20	15.3	186
Dibenz(a,h)anthracene*+								0.35	
Fluoranthene	26.1	26.9	27.5	22.4	25.73	2.29	8.9	33.6	77
Fluorene*+	0.94	1.1	0.88	1.59	1.13	0.32	29	1.5	75
Perylene+	1.3	1.14	1.44	1.5	1.35	0.16	12	1.05	128
Phenanthrene	4.96	4.23	5.64	6.05	5.22	0.8	15	5.6	93
C1-phenanthrenes + anthracenes*	19.4	14.7	18.2	19.5	17.95	2.25	13	8.2	219
C2-phenanthrenes + anthracenes*	49	46.3	51.8	49.7	49.20	2.27	4.6	35.1	140
C3-phenanthrenes + anthracenes									
C4-phenanthrenes + anthracenes									
Pyrene	28.1	25.9	30.4	31.1	28.88	2.36	8.2	34.1	85
Sum of benzofluoranthenes*	13.9	11.14	15.1	15	13.79	1.85	13	11.3	122
Benzo(g,h,i)perylene	2.14	1.99	1.26	0.65	1.51	0.69	46	2.47	61
Indeno(1,2,3-cd)pyrene+	1.43	1.25	0.51	0.53	0.93	0.48	52	1.8	52
INTERNAL STD % RECOVERY									
Phenanthrene-d10	92	100	85	95	93	6	7		
Perylene-d12	42	61	25	34	41	15	38		

*Noncertified concentrations, + Concentrations under the target MDLs

MDL STUDY ON MARINE SEDIMENT PAHs ID:MS9 DECEMBER 1991

MDL Study SEDIMENT	ng/g							ng/g Dry W			ng/g Dry W
	11046	11047	11048	11050	11051	11052	11054				
PAHs	MDL01	MDL02	MDL03	MDL05	MDL06	MDL07	MDL09	AVERAGE	% REC	STDEV	MDL
Anthracene	24.91	24.15	25.17	22.44	23.05	22.32	25.5	23.9	96	1.3	4
Benz(a)anthracene	23.74	24.68	31.33	24.07	24.85	23.56	24.5	25.3	101	2.7	9
Benzo(a)pyrene	22.07	25.31	30.46	21.3	23.08	21.59	22.0	23.7	95	3.3	10
Benzo(e)pyrene	24.04	27.5	32.28	27	25.63	24.49	24.5	26.5	106	2.9	9
Chrysene	24.24	26.84	31.76	25.65	25.32	26.18	24.2	26.3	105	2.6	8
Dibenz(a,h)anthracene	18.84	20.51	26.44	21.72	21.7	18.89	18.9	21.0	84	2.7	9
Fluoranthene	26.24	26.98	32.2	26.89	27.14	29.15	25.5	27.7	111	2.3	7
Fluorene	24.18	22.82	22.3	22.92	21.1	24.96	24.6	23.3	93	1.4	4
Perylene	20.78	23.34	29.12	20.7	23.93	19.99	21.0	22.7	91	3.2	10
Phenanthrene	27.66	26.38	27.58	26.04	25.67	27.83	27.3	26.9	108	0.9	3
C1-phenanthrenes + anthracenes	27.7	26.16	30.24	26.65	25.45	27.02	27.5	27.2	109	1.5	5
C2-phenanthrenes + anthracenes	26.29	25.06	29.91	24.76	25.15	24.95	25.0	25.9	103	1.8	6
C3-phenanthrenes + anthracenes											
C4-phenanthrenes + anthracenes											
Pyrene	26.31	27.37	31.49	26.05	27.52	29.14	27.9	28.0	112	1.9	6
Sum of benzofluoranthenes	46.09	51.78	64.02	49.01	45.43	47.13	46.7	50.0	100	6.5	21
Benzo(g,h,i)perylene	18.84	23.7	28.57	22.1	22.53	19.41	18.5	21.9	88	3.6	11
Indeno(1,2,3-cd)pyrene	17.74	22.1	28.24	21.06	21.33	18.66	18.8	21.1	85	3.5	11
INTERNAL STD % RECOVERY											
Phenanthrene-d10*	69	75	68	82	74	67	74	73		5	
Perylene-d12											

* Based on d10-phenanthrene as internal standard for all analytes.

MDL STUDY ON MARINE TISSUE PAHs ID:MS9 DECEMBER 1991

MDL Study TISSUE	ng/g									ng/g				% REC	% REC	
	10998	10999	11000	11001	11017	11018	11019	11020	10997	Dry W				10987	10988	LCS % REC
PAHs	MDL01	MDL02	MDL03	MDL04	MDL05	MDL06	MDL07	MDL08	MDL09	AVERAGE	% REC	STDEV	MDL	LCS3	LCS4	AVERAGE
Anthracene	12.4	11.4	12.1	11.3	10.9	8.7	10.3	9.8	11.7	54.8	110	5.9	17	100	97	99
Benz(a)anthracene	9.2	8.2	5.9	7.1	6.8	5.5	6.6	6.1	8.3	35.3	71	6.3	18	63	59	61
Benzo(a)pyrene	10.8	10.2	10.8	10.0	10.5	11.5	11.3	10.2	10.8	53.3	107	2.5	7	100	96	98
Benzo(e)pyrene	11.2	10.8	11.7	14.5	12.7	11.5	10.3	10.9	10.3	57.7	115	6.8	20	126	110	118
Chrysene	10.0	9.8	6.4	7.7	8.4	6.3	7.6	6.7	9.9	40.4	81	7.6	22	71	69	70
Dibenz(a,h)anthracene	4.8	4.4	4.2	3.6	5.7	3.4	5.1	4.1	4.6	22.1	44	3.6	10	48	34	41
Fluoranthene	10.0	8.8	8.6	8.3	8.5	8.3	8.3	7.6	9.0	42.9	86	3.2	9	80	75	78
Fluoren	8.3	8.0	8.6	8.7	8.5	8.8	8.5	8.4	8.4	42.3	85	1.2	3	75	73	74
Perylene	10.1	10.2	10.6	9.4	10.2	9.7	11.1	10.0	10.2	50.8	102	2.4	7	94	94	94
Phenanthrene	9.2	8.7	9.0	9.1	9.1	9.0	8.6	8.2	8.9	44.3	89	1.6	5	82	78	80
C1-phenanthrenes + anthracenes	9.7	8.5	9.5	8.6	8.4	8.7	8.2	7.6	9.0	43.5	87	3.3	10	83	76	80
C2-phenanthrenes + anthracenes	9.8	8.9	8.9	8.4	8.8	9.1	8.4	8.0	8.8	43.9	88	2.6	7	84	78	81
C3-phenanthrenes + anthracenes																
C4-phenanthrenes + anthracenes																
Pyrene	10.1	9.2	8.6	8.7	8.6	8..27	8.5	7.8	9.1	44.1	88	3.4	10	80	75	78
Sum of benzofluoranthenes	22.4	21.4	22.4	21.3	24.6	30.66^	26.25^	24.6	20.5	112.2	112	7.9	25	132	122	127
Benzo(g,h,i)perylene	4.2	4.1	3.2	2.7	5.2	3.0	3.8	3.3	3.9	18.6	37	3.8	11	39	27	33
Indeno(1,2,3-cd)pyrene	4.8	4.1	4.1	3.4	6.0	3.6	5.1	4.1	4.4	22.0	44	4.0	12	51	35	43
INTERNAL STD % RECOVERY																
Phenanthrene-d10	88	90	81	78	81	88	94	80	100	87		7		99	99	99
Perylene-d12	49	55	20	35	39	17	33	24	64	37		16		34	32	33

^ VALUE DISCARDED

MDL STUDY ON MARINE SEDIMENT PESTICIDES/PCBs DB-5 DECEMBER 1991

MDL study SEDIMENT	DB-5								ng/g			ng/g	MATRIX	MATRIX	% REC	%REC	LCS % REC
PCB congeners	MDL01	MDL02	MDL03	MDL04	MDL06	MDL07	MDL08	MDL09	AVERAGE	% REC	STDEV	MDL	1218-1	1218-2	LCS1	LCS2	AVERAGE
8	8.47	8.46	8.12	11.18	9.11	7.02	10.05	8.78	0.89	74	0.13	0.38	2.57	3.63	34	51	43
18	36.93	40.24	39.23	54.82	40.15	34.71	46.83	45.28	4.50	352	0.64	1.93	25.76	36.99	44	58	51
28	6.75	8.85	8.07	11.32	9.12	7.03	7.78	8.45	0.90	70	0.14	0.43	0.96		34	49	42
44	5.67	6.19	6.69	8.77	8.42	6.33	6.56	7.28	0.75	58	0.11	0.33	1.94	3.90	27	40	34
52	6.8	8.72	8.24	10.92	10.39	7.61	8.52	8.89	0.94	73	0.14	0.41	3.10	5.90	34	57	46
66	3.3	5.53	3.61	4.33	3.76	3.52	4.53	3.82	0.42	34	0.07	0.22			26	35	31
101	4.87	5.31	5.39	6.36	5.68	5.13	6.83	5.66	0.59	47	0.07	0.19			38	54	46
105	3.73	3.92	4.02	4.57	4.09	3.91	4.16	4.14	0.42	34	0.02	0.07			31	40	36
118	5.73	6.21	6.25	7.4	6.75	5.98	7.22	6.57	0.67	54	0.06	0.18			43	57	50
128	3.25	3.48	3.65	3.94	3.49	3.34	4	3.4	0.36	30	0.03	0.08			27	34	31
138	7.04	5.89	5.59	6.74	6.64	5.75	6.2	8.6	0.71	55	0.10	0.29			43	56	50
153	3.64	3.53	3.98	4.08	4.2	3.52	4.36	3.62	0.40	32	0.03	0.10			26	35	31
170	3.69	4.51	4.27	4.24	4.18	3.87	4.23	3.71	0.42	34	0.03	0.09			46	36	41
180	5.31	5.51	5.67	5.98	5.49	5.47	6.13	6.05	0.58	48	0.03	0.09			52	57	55
187	5.27	5.39	5.67	6.08	5.48	4.94	6.22	5.56	0.57	46	0.04	0.13			41	53	47
195	5.99	6.07	6.83	6.35	5.84	5.65	6.26	5.49	0.61	51	0.04	0.13			47	56	52
206	2.95	2.97	3.09	3.02	2.9	2.69	2.9	2.81	0.29	24	0.01	0.04			27	35	31
209	8.02	7.23	7.68	8.09	6.45	6.13	5.58	7.1	0.71	59	0.09	0.27			54	72	63
OCN % recovery	140	144	180	142	106	175	134	145	144		2				160	135	148
Pesticides																	
Aldrin	9.09	11.63	10.02	11.83	13.86	9.97	8.43	11.12	1.10	179	0.17	0.52	16.61	16.34	179	194	187
alpha-chlordane	5.3	6.22	5.08	5.72	6.02	4.94	5.46	5.5	0.58	92	0.04	0.13			93	96	95
trans-nonachlor	4.41	2.85	3.56	2.48	2.85	4.68	4.57	3.24	0.36	60	0.09	0.26			81	86	84
Heptachlor	7.16	8.6	7.42	9	10.28	7.67	6.54	8.6	0.85	136	0.12	0.36	5.11	6.62	78	85	82
Heptachlor epoxide	4.78	5.44	4.95	5.78	5.43	4.76	5.2	5.36	0.53	87	0.04	0.11			86	86	86
Hexachlorobenzene*	32.25^	16.4	11.56	14.51	14.35	12.71	12.15	16.74	1.64	234	0.20	0.64	5.13	6.59	167	140	154
Lindane(gamma-BHC)	7.66	9.22	7.89	9.74	8.56	7.57	7.52	9.47	0.88	141	0.09	0.27	2.06		118	126	122
Mirex	10.66	9.67	9.09	8.84	13.17	9.99	9.8	9.58	1.00	168	0.14	0.41	9.78	7.48	176	157	167
o,p'-DDD	10.36	13.52	12.43	13.42	10.66	13.02	11.59	11.65	1.25	101	0.12	0.36			112	98	105
p,p'-DDD	11.55	13.5	12.6	13.85	14.23	13.67	13.21	14.62	1.35	112	0.10	0.29			108	92	100
o,p'-DDE*^	13.19	13.35	14.27	14.82	14.04	17.58	16.48	16.87	1.52	126	0.17	0.50			121	115	118
p,p'-DDE*	14.84	17.43	16.57	17.76	16.5	16.28	16	17.34	1.68	138	0.09	0.28			142	121	132
o,p'-DDT	12.19	12.38	11.83	12.49	13.5	12.66	11.95	13.32	1.26	105	0.06	0.18			105	97	101
p,p'-DDT	8.85	8.56	8.47	9.33	20.87^	7.48	7.68	12.96	1.08	75	0.18	0.58			108	92	100
gamma-chlor % recov.	54	54	61	62	40	59	58	51	55		1				52	64	58

^COMPOUND PRESENTS CHROMATOGRAPHIC CO-ELUTION

MDL STUDY ON MARINE TISSUE PESTICIDES/PCBs DB-5 GC-3 DECEMBER 1991

MDL study TISSUE	DB-5	GC-3							ng/g			ng/g	MATRIX	MATRIX	% REC	% REC	LCS % REC
PCB congeners	MDL01	MDL02	MDL03	MDL04	MDL05	MDL06	MDL07	MDL08	AVERAGE	% REC	STDEV	MDL	1218-3	1218-4	LCS3	LCS4	AVERAGE
8	12.38	12.85	13.2	12.99	12.78	14.17	13.55	13.22	2.63	110	0.11	0.32	0.49	1.06	67	130	99
18	10.19	10.45	10.4	10.83	10.4	11.64	11.02	10.7	2.14	89	0.09	0.28			125	127	126
28	8.53	8.78	8.92	8.9	8.47	9.4	8.61	8.35	1.75	73	0.07	0.20	4.93	2.95	110	110	110
44	5.68	5.9	5.99	6.42	6.88	7.3	7.49	6.89	1.31	55	0.13	0.40	2.1	1.28	70	88	79
52	12	13.38	13.32	11.74	13.28	13.79	12.13	13.23	2.57	107	0.15	0.46	5.66	4.05	94	126	110
66	7.79	8.12	7.88	7.81	7.82	9.2	8.03	7.75	1.61	67	0.10	0.29	4.52	3.57	60	78	69
101	8.99	10.08	9.19	9.93	9.61	10.37	9.76	8.78	1.92	80	0.11	0.33			98	125	112
105	6.64	6.68	6.32	6.61	6.22	7.5	6.58	6.23	1.32	55	0.08	0.25	3.29	2.81	90	122	106
118	13.84	13.73	12.94	12.66	12.94	14.93	13.32	12.34	2.67	111	0.16	0.49	7.74	7	114	130	122
128	6.57	6.55	5.97	6.09	5.82	6.85	6.08	5.75	1.24	52	0.08	0.24	2.09	1.45	56	68	62
138	17.39	17.84	18.31	17.72	17.12	18.63	17.21	15.54	3.49	146	0.19	0.56	13.58	9.93	116	136	126
153	12.14	11.89	14.46	12.24	11.69	12.71	11.58	10.84	2.44	102	0.21	0.64	19.51	17.93	114	135	125
170	5.49	4.89	5.55	5.05	4.36	6.28	4.51	4.9	1.03	43	0.12	0.37					
180	14.33	13.56	13.24	12.66	12.26	14.78	12.76	12.1	2.64	110	0.19	0.58	5.39	5.08	98	118	108
187	11.56	11.79	11.2	11.28	11.07	12.35	11.33	10.9	2.29	95	0.09	0.28	5.55	3.91	100	118	109
195	10.16	10.14	9.47	9.4	9.05	10.71	9.46	9.07	1.94	81	0.12	0.35			98	120	109
206	5.36	5.27	5.59	5.83	5.52	5.36	5.46	4.9	1.08	45	0.05	0.16			80	98	89
209	10.42	10.27	10.31	10.7	10.14	10.91	10.35	9.9	2.08	86	0.06	0.19			109	124	117
OCN % recovery	108	107	77	104	78	120	106	101	100		15						
Pesticides																	
Aldrin	5.52	5.84	5.69	5.29	5.19	5.81	5.54	5.22	1.10	92	0.05	0.15	1.28	0.61	111	111	111
alpha-chlordane	8.73	8.71	9.12	8.71	8.71	9.59	8.67	9.08	1.78	149	0.07	0.20	7.3	5.43	84	84	84
trans-nonachlor	11.69	11.36	12.18	11.73	12.8	12.47	12.11	12.13	2.41	201	0.09	0.28	7.76	7.22	85	85	85
Heptachlor	5.68	5.64	5.73	5.96	5.88	5.67	5.81	5.83	1.16	96	0.02	0.07	1.39	0.88	122	122	122
H ptachlor epoxide	3.82	4.12	4	3.6	3.7	3.96	4.08	3.42	0.77	64	0.05	0.15	3.07	1.56	86	76	81
Hexachlorobenzene	24.93	17.99	20.39	22.6	30.98	22.2	22.29	26.81	4.70	392	0.80	2.41	9.86	12.12	167	164	166
Lindane(gamma-BHC)	3.55	4.69	3.53	3.52	3.18	4.03	4.22	4.22	0.77	64	0.10	0.30	1.84	0.95	118	126	122
Mirex	6.04	6.29	4.99	5.58	5.81	4.7	4.51	5.3	1.08	90	0.13	0.38	2.87	1.84	176	157	167
o,p'-DDD	8.49	8.55	7.98	7.69	7.42	8.2	7.64	7.62	1.59	66	0.09	0.26	2.78	1.49	112	98	105
p,p'-DDD	18.01	17.24	17.13	16.06	15.65	19.1	16.02	15.7	3.37	141	0.25	0.74	12.92	10.22	108	92	100
o,p'-DDE	7.45	8.39	7.37	7.55	7.42	8.29	7.41	7.02	1.52	63	0.10	0.29	2.56	1.94	121	115	118
p,p'-DDE	24.54	25.39	26.61	27.44	31.88	33.13	32.27	30.29	5.79	241	0.67	2.01	20.58	20.7	142	121	132
o,p'-DDT	13.54	13.17	12.54	12.2	11.84	12.39	11.78	12.03	2.49	104	0.13	0.38	4.7	2.7	105	97	101
p,p'-DDT	6.5	5.99	5.86	5.79	5.81	6.39	5.75	6.07	1.20	50	0.06	0.17	12.92	10.22	50	49	50
gamma-chlor % recov.	99	104	72	101	73	106	105	98	95		1.40						

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MEMORANDUM

Date: February 10, 1992

Subject: Review of Trace Metals Analysis Performance Evaluation data for Portsmouth Ecological Risk Assessment

From: Warren S. Boothman

To: Robert K. Johnston
Naval Oceans Systems Center, San Diego

Performance evaluation sample analysis

In October 1991, four samples, consisting of two sediments and two biological tissues, were delivered to Ceimic Corporation for blind chemical analysis. Appropriate standard reference materials (SRM) were analyzed along the samples to provide for analytical quality assurance (QA). The results for the marine tissue samples were received December 6, 1991; results for the sediment samples subsequently arrived December 18, 1991. Method detection limits (MDL) were to be determined as part of the Performance Evaluation. Those results were delivered to ERLN on January 27, 1992, with an addendum received February 3, 1992. The results of both evaluations are discussed below.

