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WORK PLAN FOR PHASE 2 COLLECTION AND ANALYSIS OF ECOLOGICAL DATA FROM THE GREAT BAY ESTUARY NSY PORTSMOUTH ME

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UNIVERSITY OF NEW HAMPSHIRE WORK PLAN FOR PHASE II

Collection and Analysis of Ecological Data From the Great Bay Estuary

March 1993

Prepared by:

Jackson Estuarine Laboratory
University of New Hampshire
85 Adams Point Rd.
Durham, NH 03824

WORK PLAN FOR PHASE II FOR THE UNH JEL

COLLECTION AND ANALYSIS OF ECOLOGICAL DATA FROM THE GREAT BAY ESTUARY

March 1993

Prepared by:

Jackson Estuarine Laboratory
University of New Hampshire
85 Adams Point Road
Durham, NH 03824

Frederick T. Short, UNH JEL Project Director

WORK PLAN

UNH Jackson Estuarine Laboratory Work Plan for the Portsmouth Naval Shipyard Project

Contract Number: N66001-92-D0092
Delivery Order Number: 0011

Task Title: COLLECTION AND ANALYSIS OF ECOLOGICAL DATA FROM THE GREAT BAY ESTUARY

3. TECHNICAL APPROACH

The aim of this study, Collection and Analysis of Ecological Data from the Great Bay Estuary, is to develop the information base necessary to assess the ecological impact of hazardous waste disposal on the Piscataqua and Great Bay Estuary. All aspects of the study will be documented in a Quality Assurance/Quality Control (QA/QC) and Health and Safety Plan. Progress will be documented with periodic Progress Reports and Interim Reports prepared after completion of field work. The final report will be accompanied with a Data Dump of ASCII files of all raw and calibrated data. The specific tasks of the work plan are explained below.

1. *Determine dispersion dynamics for the Great Bay Estuary.*

During this project, work will be done to determine dispersion dynamics for the Piscataqua and Great Bay Estuary. Completion of this task will provide detailed information on the fate and transport of organic and metal contaminants in the Estuary by conducting quasi-synoptic surveys of current regimes using an acoustic doppler profiler and realtime measurements of the physical and chemical properties of the water column. In addition, dye-dispersion studies will be conducted in the vicinity of the Shipyard to directly measure dispersion of material released from the Shipyard. The results of the field studies will be incorporated into hydrodynamic and contaminant transport models currently under development.

The research vessel *R/V ECOS* will conduct realtime surveys of many of the physical and hydrological parameters in the estuary. The *R/V ECOS* will record the tidal cycles off the Police pier and near Clark Island. Fresh water and salt water flow regimes will be addressed by measuring the salinity on each transect undertaken by the *R/V ECOS*. Temperature and salinity will be recorded on all transects. The salinity gradient will be used in the calibration of a pollutant fate model. Measurements of pH, dissolved oxygen, chlorophyll fluorescence, and oils fluorescence will be conducted.

Replicate water samples will be collected during *R/V ECOS* cruises in Portsmouth Harbor and Great Bay Estuary. Samples will be taken at selected sites in the cross channel and longitudinal transects, and at fixed stations during flood, mid-ebb, ebb, and mid-flood tidal stages following JEL SOP 1.05 for water sample collection, resulting in 204 discrete water samples. Samples will be immediately iced and transported to Jackson Estuarine Laboratory within four hours for processing.

Sample processing, filtrate preparation and chlorophyll analysis will be conducted according to JEL SOP 1.06. Results of chlorophyll analysis will be used to calibrate continuous fluorimetric readings collected by the *R/V ECOS*, and to examine water column primary productivity during tidal stages at transect and fixed station sites. Filtrate will be analyzed for dissolved inorganic $PO3_4$- according to JEL SOP 1.08. Dissolved ammonium (method 11-107-06-1-C) and nitrite/nitrate (method 30-107-04-A) will be analyzed on a LACHAT *Quick-Chem* nutrient autoanalyzer. Results of nutrient analysis will be used in conjunction with doppler current measurements to determine nutrient flux patterns and sources of nutrient loading in the estuary.

Additional replicate water samples for microbial analysis will be collected in conjunction with those just described. Microbial sample processing and analysis will be described in a separate section. Concomitantly, water samples will be collected and provided to NRaD to screen for organic contaminants.

A dye study using rhodamine-wt will be conducted on flood tide and ebb tide. Historical freshwater inflow data will be used to determine flushing rates and residence times. An estimate of the dispersion coefficients will be calculated. These results will be then incorporated into the contaminant transport model. The dispersion coefficients will be calculated based on known rodamine concentrations as collected by the *R/V ECOS*. These concentrations will also be compared with aerial photographs taken of the river as the rhodamine traveled through it. The photographs will determine the overall coherency of the rhodamine and help determine at what point on the river the rodamine broke up into 'patches', which could bias the concentration results. Simulations of runoff from disposal areas based on dispersion coefficients will be done in the pollutant fate model.

Currents will be measured throughout the summer at a number of stations (Fig. 1). Current measurements will also be taken around the estuary over twenty-four hour cycles. This will be done by employing S-4 current meters on fixed moorings. After at least one tidal cycle data from the S-4 will be downloaded before it is moved to another station on the river. Once downloaded, the data will be interpreted in the field using the S-4 software. The software is able to interpret the data and plot velocity vs. time plots. These plots can then be analyzed on site in order to determine the validity of the data before the S-4 is moved to a new location. The bottom current measurements obtained suing the S-4 current meters will be used to check the *R/V ECOS* data and try to explain why the river bottom is sometimes difficult to "see" acoustically. The same data combined with the *R/V ECOS* data may be used to compute the bedload transport. Using the Brown-Einstein approach, bedload flux may be calculated for various portions

of the river. Eventually sedimentation rates due to bedload transport will be calculated at several selected locations in the river.

The dispersion coefficients, developed from the dye and current data, will then be incorporated into the transport model. A coefficient will be determined in each computational cell of the TOXIWASP model. These will be used as calibration parameters within the model. Progress will be documented with periodic Progress Reports and Interim Reports prepared after completion of field work. Final reports will be accompanied with a Data Dump of ASCII files of all raw and calibrated data, following the procedures outlined in the Data Management Plan. Dr. Robin Swift will function as the QA/QC person responsible for the quality of the hydrodynamic data.

2. ***Fingerprint sources of fecal contaminants.***

Water column and sediment samples will be collected for analysis to determine sources of fecal contamination in Portsmouth Harbor. For each sample station and time, duplicate samples will be collected in sterile 1 liter plastic bottles using a hand-grab method for sampling at approximately 15 cm below the water surface. All water samples will be assayed within 8 hours of collection and kept at 5° C until all analyses are complete. Based on Phase I results, water samples will be collected from six sites each month to determine the trends of contaminant concentrations near areas of concern. The six sites will be the same as studies in Phase I, and sample collection will be coincident with samples collected for nutrient analyses.

Selected samples collected as part of the *R/V ECOS* cruises will also be analyzed for microbial contaminants (see Task 1). Samples collected for microbial analysis will be coincident with samples collected for nutrient analyses to allow for better interpretation of the sources (fecal vs. nonfecal pollution) of nutrient contamination. Samples will be collected at four tidal stages at the discreet sample stations identified for study at five different transect sites (Fort Foster, Dover Point, Police Dock, Clark Cover, Seavey Island). Results should provide useful information for determining transport patterns for suspended contaminants at the different sites. Samples will also be collected during the longitudinal cruises of the whole Great Bay Estuary at low and high tides. Samples stations will coincide with the fifteen identified for nutrient sampling. Analysis of these samples should show spatial differences in the level of fecal contamination in the estuary, and integration with other information should allow for assessment of mixing and dilution patterns for suspended contaminants in relation to sources of contamination and different water masses. Again, the coincidence of nutrient and microbial sampling will allow for a better understanding of sources and fate of nutrients. Comparisons of microbial contaminant levels at the same sites on consecutive days at high and low tides should also give a better understanding of the movement and mixing of water masses in the estuary.

Selected sediment samples collected as part of Tasks 3 and 4 will be analyzed for fecal microbial contaminants. These tasks involve sampling river and salt marsh sediments, and sites will be chosen by the investigators involved in the study of these

two habitats. Microbial sampling and analysis will be coordinated with these other investigations. Generally, subsamples from sediment cores will be collected at different depths, depending on the profiles and lengths of the cores. Results will reflect potential temporal differences in fecal contamination of suspended sediments in the estuary, and can be compared with geochronological analyses to gain a better understanding of the history of pollution in the estuary. If the geochronological analyses are successful, sediment cores will be resampled based on the actual chronology of the sedimentation reflected at different depths and reanalyzed for fecal-borne microbial contaminants to gain a more exact understanding of the temporal trends for fecal contamination. Comparison of levels in the salt marshes and the river bottom sediments will show any differences in accumulation patterns of suspended contaminants in these two habitats.

For water samples, the ERL-N membrane filtration (MF) methods ERL-N SOP 1.03.014, 1.03.015, and 1.03.016 will be used for enumeration of *Clostridium perfringens*, enterococci, and fecal coliforms/*Escherichia coli*, respectively. The ERL-N SOP 1.03.015 will be modified by excluding indoxyl-B-D-glucoside from the mE medium and instead using esculin iron agar to enumerate appropriate enterococci colonies.

The only microorganism to be used as an indicator of fecal contamination in sediments is the spore-forming *Clostridium perfringens*. JEL SOP 1.09 will be used for enumeration of *C. perfringens*. Prior preparation of the sediments will involve aseptic collection of replicate subsamples from sediment cores (see sections 3 and 4), weighing appropriate amounts, diluting 1:1 (or other appropriate dilution) in sterile PBS, and blending in a Waring blender for 1 minute. Triplicate sediment aliquots will be dried at 105° C to determine sediment dry weight.

Progress will be documented with periodic Progress Reports and Interim Reports prepared after completion of field work. Final reports will be accompanied with a Data Dump of ASCII files of all raw and calibrated data.

3. *Evaluate sediment dynamics.*

An evaluation of sedimentation processes and potential accumulation of contaminants will be conducted in the Lower Piscataqua River Estuary. This task will provide detailed information on sediment movement and deposition in the lower Estuary. Based on the existing sediment distribution map, a sediment accumulation and monitoring program will be developed and implemented to determine sedimentation processes in the lower Estuary.

Sedimentation rates will be measured utilizing sediment traps at sites where contaminants may be deposited as reflected by muddy bottoms. It is anticipated that the primary site where sediment traps will deployed will be in the cove behind Clark Island. It is anticipated a moored sediment trap array will be used. Approximately 1 L bottles with a length/width ratio between 3 to 5 will be mounted on a wooden frame attached to a tethered line. It is anticipated 4 bottles will be positioned at each of two

depths on each mooring. Two moorings are presently planned. The arrays will be deployed for periods ranging from 1 week to 1 month. Due to the inherent problems with utilizing settling traps in estuarine environments due to currents, waves or fouling organisms, the settling traps and deployment strategies will be modified as necessary. It is anticipated that deployments will begin in spring, 1993 and extend through summer, 1993. An SOP is not available for the settling trap work at this time, as part of the effort is to develop the appropriate methodology for this system. We will be using previously utilized methods and then developing the best methodology.