Sediments

Sample TM-1 (Table 1) is a highly contaminated sediment which had been previously analyzed for total metals content by the U.S. EPA National Enforcement Center (NEIC) in Denver, CO. With the exception of mercury, the recoveries of all metals for which concentrations had been determined by NEIC are greater than 82%, with most within 90-110%. The range of recoveries of metals from the estuarine sediment SRM was similar to that found for TM-1. The mercury concentrations determined in TM-1 by Ceimic were quite low and variable, relative to NEIC's results. Similarly, while no reference value for tin was determined by NEIC in this sediment, the tin determinations were also variable (relative standard deviation of 12%).

Sample TM-2 is a relatively clean, coastal sediment analyzed at ERL-N. Recoveries are lower for this sample, relative to the ERLN results. However, the sediment was analyzed only once at ERLN, so the consistent recovery values for most of the metals, along with the good results obtained for the SRM which is a similar type

Table 1. Sediment sample results

	TM-1			TM-2			1646
		NEIC			ERLN		SRM
	Mean ± S.D.	value	Recovery	Mean ± S.D.	value	Recovery	Recovery
Al	54.2 ± 0.0	65.7	82%	67.2 ± 0.3	51.7	130.0%	89.1%
As	13.4 ± 0.2	14.0	96	13.0 ± 0.5	12.4	104.8	91.4
Cd	25.0 ± 0.2	23	109	0.48 ±0.07	0.63	76.2	86.5
Cr	1650 ± 22	1750	94	66.5 ± 3.2	94.8	70.1	90.0
Cu	2685 ± 43	2720	99	25.2 ± 1.1	33.0	76.4	81.6
Fe	36.3 ± 0.2	39.1	93	34.7 ± 0.6	48.8	71.0	94.0
Pb	450 ± 3	360	125	21.6 ± 1.7	28.0	77.3	98.9
Mn	454 ± 5	520	87	1565 ± 35	2233	70.1	87.2
Hg	0.62 ± 0.25	1.99	31	nd	nd		N/A
Ni	183 ± 0	169	108	32.5 ± 1.2	49.4	65.7	85.0
Ag	18.0 ± 0.3	16	113		n d		N/A
Sn	129 ± 15			3.4 ± 1.6	2.3	147.8	N/A
Zn	1389 ± 15	1380	101	105 ±0.94	174	60.5	105.7

Concentrations in µg/g dry except for Al and Fe in mg/g dry.

of sediment matrix, suggest that the ERLN values might just as easily be somewhat high as the Ceimic values low. Again, however, the tin values obtained were both high, relative to the ERLN data, and quite variable (± 47%), indicating a problem with this determination.

The Ceimic report does recognize the elevated tin concentrations in the procedural blank, so it is reasonable to believe their results for these analyses will improve. It should also be noted that the most recent NOAA laboratory intercomparison for analysis of trace metals in marine sediments and tissues states that "reliable analysis of marine samples ... for tin is apparently possible by only a small number of experienced laboratories." The low mercury recoveries remain a problem. Because of the sealed vessels employed, the anticipated use of microwave-heated digestions should improve Ceimic's ability to digest sediments without loss of mercury from the sample; however, sample sizes may not be increased sufficiently to greatly improve the method detection limits. The problems noted in the report regarding sample storage may prove to be key to improving the apparent recovery of this element.

Tissues

Overall the results (Table 2) for the tissue samples TM-1, a bivalve homogenate containing moderate concentrations of trace metals, and TM-2, a reference fish tissue presenting low metals concentrations, are very similar to those for the sediment samples, i.e. mercury recovery was low (<60% for both the SRM and TM-2) and the tin results variable (again, there were no established reference values for tin in these tissues). In addition, recovery

Table 2. Tissue sample results

	TM-1 Mussel			TM-2 Dogfish		
	Mean ± S.D.	Reference value	Recovery	Mean ± S.D.	Reference value	Recovery
Al	375 ± 22	270	139%	11.1 ± 0.4		
As	8.1 ± 0.5			12.4 ± 0.5	17.7	70%
Cd	1.81 ± 0.03	2.08	87	0.081 ± 0.000	0.086	94
Cr	2.40 ± 0.09	2.15	112	3.35 ± 0.17	3.60	93
Cu	11.8 ± 0.3	12.8	92	4.82 ± 0.07	5.22	92
Fe	472 ± 8.5	450	105	63.7 ± 0.7	63.6	100
Pb	0.71 ± 0.25	9.11	74	0.32 ± 0.01	0.40	79
Mn	26.9 ± 0.8	26.8	100	1.71 ± 0.34	1.32	130
Hg	0.106 ± 0.008			0.466 ± 0.004	0.798	58
Ni	6.50 ± 0.26	6.84	95	1.19 ± 0.09	1.20	99
Ag	0.23 ± 0.00			0.15 ± 0.00		
Sn	1.44 ± 0.32			1.98 ± 0.13		
Zn	120 ± 2.5	135	89	17.4 ± 0.05	21.3	82

Concentrations in μg/g dry except for Al and Fe in mg/g dry.

of lead was only 75-80% for either of the tissue samples, slightly lower than the 86.5% recovery from the SRM. While this is not as severe a problem as with tin or mercury, it would appear to warrant some further method development.

The Ceimic report also concerns itself with apparently low (66%) recovery of aluminum from the SRM. Recent studies have indicated that low recovery of aluminum results from incomplete dissolution of clay mineral particles found within the organism tissues. The apparently high recovery of aluminum from sample TM-1 relative to that determined by ERLN, compared to the low SRM recovery, probably reflects somewhat more efficient dissolution of the mineral aluminum by Ceimic's method than that used at ERLN. Since this material does not constitute an environmentally significant contamination source, however, such low recoveries may be acceptable.

Method detection limits

With the exception of mercury and silver in tissues, all of the method detection limits obtained by Ceimic Corporation (Table 3) are substantially higher than the target MDL's specified in the project QA/QC plan. However, this may be due to the target values, in many cases, being unnecessarily low. When compared with detection limits reported by National Status and Trends (NS&T) laboratories, it can be seen that many target MDL's are below the NS&T limits. Therefore, the limits obtained by Ceimic may also be evaluated by comparison with the NS&T detection limits and with minimum trace metal concentrations likely to be encountered in typical marine sample matrices. For most elements in both the

Table 3. Method detection limits

Analyte	Target MDL	Matrix	MDL Obtained	NS&T MDLs 1988 - 1989	"Typical" minimum concentrations
Al	0.18	Tissue	8.17		26.
		Sediment	10.7		32000.
As	0.08	Tissue	3.2	2.0 - 6.6	14.0
		Sediment	0.52	0.09 - 2.1	3.5
Cd	0.005	Tissue	0.050	0.073 - 0.63	0.035
		Sediment	0.13	0.02 - 0.09	0.15
Cr	0.01-0.7	Tissue	1.85	0.16 - 0.4	1.4
		Sediment	1.65	0.35 - 6.0	41.
Cu	0.01-0.7	Tissue	2.01	0.46 - 9.9	2.8
		Sediment	4.55	0.09 - 2.4	6.7
Fe	0.5	Tissue	6.6		15.2
		Sediment	7.6		18000.
Pb	0.01-0.7	Tissue	0.13	0.56 - 0.66	0.37
		Sediment	0.81	0.2 - 2.2	2.7
Mn	0.01	Tissue	0.60		0.73
		Sediment	0.97		266.
Hg	0.125	Tissue	0.079	0.036	0.064
		Sediment	0.448	0.004 - 0.010	
Ni	0.01-0.7	Tissue	0.82	0.63 - 0.83	0.72
		Sediment	2.76	0.07 - 2.1	16.
Ag	0.01-0.7	Tissue	0.091	0.033 - 0.04	
		Sediment	0.15	0.01 - 0.07	< 0.02
Sn	0.075	Tissue	3.43	0.14	0.93
		Sediment	0.81	0.058 - 0.2	0.95
Zn	0.003	Tissue	6.7	6.3 - 17	21.
		Sediment	1.1	1.0 - 3.3	62.

sediment and tissue matrices, the MDL's obtained by Ceimic are within the range of detection limits reported by the NS&T labs and are less than or similar to the minimum concentrations determined in typical samples. In some cases, e.g. major elements in sediments, the limits are 1-3 orders of magnitude lower than the *minimum* concentrations likely to be encountered. The results in general seem quite acceptable; however, problems do exist for specific elements and matrices.

As seen with the analysis of the unknown samples discussed previously, tin and mercury continue to present analytical difficulties. MDL's determined for these two elements exceed the NS&T detection limits by factors of 4-100. The limits also exceed the "typical" minimum concentrations, although the limits for mercury in tissues and tin in sediments are very similar to likely minimum concentrations. The mercury results are somewhat encouraging, however, as the high MDL is the result of very low analytical values in two of the seven subsamples; if those two results were thrown out, the resulting variability would be greatly decreased and the calculated MDL (0.087 $\mu g/g$) would be acceptable. The results for analysis of tin in tissues are also highly variable (and thus the high MDL) with no clear prospect of improving. Clearly this is a problem which must be addressed.

Several minor questions exist for the MDL's determined for the other elements. The limits determined for silver in both tissues and sediments are slightly higher than the NS&T limits. Because we have little data on how low concentrations in "real-life" samples can be expected, these values are most likely satisfactory. In a similar vein, the limits obtained for chromium in tissues and copper in sediments are somewhat higher than those reported by the NS&T labs, but are comparable to the minimum concentrations likely to be encountered. These limits may thus be considered marginally acceptable.

R commendations

Ceimic's results for the trace metals performance evaluation were, for the most part, very good for both sediment and tissue analyses. Only a few problems exist, and these have been noted already by Ceimic in its reports. The results do indicate that Ceimic is, in general, capable of performing these analyses reliably and that, with a slight amount of further method refinement, their analytical results can be accepted with reasonable certainty.

The specific problems that should be addressed include mercury and tin determinations in both sediment and tissue samples and determination of lead in tissues. The most serious problem appears to be the analysis of mercury. However, the problems of low recovery and high detection limits are related, so that if the intermittent recovery problems can be eliminated, the detection limit problem is also likely to be alleviated. While the problems with tin are also being addressed by Ceimic, there does not appear to be any immediate resolution likely; further efforts will be needed to produce reliable data for this element.

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Performance Evaluation Results for Trace Metals in Marine Sediments

Ceimic Corporation

Inorganic Chemistry Laboratory

December 18, 1991

Project Overview

Two marine sediment samples were provided Ceimic Corporation by the U.S EPA Environmental Research Laboratory at Narragansett as part of a performance evaluation effort for marine samples. The results of our trace metal analyses of the two sediment samples TM-1 and TM-2, are included in this report. Also included as part of our effort is a brief summary of the procedures employed and instrumentation used.

Analytical Method

All sediment samples provided by EPA were processed in the same fashion as the Standard Reference Material (SRM) Estuarine Sediment 1646, available from the U.S. National Institute of Standards and Technology. A "wet weight" aliquot of individual TM-1 and TM-2 sediment samples and SRM subsamples was used in the wet digestion procedure, and a seperate aliquot was freeze dried and used to determine dry sediment weight. Dry sediment weights used in the digestion procedure (Table 1), were calculated from the Dry to Wet Weight Ratio determined from non-freeze dried and freeze dried sediment samples.

Table 1.

Dry sediment weights used in the wet digestion procedures. Dry sediment weight for all samples was calculated from the dry/wet weight ratios of seperate sediment aliquots that were freeze dried.

Sample Id	Subsample	Dry Sediment Weight, g	Dry/Wet Ratio x 100
SRM 1646	1001	0.418	no change
	1002	0.291	"
	1003	0.278	"
TM-1	S-102	0.144	24.9
	S-103	0.161	"
TM-2	S-201	0.141	35.8
	S-202	0.182	"
	S-203	0.237	"

Total sediment digestions were carried out on a hot plate using teflon digestion vessels with teflon watchglasses. Sediment samples were rinsed

into the teflon vessels subsequent to wet weight determinations using 6ml of concentrated Baker Instra-Analyzed HNO_3. Samples were allowed to cold digest overnight, and following this period 3ml of redistilled concentrated HF was added. Following HF additions watchglasses were place atop each beaker and heat was applied. After about 36 hours, watchglasses were removed and samples were brought to near dryness. At this point an additional 10ml of HF, and 5ml of concentrated HNO_3 was added to each vessel. Watchglasses were put in place and sediment samples were gently refluxed. As a final digestion step, samples were brought to near dryness and 10ml of 1N HNO_3 was added to each vessel along with 4ml of a 30% hydrogen peroxide solution (Aldrich Chemical Co.). Samples were again refluxed at moderate heat and were brought to near dryness. All samples were brought to a final 50ml volume in the digestion beaker using a 1N HNO_3 solution. Once samples were brought to a final 50ml volume in the digestion beaker, they were allowed to equilibrate for about four hours before the filtration step. Digested samples were filtered through acid-cleaned 0.4 um pore size Nucleopore Membranes and the filtrate dispensed into acid-cleaned High Density Polyethylene (HDPE) storage bottles. Procedural blank samples were treated in the same fashion as sediment samples and were carried through the entire digestion and analytical procedures. All digestion procedures were carried out in a Class-100 laminar flow clean bench with effluent air emptying into an evacuation hood.

Because there were certain problems with the analysis of tissues that were perhaps related to loss of Hg in the storage vessels, a filtered10ml of aliquot of each sediment sample was immediately dispensed into individual Hg reaction vessels and each solution was fixed with a concentrated potassium permanganate solution. In our previous note on Hg levels in marine tissue, it was mentioned that the immediate preparation of the Hg sample might improve recovery of this element.

With the exception of Hg, all metal samples were analyzed by Graphite Furnace Atomic Absorption Spectrophotometry or Inductively Coupled Plasma Spectroscopy, using either the Perkin Elemer Model 5100 AAS, equipped with Zeeman Background Correction and AS-60 Autosampler, or using the Perkin Elmer Model P40 ICP. Hg determinations were made using a cold vapor technique with the Coleman Model 50B Mercury Analyzer. The instrumental method used for each trace element is provided in Table 2.

Results

Concentrations observed in the procedural blank sample is reported in Table 2. In most instances blank levels were not significantly different from instrumental background and in these cases the blanks were labeled not detectable. In instances where blanks were significant, sample concentrations were corrected by procedural blank levels.

The concentration of trace metal found in subsamples of Estuarine Sediment SRM 1646 are reported in Table 3, and the average metal concentrations observed in this study are compared to expected SRM levels.

Trace metal concentrations found for EPA TM-1 and TM-2 Sediment Evaluation samples are reported in Tables 4 and 5, respectively.

Problem Areas and Remedies

A significant effort was made to get these sediment samples into solution using the wet digestion technique described. The classic "hot plate" technique is thorough judging from SRM recoveries, but the time involved in the total HF digestion of sediment samples was considerable. In this same regard, the longer a procedural period necessary for digestion the greater the potential for metal contamination. To aleviate the time element involved in the digestion of sediment samples a CEM Model 2000 Microwave Digestion System was purchased and will be used for future sediment digestions. The use of this system will provide for a more controlled digestion environment coupled with a shorter digestion period. We feel that the positive aspects of the microwave system will permit a greater sample output with the potential of increasing metal recoveries.

Mercury levels in the Estuarine Sediment SRM 1646 are the same as concentrations found in the Oyster Tissue SRM 1566a (ie. 0.063 ug/g), but because a much smaller amount of material was used in the sediment digestion (about 0.2 to 0.4 g, dry sediment weight) as compared with the tissue digestion (about 2.5 g, dry tissue weight) the recovery of Hg in the sediment SRM could not be evaluated. Although it was known at the outset that SRM 1646 Hg could not be recovered, it was hoped that the other sediments would provide sufficient Hg levels for accurate measurement. This did not turn out to be the case, and in part the amount of material used in the digestion was not sufficient. The use of a microwave technique might allow digestion of greater amounts of sediment, thus permit the evaluation of Hg in SRM and other sediments in future samples.

It was interesting to note that Al recoveries in sediment SRM were greater than found for tissue samples. The recovery of sediment Al was on the order of 89%, compared to a 66% recovery of Al in Tissue SRM. It may be that the halide concentration involved in the sediment technique may have prevented or slowed aluminum-oxide formation thus allowing for greater recovery. It should also be noted that sediment Al measurements were made shortly after the samples had been filtered (within four hours). For subsequent tissue and sediment samples Al measurements will be made at the earliest possible moment after the samples are filtered.

As a final note on Al, tissue samples were re-analyzed by a Neutron Activation technique as a check on tissue recoveries. The results of the Neutron Activation Analysis were virtually the same as those previously reported for SRM and TM-1 tissue samples. There was about a factor of two difference in the low levels of Al observed by ICP and NAA in TM-2 Tissues, the higher values were observed using the NAA technique (a copy of this data will be furnished upon request).

Observed tin levels were variable regardless of the sample analyzed, with Relative Standard Deviations ranging from around16 to 57%, for all the sediment suites evaluated. The procedural blank was on the order of 13 ug/l, which accounted for roughly half of the signals observed for SRM and TM-2 sediment samples. Because different digestion vessels were used in sediment and tissue digestions (ie. teflon versus quartz for sediment and tissue digestions, respectively), it was not possible to determine whether the digestion vessels were factors in contaminating the samples. However, it does appear that tin is being added to samples regardless of digestion vessel type, and this points to the concentrated reagents that are employed in these procedures. We will continue our efforts to establish the cause of elevated tin in our procedural blank samples.

Table 2.

A summary of trace metal concentrations measured in procedural blanks. Procedural Blanks were processed in the same fashion as samples, and carried through the entire sediment digestion procedure. Where warranted samples were corrected by procedural blanks. Concentrations are reported as ug/l.

Analyte	Procedural Blank Concentrations, ug/l S-001	Instrumental Method
Aluminum	Nd	ICP
Arsenic	1.8	GFAAS
Cadmium	Nd	GFAAS
Chromium	Nd	ICP
Copper	Nd	ICP
Iron	Nd	ICP
Lead	Nd	GFAAS
Manganese	Nd	ICP
Mercury	Nd	CV
Nickel	Nd	ICP
Silver	Nd	GFAAS
Tin	13.0	GFAAS
Zinc	Nd	ICP

Nd indicates not detected

ICP = Inductively Coupled Plasma
GFAAS = Graphite Furnace Atomic Absorption Spectrophotometry
CV = Cold Vapor

TABLE2 RECOVERY STUDY OF PAHs IN LCSs TISSUES CEIMIC

LAB CONTROL SPIKES	10738	10739	10740					10854	10855				
PAHs ng/g	125	125	125	AVER	STDV	RSD	% REC	12.5	12.5	AVER	STDV	RSD	% REC
Anthracene	4.4	4.39	4.4	4.40	0	0	88	4.5	4.76	4.63	0.18	4	93
Benz(a)anthracene	4.59	4.33	4.49	4.47	0.1	3	89	7.38	8.67	8.03	0.91	11	161
Benzo(a)pyrene	5.77	5.46	5.38	5.54	0.2	4	111	6.94	6.42	6.68	0.37	6	134
Benzo(e)pyrene	6.14	5.58	5.65	5.79	0.3	5	116	8.2	7.55	7.88	0.46	6	158
Chrysene	7.08	7.41	6.96	7.15	0.2	3	143	9.16	11	10.1	1.30	13	202
Dibenz(a,h)anthracene	4.83	3.87	4.25	4.32	0.5	11	86	5.43	3.44	4.44	1.41	32	89
Fluoranthene	4.73	4.45	4.51	4.56	0.1	3	91	5.42	5.3	5.36	0.08	2	107
Fluorene	4.4	4.39	4.42	4.40	0	0	88	3.84	3.6	3.72	0.17	5	74
Perylene	5.36	5.3	5.04	5.23	0.2	3	105	5.4	5.26	5.33	0.10	2	107
Phenanthrene	4.59	4.33	4.49	4.47	0.1	3	89	5.08	5.15	5.12	0.05	1	102
C1-phenanthrenes + anthracenes	4.76	4.4	4.5	4.55	0.2	4	91	5.23	5.38	5.31	0.11	2	106
C2-phenanthrenes + anthracenes	4.94	4.59	4.7	4.74	0.2	4	95	5.2	5.12	5.16	0.06	1	103
C3-phenanthrenes + anthracenes													
C4-phenanthrenes + anthracenes													
Pyrene	4.86	4.48	4.61	4.65	0.2	4	93	5.57	5.5	5.54	0.05	1	111
Sum of benzofluoranthenes	12.6	12.3	12.1	12.3	0.3	2	123	7.7	7.56	7.63	0.10	1	76
Benzo(g,h,i)perylene	4.83	3.87	4.25	4.32	0.5	11	86	6.26	3.1	4.68	2.23	48	94
Indeno(1,2,3-cd)pyrene	4.96	3.77	4.28	4.34	0.6	14	87	6.92	3.82	5.37	2.19	41	107
INTERNAL STD % RECOVERY													
Phenanthrene-d10	116	120	111	116	5	4		93	135	114	30	26	
Perylene-d12	78	69	74	74	5	6		55	58	57	2	4	

TABLE 3 ANALYSIS OF ORGANISM OR-1 (910566-08) PAHS

Organism OR-1 ng/g	Blank01	Blank02	08A	08B	08C				
PAHs	10852	10853	10858	10859	10860	AVERAGE	STDV	RSD	DRY WEIGHT
Anthracene			0.94	0.97	0.89	0.93	0.04	4	6.7
Benz(a)anthracene			5.81	6.07	6.26	6.05	0.23	4	43.2
Benzo(a)pyrene			1.68	1.95	1.72	1.78	0.15	8	12.7
Benzo(e)pyrene			6.13	6.07	6.88	6.36	0.45	7	45.4
Chrysene	0.37		17.5	17.8	18.2	17.83	0.35	2	127.4
Dibenz(a,h)anthracene									
Fluoranthene	1.39	0.71	10.8	11.6	12.1	11.50	0.66	6	82.1
Fluorene									
Perylene									
Phenanthrene	1.56	1.29	2.67	2.89	2.68	2.75	0.12	5	19.6
C1-phenanthrenes + anthracenes	0.19	0.19	3.37	4.24	4.24	3.95	0.5	13	28.2
C2-phenanthrenes + anthracenes	0.15		4.94	5.78	5.94	5.55	0.54	10	39.7
C3-phenanthrenes + anthracenes			2.41	2.6	2.6	2.54	0.11	4	18.1
C4-phenanthrenes + anthracenes									
Pyrene	2.01	2.17	9.78	18.6	9.63	12.67	5.14	41	90.5
Sum of benzofluoranthenes	0.66		10	9.95	11.3	10.42	0.77	7	74.4
Benzo(g,h,i)perylene									
Indeno(1,2,3-cd)pyrene									
INTERNAL STD % RECOVERY									
Phenanthrene-d10	98	103	95	76	83	85	10	11	
Perylene-d12	49	42	18	13	16	16	3	16	

TABLE 4. RECOVERY STUDY OF PESTICIDES/PCBs IN SRM 1974 TISSUE DB-5 COLUMN CEIMIC

SRM 1974 ng/g	DB-5								
PCB congeners	ACTUAL	1125-01	1125-02	1203-01	1203-02	AVERAGE	STDV	RSD	% RECOVERY
8									
18	3	1.48	0.92	0.78	0.85	1.01	0.32	32	34
28	7.6	5.58	3.68	3.17	3.4	3.96	1.10	28	52
44	8	3.17	1.94	1.78	1.89	2.20	0.65	30	27
52	12	4.89	3.07	2.64	2.86	3.37	1.03	31	28
66	13.6	8.6	5.01	5.42	5.75	6.20	1.63	26	46
101	13	5.74	3.29	3.6	3.86	4.12	1.10	27	32
105	5.6	2.82	1.45	2.24	2.25	2.19	0.56	26	39
118	13.6	6.65	3.52	4.29	4.51	4.74	1.34	28	35
128	1.9	1.01	0.44	0.6	0.62	0.67	0.24	36	35
138	14	6	3.04	3.75	3.71	4.13	1.29	31	29
153	18	6.09	3.28	3.54	4.06	4.24	1.27	30	24
170									
180	1.7	1.07	0.46	0.61	0.62	0.69	0.26	38	41
187	3.7	1.86	0.86	1.1	1.15	1.24	0.43	35	34
195									
206									
209									
OCN % recovery		119	66^	130	123	124	6	4	
Pesticides									
Aldrin									
alpha-chlordane	3.2	1.08	1.08	1	0.97	1.03	0.06	5	32
trans-nonachlor	2.6	0.89	0.91	0.76	0.74	0.83	0.09	11	32
Heptachlor									
Heptachlor epoxide									
Hexachlorobenzene									
Lindane(gamma-BHC)									
Mirex									
_,p'-DDD	2.5	0.86	1.01	0.63	0.58	0.77	0.20	26	31
p,p'-DDD	8.4	3.94	3.74	3.21	2.94	3.46	0.46	13	41
o,p'-DDE*	0.72	2.19	2.19	1.64	1.64	1.92	0.32	17	266
p,p'-DDE	5.9	3.76	3.63	2.98	2.95	3.33	0.42	13	56
o,p'-DDT	0.4	0.15	0.24	0.13	0.16	0.17	0.05	28	43
p,p'-DDT	0.3	0.26	0.18	0.05	0.06	0.14	0.10	73	46
gamma-chlor % recov.		203	213	184	184	196	14	7	

*COMPOUND SHOWS CO-ELUTION ON THIS COLUMN ^ESTIMATED RECOVERY

TABLE 5 RECOVERY STUDY OF PESTICIDES/PCBs IN SRM 1974 TISSUE DB-17 COLUMN

SRM 1974 ng/g	DB-17								
PCB congeners	ACTUAL	1125-01	1125-02	1203-01	1203-02	AVERAGE	STDV	RSD	% RECOVERY
8									
18*	3	2.74	3.19	2.42	2.01	2.59	0.50	19	86
28	7.6	7.69	8.85	5.45	4.64	6.66	1.95	29	88
44	8	2.99	3.41	2.29	1.9	2.65	0.68	26	33
52	12	4.55	5.16	3.39	2.83	3.98	1.06	27	33
66	13.6	5.32	5.94	4.08	3.44	4.70	1.14	24	35
101	13	4.43	4.86	5.39	3.95	4.66	0.61	13	36
105	5.6	2.67	2.82	2.17	1.96	2.41	0.41	17	43
118*	13.6	8.81	9.42	6.9	5.98	7.78	1.61	21	57
128	1.9	0.94	0.97	0.93	0.86	0.93	0.05	5	49
138	14	4.58	4.78	3.92	3.51	4.20	0.59	14	30
153	18	5.29	5.55	4.42	3.81	4.77	0.80	17	26
170									
180	1.7	0.84	0.84	0.96	0.92	0.89	0.06	7	52
187*	3.7	5.21^	5.46^	1.43	1.24	1.34	0.13	10	36
195									
206									
209									
OCN % recovery		134	114	121	147	134	18	14	
Pesticides									
Aldrin	3.2	3.54	3.39	2.4	2.59	2.98	0.57	19	93
alpha-chlordane	2.6	1.22	1.18	1.06	1.1	1.14	0.07	6	44
trans-nonachlor									
Heptachlor									
Heptachlor epoxide									
Hexachlorobenzene									
Lindane(gamma-BHC)									
Mirex									
o,p'-DDD*	2.5	8.81	9.42	6.9	5.98	7.78	1.61	21	311
p,p'-DDD	8.4	1.97	1.8	1.77	1.8	1.84	0.09	5	22
o,p'-DDE	0.72	0.49	0.51	0.21	0.22	0.36	0.16	46	50
p,p'-DDE	5.9	3.33	3.79	2.05	2.37	2.89	0.81	28	49
o,p'-DDT	0.4	0.25	0.23	0.49	0.52	0.37	0.15	41	93
p,p'-DDT*	0.3	5.21^	5.46^	0.21	0.26	0.24	0.04	15	78
gamma-chlor % recov.		217	217	212	193	203	13	7	

* ^ COMPOUND MAY SHOW CO-ELUTION ON THIS COLUMN

TABLE6 ANALYSIS OF ORGANISM OR-1 (910566-08) PESTICIDES/PCBs DB-5 COLUMN

Organism OR-1 ng/g	DB-5							SRM 1974	BIAS
PCB congeners	566-08A	566-08B	566-08C	AVERAGE	STDV	RSD	DRY WEIGHT	% RECOVERY	CORRECTION
8	0.26	0.5	0.28	0.35	0.13	38	2.5		2.5
18	0.18	0.45	0.22	0.28	0.15	51	2.0	34	6.0
28	0.46	0.91	0.58	0.65	0.23	36	4.64	52	8.9
44	0.34	0.71	0.43	0.49	0.19	39	3.5	27	12.8
52	0.51	1.07	0.65	0.74	0.29	39	5.3	28	18.9
66	0.61	1.17	0.6	0.79	0.33	41	5.7	46	12.4
101	1.74	3.52	2.29	2.52	0.91	36	18.0	32	56.7
105	0.64	1.34	0.94	0.97	0.35	36	7.0	39	17.8
118	1.15	2.13	1.59	1.62	0.49	30	11.6	35	33.3
128	0.29	0.46	0.38	0.38	0.09	23	2.7	35	7.7
138	2.28	4.02	3.07	3.12	0.87	28	22.3	29	75.7
153	3.36	6.55	4.44	4.78	1.62	34	34.2	24	145.0
170	0.16	0.24	0.18	0.19	0.04	22	1.4		1.4
180	0.42	0.68	0.56	0.55	0.13	24	4.0	41	9.7
187	1.06	1.9	1.42	1.46	0.42	29	10.4	34	31.1
195									
206									
209	0.26	0.73	0.37	0.45	0.25	54	3.2		3.2
OCN % recovery	160	96	122	126	32	26			
Pesticides									
Aldrin									
alpha-chlordane	0.56	0.68	0.64	0.63	0.1	10	4.5	32	13.9
trans-nonachlor	0.59	0.75	0.71	0.68	0.08	12	4.9	32	15.4
Heptachlor	0.04	0.08	0.02	0.05	0.03	65	0.33		0.33
Heptachlor epoxide	0.02	0.02	0.02	0.02	0.00	0	0.14		0.14
Hexachlorobenzene	0.22	0.27	0.29	0.26	0.04	14	1.9		1.86
Lindane(gamma-BHC)	0.01	0.01	0.01	0.01	0.00	0	0.07		0.07
Mirex	0.36	0.38	0.41	0.38	0.03	7	2.7		2.74
o,p'-DDD	0.08	0.08	0.12	0.09	0.02	25	0.67	31	2.2
p,p'-DDD	3.36	3.42	3.75	3.51	0.21	6	25.1	41	60.9
o,p'-DDE								266	
p,p'-DDE	3.88	4.12	4.31	4.10	0.22	5	29.3	56	51.9
o,p'-DDT	0.41	0.55	0.57	0.51	0.09	17	3.6	43	8.6
p,p'-DDT	0.01	0.03	0.02	0.02	0.01	50	0.14	46	0.31
gamma-chlor % recov.	124	118	108	117	8	7			

TABLE 7 ANALYSIS OF ORGANISM OR-1 (910566-08) PESTICIDES/PCBs DB-17 COLUMN

Organism OR-1 ng	DB-17							SRM 1974	BIAS
PCB congeners	566-08A	566-08B	566-08C	AVERAGE	STDV	RSD	DRY WEIGHT	% RECOVERY	CORRECTION
8	0.5	0.51	0.44	0.48	0.04	8	3.5		3.5
18*	0.77	0.67	0.65	0.70	0.06	9	5.0	86	5.8
28	1.15	1.14	1	1.10	0.08	8	7.8	88	8.9
44	0.94	0.93	0.83	0.90	0.06	7	6.4	33	19.4
52	1.93	1.94	1.78	1.88	0.09	5	13.5	33	40.5
66	1.3	1.29	1.09	1.23	0.12	10	8.8	35	25.4
101	2.12	2.16	2.02	2.10	0.07	3	15.0	36	41.9
105	0.96	0.93	0.84	0.91	0.06	7	6.5	43	15.1
118*	4.05	4.14	3.88	4.02	0.13	3	28.7	57	50.3
128	0.57	0.48	0.45	0.50	0.06	12	3.6	49	7.3
138	2.73	2.82	2.64	2.73	0.09	3	19.5	30	65.0
153	3.93	4.08	3.8	3.94	0.14	4	28.1	26	106.2
170	0.23	0.23	0.27	0.24	0.02	9	1.7		1.7
180	0.86	0.73	0.68	0.76	0.09	12	5.4	52	10.3
187*	1.52	1.5	1.42	1.48	0.05	4	10.6	36	29.4
195	0.12	0.13	0.14	0.13	0.01	8	0.93		0.9
206	0.39	0.39	0.27	0.35	0.07	20	2.5		2.5
209	0.41	0.5	0.37	0.43	0.07	16	3.0		3.0
OCN % recovery	150	134	148	144	9	6			
Pesticides									
Aldrin	0.17	0.2	0.18	0.18	0.02	8	1.3		1.3
alpha-chlordane	1.13	1.28	1.11	1.17	0.09	8	8.4	93	9.0
trans-nonachlor	1.33	1.41	1.38	1.37	0.04	3	9.8	44	22.3
Heptachlor	0.41	0.42	0.42	0.42	0.01	1	3.0		3.0
Heptachlor epoxide	0.13	0.14	0.14	0.14	0.01	4	1.0		1.0
Hexachlorobenzene	0.14	4.81	0.18	1.71	2.68	157	12.2		12.2
Lindane(gamma-BHC)	0.77	0.67	0.65	0.70	0.06	9	5.0		5.0
Mirex	0.16	0.15	0.1	0.14	0.03	24	1.0		1.0
o,p'-DDD*	4.05	4.14	3.88	4.02	0.13	3	28.7	311	9.2
p,p'-DDD	1.58	1.64	1.61	1.61	0.03	2	11.5	22	52.6
o,p'-DDE	0.31	0.33	0.31	0.32	0.01	4	2.3	50	4.5
p,p'-DDE	3.35	3.66	3.63	3.55	0.17	5	25.3	49	51.8
o,p'-DDT	1.01	0.91	0.83	0.92	0.09	10	6.5	93	7.0
p,p'-DDT*								78	
gamma-chlor % recov.	187	154	160	167	18	11			

* COMPOUND SHOWS CO-ELUTION ON THIS COLUMN

CEIMIC
CORPORATION
"Analytical Chemistry for Environmental Management"

PERFORMANCE EVALUATION RESULTS

FOR

PAHs, PESTICIDES AND PCBs

IN

MARINE SEDIMENT

CEIMIC CORPORATION

ORGANIC CHEMISTRY LABORATORY

DECEMBER 12, 1991

10 Dean Knauss Drive, Narragansett, R.I. 02882 • (401) 782-8900 • FAX (401) 782-8905

PROJECT OVERVIEW

Three (3) marine sediment samples were provided to Ceimic Corporation by U.S. EPA Environmental Research Laboratory at Narragansett as part of a performance evaluation effort for marine samples. The results of our organic analysis of the sediment samples OR-1, OR-2 and OR-3 are included in this report.