If necessary, surficial bottom sediment samples will be collected at the sites where sediment traps will be deployed (approximately at the time of the first deployment) and at other locations where additional sediment textural information is needed. It is anticipated the samples will be collected with a Shipex or similar sediment sampler. The bottom sediment samples will be collected and analyzed for textural characteristics to allow a comparison to be made between the materials settling through the water column and substrate.

Sediment deposition rates (accretion) will be determined at selected sites utilizing cores and radionuclide dating techniques. Cores will be obtained using suitable methodologies to minimize disturbing the sediment column (compaction or mixing). Anticipated methodologies include gravity coring in deeper water (revised JEL SOP 1.10, attached); vibracoring and hand coring in marshes or shallow subtidal sites. Recovered cores will be closely scrutinized for evidence of any disruptions due to coring techniques or physical or biological mixing. Recovered cores will be transported (normally in a vertical position) to JEL, where they will be opened, described, photographed and sampled for moisture and organic content (combustion at 450°), bulk density, grain size and radionuclide analyses (revised JEL SOP 1.11, attached). The sedimentation rates and geochronology of the cores will be determined from Cs-137 and Pb-210 analyses which will be contracted to another laboratory (UNH Glacier Research Group). It is anticipated a total of 8 cores will be taken. The sampling sites will be selected based on results from Phase I work (contaminant levels and substrate characteristics). The cores will be subsampled according to JEL SOP 1.10 as modified for sampling sediment chemistry.

We will develop information on the movement of suspended sediment plumes in conjunction with data obtained from the NCCOSC-deployed sensors (transmissometer, turbidimeter, and acoustic doppler profiling system). Water samples will be collected via shipboard (*R/V ECOS*) pumping systems during periods when the transmissometer and turbidimeter are being used to provide point samples for calibration. The water samples will be analyzed for total suspended sediment concentrations via filtration techniques and % organic content, normally via combustion (450°) (JEL SOP 1.16, attached). Selected samples will be analyzed for particulate carbon and nitrogen using an elemental analyzer (Carlo Erba) to develop a relationship between % particulate carbon and nitrogen and % combustibles for a wide range of sediment types.

The impact of tidal current on sediment loads will be determined at selected sites by measuring current velocities and suspended sediment concentrations through the water column at a fixed station over a portion of a tidal cycle. Current velocity will be

measured with the shipboard acoustic doppler profiler. Total suspended sediment concentrations will be determined on several samples taken through the water column from within 1 meter of the bottom to the surface. Normally, suspended sediment sampling will be done at a maximum of 1 hour intervals. In addition, the turbidity of the water column will be determined with the shipboard transmissometer and turbidimeter. In order to assess sources and sinks of suspended sediments in the lower estuary, the distribution of the suspended load will be determined by measuring suspended sediment concentrations at 5 channel cross sections extending from the mouth of the estuary to the confluence of the upper Piscataqua River and Little Bay at Dover Point. Sampling will be nearly continuous over 12 to 13 hour periods in order to encompass all phases of a tidal cycle. Sampling will be repeated at a maximum of 1 hour intervals under normal circumstances. Water samples will be collected for suspended sediment analysis (JEL SOP 1.16, attached) via shipboard pumping systems in conjunction with the transmissometer and turbidimeter measurements or with a JEL submersible pump. As frequently as possible, measurements will be made through the water column in order to examine any stratification. Consequently, snapshots of the suspended sediment concentrations and water clarity will be made over tidal cycles. Examination of all the channel cross sections will provide a quasi-synoptic description of the suspended sediment distribution in the lower and middle estuary. This information will be enhanced by measuring the suspended sediment concentrations and water clarity along an axial transect run from the mouth of the estuary to a major source of fresh water (the Squamscott River).

We will evaluate geotechnical characteristics of sediments in potential contaminant depositional sites in the lower Estuary. In order to assess relationships among the geotechnical properties of the sediment and the geochemical assimilation of contaminants, sediment samples will be analyzed for grain size, total organic carbon and particulate carbon and nitrogen (JEL SOP 1.11). Grain size will be determined using well established methodologies. Total organic carbon will be determined via combustion at 450°C, while particulate carbon and nitrogen will be determined with a Carlo Erba analyzer. In addition, sediment samples for chemistry will be collected and preserved for acid volatile sulfide (AVS) analysis. Progress will be documented with periodic Progress Reports and Interim Reports prepared after completion of field work. Final reports will be accompanied with a Data Dump of ASCII files of all raw and calibrated data.

4. ***Evaluate the potential ecological effects of contaminants from PNS on salt marsh and benthic ecology.***

<u>*Salt marsh*</u>

Salt marsh sampling stations for the PNS and reference areas in Great Bay Estuary and in York River Estuary are shown in Figure 1. Sampling sites for each sampling activity will be selected by the principal investigator.

Salt marshes will be sampled to determine the abundance and health of plants and animals (epibenthic macroinvertebrates will be identified to species). Since salt marshes

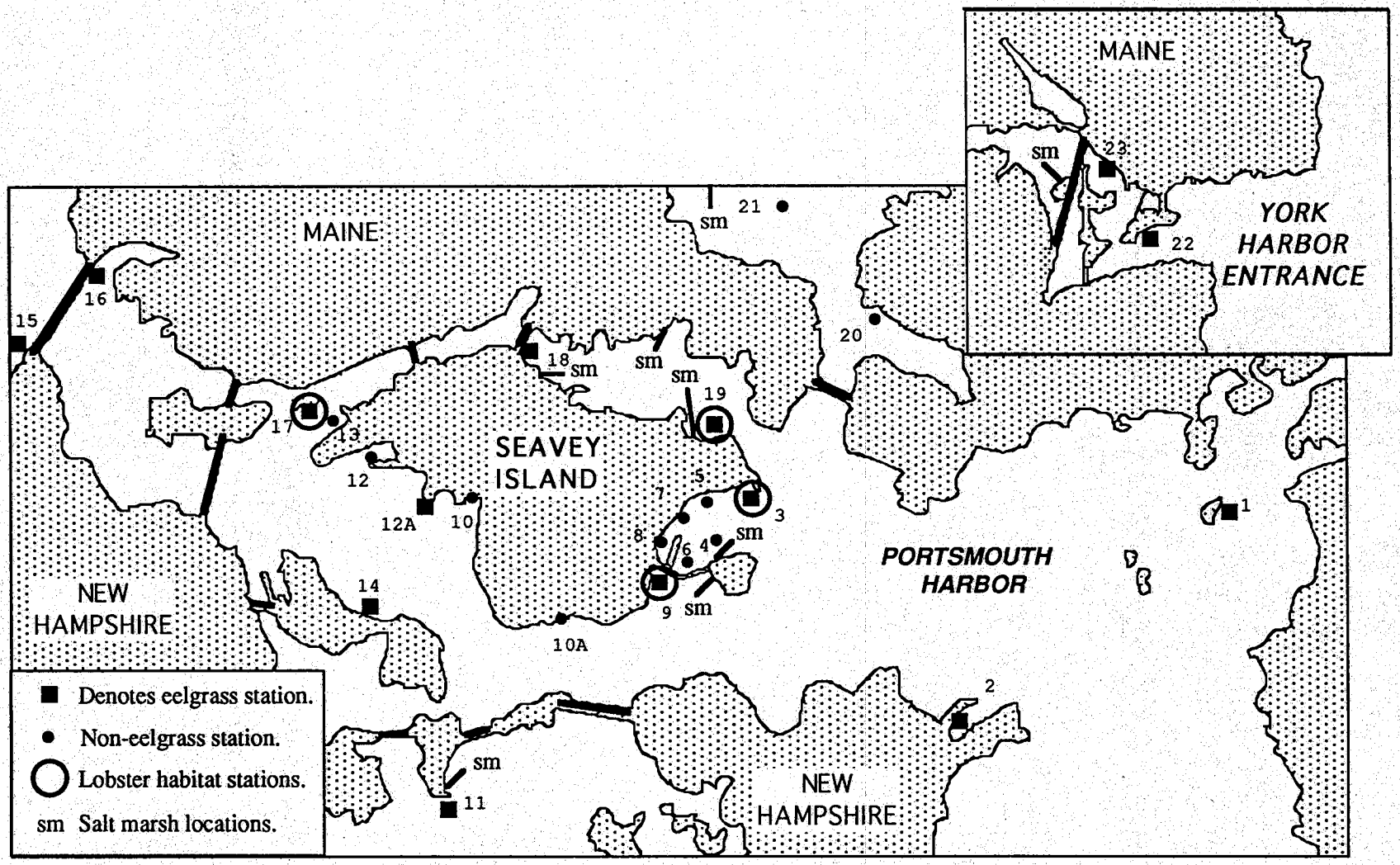

Figure 1: Location of Portsmouth Harbor and York River sampling stations showing eelgrass stations where habitat for juvnile lobsters is being investigated, and salt marshes.

are characterized by their emergent plants which normally form monospecific stands, a set of five replicate samples will be taken in each of the major plant associations within each marsh. Salt marsh plants will be sampled for abundance (% cover in 1 m^2 quadrats, and stem densities in 1/16 m^2 quadrats), vigor (height) and reproductive effort. The abundance of salt marsh epibenthic macroinvertebrates will be determined by counting live animals in 1/16 m^2 quadrats.

Tissue samples of the dominant salt marsh grass in each of the plant associations occurring at each marsh investigated will be collected, rinsed in tap water, and frozen for chemical analysis (metals) by the designated analytical testing laboratory using appropriate Quality Control and Chain-of-Custody procedures.

Sediment cores for the purposes of toxic chemical analysis will be collected from each plant sampling quadrat of each marsh investigated. Determination will be made of soil bulk properties that influence contaminant movement and fate, and also microbial indicators of sewage contamination will be measured. Five sediment cores, one from each of the salt marsh plant associations at each site, will each be split, one half of each archived, and the other composited to form one sample, which will be immediately frozen for chemical analysis by the designated analytical testing laboratory using appropriate quality control and chain of custody procedures. Sediments will be examined for contaminant compounds targeted during Phase I activities. The remainder of each set of five cores will be kept at 5°C as archived samples for the remainder of the project.

Five sediment core replicates will be taken from each physiognomic unit (high marsh and low marsh) at each marsh for the following analyses: description of sediment character, combustible organic carbon and grain size analysis, which will provide a picture of the sedimentary processes and environment in the sampled areas. The abundance of the microbe, *Clostridium perfringens*, will be determined in selected sediment core samples and will serve as an indicator of human sewage contamination of the sediments. A composite of the replicates will be frozen and submitted for chemical analyses (metals and organics).