ANALYTICAL METHOD

The sediment sample provided by EPA were processed in the same fashion as the Standard Reference Material (SRM) Marine Sediment 1941, available from the U.S. National Institute of Standards and Technology.

All the results submitted were obtained by using the "Standard Operating Procedures for the Conduct of Marine Environmental Sampling and Analysis", ERL-N Contribution No. 1263, February 1991 with minor modifications.

The Internal Standards used for the analysis of PAH's were d_{10}-Phenanthene and d_{12}-Perylene spiked in the range of 270 - 700 at ng/g wet weight. The external standard was d_{10}-Acenapthene spiked the same level as the internal standard.

The Internal Standard used for the analysis of Pesticides was gamma-chlordene spiked in the range of 1.3 - 3.3 ng/g wet weight. For the analysis of PCB's the internal standards was OCN spiked in the range of 13 - 33 ng/g wet weight. The external standard used was DBC spiked at the same levels as OCN.

RESULTS

A. Polycyclic Aromatic Hydrocarbons (PAHs)

Table 1

Concentrations of PAH's measured in SRM Marine Sediment 1941.

Individual concentrations observed for each of five (5) subsamples of SRM 1941 are reported along with Average, Standard Deviation (STDV), and Relative Standard Deviation (RSD). Average concentrations were compared to expected SRM 1941 values and a percent (%) recovery estimated. All PAH's concentrations are reported in ng/g on a Wet Weight basis.

Recoveries for the Internal Standard used are also reported.

Table 2

Recovery Study of PAHs in Laboratory Control Samples.

In this study the subsamples were spiked with all target PAHs at a concentration of 170 ng/g Wet Weight basis assuming a initial weight of 15 g of sediment.

Individual concentrations observed for each of the subsamples are reported along with Average, Standard Deviation (STDV), and Relative Standard Deviation (RSD) for each of the two studies. Average concentrations were compared to spiked values and a percent (%) recovery estimated.

Recoveries for the Internal Standard used are also reported.

Table 3

A summary of PAHs concentrations measured in subsamples of EPA Marine Sediment OR-1.

Subsamples concentrations are reported along with the Average, Standard Deviation (STDV), and Relative Standard Deviation (RSD) for each analyte.

The results of the analysis of two (2) method blanks provided numbers at below the target MDL.

Recoveries for the Internal Standard used are also reported.

Table 4

A summary of PAHs concentrations measured in subsamples of EPA marine Sediment OR-2.

Subsamples concentrations are reported along with the Average, Standard Deviation (STDV), and Relative Standard Deviation (RSD) for each analyte.

The results of the analysis of two (2) method blanks provided numbers at below the target MDL.

Recoveries for the Internal Standard used are also reported.

Table 5

A summary of PAHs concentrations measured in subsamples of EPA marine Sediment OR-3.

Subsamples concentrations are reported along with the Average, Standard Deviation (STDV), and Relative Standard Deviation (RSD) for each analyte.

The results of the analysis of two (2) method blanks provided numbers at below the target MDL.

Recoveries for the Internal Standard used are also reported.

B. **Polychlorinated Biphenyls and Chlorinated Pesticides.**

Table 7

Concentrations of PCBs/Pesticides measured in SRM Marine Sediment 1941 using a DB-5 capillary column.

Individual concentrations observed for each of three (3) subsamples of SRM 1941 are reported along with Average, Standard Deviation (STDV), and Relative Standard Deviation (RSD). Average concentrations were compared to expected SRM 1941 values and a percent (%) recovery estimated. All PCBs/Pesticides concentrations are reported in ng/g on a Wet Weight basis.

Recoveries for the Internal Standard used are also reported.

Table 8

A summary of PCBs/Pesticides concentrations measured in subsamples of EPA Marine Sediment OR-1 using a DB-5 capillary column.

Concentrations are reported along with the Average, Standard Deviation (STDV), Relative Standard Deviation (RSD) and Bias Correction based on the Percent Recovery of SRM 1974 for each analyte. There were no target analytes detected in the method blanks above the target detection limits.

Recoveries for the Internal Standard used are also reported.

Table 9

A summary of PCBs/Pesticides concentrations measured in subsamples of EPA Marine Sediment OR-2 using a DB-5 capillary column.

Concentrations are reported along with the Average, Standard Deviation (STDV), Relative Standard Deviation (RSD) and Bias Correction based on the Percent Recovery of SRM 1974 for each analyte. There were no target analytes detected in the method blanks above the target detection limits.

Recoveries for the Internal Standard used are also reported.

Table 10

A summary of PCBs/Pesticides concentrations measured in subsamples of EPA Marine Sediment OR-3 using a DB-5 capillary column.

Concentrations are reported along with the Average, Standard Deviation (STDV), Relative Standard Deviation (RSD) and Bias Correction based on the Percent Recovery of SRM 1974 for each analyte. There were no target analytes detected in the method blanks above the target detection limits.

Recoveries for the Internal Standard used are also reported.

PROBLEM AREAS

On the DB-5 capillary column the response of the internal standard used to quantitate PCB congeners was variable compared to the response of the internal standard used to quantitate pesticides. This observation is reflected by RSD of each PCB congener analyte reported from the DB-5.

The evaluation of the internal standard for the PCB congeners from the DB-5 column occurs during the end of the temperature program when the column temperature is approaching 300° C and column bleed is characteristically high. Variability in response may be attributed to difficulty of integration.

A retention time shift of about + 0.30 min. occurred in the gas chromotography of the F1 fractions of replicated EPA marine sediment samples OR1 - A, B and C. F2 fractions did not exhibit a retention time shift. The external standard DBC shifted in the F1 fraction of OR1 along with the internal standards demonstrating a matrix effect. No explanation has been determined

TABLE 1 RECOVERY STUDY OF PAHs IN SRM 1941 CEIMC

SRM 1941 ng/g	50	50	50	10	10	Wet W			Dry W	
PAHs	1121-01	1121-02	1121-03	1121-04	1121-05	AVERAGE	STDV	RSD	ACTUAL	% RECOVERY
Anthrac n	127	140	138	129	225	152	41	27	202	78
Benz(a)anthracene	592	563	495	583	608	568	44	8	550	108
Benzo(a)pyrene	507	550	535	560	612	553	39	7	670	86
Benzo(e)pyrene*	629	635	644	743	752	681	61	9	573	124
Chrysene*	846	760	683	933	862	817	97	12	702	121
Dibenz(a,h)anthracene										
Fluoranthene	752	925	975	941	892	897	86	10	1220	77
Fluorene*	52	49	46	50	74	54	11	21	104	54
Perylene	306	339	318	391	454	362	61	17	422	89
Phenanthrene	346	390	377	391	440	389	34	9	577	70
C1-phenanthrenes + anthracenes	386	452	450	452	516	451	46	10	660	71
C2-phenanthrenes + anthracenes	407	467	484	502	544	481	50	10	472	106
C3-phenanthrenes + anthracenes										
C4-phenanthrenes + anthracenes										
Pyrene	664	826	854	856	819	804	80	10	1080	78
Sum of benzofluoranthenes	1782	1695	1644	2125	2066	1862	219	12	1721	113
Benzo(g,h,i)perylene	451	401	433	604	667	511	117	23	516	103
Indeno(1,2,3-cd)pyrene	406	367	396	593	664	485	134	28	569	89
INTERNAL STD % RECOVERIES										
Ph nanthrene-d10	84	94	88	94^	67	83	12	14		
Perylene-d12	37	57	64	51^	41	50	13	26		

*Noncertified concentrations ^Estimated recovery

MDL STUDY ON MARINE SEDIMENT PAHs ID:MS9 DECEMBER 1991

MDL Study SEDIMENT	ng/g							ng/g			ng/g
	11046	11047	11048	11050	11051	11052	11054	Dry W			Dry W
PAHs	MDL01	MDL02	MDL03	MDL05	MDL06	MDL07	MDL09	AVERAGE	% REC	STDEV	MDL
Anthracene	24.91	24.15	25.17	22.44	23.05	22.32	25.5	23.9	96	1.3	4
Benz(a)anthracene	23.74	24.68	31.33	24.07	24.85	23.56	24.5	25.3	101	2.7	9
Benzo(a)pyrene	22.07	25.31	30.46	21.3	23.08	21.59	22.0	23.7	95	3.3	10
Benzo(e)pyrene	24.04	27.5	32.28	27	25.63	24.49	24.5	26.5	106	2.9	9
Chrysene	24.24	26.84	31.76	25.65	25.32	26.18	24.2	26.3	105	2.6	8
Dibenz(a,h)anthracene	18.84	20.51	26.44	21.72	21.7	18.89	18.9	21.0	84	2.7	9
Fluoranthene	26.24	26.98	32.2	26.89	27.14	29.15	25.5	27.7	111	2.3	7
Fluorene	24.18	22.82	22.3	22.92	21.1	24.96	24.6	23.3	93	1.4	4
Perylene	20.78	23.34	29.12	20.7	23.93	19.99	21.0	22.7	91	3.2	10
Phenanthrene	27.66	26.38	27.58	26.04	25.67	27.83	27.3	26.9	108	0.9	3
C1-phenanthrenes + anthracenes	27.7	26.16	30.24	26.65	25.45	27.02	27.5	27.2	109	1.5	5
C2-phenanthrenes + anthracenes	26.29	25.06	29.91	24.76	25.15	24.95	25.0	25.9	103	1.8	6
C3-phenanthrenes + anthracenes											
C4-phenanthrenes + anthracenes											
Pyren	26.31	27.37	31.49	26.05	27.52	29.14	27.9	28.0	112	1.9	6
Sum of benzofluoranthenes	46.09	51.78	64.02	49.01	45.43	47.13	46.7	50.0	100	6.5	21
Benzo(g,h,i)perylene	18.84	23.7	28.57	22.1	22.53	19.41	18.5	21.9	88	3.6	11
Indeno(1,2,3-cd)pyrene	17.74	22.1	28.24	21.06	21.33	18.66	18.8	21.1	85	3.5	11
INTERNAL STD % RECOVERY											
Phenanthrene-d10*	69	75	68	82	74	67	74	73		5	
Perylene-d12											

* Based on d10-phenanthrene as internal standard for all analytes.

MDL STUDY ON MARINE TISSUE PAHs ID:MS9 DECEMBER 1991

MDL Study TISSUE	ng/g									ng/g				% REC	% REC	
	10998	10999	11000	11001	11017	11018	11019	11020	10997	Dry W				10987	10988	LCS % REC
PAHs	MDL01	MDL02	MDL03	MDL04	MDL05	MDL06	MDL07	MDL08	MDL09	AVERAGE	% REC	STDEV	MDL	LCS3	LCS4	AVERAGE
Anthracene	12.4	11.4	12.1	11.3	10.9	8.7	10.3	9.8	11.7	54.8	110	5.9	17	100	97	99
Benz(a)anthracene	9.2	8.2	5.9	7.1	6.8	5.5	6.6	6.1	8.3	35.3	71	6.3	18	63	59	61
Benzo(a)pyrene	10.8	10.2	10.8	10.0	10.5	11.5	11.3	10.2	10.8	53.3	107	2.5	7	100	96	98
Benzo(e)pyrene	11.2	10.8	11.7	14.5	12.7	11.5	10.3	10.9	10.3	57.7	115	6.8	20	126	110	118
Chrysene	10.0	9.8	6.4	7.7	8.4	6.3	7.6	6.7	9.9	40.4	81	7.6	22	71	69	70
Dibenz(a,h)anthracene	4.8	4.4	4.2	3.6	5.7	3.4	5.1	4.1	4.6	22.1	44	3.6	10	48	34	41
Fluoranthene	10.0	8.8	8.6	8.3	8.5	8.3	8.3	7.6	9.0	42.9	86	3.2	9	80	75	78
Fluorene	8.3	8.0	8.6	8.7	8.5	8.8	8.5	8.4	8.4	42.3	85	1.2	3	75	73	74
Peryl ne	10.1	10.2	10.6	9.4	10.2	9.7	11.1	10.0	10.2	50.8	102	2.4	7	94	94	94
Phenanthrene	9.2	8.7	9.0	9.1	9.1	9.0	8.6	8.2	8.9	44.3	89	1.6	5	82	78	80
C1-phenanthrenes + anthracenes	9.7	8.5	9.5	8.6	8.4	8.7	8.2	7.6	9.0	43.5	87	3.3	10	83	76	80
C2-phenanthrenes + anthracenes	9.8	8.9	8.9	8.4	8.8	9.1	8.4	8.0	8.8	43.9	88	2.6	7	84	78	81
C3-phenanthrenes + anthracenes																
C4-phenanthrenes + anthracenes																
Pyrene	10.1	9.2	8.6	8.7	8.6	8..27	8.5	7.8	9.1	44.1	88	3.4	10	80	75	78
Sum of benzofluoranthenes	22.4	21.4	22.4	21.3	24.6	30.66^	26.25^	24.6	20.5	112.2	112	7.9	25	132	122	127
Benzo(g,h,i)perylene	4.2	4.1	3.2	2.7	5.2	3.0	3.8	3.3	3.9	18.6	37	3.8	11	39	27	33
Indeno(1,2,3-cd)pyrene	4.8	4.1	4.1	3.4	6.0	3.6	5.1	4.1	4.4	22.0	44	4.0	12	51	35	43
INTERNAL STD % RECOVERY																
Phenanthrene-d10	88	90	81	78	81	88	94	80	100	87		7		99	99	99
Perylene-d12	49	55	20	35	39	17	33	24	64	37		16		34	32	33