The quality of the salt marsh habitats will be evaluated and the extent and/or potential of impact from contaminants on habitat quality and trophic transport will be assessed. Progress will be documented with periodic Progress Reports and Interim Reports prepared after completion of field work. Final reports will be accompanied with a Data Dump of ASCII files of all raw and calibrated data, according to the Data Management Plan.

Benthic ecology

Dr. Ray Grizzle, a subcontractor at Campbell University in North Carolina, will assess existing data (Johnston et al. 1992) on faunal benthos and environmental conditions at 23 sites with respect to needs for additional sampling. With the goal of describing spatial patterns in the sampling area and relating spatial variations in faunal benthos to pollutant distribution, we will quantitatively analyze available benthic and

environmental data. Then, we will re-sample sediments and benthos at selected sites, and provide appropriate processing of the samples and quantitative analyses of the resulting data.

Existing data on faunal benthos and environmental conditions at 23 sites in the Portsmouth Harbor area will be assessed by examining field notes on sampling conditions, variability among replicate samples, and other available information. This assessment will be done to determine the usefulness of the benthic data for further analyses, and to determine if additional sediment/benthos samples should be taken. If this assessment indicates that additional samples are needed, selected sites will be re-sampled as soon as possible using coring devices and/or appropriate grab type samples. As many samples as possible during these additional post-1991 sampling efforts will be taken using a new coring device that provides a sample suitable for obtaining sediment profile imaging (SPI) data. The SPI data will be used in conjunction with the benthic data obtained by "traditional" techniques in order to address the usefulness of SPI in future studies.

A variety of univariate analyses (e.g. species numbers, community abundances) and classification techniques will be used to characterize spatial patterns in the available benthic data. In addition, ordination techniques will be used to provide multivariate analyses of spatial aspects of the benthic data and corresponding environmental data. Similar univariate and multivariate analyses will be used on a data set comprised of existing data and any additional post-1991 data that may be collected. These will be primarily carried out in order to look for variations in benthos that may be related to distribution of pollutants.

At the completion of this assessment, we will evaluate the impact of PNS on the benthic community in the surrounding estuary. As part of the long-term monitoring plan, we will evaluate and implement a seasonal monitoring plan for benthic organisms as appropriate. Progress will be documented with periodic Progress Reports and Interim Reports prepared after completion of field work. Final reports will be accompanied with a Data Dump of ASCII files of all raw and calibrated data, according to the Data Management Plan.

5. ***Determine bioaccumulation and toxicological effects of contaminants on lobster and winter flounder.***

<u>Lobster</u>

We will develop and implement a sampling program to assess the bioaccumulation potential of contaminants in lobsters (*Homarus americanus*). Juvenile lobsters have been found inhabiting mud burrows within eelgrass beds in the vicinity of the Portsmouth Naval Shipyard (Johnston et al. 1992). The discovery of lobsters utilizing these eelgrass habitats gave rise to the idea of sampling and measuring the body tissues of long-term resident organisms living within an area of potential contamination. Lobsters have proven to be an excellent indicator of organic and metal contamination and are ideal for use as an indicator of contaminant accumulation (R. Pruell, EPA-ERLN, pers. comm.).

First we will determine if juvenile lobster populations are resident within the eelgrass beds at sites around Seavey Island, and we will document lobster use of those habitats. Using SCUBA and underwater video, we will quantify the number of lobster burrows within eelgrass beds around Seavey. Lobster burrows will be counted and mapped and distribution of burrows will be monitored over the summer of 1993 to determine changes in use patterns of the habitat by lobsters. A mark/recapture study at these sites through the spring of 1993 will be done on juvenile lobsters. The animals will be tagged nondestructively upon capture (at least 50 juveniles/site or a minimum total of 200 juveniles to be tagged) so that we can determine the stability of the populations as well as their health and abundance, and thereby know to what extent the population reflects accumulated contaminants originating at the Shipyard (Figure 1). Additionally, an appropriate reference population from the Gulf of Maine at the Isle of Sholes will be sampled. The Isles of Shoals site will provide juvenile lobsters that have grown up in an offshore environment away from any major sources of contaminants. Reference juveniles and adults will both be taken from this area, as far removed from sources of contamination as possible, for comparison to lobster populations in proximity to the Shipyard. Juvenile lobsters collected from each of the 4 sites around the Shipyard (previously tagged animals, Figure 1) and from the reference site (9 lobsters/site = 45 juveniles total). Adult and subadult lobsters will also be collected from around the Shipyard (5 of each size) and from the reference site (5 of each size).

To determine if lobsters in residence near potential contaminant release sites accumulate toxic contaminants within their body, we will sample muscle tissue from the tail and claw of juvenile lobsters a as well as the hepatopancreas, which previous research has shown to be a good indicator of contamination as it concentrates toxic contaminants. After each capture, some animals will be destroyed and their flesh and hepatopancreas analysed for the presence of chemical contaminants. Adult lobsters will be sampled as well, since it is the adult population that poses an actual threat to human consumers. Dissection of flesh and hepatopancreas extraction will be conducted at Jackson Estuarine Laboratory using ERL-N SOP for the preparation of "Marine Tissues for Organic and Inorganic Analysis". Composite samples (discrete samples for both organic and inorganic analyses) will be prepared for each season for reference and Portsmouth Harbor sites, resulting in 50 organic and 50 inorganic samples per season. Prelabeled sample containers for all samples will be provided to JEL by ERL-N. Samples will be packed and shipped according to the aforementioned SOPs and accompanied by Chain-of-Custody forms. Progress will be documented with periodic Progress Reports and Interim Reports prepared after completion of field work. Final reports will be accompanied with a data dump of ASCII files of all raw and calibrated data.

Winter flounder

Adult winter flounder (*Pseudopleuronectes americanus*) will be collected in the spring of 1993 and the fall of 1993 in Portsmouth Harbor and from reference sites in the Gulf of Maine. Harbor collections will be made by contracting the services of a commercial trawler and making a series of 15 minute tows using a beam trawl constructed for use in the harbor. A rough estimate of population abundance for winter flounder will be made from the results of the trawls. Reference population fish will be purchased from

a commercial trawler fishing in the Gulf of Maine. Fish will be obtained the day of capture, and the location of capture will be noted. Fish from each tow, and from the reference population, will be enumerated, measured, examined for external lesions and abnormalities, placed on ice and transported to Jackson Estuarine Laboratory for dissection and tissue extraction.

Dissection of flesh and liver extraction will be conducted at Jackson Estuarine Laboratory using ERL-N SOP for the preparation of "Marine Tissues for Organic and Inorganic Analysis". Five composite samples (discrete samples for both organic and inorganic analyses) will be prepared for each season for reference and Portsmouth Harbor sites, resulting in 10 organic and 10 inorganic samples per season. Dissection and removal of flounder spleen will be conducted according to ERL-N SOP for "Dissection of Flounder Spleen for Histological Examination". Prelabeled sample containers for all samples will be provided to JEL by ERL-N. Samples will be packed and shipped according to the aforementioned SOPs and accompanied by Chain-of-Custody forms. Progress will be documented with periodic Progress Reports and Interim Reports prepared after completion of field work. Final reports will be accompanied with a data dump of ASCII files of all raw and calibrated data.

Upon completion of the field sampling and laboratory analyses for lobster and flounder, we will evaluate the ecological risk of bioaccumulation of PNS contaminants to this portion of the marine demersal food chain. Based on the sediment contaminant results from our earlier study (Johnston et al. 1991), we will evaluate the feasibility of developing a food chain model for contaminants of interest. The need for such an investigation beyond this study will depend on whether the lobster and/or flounder results show evidence of bioaccumulation for any contaminants possibly originating from Shipyard activities.

6. *Develop a long-term monitoring strategy.*

We will develop a long-term monitoring strategy to determine the long-term effects of contaminant release for input into the strategic risk management plan. This will evaluate information on short-term and long-term variability of the important ecosystem parameters to be monitored in the estuary. The task will include an intensive sampling interval, conducted during an ecologically critical period to establish the necessary baseline for evaluating long-term effects.

Additionally, we will develop a seasonal long-term monitoring plan for conducting sampling for chemical residue analysis and providing samples to the designated analytical testing laboratory using appropriate Quality Control and Chain-of-Custody procedures. Samples could include mussels, eelgrass, and other species as appropriate, seep samples, and samples of selected surface sediments.

Biological and toxicological analysis will be done on selected species in order to monitor the health and abundance patterns of species, as appropriate, and to evaluate

toxicological effects of target contaminants on selected sentinel species. Progress will be documented with periodic Progress Reports and Interim Reports.

7. *Provide technical support at information exchange proceedings.*

Technical support will be provided to the Navy at information exchange proceedings by appropriate scientists working on the project. This will include attending meetings and providing input to the administrative record, as required, and attending public hearings and workshops, as appropriate. Upon approval for public release by NRaD, we will present research results at technical seminars and workshops, as required.

Dr. Ward, the project manager, will provide ongoing coordination with and obtain assistance from PNS, as required to carry out the tasks defined in this statement of work. He will obtain the necessary sampling permits and provide ongoing coordination with appropriate State and Federal agencies to carry out the tasks defined in this work plan.

8. *Document validity of the data by preparing a Quality Assurance/Quality Control (QA/QC) plan.*

The validity of the data will be documented by preparing a Quality Assurance/Quality Control (QA/QC) plan. The QA/QC plan will present, in sufficient detail, information on Chain-of-Custody procedures/, standard operating procedures, analytical method descriptions, and other QA/QC procedures. Health and safety plans for workers, and other information required to document the acceptability of data, will be included in the document.

At present three QA/QC officers have been identified for project activities. Dr. David Burdick will have the major QA/QC responsibilities for all JEL investigators and will oversee the general chain-of-custody procedures, SOP's, analytical method descriptions and other QA/QC procedures. However, Dr. Burdick is also a principal investigator for the project's work in salt marsh systems. Dr. Larry Ward will act as QA/QC officer with regard to the salt marsh investigation. Dr. Robert Swift has been designated the QA/QC officer for the computer modelling effort being conducted by UNH Ocean Engineering program.

BATTELLE MARINE SCIENCES LABORATORY WORK PLAN

Analytical Chemistry for the Estuarine Ecological Risk Assessment Case Study for Naval Shipyard Portsmouth, Kittery, Maine

March 1993

Prepared By:

Battelle Pacific Northwest Laboratories
Marine Sciences Laboratory
439 West Sequim Bay Rd.
Sequim, WA 98382

QUALITY ASSURANCE PROJECT PLAN (QAPjP)

ANALYTICAL CHEMISTRY FOR THE ESTUARINE ECOLOGICAL RISK ASSESSMENT AT NAVAL SHIPYARD PORTSMOUTH, MAINE

Issue Date:

E.A. Crecelius, Program Manager (Concurrence) — 3-11-93 Date

L.F. Lefkovitz, Project Manager (Concurrence) (206) 681-3626 — 3/11/93 Date

R. Cuello, Quality Engineer (Concurrence) — 3/11/93 Date

R.M. Ecker, Manager Marine Sciences Laboratory (Approval) — 3/12/93 Date

RK Johnston, NCCOSC (Approval) — 3/15/93 Date

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QA Plan Distribution List

CW Apts	RM Ecker	LF Lefkovitz
EA Crecelius	TJ Gilfoil	
R Cuello	RR LaBarge	

3.0 INTRODUCTION

3.1 Title:

QA Project Plan (QAPjP) for the Project: Analytical Chemistry for the Estuarine Ecological Risk Assessment at Naval Shipyard Portsmouth, Maine.