^ VALUE DISCARDED

MDL STUDY ON MARINE SEDIMENT PESTICIDES/PCBs DB-5 DECEMBER 1991

MDL study SEDIMENT	DB-5								ng/g			ng/g	MATRIX	MATRIX	% REC	%REC	LCS % REC
PCB congeners	MDL01	MDL02	MDL03	MDL04	MDL06	MDL07	MDL08	MDL09	AVERAGE	% REC	STDEV	MDL	1218-1	1218-2	LCS1	LCS2	AVERAGE
8	8.47	8.46	8.12	11.18	9.11	7.02	10.05	8.78	0.89	74	0.13	0.38	2.57	3.63	34	51	43
18	36.93	40.24	39.23	54.82	40.15	34.71	46.83	45.28	4.50	352	0.64	1.93	25.76	36.99	44	58	51
28	6.75	8.85	8.07	11.32	9.12	7.03	7.78	8.45	0.90	70	0.14	0.43	0.96		34	49	42
44	5.67	6.19	6.69	8.77	8.42	6.33	6.56	7.28	0.75	58	0.11	0.33	1.94	3.90	27	40	34
52	6.8	8.72	8.24	10.92	10.39	7.61	8.52	8.89	0.94	73	0.14	0.41	3.10	5.90	34	57	46
66	3.3	5.53	3.61	4.33	3.76	3.52	4.53	3.82	0.42	34	0.07	0.22			26	35	31
101	4.87	5.31	5.39	6.36	5.68	5.13	6.83	5.66	0.59	47	0.07	0.19			38	54	46
105	3.73	3.92	4.02	4.57	4.09	3.91	4.16	4.14	0.42	34	0.02	0.07			31	40	36
118	5.73	6.21	6.25	7.4	6.75	5.98	7.22	6.57	0.67	54	0.06	0.18			43	57	50
128	3.25	3.48	3.65	3.94	3.49	3.34	4	3.4	0.36	30	0.03	0.08			27	34	31
138	7.04	5.89	5.59	6.74	6.64	5.75	6.2	8.6	0.71	55	0.10	0.29			43	56	50
153	3.64	3.53	3.98	4.08	4.2	3.52	4.36	3.62	0.40	32	0.03	0.10			26	35	31
170	3.69	4.51	4.27	4.24	4.18	3.87	4.23	3.71	0.42	34	0.03	0.09			46	36	41
180	5.31	5.51	5.67	5.98	5.49	5.47	6.13	6.05	0.58	48	0.03	0.09			52	57	55
187	5.27	5.39	5.67	6.08	5.48	4.94	6.22	5.56	0.57	46	0.04	0.13			41	53	47
195	5.99	6.07	6.83	6.35	5.84	5.65	6.26	5.49	0.61	51	0.04	0.13			47	56	52
206	2.95	2.97	3.09	3.02	2.9	2.69	2.9	2.81	0.29	24	0.01	0.04			27	35	31
209	8.02	7.23	7.68	8.09	6.45	6.13	5.58	7.1	0.71	59	0.09	0.27			54	72	63
OCN % recovery	140	144	180	142	106	175	134	145	144		2				160	135	148
Pesticides																	
Aldrin	9.09	11.63	10.02	11.83	13.86	9.97	8.43	11.12	1.10	179	0.17	0.52	16.61	16.34	179	194	187
alpha-chlordane	5.3	6.22	5.08	5.72	6.02	4.94	5.46	5.5	0.58	92	0.04	0.13			93	96	95
trans-nonachlor	4.41	2.85	3.56	2.48	2.85	4.68	4.57	3.24	0.36	60	0.09	0.26			81	86	84
Heptachlor	7.16	8.6	7.42	9	10.28	7.67	6.54	8.6	0.85	136	0.12	0.36	5.11	6.62	78	85	82
Heptachlor epoxide	4.78	5.44	4.95	5.78	5.43	4.76	5.2	5.36	0.53	87	0.04	0.11			86	86	86
Hexachlorobenzene*	32.25^	16.4	11.56	14.51	14.35	12.71	12.15	16.74	1.64	234	0.20	0.64	5.13	6.59	167	140	154
Lindane(gamma-BHC)	7.66	9.22	7.89	9.74	8.56	7.57	7.52	9.47	0.88	141	0.09	0.27	2.06		118	126	122
Mirex	10.66	9.67	9.09	8.84	13.17	9.99	9.8	9.58	1.00	168	0.14	0.41	9.78	7.48	176	157	167
o,p'-DDD	10.36	13.52	12.43	13.42	10.66	13.02	11.59	11.65	1.25	101	0.12	0.36			112	98	105
p,p'-DDD	11.55	13.5	12.6	13.85	14.23	13.67	13.21	14.62	1.35	112	0.10	0.29			108	92	100
o,p'-DDE*^	13.19	13.35	14.27	14.82	14.04	17.58	16.48	16.87	1.52	126	0.17	0.50			121	115	118
p,p'-DDE*	14.84	17.43	16.57	17.76	16.5	16.28	16	17.34	1.68	138	0.09	0.28			142	121	132
o,p'-DDT	12.19	12.38	11.83	12.49	13.5	12.66	11.95	13.32	1.26	105	0.06	0.18			105	97	101
p,p'-DDT	8.85	8.56	8.47	9.33	20.87^	7.48	7.68	12.96	1.08	75	0.18	0.58			108	92	100
gamma-chlor % recov.	54	54	61	62	40	59	58	51	55		1				52	64	58

^COMPOUND PRESENTS CHROMATOGRAPHIC CO-ELUTION

MDL STUDY ON MARINE TISSUE PESTICIDES/PCBs DB-5 GC-3 DECEMBER 1991

MDL study TISSUE	DB-5	GC-3							ng/g			ng/g	MATRIX	MATRIX	% REC	% REC	LCS % REC
PCB congeners	MDL01	MDL02	MDL03	MDL04	MDL05	MDL06	MDL07	MDL08	AVERAGE	% REC	STDEV	MDL	1218-3	1218-4	LCS3	LCS4	AVERAGE
8	12.38	12.85	13.2	12.99	12.78	14.17	13.55	13.22	2.63	110	0.11	0.32	0.49	1.06	67	130	99
18	10.19	10.45	10.4	10.83	10.4	11.64	11.02	10.7	2.14	89	0.09	0.28			125	127	126
28	8.53	8.78	8.92	8.9	8.47	9.4	8.61	8.35	1.75	73	0.07	0.20	4.93	2.95	110	110	110
44	5.68	5.9	5.99	6.42	6.88	7.3	7.49	6.89	1.31	55	0.13	0.40	2.1	1.28	70	88	79
52	12	13.38	13.32	11.74	13.28	13.79	12.13	13.23	2.57	107	0.15	0.46	5.66	4.05	94	126	110
66	7.79	8.12	7.88	7.81	7.82	9.2	8.03	7.75	1.61	67	0.10	0.29	4.52	3.57	60	78	69
101	8.99	10.08	9.19	9.93	9.61	10.37	9.76	8.78	1.92	80	0.11	0.33			98	125	112
105	6.64	6.68	6.32	6.61	6.22	7.5	6.58	6.23	1.32	55	0.08	0.25	3.29	2.81	90	122	106
118	13.84	13.73	12.94	12.66	12.94	14.93	13.32	12.34	2.67	111	0.16	0.49	7.74	7	114	130	122
128	6.57	6.55	5.97	6.09	5.82	6.85	6.08	5.75	1.24	52	0.08	0.24	2.09	1.45	56	68	62
138	17.39	17.84	18.31	17.72	17.12	18.63	17.21	15.54	3.49	146	0.19	0.56	13.58	9.93	116	136	126
153	12.14	11.89	14.46	12.24	11.69	12.71	11.58	10.84	2.44	102	0.21	0.64	19.51	17.93	114	135	125
170	5.49	4.89	5.55	5.05	4.36	6.28	4.51	4.9	1.03	43	0.12	0.37					
180	14.33	13.56	13.24	12.66	12.26	14.78	12.76	12.1	2.64	110	0.19	0.58	5.39	5.08	98	118	108
187	11.56	11.79	11.2	11.28	11.07	12.35	11.33	10.9	2.29	95	0.09	0.28	5.55	3.91	100	118	109
195	10.16	10.14	9.47	9.4	9.05	10.71	9.46	9.07	1.94	81	0.12	0.35			98	120	109
206	5.36	5.27	5.59	5.83	5.52	5.36	5.46	4.9	1.08	45	0.05	0.16			80	98	89
209	10.42	10.27	10.31	10.7	10.14	10.91	10.35	9.9	2.08	86	0.06	0.19			109	124	117
OCN % recovery	108	107	77	104	78	120	106	101	100		15						
Pesticides																	
Aldrin	5.52	5.84	5.69	5.29	5.19	5.81	5.54	5.22	1.10	92	0.05	0.15	1.28	0.61	111	111	111
alpha-chlordane	8.73	8.71	9.12	8.71	8.71	9.59	8.67	9.08	1.78	149	0.07	0.20	7.3	5.43	84	84	84
trans-n nachlor	11.69	11.36	12.18	11.73	12.8	12.47	12.11	12.13	2.41	201	0.09	0.28	7.76	7.22	85	85	85
Heptachlor	5.68	5.64	5.73	5.96	5.88	5.67	5.81	5.83	1.16	96	0.02	0.07	1.39	0.88	122	122	122
Heptachlor poxide	3.82	4.12	4	3.6	3.7	3.96	4.08	3.42	0.77	64	0.05	0.15	3.07	1.56	86	76	81
Hexachlorobenzene	24.93	17.99	20.39	22.6	30.98	22.2	22.29	26.81	4.70	392	0.80	2.41	9.86	12.12	167	164	166
Lindane(gamma-BHC)	3.55	4.69	3.53	3.52	3.18	4.03	4.22	4.22	0.77	64	0.10	0.30	1.84	0.95	118	126	122
Mirex	6.04	6.29	4.99	5.58	5.81	4.7	4.51	5.3	1.08	90	0.13	0.38	2.87	1.84	176	157	167
o,p'-DDD	8.49	8.55	7.98	7.69	7.42	8.2	7.64	7.62	1.59	66	0.09	0.26	2.78	1.49	112	98	105
p,p'-DDD	18.01	17.24	17.13	16.06	15.65	19.1	16.02	15.7	3.37	141	0.25	0.74	12.92	10.22	108	92	100
o,p'-DDE	7.45	8.39	7.37	7.55	7.42	8.29	7.41	7.02	1.52	63	0.10	0.29	2.56	1.94	121	115	118
p,p'-DDE	24.54	25.39	26.61	27.44	31.88	33.13	32.27	30.29	5.79	241	0.67	2.01	20.58	20.7	142	121	132
o,p'-DDT	13.54	13.17	12.54	12.2	11.84	12.39	11.78	12.03	2.49	104	0.13	0.38	4.7	2.7	105	97	101
p,p'-DDT	6.5	5.99	5.86	5.79	5.81	6.39	5.75	6.07	1.20	50	0.06	0.17	12.92	10.22	50	49	50
gamma-chlor % recov.	99	104	72	101	73	106	105	98	95		1.40						

United States Environmental Protection Agency
Environmental Research Laboratory
27 Tarzwell Drive
Narragansett, Rhode Island 02882
Environmental Chemistry Group

MEMORANDUM

Date: February 10, 1992

Subject: Review of Trace Metals Analysis Performance Evaluation data for Portsmouth Ecological Risk Assessment

From: Warren S. Boothman

To: Robert K. Johnston
Naval Oceans Systems Center, San Diego

Performance evaluation sample analysis

In October 1991, four samples, consisting of two sediments and two biological tissues, were delivered to Ceimic Corporation for blind chemical analysis. Appropriate standard reference materials (SRM) were analyzed along the samples to provide for analytical quality assurance (QA). The results for the marine tissue samples were received December 6, 1991; results for the sediment samples subsequently arrived December 18, 1991. Method detection limits (MDL) were to be determined as part of the Performance Evaluation. Those results were delivered to ERLN on January 27, 1992, with an addendum received February 3, 1992. The results of both evaluations are discussed below.

Sediments

Sample TM-1 (Table 1) is a highly contaminated sediment which had been previously analyzed for total metals content by the U.S. EPA National Enforcement Center (NEIC) in Denver, CO. With the exception of mercury, the recoveries of all metals for which concentrations had been determined by NEIC are greater than 82%, with most within 90-110%. The range of recoveries of metals from the estuarine sediment SRM was similar to that found for TM-1. The mercury concentrations determined in TM-1 by Ceimic were quite low and variable, relative to NEIC's results. Similarly, while no reference value for tin was determined by NEIC in this sediment, the tin determinations were also variable (relative standard deviation of 12%).

Sample TM-2 is a relatively clean, coastal sediment analyzed at ERL-N. Recoveries are lower for this sample, relative to the ERLN results. However, the sediment was analyzed only once at ERLN, so the consistent recovery values for most of the metals, along with the good results obtained for the SRM which is a similar type

Table 1. Sediment sample results

	TM-1			TM-2			1646
		NEIC			ERLN		SRM
	Mean ± S.D.	value	Recovery	Mean ± S.D.	value	Recovery	Recovery
Al	54.2 ± 0.0	65.7	82%	67.2 ± 0.3	51.7	130.0%	89.1%
As	13.4 ± 0.2	14.0	96	13.0 ± 0.5	12.4	104.8	91.4
Cd	25.0 ± 0.2	23	109	0.48 ±0.07	0.63	76.2	86.5
Cr	1650 ± 22	1750	94	66.5 ± 3.2	94.8	70.1	90.0
Cu	2685 ± 43	2720	99	25.2 ± 1.1	33.0	76.4	81.6
Fe	36.3 ± 0.2	39.1	93	34.7 ± 0.6	48.8	71.0	94.0
Pb	450 ± 3	360	125	21.6 ± 1.7	28.0	77.3	98.9
Mn	454 ± 5	520	87	1565 ± 35	2233	70.1	87.2
Hg	0.62 ± 0.25	1.99	31	nd	nd		N/A
Ni	183 ± 0	169	108	32.5 ± 1.2	49.4	65.7	85.0
Ag	18.0 ± 0.3	16	113		n d		N/A
Sn	129 ± 15			3.4 ± 1.6	2.3	147.8	N/A
Zn	1389 ± 15	1380	101	105 ±0.94	174	60.5	105.7

Concentrations in µg/g dry except for Al and Fe in mg/g dry.

of sediment matrix, suggest that the ERLN values might just as easily be somewhat high as the Ceimic values low. Again, however, the tin values obtained were both high, relative to the ERLN data, and quite variable (± 47%), indicating a problem with this determination.

The Ceimic report does recognize the elevated tin concentrations in the procedural blank, so it is reasonable to believe their results for these analyses will improve. It should also be noted that the most recent NOAA laboratory intercomparison for analysis of trace metals in marine sediments and tissues states that "reliable analysis of marine samples ... for tin is apparently possible by only a small number of experienced laboratories." The low mercury recoveries remain a problem. Because of the sealed vessels employed, the anticipated use of microwave-heated digestions should improve Ceimic's ability to digest sediments without loss of mercury from the sample; however, sample sizes may not be increased sufficiently to greatly improve the method detection limits. The problems noted in the report regarding sample storage may prove to be key to improving the apparent recovery of this element.

Tissues

Overall the results (Table 2) for the tissue samples TM-1, a bivalve homogenate containing moderate concentrations of trace metals, and TM-2, a reference fish tissue presenting low metals concentrations, are very similar to those for the sediment samples, i.e. mercury recovery was low (<60% for both the SRM and TM-2) and the tin results variable (again, there were no established reference values for tin in these tissues). In addition, recovery

Table 2. Tissue sample results

	TM-1 Mussel			TM-2 Dogfish		
	Mean ± S.D.	Reference value	Recovery	Mean ± S.D.	Reference value	Recovery
Al	375 ± 22	270	139%	11.1 ± 0.4		
As	8.1 ± 0.5			12.4 ± 0.5	17.7	70%
Cd	1.81 ± 0.03	2.08	87	0.081 ± 0.000	0.086	94
Cr	2.40 ± 0.09	2.15	112	3.35 ± 0.17	3.60	93
Cu	11.8 ± 0.3	12.8	92	4.82 ± 0.07	5.22	92
Fe	472 ± 8.5	450	105	63.7 ± 0.7	63.6	100
Pb	0.71 ± 0.25	9.11	74	0.32 ± 0.01	0.40	79
Mn	26.9 ± 0.8	26.8	100	1.71 ± 0.34	1.32	130
Hg	0.106 ± 0.008			0.466 ± 0.004	0.798	58
Ni	6.50 ± 0.26	6.84	95	1.19 ± 0.09	1.20	99
Ag	0.23 ± 0.00			0.15 ± 0.00		
Sn	1.44 ± 0.32			1.98 ± 0.13		
Zn	120 ± 2.5	135	89	17.4 ± 0.05	21.3	82

Concentrations in μg/g dry except for Al and Fe in mg/g dry.

of lead was only 75-80% for either of the tissue samples, slightly lower than the 86.5% recovery from the SRM. While this is not as severe a problem as with tin or mercury, it would appear to warrant some further method development.

The Ceimic report also concerns itself with apparently low (66%) recovery of aluminum from the SRM. Recent studies have indicated that low recovery of aluminum results from incomplete dissolution of clay mineral particles found within the organism tissues. The apparently high recovery of aluminum from sample TM-1 relative to that determined by ERLN, compared to the low SRM recovery, probably reflects somewhat more efficient dissolution of the mineral aluminum by Ceimic's method than that used at ERLN. Since this material does not constitute an environmentally significant contamination source, however, such low recoveries may be acceptable.