3.2 Scope:

To chemically analyze marine sediment, tissue and elutriate samples collected as part of the Estuarine Ecological Risk Assessment at Naval Shipyard Portsmouth. The administration of this project is under the direction of the Marine Sciences Laboratory (MSL) of the Earth and Environmental Sciences Center, Pacific Northwest Laboratories (PNL).

3.3 Client:

Naval Command Control and Ocean Surveillance Center (NCCOSC) and Environmental Research Laboratory Narrangansett

3.4 Authorizing Document:

20898

3.5 QA Requirements Specification(s):

ASME NQA-I AS DELINEATED IN PNL-MA-70

Impact Level III activities shall comply with the Good Practices Standard (GPS) provided in Part 2 of PNL-MA-70, PNL QA Manual. This QAPjP also identifies client QA requirements and any imposed exclusions or limitations to PNL procedure requirements. If other quality-related activities are later performed, the appropriate PNL-MA-70 requirements and procedures shall be applied, unless specifically excluded.

3.6 QA Program/Organization:

The PNL GPS document establishes the minimum quality assurance requirements for work within the laboratory. Every staff member conducts their work in accordance with the GPS. The project organization with key personnel identified is located in Exhibit 5.1, Project Interfaces.

3.7 Impact Level:

The Analytical Chemistry for the Estuarine Ecological Risk Assessment at Naval Shipyard Portsmouth, Maine project has been classified overall as Impact Level (IL) III. All tasks within the project have been classified as IL III, therefore a Work Breakdown Structure (WBS) with corresponding Impact Levels is not attached.

3.8 Special Client Requirements:

Analytical Chemistry Quality Assurance and Quality Control Protocols, Criteria, and Corrective Action for the Estuarine Ecological Risk Assessment at Naval Shipyard Portsmouth, Maine - Addendum, February 2, 1993.

3.9 Other Requirements, Direction or Planning:

See sections 4 through 18 of this QAPjP.

4.0 PROJECT DESCRIPTION

This QAPjP addresses all of the various types of activities that the Analytical Chemistry for the Estuarine Ecological Risk Assessment at Naval Shipyard Portsmouth, Maine project might potentially perform.

4.1 Objectives

The objectives of this project are to perform chemical analysis of sediments, tissues and elutriate samples collected as part of the Estuarine Ecological Risk Assessment at Naval Shipyard Portsmouth.

4.2 Approach

The approach for meeting the objectives of Section 4.1 is documented in this QAPjP.

4.3 Change Control (Scope, Schedule, Budget)

Requests for changes in project scope, schedule or budget must be documented and receive approval from the client.

5.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

Line authority, Quality Assurance authority, support within MSL and interfaces with the client are shown in Exhibit 5.1. The responsibilities of key PNL personnel are summarized in Section 5.1.

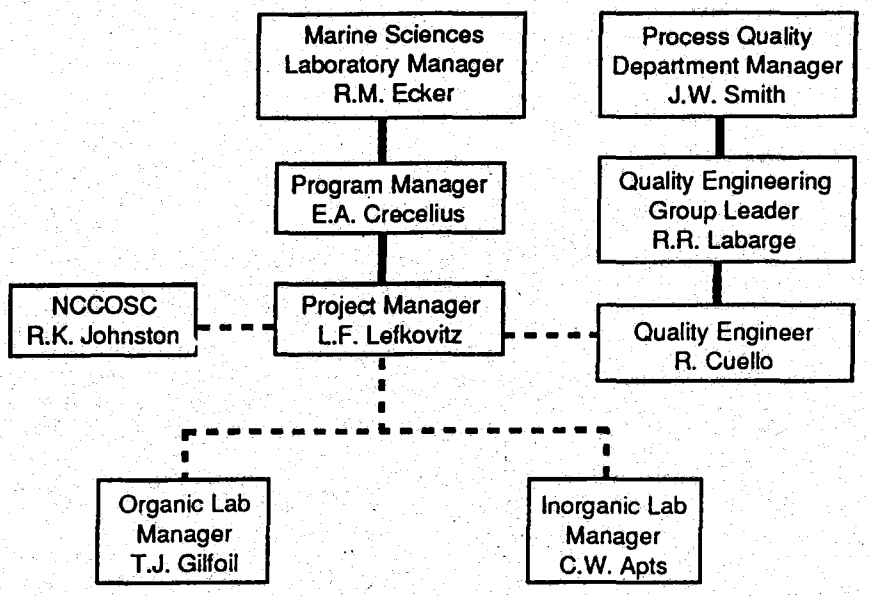
Changes to organizational/interface structures shown in Exhibit 5.1 that do not reflect a change in the overall scope of the activities or a change of requirements will not require a QAPjP revision but will be incorporated in the next required revision of the QAPjP.

5.1 Responsibilities of Key Personnel

Personnel	Responsibilities
Marine Sciences Laboratory Manager	Provides management review of project. Assures appropriate and qualified staff are available.
Program Manager	Provides overall direction of the project for PNL, the Marine Sciences Laboratory, and the client. Ensures that all project objectives are accomplished in a timely manner and within the program budget. Assigns qualified staff to the project. Has direct contact with the PNL Quality Engineer and the client.
Project Manager	Provides planning and management assistance to Program Manager by developing planning documents, directing day-to-day activities to accomplish the program objectives, and coordinating tasks, personnel, and schedules. Manages the project budget and schedules.
Lab Manager	Oversees day-to-day activities in the laboratory. Is responsible for laboratory facilities and test equipment, training of laboratory personnel, and providing direction to project staff. Ensures that laboratory staff are kept current with procedures, investigates suspect results, and reviews laboratory records. Works closely with project manager to coordinate schedules and personnel. Performs QC review of analytical results.

Project Staff	Perform chemical analysis activities in accordance with methods identified in the planning documents. Works under supervision of Lab Manager.
Quality Engineer	Provides QA support at all levels, in such areas as QA requirement guidance and interpretation, audit preparation, QA Plan development or revision, resolving QA problems and document review. Provides independent oversight to verify the project activities are being conducted in a manner consistent with applicable requirements identified in this QA Plan. Also responsible for the review and oversight of the quality of data generated from the chemical and biological analyses.

EXHIBIT 5.1 Project Interfaces



6.0 QA OBJECTIVES AND QUALITY CONTROL CHECKS FOR MEASUREMENT DATA

The characteristics used to define data quality are accuracy, precision, completeness, comparability, representativeness and method detection limit. The definition and application of these parameters to this project are discussed below. Data quality objectives (DQOs) for accuracy, precision, and completeness are shown in Table 6.1. Table 6.1 also contains the applicable QC measurements and the minimum frequency they need to be performed during the chemical analysis of the sediments, tissues, and elutriates.

The precision and accuracy objectives specified in Table 6.1 are based on standard method performance information, when available, and historical laboratory performance. Table 6.2 contains a list of the parameters to be analyzed along with their associated target method detection limits. Table 6.3 is a reference list of the applicable chemical analytical methods that will be used on this project.

6.1 DQO Definitions

ACCURACY - a measure of the bias of a system or measurement. It is the closeness of agreement between an observed value and an accepted value.

For this project, accuracy of chemical analysis will be determined through the analysis of matrix spikes, surrogate internal standards, method blanks, calibration checks and, when available, standard reference material (SRM). SRMs are materials that have been certified by a recognized authority (e.g., National Institute of Standards and Technology) and which are treated and analyzed as an actual sample. Matrix spikes will be performed by adding a known quantity of target analytes into a sample and preparing and analyzing the sample the same as a regular sample. Surrogate internal standards will be spiked into each sample just prior to extraction and will be used to monitor the method performance. Method blanks will be used to measure contamination associated with laboratory processing and analyses.

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 more than 4 times and no less than 2 times the sample value.

For measurements where matrix spikes are used, percent recovery shall be used.

$$\%R = 100 \times \frac{S - U}{C_{sa}}$$

%R = percent recovery
S = measured concentration in spiked aliquot
U = measured concentration in unspiked aliquot
C_{sa} = actual concentration of spike added

For situations where a SRM is used, recovery shall be used.

$$R = \frac{C_1}{C_2} \times 100$$

R = recovery
C_1 = measured value
C_2 = certified value

For situations where calibration checks are used, percent difference shall be used.

$$PD = \frac{C_1 - C_2}{C_2} \times 100$$

PD = percent difference
C_1 = measured calibration check value
C_2 = original calibration value

PRECISION - a measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions.

For this project, measures of analytical precision will be determined by the analysis of laboratory duplicates. Laboratory duplicates will be prepared by homogenizing and splitting a sample in the laboratory, and carrying the subsamples through the entire analytical process. Precision will be expressed in terms of the relative percent difference (RPD) for all laboratory duplicates.

$$RPD = \frac{(C_1 - C_2)}{(C_1 + C_2)/2} \times 100$$

RPD = relative percent difference
C_1 = larger of the two observed values
C_2 = smaller of the two observed values

COMPLETENESS - a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions.

Target completeness values are 90% for sample analysis. Defined as follows for all measurements:

$$\%C = 100 \times \frac{V}{n}$$

% C = percent completeness
V = number of measurements judged valid
n = total number of measurements necessary to achieve a specified statistical level of confidence in decision making

DETECTION LIMIT - Detection limit is the minimum concentration of a substance that can be measured and reported. Method Detection Limit (MDL) is the minimum concentration of a substance that can be identified, measured, and reported with 99 percent confidence that the analyte concentration is greater than zero. MDLs are determined from seven replicate analyses of a sample of a given matrix of either blanks, low level spikes, or SRMs. MDLs shall be established for all parameters and should be generated within the 12 months prior to the sample analyses with which they are reported. Target MDLs for the parameters of interest are presented in Table 6.2. MDL is defined as follows:

$$MDL = t_{(n-1,\ 1-\infty = 0.99)} \times S$$

MDL = method detection limit
S = standard deviation of the replicate analyses
$t_{(n-1,\ 1-\infty = 0.99)}$ = Students' t-value appropriate to a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom

The achieved MDLs should be within a factor of two of the target MDL, or alternatively, within a factor of two of the "typical" marine minimum concentration. While the achieved MDLs may

vary as a result of sample matrix, the achieved MDLs for organics will be based on a sample size of 30g for sediments, 20g for tissues, and 500 mL for elutriates while the achieved MDLs for inorganics will be based on a sample size of 10g for sediments, 10g for tissues, and 500 mL for elutriates.

Limit of Quantification (LOQ) is the level above which quantitative results may be obtained with a specified degree of confidence. LOQ is defined as 10 times the standard deviation of replicate analyses from the achieved MDL study or the target MDL, whichever is higher.

Instrument Detection LImit (IDL) is the smallest signal above background noise that an instrument can detect reliably.

REPRESENTATIVENESS - expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition.

Representativeness will be ensured by the proper handling and storage of samples and analysis within the specified holding times so that the material analyzed reflects the material collected as accurately as possible.

COMPARABILITY - expresses the confidence with which one data set can be compared to another.

Comparability for this project will not be quantified, but will be addressed through the use of recognized laboratory methods. The use of standard reporting units also will facilitate comparability with other data sets (see Section 10.3).

6.2 Corrective Action for Results Outside Established DQOs

Results outside the established criteria in Tables 6.1 and 6.2 shall be brought to the attention of the Lab Manager and Project Manager who shall determine and document the appropriate corrective action. These actions may include, but are not limited to, review of data and calculations, flagging of suspect data (flagging requirements are addressed in Section 10.3) or reprepping and/or re-analyses of individual or entire batches of samples. The client will be notified prior to the reprepping of any samples. The following describes guidelines to be followed when established criteria are not met.

For all organic and inorganic analyses, a Preliminary QC Checklist (see Exhibit 6.1 for an example) shall be prepared by the analyst immediately following analysis of a batch of samples. This checklist shall be used to identify any QC problems that might have occurred and provides a mechanism to determine corrective action at an early stage of the data review process.

Matrix Spikes - All matrix spike recoveries which are outside the established DQOs shall be noted in the narrative and flagged on the final data report. 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 quality control criteria.

Surrogates - Surrogate compounds; representative of the analytes of interest, will be added in known quantities prior to extraction for organics. If surrogate recoveries are outside the 30 - 130% warning limit and there is a > 50% difference between SRM surrogate recoveries and sample surrogate recoveries, than the samples needs to be re-extracted and re-analyzed. If after re-analysis, the same recoveries are outside the limits, the problem will be considered a matrix effect and a third re-extraction and re-analysis is not required.

Replicates - All samples associated with laboratory duplicates that are outside the established RPD control limits will be noted in the narrative and flagged in the final data report. In addition, no more than 35% of all RPDs within a set of analytes can be >30% RPD (for analytes > LOQ). If there are more than 35%, that sample batch must be considered for reprepping and/or re-analysis based on the other quality control criteria.

SRMs - SRM values exceeding the recovery range from the certified value should be noted in the narrative and flagged in the final data report. In addition, if the acceptable limits established in Table 6.1 for SRMs are exceeded, then the batch of samples associated with the out of control SRMs must be considered for re-analysis based on the other quality control criteria.

Calibration Check Standards (CCS) - If the CCSs fall outside the criteria established in Table 6.1, then that batch of samples associated with the out of control CCSs must be re-analyzed.

Method Blanks - Any blank values detected above the established criteria should be noted in the narrative and the corresponding data should be flagged as blank contaminated. If the problem significantly affects the sample data for that batch re-analysis may be necessary.

6.3 Holding Times

Holding times for analytical chemistry begin the day of sample receipt at the laboratory. These holding times and requirements are listed below. After receipt at the laboratory, all sediment and tissue samples shall be held frozen (-20 ± 10°C) until extraction (organics) or freeze drying (metals) is complete All elutriate samples shall be held refrigerated (4 ± 2°C) until extracted. All extracts shall be held frozen (-20 ± 10°C) until analyses.

Analysis	Holding Time
Sediment	
Metals (except Mercury)	6 months
Mercury	28 days
Pesticides/PAH/PCB	60 days to extraction (*); 40 days (to analysis after extraction)
Tissue	
Metals (except Mercury)	6 months
Mercury	28 days
Pesticides/PAH/PCB	60 days to extraction (*); 40 days (to analysis after extraction)
Elutriate	
Metals (except Mercury)	6 months
Mercury	28 days
Pesticides/PAH/PCB	10 days to extraction; 40 days (to analysis after extraction)

* If sediments and tissues are held frozen (-20°C), holding times may be extended up to 6 months (Puget Sound Estuary Program, Recommended Guidelines for Measuring Organic Compounds in Puget Sound Sediment and Tissue Samples, EPA, December 1989)

TABLE 6.1 Data Quality Objectives for Sediment, Tissue and Elutriate Chemistry

Parameter	QC Measurement	Frequency	Acceptable Limits
PCB/Pesticides, PAHs	Laboratory Reagent Blank	1 per 20 samples	• < LOQ
	Calibration Check Standards	Beginning and end of batch and every 10 samples	• <25%[a]; • no more than 2 PDs for each calibration check can be > 25%[a]
	Surrogate Internal Standards	Each sample	• 30 - 130%[b] is the warning limit; • recommended control limit is >50% difference between SRM surrogate and sample surrogate recoveries
	Matrix Spike	1 per 20 samples	• 50 - 150%[b]
	Laboratory Duplicates	1 per 20 samples	• <30%[c] for analytes > LOQ; • no more than 35% of all RPDs within a set of analytes (i.e., PAHs or PCB/Pesticides) can be >30%[c]
	Standard Reference Material	1 per 20 samples	• ±40%[d] (for analytes > LOQ); • no more than 35% of the all SRM recoveries within a set of analytes (i.e., PAHs or PCB/Pesticides) can exceed ±40%[d]; • the overall average recoveries should be ±35%[e]
Al, Ag, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sn, Zn	Laboratory Reagent Blank[f]	1 per 20 samples	• < LOQ
	Calibration Check Standards[g]	Beginning and end of batch and every 10 samples	• <25%[a] for Hg, <15%[a] for all other metals; • no more than 2 PDs can be > 15%[a] (does not include Hg)
	Matrix Spike[f]	1 per 20 samples	• 85 - 115%[b]
	Laboratory Duplicates	1 per 20 samples	• <50%[c] for Al and Fe, <20%[c] for all other metals for analytes > LOQ; • no more than 35% of all RPDs (except Al and Fe) can be >30%[c]
	Standard Reference Material	1 per 20 samples	• ±25%[d] for Hg, ±20%[d] for all other metals (for analytes > LOQ); • no more than 15% of all SRM recoveries can be outside the SRM recovery ranges

(a) Percent Difference (PD)
(b) Percent Recovery
(c) Relative Percent difference (RPD)
(d) SRM Percent Recovery
(e) [The Σ of all SRM recoveries (in percent) divided by the number of recoveries calculated] x 100
(f) Applies to AA and ICP/MS only
(g) For metals, the Calibration Check Standard will be an analysis of a SRM

TABLE 6.2 List of Analytes, Methods and Target MDLs[a]

Analyte	Reference Method	Sediment MDL	Tissue MDL	Elutriate MDL
Metals				
Aluminum	XRF	19800 µg/g	N/A	N/A
Arsenic	XRF	2.5 µg/g	N/A	N/A
Cadmium	GFAA	0.1 µg/g	N/A	N/A
Chromium	XRF	33 µg/g	N/A	N/A
Copper	XRF	5.5 µg/g	N/A	N/A
Iron	XRF	2600 µg/g	N/A	N/A
Lead	XRF	6.2 µg/g	N/A	N/A
Manganese	XRF	50 µg/g	N/A	N/A
Mercury	CVAA	0.01 µg/g	N/A	N/A
Nickel	XRF	7.5 µg/g	N/A	N/A
Silver	GFAA	0.04 µg/g	N/A	N/A
Tin	ICP/MS	0.5 µg/g	N/A	N/A
Zinc	XRF	7.8 µg/g	N/A	N/A
Aluminum	ICP/MS	N/A	34 µg/g	N/A
Arsenic	XRF	N/A	1.2 µg/g	N/A
Cadmium	ICP/MS	N/A	0.44 µg/g	N/A
Chromium	ICP/MS	N/A	0.40 µg/g	N/A
Copper	XRF	N/A	2.7 µg/g	N/A
Iron	XRF	N/A	26 µg/g	N/A
Lead	ICP/MS	N/A	0.09 µg/g	N/A
Manganese	XRF	N/A	1.8 µg/g	N/A
Mercury	CVAA	N/A	0.006 µg/g	N/A
Nickel	ICP/MS	N/A	0.54 µg/g	N/A
Silver	ICP/MS	N/A	0.30 µg/g	N/A
Zinc	XRF	N/A	27 µg/g	N/A
Aluminum	GFAA	N/A	N/A	10.0 µg/L
Arsenic	HAA	N/A	N/A	0.5 µg/L
Cadmium	GFAA, ICP/MS	N/A	N/A	0.2 µg/L
Chromium	GFAA	N/A	N/A	1.0 µg/L
Copper	GFAA, ICP/MS	N/A	N/A	0.2 µg/L
Iron	GFAA	N/A	N/A	20.0 µg/L
Lead	GFAA, ICP/MS	N/A	N/A	0.2 µg/L
Manganese	GFAA	N/A	N/A	0.5 µg/L
Mercury	CVAF	N/A	N/A	0.001 µg/L
Nickel	GFAA, ICP/MS	N/A	N/A	0.2 µg/L
Silver	GFAA, ICP/MS	N/A	N/A	0.01 µg/L
Tin	ICP/MS	N/A	N/A	0.05 µg/L
Zinc	GFAA	N/A	N/A	1.0 µg/L
Chlorinated Pesticides				
Aldrin	NOAA	0.6 ng/g	0.6 ng/g	0.05 µg/L
α-Chlordane	NOAA	0.6 ng/g	0.6 ng/g	0.05 µg/L
γ-BHC (Lindane)	NOAA	0.6 ng/g	0.6 ng/g	0.05 µg/L
o,p'-DDD	NOAA	0.6 ng/g	0.6 ng/g	0.05 µg/L
p,p'-DDD	NOAA	0.6 ng/g	0.6 ng/g	0.05 µg/L
o,p'-DDE	NOAA	0.6 ng/g	0.6 ng/g	0.05 µg/L
p,p'-DDE	NOAA	0.6 ng/g	0.6 ng/g	0.05 µg/L
o,p'-DDT	NOAA	0.6 ng/g	0.6 ng/g	0.05 µg/L
p,p'-DDT	NOAA	0.6 ng/g	0.6 ng/g	0.05 µg/L