Method detection limits

With the exception of mercury and silver in tissues, all of the method detection limits obtained by Ceimic Corporation (Table 3) are substantially higher than the target MDL's specified in the project QA/QC plan. However, this may be due to the target values, in many cases, being unnecessarily low. When compared with detection limits reported by National Status and Trends (NS&T) laboratories, it can be seen that many target MDL's are below the NS&T limits. Therefore, the limits obtained by Ceimic may also be evaluated by comparison with the NS&T detection limits and with minimum trace metal concentrations likely to be encountered in typical marine sample matrices. For most elements in both the

Table 3. Method detection limits

Analyte	Target MDL	Matrix	MDL Obtained	NS&T MDLs 1988 - 1989	"Typical" minimum concentrations
Al	0.18	Tissue	8.17		26.
		Sediment	10.7		32000.
As	0.08	Tissue	3.2	2.0 - 6.6	14.0
		Sediment	0.52	0.09 - 2.1	3.5
Cd	0.005	Tissue	0.050	0.073 - 0.63	0.035
		Sediment	0.13	0.02 - 0.09	0.15
Cr	0.01-0.7	Tissue	1.85	0.16 - 0.4	1.4
		Sediment	1.65	0.35 - 6.0	41.
Cu	0.01-0.7	Tissue	2.01	0.46 - 9.9	2.8
		Sediment	4.55	0.09 - 2.4	6.7
Fe	0.5	Tissue	6.6		15.2
		Sediment	7.6		18000.
Pb	0.01-0.7	Tissue	0.13	0.56 - 0.66	0.37
		Sediment	0.81	0.2 - 2.2	2.7
Mn	0.01	Tissue	0.60		0.73
		Sediment	0.97		266.
Hg	0.125	Tissue	0.079	0.036	0.064
		Sediment	0.448	0.004 - 0.010	
Ni	0.01-0.7	Tissue	0.82	0.63 - 0.83	0.72
		Sediment	2.76	0.07 - 2.1	16.
Ag	0.01-0.7	Tissue	0.091	0.033 - 0.04	
		Sediment	0.15	0.01 - 0.07	< 0.02
Sn	0.075	Tissue	3.43	0.14	0.93
		Sediment	0.81	0.058 - 0.2	0.95
Zn	0.003	Tissue	6.7	6.3 - 17	21.
		Sediment	1.1	1.0 - 3.3	62.

sediment and tissue matrices, the MDL's obtained by Ceimic are within the range of detection limits reported by the NS&T labs and are less than or similar to the minimum concentrations determined in typical samples. In some cases, e.g. major elements in sediments, the limits are 1-3 orders of magnitude lower than the *minimum* concentrations likely to be encountered. The results in general seem quite acceptable; however, problems do exist for specific elements and matrices.

As seen with the analysis of the unknown samples discussed previously, tin and mercury continue to present analytical difficulties. MDL's determined for these two elements exceed the NS&T detection limits by factors of 4-100. The limits also exceed the "typical" minimum concentrations, although the limits for mercury in tissues and tin in sediments are very similar to likely minimum concentrations. The mercury results are somewhat encouraging, however, as the high MDL is the result of very low analytical values in two of the seven subsamples; if those two results were thrown out, the resulting variability would be greatly decreased and the calculated MDL (0.087 $\mu g/g$) would be acceptable. The results for analysis of tin in tissues are also highly variable (and thus the high MDL) with no clear prospect of improving. Clearly this is a problem which must be addressed.

Several minor questions exist for the MDL's determined for the other elements. The limits determined for silver in both tissues and sediments are slightly higher than the NS&T limits. Because we have little data on how low concentrations in "real-life" samples can be expected, these values are most likely satisfactory. In a similar vein, the limits obtained for chromium in tissues and copper in sediments are somewhat higher than those reported by the NS&T labs, but are comparable to the minimum concentrations likely to be encountered. These limits may thus be considered marginally acceptable.

Recommendations

Ceimic's results for the trace metals performance evaluation were, for the most part, very good for both sediment and tissue analyses. Only a few problems exist, and these have been noted already by Ceimic in its reports. The results do indicate that Ceimic is, in general, capable of performing these analyses reliably and that, with a slight amount of further method refinement, their analytical results can be accepted with reasonable certainty.

The specific problems that should be addressed include mercury and tin determinations in both sediment and tissue samples and determination of lead in tissues. The most serious problem appears to be the analysis of mercury. However, the problems of low recovery and high detection limits are related, so that if the intermittent recovery problems can be eliminated, the detection limit problem is also likely to be alleviated. While the problems with tin are also being addressed by Ceimic, there does not appear to be any immediate resolution likely; further efforts will be needed to produce reliable data for this element.

cc: Linda Dietz, NORTHDIV
Richard Pruell, ERL-N
William Nelson, ERL-N
Norm Rubinstein, ERL-N

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Performance Evaluation Results for Trace Metals in Marine Sediments

Ceimic Corporation

Inorganic Chemistry Laboratory

December 18, 1991

into the teflon vessels subsequent to wet weight determinations using 6ml of concentrated Baker Instra-Analyzed HNO_3. Samples were allowed to cold digest overnight, and following this period 3ml of redistilled concentrated HF was added. Following HF additions watchglasses were place atop each beaker and heat was applied. After about 36 hours, watchglasses were removed and samples were brought to near dryness. At this point an additional 10ml of HF, and 5ml of concentrated HNO_3 was added to each vessel. Watchglasses were put in place and sediment samples were gently refluxed. As a final digestion step, samples were brought to near dryness and 10ml of 1N HNO_3 was added to each vessel along with 4ml of a 30% hydrogen peroxide solution (Aldrich Chemical Co.). Samples were again refluxed at moderate heat and were brought to near dryness. All samples were brought to a final 50ml volume in the digestion beaker using a 1N HNO_3 solution. Once samples were brought to a final 50ml volume in the digestion beaker, they were allowed to equilibrate for about four hours before the filtration step. Digested samples were filtered through acid-cleaned 0.4 um pore size Nucleopore Membranes and the filtrate dispensed into acid-cleaned High Density Polyethylene (HDPE) storage bottles. Procedural blank samples were treated in the same fashion as sediment samples and were carried through the entire digestion and analytical procedures. All digestion procedures were carried out in a Class-100 laminar flow clean bench with effluent air emptying into an evacuation hood.

Because there were certain problems with the analysis of tissues that were perhaps related to loss of Hg in the storage vessels, a filtered10ml of aliquot of each sediment sample was immediately dispensed into individual Hg reaction vessels and each solution was fixed with a concentrated potassium permanganate solution. In our previous note on Hg levels in marine tissue, it was mentioned that the immediate preparation of the Hg sample might improve recovery of this element.

With the exception of Hg, all metal samples were analyzed by Graphite Furnace Atomic Absorption Spectrophotometry or Inductively Coupled Plasma Spectroscopy, using either the Perkin Elemer Model 5100 AAS, equipped with Zeeman Background Correction and AS-60 Autosampler, or using the Perkin Elmer Model P40 ICP. Hg determinations were made using a cold vapor technique with the Coleman Model 50B Mercury Analyzer. The instrumental method used for each trace element is provided in Table 2.

Project Overview

Two marine sediment samples were provided Ceimic Corporation by the U.S EPA Environmental Research Laboratory at Narragansett as part of a performance evaluation effort for marine samples. The results of our trace metal analyses of the two sediment samples TM-1 and TM-2, are included in this report. Also included as part of our effort is a brief summary of the procedures employed and instrumentation used.

Analytical Method

All sediment samples provided by EPA were processed in the same fashion as the Standard Reference Material (SRM) Estuarine Sediment 1646, available from the U.S. National Institute of Standards and Technology. A "wet weight" aliquot of individual TM-1 and TM-2 sediment samples and SRM subsamples was used in the wet digestion procedure, and a seperate aliquot was freeze dried and used to determine dry sediment weight. Dry sediment weights used in the digestion procedure (Table 1), were calculated from the Dry to Wet Weight Ratio determined from non-freeze dried and freeze dried sediment samples.

Table 1.

Dry sediment weights used in the wet digestion procedures. Dry sediment weight for all samples was calculated from the dry/wet weight ratios of seperate sediment aliquots that were freeze dried.

Sample Id	Subsample	Dry Sediment Weight, g	Dry/Wet Ratio x 100
SRM 1646	1001	0.418	no change
	1002	0.291	"
	1003	0.278	"
TM-1	S-102	0.144	24.9
	S-103	0.161	"
TM-2	S-201	0.141	35.8
	S-202	0.182	"
	S-203	0.237	"

Total sediment digestions were carried out on a hot plate using teflon digestion vessels with teflon watchglasses. Sediment samples were rinsed

It was interesting to note that Al recoveries in sediment SRM were greater than found for tissue samples. The recovery of sediment Al was on the order of 89%, compared to a 66% recovery of Al in Tissue SRM. It may be that the halide concentration involved in the sediment technique may have prevented or slowed aluminum-oxide formation thus allowing for greater recovery. It should also be noted that sediment Al measurements were made shortly after the samples had been filtered (within four hours). For subsequent tissue and sediment samples Al measurements will be made at the earliest possible moment after the samples are filtered.

As a final note on Al, tissue samples were re-analyzed by a Neutron Activation technique as a check on tissue recoveries. The results of the Neutron Activation Analysis were virtually the same as those previously reported for SRM and TM-1 tissue samples. There was about a factor of two difference in the low levels of Al observed by ICP and NAA in TM-2 Tissues, the higher values were observed using the NAA technique (a copy of this data will be furnished upon request).

Observed tin levels were variable regardless of the sample analyzed, with Relative Standard Deviations ranging from around16 to 57%, for all the sediment suites evaluated. The procedural blank was on the order of 13 ug/l, which accounted for roughly half of the signals observed for SRM and TM-2 sediment samples. Because different digestion vessels were used in sediment and tissue digestions (ie. teflon versus quartz for sediment and tissue digestions, respectively), it was not possible to determine whether the digestion vessels were factors in contaminating the samples. However, it does appear that tin is being added to samples regardless of digestion vessel type, and this points to the concentrated reagents that are employed in these procedures. We will continue our efforts to establish the cause of elevated tin in our procedural blank samples.

Results

Concentrations observed in the procedural blank sample is reported in Table 2. In most instances blank levels were not significantly different from instrumental background and in these cases the blanks were labeled not detectable. In instances where blanks were significant, sample concentrations were corrected by procedural blank levels.

The concentration of trace metal found in subsamples of Estuarine Sediment SRM 1646 are reported in Table 3, and the average metal concentrations observed in this study are compared to expected SRM levels.

Trace metal concentrations found for EPA TM-1 and TM-2 Sediment Evaluation samples are reported in Tables 4 and 5, respectively.

Problem Areas and Remedies

A significant effort was made to get these sediment samples into solution using the wet digestion technique described. The classic "hot plate" technique is thorough judging from SRM recoveries, but the time involved in the total HF digestion of sediment samples was considerable. In this same regard, the longer a procedural period necessary for digestion the greater the potential for metal contamination. To aleviate the time element involved in the digestion of sediment samples a CEM Model 2000 Microwave Digestion System was purchased and will be used for future sediment digestions. The use of this system will provide for a more controlled digestion environment coupled with a shorter digestion period. We feel that the positive aspects of the microwave system will permit a greater sample output with the potential of increasing metal recoveries.

Mercury levels in the Estuarine Sediment SRM 1646 are the same as concentrations found in the Oyster Tissue SRM 1566a (ie. 0.063 ug/g), but because a much smaller amount of material was used in the sediment digestion (about 0.2 to 0.4 g, dry sediment weight) as compared with the tissue digestion (about 2.5 g, dry tissue weight) the recovery of Hg in the sediment SRM could not be evaluated. Although it was known at the outset that SRM 1646 Hg could not be recovered, it was hoped that the other sediments would provide sufficient Hg levels for accurate measurement. This did not turn out to be the case, and in part the amount of material used in the digestion was not sufficient. The use of a microwave technique might allow digestion of greater amounts of sediment, thus permit the evaluation of Hg in SRM and other sediments in future samples.

Table 2.

A summary of trace metal concentrations measured in procedural blanks. Procedural Blanks were processed in the same fashion as samples, and carried through the entire sediment digestion procedure. Where warranted samples were corrected by procedural blanks. Concentrations are reported as ug/l.

Analyte	Procedural Blank Concentrations, ug/l S-001	Instrumental Method
Aluminum	Nd	ICP
Arsenic	1.8	GFAAS
Cadmium	Nd	GFAAS
Chromium	Nd	ICP
Copper	Nd	ICP
Iron	Nd	ICP
Lead	Nd	GFAAS
Manganese	Nd	ICP
Mercury	Nd	CV
Nickel	Nd	ICP
Silver	Nd	GFAAS
Tin	13.0	GFAAS
Zinc	Nd	ICP

Nd indicates not detected.

ICP = Inductively Coupled Plasma
GFAAS = Graphite Furnace Atomic Absorption Spectrophotometry
CV = Cold Vapor

Table 3.

Concentrations of trace elements measured in Standard Reference Material (SRM) Estuarine Sediment 1646, prepared by the U.S. National Institute of Standards and Technology. Individual concentrations observed for each of three subsamples of SRM 1646 are repoted along with the Mean, Standard Deviation, and Relative Standard Deviation (RSD). Average metal concentrations observed were compared to expected SRM 1646 values and a % recovery was estimated. Metal concentrations are reported in ug/g Dry Weight, unless otherwise noted.

Concentrations in ug/g, except where noted for

Analyte	Estuarine Sediment SRM 1646 Subsamples 1001	1002	1003	Observed SRM Mean ± Std. Dev.	RSD(%)	Expected SRM Mean ± Std. Dev.	% Recovery
Aluminum*	50.8	57.5	58.9	55.7 ± 4.3	7.8	62.5 ± 2.0	89.1
Arsenic	11.3	9.9	10.6	10.6 ± 0.7	6.6	11.6 ± 1.3	91.4
Cadmium	0.31	-	0.32	0.32 ± 0.07	2.2	0.36 ± 0.07	86.5
Chromium	68.4	67.7	69.1	68.4 ± 0.7	1.0	76. ± 3.	90.0
Copper	13.9	14.4	15.8	14.7 ± 1.0	6.7	18. ± 3.	81.6
Iron*	31.5	31.3	31.6	31.5 ± 0.2	0.5	33.5 ± 1.0	94.0
Lead	26.0	29.2	28.4	27.9 ± 1.7	6.0	28.2 ± 1.8	98.9
Manganese	324.	329.	328.	327. ± 2.6	0.8	375. ± 20.	87.2
Mercury**	nd	nd	nd	- -	-	0.063 ± 0.0012	-
Nickel	27.3	-	27.0	27.2 ± 0.2	0.8	32. ± 3.	85.0
Silver***	nd	nd	nd	- -	-	- -	-
Tin***	4.5	4.4	2.3	3.7 ± 1.2	33.5	- -	-
Zinc	121.	197.	122.	146. ± 44.	29.8	138. ± 6.	105.7

* Al and Fe concentrations in mg/g Dry Weight
** Hg concentrations were not detected (nd) using SRM sediment weights of 0.4 g, or less.
*** Ag and Sn levels in SRM 1646 are not certified thus recoveries cannot be established.

Table 4.

A summary of trace metal concentrations measured in subsamples of EPA Marine Sediment TM-1. Subsample concentrations are reported along with the Mean, Standard Deviation, and Relative Standard Deviation (RSD) for each element. Concentrations reported are in ug/g Dry Sediment Weight, except for Al and Fe which are mg/g Dry Sediment Weight.

	TM-1 EPA Marine Sediment Concentrations in ug/g, Dry Wt.				
	TM-1 Subsamples		Observed EPA TM-1		
Analyte	S-102	S-103	Mean	± Std. Dev.	RSD(%)
Aluminum*	54.2	54.1	54.2	± 0.1.	0.1
Arsenic	13.6	13.2	13.4	± 0.3	2.1
Cadmium	24.8	25.2	25.0	± 0.3	1.1
Chromium	1672.	1628.	1650.	± 31.	1.9
Copper	2728.	2642.	2685.	± 60.	2.3
Iron*	36.1	36.5	36.3	± 0.3	0.8
Lead	447.	453.	450.	± 4.	0.9
Manganese	458.	449.	453.	± 6.	1.4
Mercury	0.87	0.37	0.62	± 0.35	57.0
Nickel	183.	183.	183.	± 0.	0.0
Silver	18.3	17.7	18.0	± 0.4	2.4
Tin	144.	114.	129.	± 21.	16.4
Zinc	1403.	1374.	1389.	± 21.	1.5

* Al and Fe concentrations are mg/g Dry Sediment Weight.

Table 5.

A summary of trace metal concentrations measured in subsamples of EPA Marine Sediment TM-2. Subsample concentrations are reported along with the Mean, Standard Deviation, and Relative Standard Deviation (RSD) for each element. All concentration are based on ug/g Dry Sediment Weight, except for Al and Fe which are in mg/g Dry Sediment Weight.

TM-2
EPA Marine Sediment
Concentrations in ug/g,
Dry Sediment Wt.

Analyte	TM-2 Subsamples S-201	S-202	S-203	Observed EPA TM-2 Mean ± Std. Dev.	RSD(%)
Aluminum*	67.2	66.8	67.5	67.2 ± 0.4	0.6
Arsenic	13.6	12.4	13.0	13.0 ± 0.6	4.6
Cadmium	0.57	0.47	0.40	0.48 ± 0.09	17.8
Chromium	70.9	64.8	63.7	66.5 ± 3.9	5.8
Copper	26.2	25.8	23.6	25.2 ± 1.4	5.6
Iron*	35.5	34.3	34.2	34.7 ± 0.7	2.1
Lead	21.2	19.8	23.9	21.6 ± 2.1	9.6
Manganese	1602.	1519.	1575.	1565. ± 42.	2.7
Mercury	bd	bd	bd	-	-
Nickel	33.3	30.8	33.3	32.5 ± 1.4	4.4
Silver	bd	bd	bd	-	-
Tin	5.5	3.2	1.5	3.4 ± 2.0	59.0
Zinc	106.	106.	104.	105. ± 1.2	1.1

* Al and Fe concentrations in mg/g Dry Sediment Weight.

Performance Evaluation Results for Trace Metals in Marine Tissues

Ceimic Corporation

Inorganic Chemistry Laboratory

December 6, 1991

Project Overview

Two marine tissue samples were provided Ceimic Corporation by the U.S EPA Environmental Research Laboratory at Narragansett as part of a performance evaluation effort for marine samples. The results of our trace metal analyses of the two tissue samples TM-1 and TM-2, are included in this report. Also included as part of our effort is a brief summary of the procedures employed and instrumentation used.