TABLE 6.2 Continued

Analyte	Reference Method	Sediment MDL	Tissue MDL	Elutriate MDL
Chlorinated Pesticides (Continued)				
Heptachlor	NOAA	0.6 ng/g	0.6 ng/g	0.05 µg/L
Heptachlor epoxide	NOAA	0.6 ng/g	0.6 ng/g	0.05 µg/L
Hexachlorobenzene	NOAA	0.6 ng/g	0.6 ng/g	0.05 µg/L
Mirex	NOAA	0.6 ng/g	0.6 ng/g	0.05 µg/L
Trans-nonachlor	NOAA	0.6 ng/g	0.6 ng/g	0.05 µg/L
PCBs				
8 (2,4')	NOAA	0.5 ng/g	0.5 ng/g	0.05 µg/L
18 (2,2',5)	NOAA	0.5 ng/g	0.5 ng/g	0.05 µg/L
28 (2,4,4')	NOAA	0.5 ng/g	0.5 ng/g	0.05 µg/L
44 (2,2',3,5')	NOAA	0.5 ng/g	0.5 ng/g	0.05 µg/L
52 (2,2',5,5')	NOAA	0.5 ng/g	0.5 ng/g	0.05 µg/L
66 (2,3',4,4')	NOAA	0.5 ng/g	0.5 ng/g	0.05 µg/L
101 (2,2',3,5,5')	NOAA	0.5 ng/g	0.5 ng/g	0.05 µg/L
105 (2,3,3',4,4')	NOAA	0.5 ng/g	0.5 ng/g	0.05 µg/L
118 (2,3',4,4',5)	NOAA	0.5 ng/g	0.5 ng/g	0.05 µg/L
128 (2,2',3,3',4,4')	NOAA	0.5 ng/g	0.5 ng/g	0.05 µg/L
138 (2,2',4,4',5,5')	NOAA	0.5 ng/g	0.5 ng/g	0.05 µg/L
153 (2,2',4,4',5,5')	NOAA	0.5 ng/g	0.5 ng/g	0.05 µg/L
170 (2,2',3,3',4,4',5)	NOAA	0.5 ng/g	0.5 ng/g	0.05 µg/L
180 (2,2',3,4',5,5',6)	NOAA	0.5 ng/g	0.5 ng/g	0.05 µg/L
187 (2,2',3,4',5,5',6)	NOAA	0.5 ng/g	0.5 ng/g	0.05 µg/L
195 (2,2',3,3',4,4',5,6)	NOAA	0.5 ng/g	0.5 ng/g	0.05 µg/L
206 (2,2',3,3',4,4',5,5',6)	NOAA	0.5 ng/g	0.5 ng/g	0.05 µg/L
209 (2,2',3,3',4,4',5,5',6,6')	NOAA	0.5 ng/g	0.5 ng/g	0.05 µg/L
PAHs				
Anthracene	NOAA	5.0 ng/g	20.0 ng/g	0.1 µg/L
Benzo(a)anthracene	NOAA	5.0 ng/g	20.0 ng/g	0.1 µg/L
Benzo(a)pyrene	NOAA	5.0 ng/g	20.0 ng/g	0.1 µg/L
Benzo(e)pyrene	NOAA	5.0 ng/g	20.0 ng/g	0.1 µg/L
Benzo(g,h,i)perylene	NOAA	5.0 ng/g	20.0 ng/g	0.1 µg/L
Chrysene	NOAA	5.0 ng/g	20.0 ng/g	0.1 µg/L
Dibenzo(a,h)anthracene	NOAA	5.0 ng/g	20.0 ng/g	0.1 µg/L
Fluoranthene	NOAA	5.0 ng/g	20.0 ng/g	0.1 µg/L
Fluorene	NOAA	5.0 ng/g	20.0 ng/g	0.1 µg/L
Indeno(1,2,3-cd)pyrene	NOAA	5.0 ng/g	20.0 ng/g	0.1 µg/L
Perylene	NOAA	5.0 ng/g	20.0 ng/g	0.1 µg/L
Phenanthrene	NOAA	5.0 ng/g	20.0 ng/g	0.1 µg/L
Pyrene	NOAA	5.0 ng/g	20.0 ng/g	0.1 µg/L
C_1 alkyl phenanthrenes plus anthracenes	NOAA	5.0 ng/g	20.0 ng/g	0.1 µg/L
C_2 alkyl phenanthrenes plus anthracenes	NOAA	5.0 ng/g	20.0 ng/g	0.1 µg/L
C_3 alkyl phenanthrenes plus anthracenes	NOAA	5.0 ng/g	20.0 ng/g	0.1 µg/L
C_4 alkyl phenanthrenes plus anthracenes	NOAA	5.0 ng/g	20.0 ng/g	0.1 µg/L

(a) Detection limits are in dry weight for all sediment and tissue parameters.

TABLE 6.3 List of Chemical Analytical Methods

GFAA	Graphite Furnace Atomic Absorbtion - SOPs **MSL-M-033, Trace Elements in Tissues and Sediments by Stabilized Temperature GFAA** and **MSL-M-032, Determination of Trace Elements in Water by Stabilized Temperature GFAA Spectrometry.**
CVAA	Cold Vapor Atomic Absorption - SOP **MSL-M-031, Total Mercury in Sediment and Tissue by CVAA.**
CVAF	Cold Vapor Atomic Fluorescence - SOP **MSL-M-027, Total Mercury in Aqueous Samples by CVAF.**
HAA	Hydride Atomic Absorption - SOP **MSL-M-035, Arsenic Speciation in Aqueous Samples.**
XRF	SOP - **7-40.48, Procedures and Quality Control for Energy Dispersive X-Ray Fluorescence Spectroscopy Using the BFP Approach With the Kevex 0810A System**
ICP/MS	EPA 6020, Inductively Coupled Plasma/Mass Spectrometry,CLP-M, Version 8.0 - Modified for the Contract Laboratory Program.
NOAA	**MacLeod, W.D., et al. "Standard analytical procedures of the NOAA National Analytical Facility," 1985-1986: Extractable toxic organic compounds, second edition. U.S. Dep. Commer. NOAA Tech. Memo. NMFS F/NWC-92. 1985.** and **Krahn et al. "New HPLC Cleanup and Revised Extraction Procedures for Organic Contaminants," NOAA Technical Memorandum NMFS F/NWC-153. 1988.** Samples will be extracted, cleaned-up and quantified in accordance with the following respective NOAA based SOPs: For Pesticides/PCBs - **MSL-M-079, Extraction and Clean-up of Sediment and Tissue for Semivolatile Organics following the Surrogate Internal Standard Method; MSL-M-080, Extraction and Clean-up of Water for Semivolatile Organics following the Surrogate Internal Standard Method;** and **MSL-M-044, Analysis of PCBs and Chlorinated Pesticides by Gas Chromatography with Electron Capture Detection** For PAHs - **MSL-M-079, Extraction and Clean-up of Sediment and Tissue for Semivolatile Organics following the Surrogate Internal Standard Method; MSL-M-080, Extraction and Clean-up of Water for Semivolatile Organics following the Surrogate Internal Standard Method;** and **MSL-M-043, Identification and Quantification of Polynuclear Aromatic Hydrocarbons by Gas Chromatography/Mass Spectrometry**

EXHIBIT 6.1 Preliminary QC Checklist Example

PRELIMINARY QC CHECKLIST **DATE:** _____

PROJECT: _____

PARAMETER: _____

BATCH: _____

BATTELLE #: _____

SAMPLES INVOLVED: _____

QC Parameter	Control Limits (1)	No. of DQO Exceedences	COMMENTS
SURROGATES: (2)	40 to 120%		
Mean Surrogate Recovery:	40 to 120%		
Recoveries outside of limits	+/- 15% from mean		
MATRIX SPIKE: (% Recoveries) MS:	40 to 120%		
MATRIX SPIKE: (% Recoveries) MSD:	40 to 120%		
MS/MSD RPDs:	+/- 30%		
REPLICATE PRECISION: (RSDs)	+/- 30%		
Method Blank (Values above DL)	Detected Values		
SRM: Difference from cert. mean	+/- 30%		

(1) Control limits listed in project quality assurance plan.
(2) Note if this based on initial extraction or after re-extracts.

Laboratory Manager: _____ Batelle MSL Program Manager: _____
Date: _____ Date: _____

7.0 ANALYTICAL PROCEDURES

Sediment, tissue and elutriate samples must be subjected to a series of chemical procedures and evaluations. These procedures and evaluations shall be governed by this QAPjP and/or Standard Operating Procedures.

Care should be taken during the processing of all samples that enough material is extracted so that the dry-weight sample size is comparable (if enough sample is available) to the sample size used to determine the MDL (for organics - 30g for sediments, 20g for tissues, and 500 mL for elutriates; for inorganics - 10g for sediments, 10g for tissues, and 500 mL for elutriates. This will insure that the MDLs are as low as possible for the sample analysis. In cases where there appears not to be enough material for the analysis, the client should be consulted to determine if it is possible to pool the samples (from appropriate replicates) to obtain enough material for a valid analysis.

7.1 Sample Analysis Scheme and Archiving Requirements

7.1.1 Sample Analysis Scheme

The maximum batch size shall be 20 samples. Table 7.1 shows an example of the minimum (5%) QA/QC samples required for the analysis of a hypothetical batch of 20 samples.

Table 7.1 Sample Analysis Scheme

Sample	Number	Description
EXTRACTED SAMPLES		
$S_1, S_2, S_3, \ldots, S_{20}$	20	Field Sample
SRM	1	Standard Reference Material
LD	1	Laboratory Duplicate
MS	1	Matrix Spike
Blank	1	Reagent Blank
Total $ES_1, \ldots, ES_{20}$	24	Extracted Samples
SEQUENCE OF ANALYSIS		
CC_1	1	Calibration Check
$ES_1, \ldots, ES_{10}$	10	Extracted Samples
CC_2	1	Calibration Check
$ES_{11}, \ldots, ES_{20}$	10	Extracted Samples
CC_3	1	Calibration Check
$ES_{21}, \ldots, ES_{24}$	4	Extracted Samples
CC_4	1	Calibration Check
Total	28	Analytical Analyses

7.1.2 Sample Archiving

If there is adequate sediment, tissue and/or elutriate sample remaining after extraction, an aliquot of the sediment and/or tissue shall be archived in a precleaned jar and stored frozen for up to 6 months after collection date. Storage location will depend on the type of sample and type of analysis (see project manager). Temperature of the archival facility shall be checked and recorded daily with a thermometer calibrated in accordance with **MSL-M-047, Calibration and Use of Thermometers.**

7.2 Chemistry Procedures

The sediment, tissue and elutriate samples must be subjected to a series of chemical evaluations following the procedures outlined in Table 6.3 and this section of the QAPjP. Potential chemical constituents to be analyzed for, as well as the corresponding standard analytical methods on which the primary analytical laboratory bases its procedures, are shown in Table 6.2 and 6.3. Appendix A contains the list of the chemical analytical SOPs that will be used on this project.

The sediment, tissue and elutriate samples shall be analyzed for the parameters using the detection limits specified in Table 6.2. If these detection limits are not achievable, attempts shall be made to achieve the lowest practical detection limits.

The analyses will be distributed as listed below. Changes to this list shall be approved by the Program Manager and the client prior to submittal to the laboratory for analysis.

Laboratory	Sediment	Tissue	Elutriate
Marine Sciences Laboratory	Metals, Pesticides, PCBs, PAHs	Metals, Pesticides, PCBs, PAHs	Metals, Pesticides, PCBs, PAHs
Pacific Northwest Laboratories	Metals (Al, As, Cr, Cu, Fe, Mn, Pb, Ni, Zn)	Metals (As, Cu, Fe, Mn, Zn)	N/A

7.2.1 Organics in Sediments and Tissues

The details of the sediment extraction procedure for PAH and PCB/pesticide analysis are presented in SOP **MSL-M-079, Extraction and Clean-up of Sediment and Tissue for Semivolatile Organics following the Surrogate Internal Standard Method**. Briefly, samples will be spiked with the surrogates. Samples will be solvent extracted and then purified using alumina/silica column chromatography followed by high-performance size-exclusion chromatography. Extracts will be quantified by the internal standard method, using surrogate internal standards.

PCB and pesticide analysis will be carried out by capillary gas chromatography with electron capture detection (GC/ECD) as described in SOP **MSL-M-044, Analysis of Polychlorinated Biphenyls and Chlorinated Pesticides by Gas Chromatography with Electron Capture Detection**. For PCBs and Pesticides, all analyses require qualitative confirmation using a second column which is different from the one used in the initial quantitative GC analyses. PAHs will be determined by capillary gas chromatography/mass spectrometry (GC/MS) using selected ion monitoring according to SOP **MSL-M-043, Identification and Quantification of Polynuclear Aromatic Hydrocarbons by Gas Chromatography/Mass Spectrometry**.

7.2.2 Organics in Elutriates

The details of the elutriate extraction procedure for PAH and PCB/pesticide analysis are presented in SOP **MSL-M-080, Extraction and Clean-up of Water for Semivolatile Organics following the Surrogate Internal Standard Method**. Samples will be spiked with the surrogates, solvent extracted and then the concentrated sample extracts will be cleaned up by alumina/silica column chromatography prior to analysis. If necessary, sulfur from sample extracts will be removed by a copper clean up procedure. Extracts will be quantified by the internal standard method, using the surrogate internal standards.

PCB and pesticide analysis will be carried out by capillary gas chromatography with electron capture detection (GC/ECD) as described in SOP **MSL-M-044, Analysis of Polychlorinated Biphenyls and Chlorinated Pesticides by Gas Chromatography with Electron Capture Detection.** For PCBs and Pesticides, all analyses require qualitative confirmation using a second column which is different from the one used in the initial quantitative GC analyses. PAHs will be determined by capillary gas chromatography/mass spectrometry (GC/MS) using selected ion monitoring according to SOP **MSL-M-043, Identification and Quantification of Polynuclear Aromatic Hydrocarbons by Gas Chromatography/Mass Spectrometry.**

7.2.3 Metals in Sediments

Energy dispersive x-ray fluorescence (XRF) spectroscopy does not require sediments to be processed beyond freeze drying and grinding. Dried subsamples of the homogenized sediment samples will be exposed to XRF for quantitation of aluminum, arsenic, chromium, copper, iron, lead, manganese, nickel, and zinc. XRF analysis will be performed according to SOP **7-40.48, Procedures and Quality Control for Energy Dispersive X-Ray Fluorescence Spectroscopy Using the BFP Approach with the Kevex 0810A System.**

For analysis by atomic absorption, additional sediment subsamples will be digested with an HNO_3/HCLO4 acid mixture and then subsequently with hydrofluoric acid according to SOP **MSL-M-007, TAMU Sediment Digestion.** The resultant digestate will then be split for analysis of cadmium and silver by graphite furnace atomic absorption (GFAA) spectrometry, mercury by cold vapor atomic absorption (CVAA), and tin by inductively coupled plasma/mass spectrometry (ICP/MS). Specific details of analytical procedures are included in SOPs **MSL-M-033, Trace Elements in Sediment and Tissues by GFAA; MSL-M-031, Total Mercury in Tissues and Sediment by CVAA**; and **EPA Method 6020.**

For all metals analyzed by atomic absorbtion and ICP/MS, results will be blank corrected by subtracting the blank absorbance readings prior to performing quantitation calculations.

7.2.4 Metals in Tissues

Energy dispersive x-ray fluorescence (XRF) spectroscopy does not require tissues to be processed beyond freeze drying and grinding. Dried subsamples of the homogenized tissue samples will be exposed to XRF for quantitation of arsenic, copper, iron, manganese, and zinc. XRF analysis will be performed according to SOP **7-40.48, Procedures and Quality Control for Energy Dispersive X-Ray Fluorescence Spectroscopy Using the BFP Approach with the Kevex 0810A System.**

For analysis by inductively coupled plasma/mass spectrometry (ICP/MS) and cold vapor atomic absorption (CVAA), additional tissue subsamples will be digested with an $HNO_3/HClO_4$ acid mixture according to SOP **MSL-M-0018, TAMU Tissue Digestion.** The resultant digestate will then be split for analysis of aluminum, cadmium, chromium, lead, nickel, and silver by ICP/MS and mercury by CVAA. Specific details of analytical procedures are included in **EPA Method 6020** and SOP **MSL-M-031, Total Mercury in Tissues and Sediment by CVAA.**

For all metals analyzed by atomic absorbtion, results will be blank corrected by subtracting the blank absorbance readings prior to performing quantitation calculations. For all metals analyzed by ICP/MS, results will be blank corrected by subtracting the signal readings prior to performing quantitation calculations.

7.2.5 Metals in Elutriates

For cadmium, copper, lead, nickel and silver; samples are extracted in accordance with SOP

MSL-M-034, APDC Extraction for Trace Metals in Water. Briefly, samples are chelated, precipitated out of solution, the filtered, The filter is digested in concentrated acid and the digestate analyzed in accordance with SOP **MSL-M-032, Determination of Trace Elements in Water by Stabilized Temperature Platform GFAA Spectrometry** or **EPA Method 6020.**

For aluminum, chromium, iron, manganese, and zinc; samples are analyzed directly in accordance with SOP **MSL-M-032, Determination of Trace Elements in Water by Stabilized Temperature Platform GFAA Spectrometry.**

For tin; samples are analyzed directly in accordance with **EPA Method 6020.**

For mercury; samples are analyzed directly in accordance with SOP **MSL-M-027, Total Mercury in Aqueous Samples by CVAF**. Briefly, this method is a CVAF technique, based upon the emission of 254 nm radiation by excited Hg° atoms in an inert gas stream. Mercuric ions in the oxidized sample are reduced to Hg° with $SnCl_2$, and then purged onto gold-coated sand traps as a means of preconcentration and interference removal. Mercury vapor is thermally desorbed to a second "analytical" gold trap, and from that into the fluorescence cell. Fluorescence (peak ares) is proportional to the quantity of mercury collected, which is quantified using a standard curve as a function of the quantity of sample purged.

For arsenic; the samples are analyzed in accordance with SOP **MSL-M-035, Arsenic Speciation in Aqueous Samples**. Briefly, arsenate, arsenite, methylarsonic acid and dimethylarsinic acid are volatilized from solution at a specific pH after reduction to the corresponding arsines with sodium borohydride. The volatilized arsines are then swept onto a liquid nitrogen cooled chromatographic trap, which upon warming, allows for a separation of species based on boiling points. The released arsines are swept by helium carrier gas into a quartz cuvette burner cell, where they are decomposed to atomic arsenic. Arsenic concentrations are then determined by atomic absorption spectroscopy.

For all metals analyzed by atomic absorbtion, results will be blank corrected by subtracting the blank absorbance readings prior to performing quantitation calculations. For all metals analyzed by ICP/MS, results will be blank corrected by subtracting the signal readings prior to performing quantitation calculations.

8.0 SAMPLE CUSTODY AND LAB DOCUMENTATION

All of the samples shall be handled in such a manner to preclude the contamination or loss of any of the samples. Following receipt of samples at the MSL, all samples shall be stored as required by section 6.3 of this QAPjP. Temperatures of the storage facilities shall be checked and recorded daily with a certified thermometer or a thermometer calibrated in accordance with **MSL-M-047, Calibration and Use of Thermometers.**

8.1 Sample Chain-of-Custody

The chain-of-custody of samples from the MSL to the Richland, Pacific Northwest Laboratories analytical XRF lab shall be controlled in accordance with **MSL-A-002, Sample Chain-of-Custody.**

8.2 Lab Documentation

Lab documentation shall be reviewed by the cognizant peer reviewer for completeness, legibility and reasonableness. This review shall be documented by signature or initials of the reviewer and date of review on the documentation. Only black ink shall be used to record information on data forms.

8.3 Corrections to Documentation

If an error is made on any field or laboratory documentation, an individual may correct the error by drawing a single line through the error and entering the correct information. The error shall not be obliterated. All non-editorial corrections shall be initialed and dated.

9.0 CALIBRATION PROCEDURES AND FREQUENCY

All measuring and test equipment (M&TE) must be controlled in accordance with PNL-MA-70 Administrative Procedure **PAP-70-1201, Calibration Control System.** All M&TE used on this project shall be traceable to the data collected and shall be calibrated before use.

Analytical Chemistry Calibration

Calibration methods for all chemical analytical processes are addressed in each specific SOP. Calibration check standard acceptance criteria are addressed in Table 6.1. As a minimum, calibrations should include:

- standards that are traceable to nationally recognized standard organization(s)
- standards that are within their expiration date
- using standard concentrations that bracket the expected concentration of the sample(s)

10.0 DATA REDUCTION, VALIDATION, AND REPORTING

The following sections briefly describe the data reduction, validation, and reporting procedures that shall be used.

10.1 Data Reduction and Reporting

Chemistry Data

Data packages for chemical analyses shall include, as applicable, the following:

1) Analytical results
   - analyte concentration
   - sample weight
   - percent moisture (for non-aqueous samples)
   - final volume of extract or diluted sample

2) Holding Times/Sample Tracking Information
   - date samples received
   - date samples extracted and/or digested
   - date analyzed for each parameter
   - Battelle log-in form with Battelle ID, client ID and batch number

3) Surrogates
   - amount of surrogate spiked, and percent recovery of each surrogate

4) Matrix Spike
   - amount spiked and percent recovery

5) Calibration Check Sample
   - amount spiked, and percent difference of each compound

6) Blank
   - identity and amount of each constituent

7) Detection Limit
   - analyte detection limits with methods of estimation

8) Chromatograms (for organic analysis)
   All chromatograms properly labeled with or traceable to:
   - sample identification
   - method identification
   - identification of retention time of analyte on the chromatograms

9) Quantitative Chromatogram Report
   - retention time of analyte
   - detector response
   - amount of analyte found
   - data and time of injection

10) Calibration
   - calibration curve of coefficients of the linear or non-linear equation which describes the calibration curve
   - concentration/response data (or relative response data) of the calibration check standards, along with dates on which they were analytically determined

11) Results of Standard Additions

12) Results of Serial Dilutions

All results will be reported in a tabular format and will include the following information:

- Results of sample analyses on a dry weight basis for sediments and tissues. Units for individual parameters and flags used to qualify the data are presented in Section 10.3 and will be noted on individual analysis results tables.
- Percent moisture for sediments and tissues
- Achieved MDLs
- Surrogate recoveries
- Results of procedural blank analyses. Data for metals will be blank corrected while organic data will not.
- Amounts expected and recovered, and percent recoveries, for matrix spikes.
- Results of duplicate analyses reported as RPD.
- Results of SRMs and recoveries.
- QA/QC summaries that identify, by analyte, whether the following QC requirements were met or not: holding times, detection limits, method blanks, matrix spikes, duplicates, SRMs, surrogates. When the QC data have exceeded the criteria, a qualification of the data will also be part of the QA/QC summaries.