At the outset of this report it should be noted that some analytical problems were encountered for some elements, as should be expected when analyzing trace elements in a marine matrix. The important issue is that these problems were recognized using quality assurance protocols that were already in place. Thus, the problems encountered for the measurement of aluminum, tin, and mercury and the corrective measures that we will pursue on subsequent samples are detailed in a later section.

Analytical Method

All tissue samples provided by EPA were processed in the same fashion as the Standard Reference Material (SRM) Oyster Tissue 1566a, available from the U.S. National Institute of Standards and Technology. In this regard, a "wet weight" aliquot of individual TM-1 and TM-2 samples and SRM subsamples was used in the wet digestion procedure, and a seperate aliquot was freeze dried and used to determine dry tissue weight. Dry tissue weights used in the digestion technique are given in Table 1. Losses of Hg that occur during freeze drying necessitated the use of wet tissue in the digestion procedure.

Table 1.

Wet and dry tissue weights of EPA Performance Evaluation samples TM-1, TM-2, and SRM 1566a Oyster Tissue samples used in the digestion procedure.

Sample ID	Subsample	Wet Tissue Wt., g	Dry Tissue Wt., g	Ratio
SRM 1566a	1001	2.59	2.49	0.96
	1002	2.56	2.46	0.96
	1003	2.49	2.39	0.96
EPA TM-1	101	10.50	1.63	0.155
	102	17.18	2.66	0.155
EPA TM-2	201	2.47	2.47	no change
	202	2.49	2.49	no change

Wet tissue weight determinations were carried out directly in quartz digestion vessels. Subsequent to weight determinations, 30ml of concentrated Baker Instra-Analyzed HNO_3 was added to each beaker. Samples were allowed to cold digest for a period of 24 hours, and following this period heat was gently applied. Once samples stopped frothing, they were covered with teflon watchglasses and moderate heat (about 120 ^{o}C) was applied. After 36 hours, watchglasses were removed and samples were brought to near dryness. At this point 10ml of 1N HNO_3 was added to each vessel along with 5ml of a 30% hydrogen peroxide solution (Aldrich Chemical Co.). Samples were again refluxed at moderate heat until solutions became clear and then were brought to near dryness. All samples were brought to a final 50ml volume in the digestion beaker using a 1N HNO_3 solution. Digested samples were filtered through acid-cleaned 0.4 um pore size Nucleopore Membranes and the filtrate dispensed into acid-cleaned High Density Polyethylene (HDPE) storage bottles. Procedural blank samples were treated in the same fashion as tissue samples and were carried through the entire digestion and analytical procedures. All digestion procedures were carried out in a Class-100 laminar flow clean bench with effluent air emptying into an evacuation hood.

With the exception of Hg, all metal samples were analyzed by Graphite Furnace Atomic Absorption Spectrophotometry or Inductively Coupled Plasma Spectroscopy, using either the Perkin Elemer Model 5100 AAS, equipped with Zeeman Background Correction and AS-60 Autosampler, or using the Perkin Elmer Model P40 ICP. Hg determinations were made using a cold vapor technique with the Coleman Model 50B Mercury Analyzer. The instrumental method used for each trace element is provided in Table 2.

Results

Concentrations observed in the procedural blank samples are reported in Table 2. In most instances blank levels were not significantly different from instrumental background and in these cases the blanks were labeled not detectable. In instances where blanks were significant, sample concentrations were corrected by procedural blank levels.

The concentration of trace metal found in subsamples of SRM1566a are reported in Table 3, and average metal concentrations observed in this study are compared to expected SRM levels.

Trace metal concentrations found for EPA TM-1 and TM-2 Evaluation samples are reported in Tables 4 and 5, respectively.

Problem Areas and Remedies

Several attempts were made to analyze Aluminum by ICP and GFAAS techniques, but regardless of the instumental technique employed, recoveries of Al in SRM samples remained low (Table 3). As a final check to establish whether there were actual losses of Al during the digestion procedure, or that some other factor might be involved in the low recovery, a Neutron Activation (NA) technique will be used to verify the results that we have reported.

Tin levels that we observed were somewhat confused due to the relatively high and variable procedural blanks (Table 2). At present we are attempting to establish the reagent or reagents causing the blank problems. Although Sn can be used to stabilize hydrogen peroxide, the Aldrich Chemical Co., uses stabilizers other than this metal. Once we establish the exact nature of the problem, I think we can expect a reasonably good result in the analysis of Sn in tissue samples.

Mercury concentrations observed in SRM 1566a samples were about half the expected SRM levels (Table 3). Although the poor recovery of Hg in SRM's may be due to the low concentrations, an effort will be made to reduce potential losses by fixing samples for Hg analysis with $KMnO_4$ immediately after samples are brought to final volume with 1N HNO_3. A recent laboratory experiment revealed that Hg standards could be held without apparent loss of the element for at least seven days when fixed with $KMnO_4$.

Table 2.

A summary of trace metal concentrations measured in procedural blanks. Procedural Blanks were processed in the same fashion as samples, and carried through the entire digestion procedure. Where warranted samples were corrected by procedural blanks. Concentrations are reported as ug/l.

	Procedural Blank Concentrations, ug/l					
Analyte	T001	T002	PBLK Mean	± Std. Dev.	RSD(%)	Instrumental Method
Aluminum	107.	131.	119.	± 17.	14.3	ICP
Arsenic	1.6	1.4	1.5	± 0.14	9.4	GFAAS
Cadmium	Nd	Nd	-		-	ICP + GFAAS
Chromium	12.8	11.1	12.0	± 1.2	10.0	GFAAS
Copper	0.4	0.0	0.2	± 0.3	-	ICP + GFAAS
Iron	Nd	Nd	-		-	ICP
Lead	Nd	Nd	-		-	GFAAS
Manganese	Nd	0.1	-		-	GFAAS
Mercury	Nd	Nd	-		-	CV
Nickel	2.6	2.1	2.35	± 0.35	15.1	GFAAS
Silver	Nd	Nd	-		-	GFAAS
Tin	23.4	7.7	15.5	± 11.1	71.6	GFAAS
Zinc	Nd	Nd	-		-	ICP

Nd indicates not detected

ICP = Inductively Coupled Plasma
GFAAS = Graphite Furnace Atomic Absorption Spectrophotometry
CV = Cold Vapor

Table 3.

Concentrations of trace elements measured in Standard Reference Material (SRM) Oyster Tissue 1566a, prepared by the U.S. National Institute of Standards and Technology. Individual concentrations observed for each of three subsamples of SRM 1566a are repoted along with the Mean, Standard Deviation, and Relative Standard Deviation (RSD). Average metal concentrations observed were compared to expected SRM 1566a values and a % recovery was estimated. All metal concentrations are reported in ug/g on a Dry Weight basis.

	Concentrations, ug/g, observed in Oyster Tissue SRM 1566a Subsamples			Observed		Expected	
Analyte	1001	1002	1003	SRM Mean ± Std. Dev.	RSD(%)	SRM Mean ± Std. Dev.	% Recovery
Aluminum	137.	133.	133.	134.3 ± 2.3	1.7	202.5 ± 12.5	66.3
Arsenic	13.5	13.2	13.2	13.3 ± 0.17	1.3	14.0 ± 1.2	95.0
Cadmium	3.98	4.39	4.18	4.18 ± 0.21	4.9	4.15 ± 0.38	100.7
Chromium	1.56	1.53	1.25	1.45 ± 0.17	11.8	1.43 ± 0.46	101.4
Copper	66.77	67.69	65.94	66.80 ± 0.88	1.3	66.3 ± 4.3	100.8
Iron	536.	531.	515.	527.1 ± 11.1	2.1	539. ± 15.	97.8
Lead	0.33	0.31	0.31	0.32 ± 0.01	3.6	0.371± 0.014	86.5
Manganese	12.44	12.72	12.21	12.46 ± 0.26	2.1	12.3 ± 1.5	101.3
Mercury	0.041	-	0.035	0.038± 0.004	11.2	0.064± 0.0067	59.4
Nickel	2.60	2.66	2.41	2.56 ± 0.13	5.1	2.25 ± 0.44	113.7
Silver	1.41	1.48	1.07	1.32 ± 0.22	16.6	1.68 ± 0.15	78.6
Tin	2.25	2.47	2.80	2.51 ± 0.28	11.0	(3)*	83.7
Zinc	823.	839.	818.	826.9 ± 10.9	1.3	830. ± 57.	99.6

* Tin concentrations in SRM 1566a are noncertified values

Table 4.

A summary of trace metal concentrations measured in subsamples of EPA Marine Tissue TM-1. Subsample concentrations are reported along with the Mean, Standard Deviation, and Relative Standard Deviation (RSD) for each element. All concentration are based on ug/g Dry Tissue Weight.

	TM-1 EPA Marine Tissue Concentrations in ug/g, Dry Wt.				
	TM-1 Subsamples		Observed EPA TM-1		
Analyte	101	102	Mean	± Std. Dev.	RSD(%)
Aluminum	396.	353.	374.	± 30.	8.1
Arsenic	8.6	7.5	8.1	± 0.78	9.6
Cadmium	1.84	1.77	1.81	± 0.05	2.7
Chromium	2.49	2.31	2.40	± 0.13	5.3
Copper	12.05	11.50	11.78	± 0.39	3.3
Iron	480.	463.	471.	± 12.	2.6
Lead	6.96	6.46	6.71	± 0.35	5.3
Manganese	27.70	26.09	26.90	± 1.14	4.2
Mercury	0.114	0.097	0.106	± 0.012	11.3
Nickel	6.75	6.24	6.50	± 0.36	5.5
Silver	0.23	0.23	0.23	± 0.00	0.0
Tin	1.76	1.11	1.44	± 0.46	31.9
Zinc	122.	117.	119.4	± 3.0	2.6

Table 5.

A summary of trace metal concentrations measured in subsamples of EPA Marine Tissue TM-2. Subsample concentrations are reported along with the Mean, Standard Deviation, and Relative Standard Deviation (RSD) for each element. All concentration are based on ug/g Dry Tissue Weight.

	TM-2 EPA Marine Tissue Concentrations in ug/g, Dry Wt.					
	TM-2 Subsamples		Observed EPA TM-2			
Analyte	201	202	Mean	±	Std. Dev.	RSD(%)
Aluminum	10.6	11.5	11.1	±	0.6	5.6
Arsenic	12.0	12.9	12.5	±	0.6	5.1
Cadmium	0.081	0.080	0.081	±	0.001	0.9
Chromium	3.52	3.18	3.35	±	0.24	7.2
Copper	4.76	4.89	4.83	±	0.09	1.9
Iron	64.4	63.0	63.7	±	1.0	1.6
Lead	0.31	0.32	0.32	±	0.01	2.2
Manganese	1.37	2.05	1.71	±	0.48	28.1
Mercury	-	a) 0.470 b) 0.422 c) 0.461	0.451	±	0.026	5.7
Nickel	1.28	1.10	1.19	±	0.13	10.7
Silver	0.16	0.15	0.16	±	0.01	4.4
Tin	2.11	1.85	1.98	±	0.18	9.1
Zinc	17.4	17.5	17.5	±	0.07	0.4

CEIMIC
CORPORATION
"Analytical Chemistry for Environmental Management"

December 27, 1991

Dr. Warren Boothman
Environmental Research Laboratory
U.S. Environmental Protection Agency
27 Tarzwell Drive
Narragansett, RI 02882

Dear Dr. Boothman:

Enclosed is the report of results for the MDL Studies on marine tissue and marine sediment for Trace Metals. This study was requested of Ceimic Corporation as part of the Laboratory Performance Evaluation for the Estuarine Ecological Risk Assessment at the Naval Shipyard in Portsmouth Maine.

Please call if you have any questions regarding this data

Sincerely,

Phyllis Shiller

Phyllis Shiller
Inorganic Laboratory
Manager

PS/11

Enclosure

10 Dean Knauss Drive, Narragansett, R.I. 02882 • (401) 782-8900 • FAX (401) 782-8905

METHOD DETECTION LIMIT (MDL) RESULTS

FOR

TRACE METALS

IN

MARINE TISSUES

AND

MARINE SEDIMENTS

CEIMIC CORPORATION

INORGANIC LABORATORY

JANUARY 28, 1992

PROJECT OVERVIEW

A method detection limit (MDL) study of marine sediments and tissue was performed for the Estuarine Ecological Risk Assessment Project. The study was performed in accordance with "Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11", from 49.CFR 43430, October 26,1984.

ANALYTICAL METHOD

For our sediment MDL study, a Silica Gel was used as the analytical medium. About 0.250 g, of silica gel was used in the spiked and non-spiked samples. In all instances a seawater matrix (0.5ml unacidified Sargasso Seawater), was added to individual subsamples. The Silica Gel 60 (particle size 0.063-0.200 mm) was obtained from EM Science. The samples were spiked with metals at appropriate levels.

For our Marine Tissue MDL study, a flounder tissue was bought at a local retail outlet, and homogenized. About 10 g of wet tissue was used in this study, or about 0.5 g dry weight. Trace metal concentrations were measured in seven unspiked and spiked subsamples.

Both tissue and sediment samples were digested using a CEM Model 2000 Microwave, equipped with teflon lined digestion vessels.

Aluminum, Chromium, Copper, Iron, Manganese, Nickel, and Zinc were analyzed by Inductively Coupled Argon Plasma Spectroscopy in Perkin Elmer Model P400 ICP. Arsenic, Cadmium, Lead, Silver, and Tin were analyzed by Graphite Furnace Atomic Absorption Spectroscopy Perkin Elmer Model 5100 AAS, equipped with Zeeman Background Correction. The mercury was analyzed by cold vapor technique Coleman Model 50B.

RESULTS

Results for the Trace Metal MDL are summarized in Tables 1, and 2, for Marine Tissues and Sediments, respectively. In each table the individual observed concentrations are reported for each of the seven spiked subsamples. All concentrations are reported as ug/g dry tissue or sediment weight. Along with the individual results, the average and standard deviation (SD) of the spiked samples are also reported. Matrix concentrations reported in Tables 1 and 2, refer to the background concentrations observed for unspiked tissue and sediment samples. The amount of spike added to the subsamples is reported as the True Spike Value (TSV), and this value was calculated by multiplying the spike solution by the

final volume of our extract and dividing this product by the dry sample weight. Our percent recoveries are defined as the average of the observed spiked sample concentrations (AVERAGE) minus the matrix concentration (MATRIX) divided by the spike added (TSV).

OBSERVATIONS

Marine Tissue MDL:

The percent recovery for aluminum in the tissue MDL study was lower than anticipated (Table 1). The low recovery may in part be that the spike solution was at a level that was twice the instrumental detection limit, and the observed tissue concentration of unspiked samples was at or below the detection limit.

Another issue is that the unspiked arsenic concentrations were greater than the range for the MDL. We found an average of about 16 ppm As dry tissue weight, and our spiking level for a proper MDL study would require a background arsenic level of between 0.2 and 1.0 ppm dry tissue weight. This element is always analyzed by GFAAS, and the MDL reported (Table 1), is erroneously high.

Nickel and zinc concentration observed in the matrix were greater than those observed in the spiked samples (Table 1). It appears that there are two sources of error, the first is that the matrix level is at the instrument detection limit (IDL), and the second is that our spikes for each element were at levels that are about twice the IDL. In the future we may decide to analyze nickel by GFAAS for low levels, and use our ICP for higher concentrations. In the case of zinc, it is felt that the vast majority of our samples (tissues and sediments) will be significantly greater than the levels observed for this study.

It should also be noted that our Performance Evaluation tissue samples had greater percent solids than the percent solids observed for flounder tissue. In this regard, we analyzed less solid material in flounder tissue than we did for our performance evaluation samples. In our future sample preparation efforts an attempt will be made to analyze a wet tissue weight that will yield approximately 1.0 g dry tissue weight.

Marine Sediment MDL:

For the most part our Marine Sediment MDL worked well (Table 2). However, in the case of mercury two of the individual subsamples had concentrations well below the other five observations, which elevated the MDL. It is reasonable to expect that the mercury MDL should be somewhat lower than our calculated value.

Table 1.

Summary of concentrations observed in Flounder tissue spiked with trace metals, along with the average concentration and standard deviation, concentration of non-spiked tissue (Matrix), the level at which the tissues were spiked (True Spike Value), and the Method Detection Limit (MDL). Concentrations reported for individual and spiked samples are based on ug/g Dry Tissue Weight. Additionally, Matrix values, True Spike Values, and Method Detection Limit are reported in ug/g, concentrations.

	Spiked Tissue Sample Number									True		Method
Analyte	119	120	121	122	123	124	125	AVG ± SD	Matrix	Spike Value	% Recovery	Detection Limit
Aluminum	28.8	31.5	30.4	24.8	25.5	26.0	27.7	27.8 ± 2.6	26.3	21.2	7.1	8.17
Arsenic*	16.7	16.4	16.2	16.0	14.0	17.2	16.6	16.2 ± 1.0				3.2
Cadmium	0.430	0.432	0.460	0.439	0.466	0.425	0.441	0.442± 0.016	0.035	0.425	95.8	0.050
Chromium	5.23	4.75	5.62	5.54	6.03	4.99	4.30	5.22 ± 0.59	1.52	4.25	87.1	1.85
Copper	6.35	6.64	7.86	6.27	7.20	5.94	6.67	6.70 ± 0.64	2.76	4.25	92.7	2.01
Iron	21.3	20.4	24.2	20.8	20.4	17.0	19.8	20.6 ± 2.1	26.3	10.6	50.9	6.6
Lead	0.574	0.601	0.629	0.533	0.572	0.509	0.613	0.576± 0.043	ND	0.531	109.0	0.13
Manganese	2.46	2.32	2.70	2.40	2.54	2.12	2.26	2.40 ± 0.19	0.73	1.59	105.0	0.60
Mercury	0.215	0.227	0.258	0.209	0.222	0.186	0.253	0.224± 0.025	0.112	0.127	88.2	0.079
Nickel	4.82	3.80	7.19	4.49	4.76	5.73	4.63	5.06 ± 1.10	5.66	4.25	-14.1	3.45
Silver	0.410	0.432	0.483	0.407	0.434	0.414	0.463	0.435± 0.029	ND	0.531	82.0	0.091
Tin	3.83	4.25	3.28	3.49	0.84	3.09	2.99	3.11 ± 1.09	0.93	1.06	203.6	3.43
Zinc	20.8	19.0	24.3	17.2	19.2	12.6	19.5	18.9 ± 3.6	26.0	2.12	-15.1	11.3

* Arsenic concentrations reported are the levels found in the unspiked tissue.

ND indicates sample is below detectable level

Table 2.

Summary of concentrations observed in Silica Gel spiked with trace metals, along with the average concentration and standard deviation, concentration observed for non-spiked silica gel (Matrix), the level at which the tissues were spiked (True Spike Value), and the Method Detection Limit (MDL). Concentrations reported for individual and spiked samples are based on ug/g Dry Sediment Weight. Additionally, Matrix values, True Spike Values, and Method Detection Limit are reported in ug/g,concentrations.

	Spiked Sediment Sample Number									True Spike	%	Method Detection
Analyte	111	112	113	114	116	117	118	AVG ± SD	Matrix	Value	Recovery	Limit
Aluminum	21.6	22.1	23.3	26.5	22.0	31.7	26.4	24.8 ± 3.4	ND	40.5	61.	10.7
Arsenic	1.62	2.04	1.92	2.09	1.95	1.81	1.68	1.87 ± 0.16	ND	2.02	93.	0.52
Cadmium	0.728	0.787	0.792	0.804	0.701	0.697	0.734	0.749± 0.041	ND	0.807	93.	0.13
Chromium	7.09	8.09	8.13	8.91	8.17	7.97	7.53	7.98 ± 0.53	ND	8.07	99.	1.65
Copper	7.09	9.57	9.38	10.70	7.59	6.77	6.95	8.29 ± 1.45	ND	8.07	103.	4.55
Iron	14.7	9.4	9.2	16.3	11.5	11.6	12.2	12.1 ± 2.4	ND	20.2	60.	7.6
Lead	2.31	2.66	2.31	2.94	2.28	2.21	2.20	2.42 ± 0.26	1.26	1.01	115.	0.81
Manganese	3.54	4.25	4.17	4.57	4.28	3.98	3.86	4.09 ± 0.31	ND	3.03	134.	0.97
Mercury	0.138	0.469	0.526	0.196	0.467	0.471	0.450	0.388± 0.142	0.263	0.241	52.	0.448
Nickel	6.72	7.23	9.58	8.48	8.56	8.57	8.11	8.18 ± 0.88	ND	8.07	101.	2.76
Silver	0.802	0.894	0.875	0.935	0.837	0.797	0.869	0.858± 0.046	ND	1.01	85.	0.15
Tin	2.28	2.51	2.11	2.67	2.55	1.91	2.57	2.37 ± 0.26	ND	2.03	117.	0.81
Zinc	4.66	5.32	5.63	5.87	5.45	5.38	5.21	5.36 ± 0.35	ND	4.05	132.	1.10

ND, indicates that metals were below detectable levels.

APPENDIX B

REVISED ANALYTICAL CHEMISRTY QUALITY ASSURANCE/ QUALITYCONTROL PROTOCOLS, CRITERIA, AND CORRECTIVE ACTION PLAN

Analytical Chemistry Quality Assurance and Quality Control Protocols, Criteria, and Corrective Action For the Estuarine Ecological Risk Assessment at Naval Shipyard Portsmouth, Maine

ADDENDUM

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Introduction

This document provides clarifications, revisions, and recommended quality control guidelines to be followed during the analysis of routine sediment, tissue, and seep samples collected as part of the Estuarine Ecological Risk Assessment at Naval Shipyard Portsmouth. Until further notice, the quality control criteria outlined in this document shall be followed for all subsequent sample analysis.

Overall

Care should be taken during the processing of all tissue samples that enough material is extracted so that the dry-weight sample size is comparable (if enough tissue is available) to the sample size used to determine the method detection limit (MDL). This will insure that the MDLs are as low as possible for the sample analysis.

Records should be kept of dry:wet ratios of the various tissue matrices. These should be consulted before determining the amount of material to be analyzed.

In cases where there appears not to be enough material for the analysis, the Project Officer should be consulted to determine if it is possible to pool the samples (from appropriate replicates) to obtain enough material for a valid analysis.

An additional flag (f) should be used for reporting results obtained between the instrument detection limit (IDL) and the (MDL). This will provide the data user with the maximum flexibility for data usage, while maintaining CLP-style, standard procedures for data verification (see Table 3 for data flags below).

The polycyclic aromatic hydrocarbons (PAH) should be measured in all routine sediments, seeps, mussel (Mytilus edulis) and lobster (Homarus americanas) hepatopancreas tissue samples.

Table 1 provides the revised control limits for organic and inorganic analysis. Table 2 lists the target MDLs for organic and inorganic analysis, and Table 3 clarifies use of data flags.

Table 1. Revised control limits.

1. Performance Evaluation	CONTROL LIMIT RSD	NUMBER ALLOWED OUT	FREQUENCY
Initial Calibration			Initial
Organics			
PAH fraction	<20%		
PCB fraction	<20%	2	
PEST fraction	<20%	2	
Inorganics	Lab develops own according to CLP SOW/90		
Detection Limits	(see Table 2)		Initial
Blind Analysis of PE organic samples, PE inorganic samples	Subject to review by Project Officers and Project QA Officers		

2. Ongoing Demonstration of Capability Analysis of Standard Reference Material (SRM) or Laboratory Control Material (LCM)	RECOVERY OF EACH ANALYTE	PERCENT ALLOWED OUT	OVERALL AVERAGE RECOVERY	FREQ: 1 PER BATCH
ORGANIC ANALYSIS				
Sediment: PAH fraction	±40%	<35%	±35%	
PCB/PEST fraction	±40%	<35%	±35%	
Tissue: PAH fraction	±40%	<35%	±35%	
PCB/PEST fraction	±40%	<35%	±35%	
INORGANIC ANALYSIS				
Sediment: Mercury (Hg)	±25%	<15%	NA	
(Al, As, Cd, Cr, Cu, Fe, Pb, Ni, Ag, Sn, Zn)	±20%			
Tissue: Mercury (Hg)	±25%	<15%	NA	
(Al, As, Cd, Cr, Cu, Pb, Ni, Ag, Zn)	±20%			

NOTES: (1) In reporting results from the analysis of standard reference materials (SRM) or laboratory control materials (LCM) any data obtained which are below the LOQ are not to be used for computing control limits. However, it is necessary to report all the results obtained from the SRM analysis (even those below the LOQ). These data will make it possible to identify matrix problems and evaluate method performance.

(2) In determining the percent of analytes allowed out, fractions may be rounded up to the nearest whole number.

3. Calibration Check using calibration standards.	CONTROL LIMIT	NUMBER ALLOWED OUT	FREQUENCY: Beginning and end of batch and every 10 samples
ORGANIC ANALYSIS			
sediments and tissues			
PAH fraction	<25%		
PCB fraction	<25%	2	
PEST fraction	<25%	2	
INORGANIC ANALYSIS			
sediments and tissues			
Mercury (Hg)	±25%	}	
all others	±15%	} 2	

4. Laboratory Reagent Blank	CONTROL LIMIT	FREQUENCY: one per batch
All analytes:	greater than 3 times MDL	

5. Laboratory Fortified Sample Matrix (matrix spike sample)	WARNING LIMIT	FREQUENCY: 5% of total samples
All analytes:	±50%	

NOTES:

(1) No control limits are specified for laboratory fortified sample matrix spike. If analytes fall outside of the ±50% recovery they should be flagged accordingly and explained in the case narrative. If more than 30% of the analytes fail to meet the ±50% recovery criteria, the batch must be considered for reprepping based on the other control criteria.

(2) Care must be taken to spike the samples within the appropriate range for the analytes of concern. An attempt should be made to spike the samples such that the spike is no less than 4 times and no more than 2 times the sample value.

6. Laboratory Duplicate	CONTROL LIMIT	PERCENT ALLOWED OUT	FREQUENCY: one per batch
Organics: (Sed and Tissue)			
PAHs	<30%RPD	<35%	
PCBs and PEST	<30%RPD	<35%	
Inorganics (Sed and Tissues)			

Al, Fe	<50%RPD	}
all others	<30%RPD	}<35%

NOTE: Both the sample and duplicate must be above the LOQ before the relative percent difference (RPD) can be calculated. It is understood that there will be a higher amount of variability in RPDs calculated for analytes near the LOQ (at 10s). Therefore discretion will be used in evaluating the control criteria for those cases.

7. Field Duplicates — NA

8. Internal Standards

	WARNING LIMITS	RECOMMENDED CONTROL LIMITS	FREQ: each sample
Organics:			
d_{10}-phenathrene PCB 198	}Outside of }30-130% }Recovery	>50% difference between SRM and sample recoveries	
Inorganics	NA		

NOTES:

(1) Internal standard recoveries are advisory limits. The laboratory must set its own warning and control limits based on the data obtained from control charts documenting recoveries. It is the responsibility of the analyst to demonstrate that the analytical process is always "in control". However, extremely low or high recoveries for the internal standards for any sample in the batch, or large differences (>50%) between the recoveries obtained for the SRM and individual samples would be grounds for reprepping the batch, based on the results of the other control criteria.

(2) It is recommended that for the PAHs d_{10}-phenanthrene, d_{12}-benzo(a)anthracene, and d_{12}-perylene and for the PCBs PCB 103 and PCB 198 be used for internal standards, if possible, to improve method accuracy and precision.

9. Injection Internal Standards. — Lab develops own

Organics:	
all matrices all analytes	} Lab will monitor } areas with control charts
Inorganics:	NA

10. Interlaboratory Calibration

	WARNING LIMIT	ALLOWED OUT	FREQUENCY: 5% of samples by matrix
Organics and Inorganics	}within	}	

all matrices	}a factor	}20%
all analytes	}of 3	}

NOTE:
The purpose of the interlaboratory calibration is to provide an independent check on the accuracy of the analysis. Variations between laboratories, inhomogeneity of the samples, and the relatively low concentrations of many of the analytes will interfere with the results. Gross differences between the laboratories will be subject to review by the Project Officers and the Project QA/QC Officers to determine if corrective action is necessary.

Table 2. Target method detection limits for analytes of concern. (See the original QA/QC Plan for list of individual analytes, if necessary). Wet weight or dry weight (DW) of the MDL is specified. (A) The analytes, matrices, and target MDLs for organic compounds. (B) The elements, matrices, target MDLs, and "typical" marine minimum concentrations for the inorganic analytes.

A. ORGANICS

Analyte	Matrix	Target MDL
Volatile Organics	seep water	.6 ug/L
PAHs	seep water	5.0 ug/L
PAHs	sediment	5.0 ng/g (DW)
PAHs	tissue	20.0 ng/g (DW)
Pesticides	seep water	.6 ug/L
Pesticides	sediment	.6 ng/g (DW)
Pesticides	tissue	.6 ng/g (DW)
PCBs	seep water	1.0 ug/L
PCBs	sediment	.5 ng/g (DW)
PCBs	tissue	.5 ng/g (DW)

Note: For the organic compounds the MDL obtained should be within a factor of two of the target MDL. Final acceptance of the MDLs is subject to review by the Project Officer and the Project QA/QC officers. Specific analytes will be evaluated on a case-by-case basis.

B. INORGANICS

Analyte	Matrix	Target MDL		"Typical" Marine Minimum Conc.	
Aluminum	seep water	75.0	ug/L	2.0	ug/L
Aluminum	sediment	Not Specified(NS)		32000.0	ug/g
Aluminum	tissue	NS		26.0	ug/g
Arsenic	seep water	3.0	ug/L	3.7	ug/L
Arsenic	sediment	1.1	ug/g (DW)	3.5	ug/g
Arsenic	tissue	4.3	ug/g (DW)	14.0	ug/g
Cadmium	seep water	0.2	ug/L	.1	ug/L
Cadmium	sediment	0.35	ug/g (DW)	.15	ug/g
Cadmium	tissue	0.055	ug/g (DW)	.035	ug/g
Chromium	seep water	3.0	ug/L	.3	ug/L
Chromium	sediment	3.16	ug/g (DW)	41.0	ug/g
Chromium	tissue	0.28	ug/g (DW)	1.4	ug/g
Copper	seep water	0.7	ug/L	.1	ug/L
Copper	sediment	1.25	ug/g (DW)	6.7	ug/g
Copper	tissue	5.0	ug/g (DW)	2.8	ug/g
Iron	seep water	20.0	ug/g	2.0	ug/L
Iron	sediment	NS		18000.0	ug/g
Iron	tissue	NS		15.2	ug/g
Lead	seep water	3.0	ug/L	.0005	ug/L
Lead	sediment	1.2	ug/g (DW)	2.7	ug/g
Lead	tissue	0.6	ug/g (DW)	.37	ug/g
Manganese	seep water	0.5	ug/L	.2	ug/L
Manganese	sediment	NS		266.0	ug/g
Manganese	tissue	NS		.73	ug/g
Mercury	seep water	5.0	ug/L	.03	ug/L
Mercury	sediment	0.007	ug/g (DW)		
Mercury	tissue	0.036	ug/g (DW)	.064	ug/g
Nickel	seep water	3.0	ug/L	1.7	ug/L
Nickel	sediment	1.08	ug/g (DW)	16.0	ug/L
Nickel	tissue	0.73	ug/g (DW)	.72	ug/g
Silver	seep water	3.0	ug/L	.002	ug/L
Silver	sediment	0.04	ug/g (DW)	.02	ug/L
Silver	tissue	0.037	ug/g (DW)		
Tin	seep water	3.0	ug/L	.01	ug/L
Tin	sediment	1.75	ug/g (DW)	0.95	ug/g
Zinc	seep water	0.1	ug/L	.5	ug/L

Zinc	sediment	2.15	ug/g (DW)	62.0	ug/g
Zinc	tissue	11.65	ug/g (DW)	21.0	ug/g

NOTES:

(1) The target MDLs for seep samples were obtained from the detection limits reported for the NCBC Davisville risk assessment pilot study (Munns et al. 1991).

(2) The target MDLs for sediment and tissue samples were obtained by calculating the midpoint of the range of actual MDLs, for each element, as reported by laboratories participating in the Status and Trends Program (NOAA 1991).

(3) The "typical" marine minimum concentrations for seep waters are those found in oceanic seawater (Brown et al. 1989). The "typical" marine minimum concentrations for sediments and seeps were those reported for "typical" samples by laboratories participating in the Status and Trends Program (NOAA 1991).

(4) For inorganic compounds the MDL obtained should be within a factor of two of the target MDL, or alternatively, within a factor of two of the "typical" marine minimum concentrations. Final acceptance of the MDLs is subject to review by the Project Officer and the Project QA/QC officers. Specific elements will be evaluated on a case-by-case basis.

(5) The analysis of tin in tissue samples has been deleted from this requirement.

Table 3. Data flags.

A. ORGANICS and INORGANICS.

Code	Description
a	analyte was not detected below the MDL shown
b	reported value is below the LOQ
c	not reported due to matrix interference
d	not quantified
e	not reported
f	reported value is below the MDL
h	quantification based on alternate internal standard
j	analysis performed with selected ion monitoring
p	value shown may be biased as determined by recovery of analyte in reference material
u	analyte was not detected at the instrument detection limit

B. INORGANICS. Additional flags allowed:

Code	Description
n	the spike recovery is out of control
s	the sample was analyzed by method of standard addition
w	analytical spike outside of 85-115% recovery
*	the duplicate is out of control
+	correlation of 0.995 was not met for the method of standard addition

References

Brown, J., A. Colling, D. Park, J. Phillips, D. Rothery, and J. Wright, 1989. Seawater: Its Composition, Properties and Behavior. Pergamon Press, Oxford, UK, 165pp.

Munns, W.R., Jr., C. Mueller, D.J. Cobb, T.R. Gleason, W.G. Nelson, G.G. Pesch, and R.K. Johnston, 1991. Marine Ecological Risk Assessment at Naval Construction Battalion Center, Davisville, Rhode Island. Naval Ocean Systems Center Technical Report 1437, San Diego, CA, 129pp.

National Oceanic and Atmospheric Administration (NOAA), 1991. Second Summary of Data on Chemical Contaminants in Sediments from the National Status and Trends Program. NOAA Technical Memorandum NOS OMA 59, Rockville, MD.