10.2 Process for Handling Suspect or Unacceptable Data

When the initial data review identifies suspect data, that data must be investigated to establish whether it reflects true conditions or an error. The investigation shall be documented. If the data value is determined to be in error, the source of the error must be investigated, the correct value established if possible, and the erroneous value replaced with

the correct value. If the investigation concludes that the data are suspect (possibly in error) but a correct value cannot be determined, the data must be flagged to indicate its suspect status.

10.3 Standard Units and Data Flags

The standard units used to report data are:

Metals	µg/g and µg/L
PAH	ng/g and µg/L
Pesticides & PCBs	ng/g and µg/L

The standard data flags used to report data shall be:

ORGANICS AND INORGANICS

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 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
n the surrogate recovery is out of control
s the sample was analyzed by method of standard addition
w matrix spike outside of recovery control limits
* the duplicate is out of control
+ correlation of 0.995 was not met for the method of standard addition

10.4 Data Validation

A series of reviews by technical personnel will be implemented to ensure that the data generated for this projects meet the data quality objectives. These reviews will include the following:

- Data will be reviewed by the laboratory personnel periodically to ensure that sample analytical activities are completely and adequately documented.

- Reviews of analytical results and supporting documentation will be the responsibility of the Lab Managers. The Lab Manager will review sample holding times, sample preservation, equipment calibration, and sample integrity. The results of QC measurements (Section 6) will be compared to pre-established criteria as a measure of data acceptability.

- All calculations performed manually will be checked for accuracy by someone other than who performed the original calculation. Checking shall be performed by qualified persons who did not participate in performing the calculations. Checking shall be documented, by signature and date on the calculation worksheet. Separate documentation is acceptable, provided traceable records are maintained.

- The following shall be performed for verification of data input into spreadsheets and/or data bases:

The staff member entering data shall assure correct entry into the software by comparing data with the hard copy of the data listing. If errors are discovered, the errors shall be corrected and a new data listing generated. When data are correctly entered, the staff member entering the data shall sign and date the correct data listing and submit it as a project record.

- A final data audit by the quality assurance engineer will be performed prior to submission of the data and report to the client. This audit ensure that the data are accurate, traceable, defensible, and complete, as compared to the planning documents. The audit procedure (**MSL-Q-005, Quality Assurance Data Audits**) is a statistical, randomized check which involves comparing selected reported values to the original data. This procedure is designed to ensure a 95 percent chance of detecting whether one percent or more reported values disagree with the original data.

10.5 Reports

Data deliverables are due to the client within 90 days from initiation of sample analyses. Appendix B contains the Data Deliverable requirements from the client. The MSL may develop its own data deliverable if:

1) The proposed data deliverable contains the information and data according to the minimum reporting requirements identified in Appendix B in an equivalent format; and

2) The proposed data deliverable format is approved by NCCOSC prior to submission. The NCCOSC will work with the MSL to assure that the data deliverable meets the specifications of this requirement in the most cost-effective manner.

11.0 SURVEILLANCE AND AUDITS

Verification surveillances are performed by the project Quality Engineer in accordance with QAP-70-1001, **Planning and Performing Surveillance**. Surveillances are performed to ensure that a specified requirement, or set of requirements, is being met. Surveillances can be performed as real time observations during the analytical process to ensure that specific applicable procedures are being implemented. Surveillance can also be performed to ensure that the resultant project data are traceable back through the analytical process, through sample handling and transportation, back to the date, location, staff, and technique used to prepare the sample.

As a minimum, at least one surveillance must be performed during the following key activities on the project:

- traceability of data
- compliance of data with data quality objectives

System audits are performed by the PNL Quality Verification (QV) Department on a periodic basis. This project is subject to inclusion in the QV audit schedule.

The results of surveillances and audits shall be made available to project and line management as well as to key individuals contacted.

12.0 SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY, AND COMPLETENESS

Because of the nature of environmental measurements, it is frequently difficult or impossible to know the "true" value of the measured parameter. The accuracy of the measured value must instead be inferred through the use of QC samples of known composition. This project uses this method to verify that the data quality objectives (DQOs) established in Tables 6.1 and 6.2 have been met. Since this project is not a monitoring project, routine procedures to monitor data

precision, accuracy, and completeness are not required. Precision, accuracy, and completeness will be calculated following equations presented in Section 6. The results will be reported in quality control tables in the final report. These results will be compared against the DQOs established in Tables 6.1 and 6.2 and this comparison will also be reported in the final report.

13.0 CORRECTIVE ACTION

The need for corrective action may be identified by the technical staff during the course of their work or through QA surveillances or audits. Each individual performing laboratory or data processing activities will be responsible for notifying the appropriate supervisory personnel of any circumstance that could affect the quality or integrity of the data.

Deviations typically result from unforeseen circumstances. Deviations apply when the quality of reportable data is indeterminate, (i.e., not objective evidence is available to substantiate data quality or to indicate that established procedures/requirements were met). All deviations from approved SOPs or this QAPjP must be documented. Depending on the severity of the deviation, the Program Manager shall determine how the deviation shall be documented (i.e., through use of a Miscellaneous Documentation Form per **MSL-A-005, Deviation from Protocols and SOPs**, establishment of a Deficiency Report per **PAP-70-1502, Controlling Deviations from QA Requirements and Established Procedures**, etc.). The following are guidelines to resolving deficiencies:

- The need for corrective action at the laboratory level, such as broken samples, improper instrument calibration, etc. will be addressed by the Lab Manager.
- Corrective actions for results outside established DQOs are addressed in section 6.2.
- See section 20.2 for information required to document changes to SOPs and QAPjPs.

14.0 QUALITY ASSURANCE REPORTS TO MANAGEMENT

Significant problems (e.g., problems affecting the quality of the work) uncovered by project personnel must be reported to line management immediately for resolution. Significant problems involving data quality or sample integrity must be thoroughly documented. Line management must be included on the distribution of all audit and surveillance reports. Significant problems encountered in day-to-day operations must be reported to line management immediately by the Program Manager.

15.0 RECORDS

Records shall be indexed and subsequently maintained in accordance with **PNL-MA-68, Records Management**. All project records shall be made available for storage after project completion and/or after client approval of the final report. The retention period for storage shall be specified on the Records Inventory/Disposition Schedule (RIDS). Records will not be turned over to the client unless specifically requested. The project Quality Engineer does not have to approve the RIDS.

16.0 PROCUREMENT CONTROL

Procurements of items and subcontracted services are governed by PNL-MA-70 Administrative Procedure **PAP-70-401, Preparation, Review, and Approval of Purchase Requisitions.**

Subcontractors used by PNL shall be required to follow the applicable requirements delineated in this QA Plan. For subcontractors that will be performing chemical analysis, a preaward evaluation of the capabilities of that supplier shall be made by either a representative of the Quality Control group or by the Project Quality Engineer. Specific sections of this QAPjP that shall be passed on to these chemical analytical labs include, as a minimum: Section 6 and 13. Other portions of

this QAPjP (e.g., requirements for training, sample chain-of-custody, etc.) may be passed on at the discretion of the Program Manager and Project Quality Engineer.

Samples submitted to analytical labs shall be accompanied with, as a minimum, directions for the following: 1) chain-of-custody; 2) analysis turnaround time; 3) QC requirements; 4) methods; and 5) notification of MSL staff when Data Quality Objective (DQO) requirements are exceeded. Corrective action for DQO exceedences shall be coordinated with MSL and analytical staff and shall follow guidance of section 6.2 of this QAPjP.

17.0 STAFF TRAINING

Staff performing activities affecting quality shall have documented training for the applicable standard operating procedures and this QAPjP. Training shall be documented in accordance with **MSL-A-006, Marine Sciences Laboratory Training** either through the issuance of training assignments for read/study training or through briefings given by the Quality Engineer, Project Manager or Lab Manager.

Current resumes of key project staff shall be maintained in the project files. The resumes should be updated annually. As a minimum, the resume shall contain the following:

- education completed (e.g., degree and major)
- work experience (employer and major responsibilities)
- licenses and certifications
- related training and qualifications

18.0 DOCUMENT CONTROL

18.1 QAPjP Control

Distribution, control and modifications of this QAPjP shall be performed in accordance with PNL-MA-70 Administrative Procedure **PAP-70-205, Quality Assurance Plans.** Distribution and control of this QAPjP will be performed by the project. A distribution list shall be maintained in project files and updated as new copies are distributed. Modifications shall be made either by revision or by issue of an Interim Change Notice. Any PNL staff may request a change to this QAPjP at any time by notifying the Program Manger or Quality Engineer.

18.2 Standard Operating Procedure Control

Distribution of Standard Operating Procedures (SOP) will be controlled in accordance with PNL-MA-70 Administrative Procedure **PAP-70-601, Document Control** by the MSL Quality Assurance Office. Formal changes to SOPs must be performed in accordance with PNL-MA-70 Administrative Procedure **PAP-70-602, Document Change Control.** Modifications shall be made either by revision or by issue of an Interim Change Notice. Any MSL staff may request a change to the SOPs at any time by notifying the Project Manger or Quality Engineer.

Deviations from SOPs should be documented on a Miscellaneous Documentation Form and shall be approved by the Project Manager.

APPENDIX A

SOP LIST

QUALITY ASSURANCE PROJECT PLAN (QAPjP)

ANALYTICAL CHEMISTRY FOR THE
ESTUARINE ECOLOGICAL RISK ASSESSMENT
AT NAVAL SHIPYARD PORTSMOUTH, MAINE

NAVAL SHIPYARD PORTSMOUTH SOP LIST

SOP No.	SOP Title
Battelle Marine Sciences Laboratory, Sequim, Washington	
MSL-A-002	Sample Chain of Custody
MSL-A-005	Deviations from Protocols and SOPs
MSL-D-001	Recording Data on Data Sheets and Laboratory Notebooks
MSL-Q-005	Quality Assurance Data Audits
MSL-M-007	TAMU Sediment Digestion
MSL-M-018	TAMU Tissue Digestion
MSL-M-027	Total Mercury in Water
MSL-M-031	Total Mercury in Sediment and Tissue by CVAA
MSL-M-032	Trace Elements in Water by Stabilized Temperature GFAA Spectrometry
MSL-M-033	Trace Elements in Tissues and Sediments by Stabilized Temperature GFAA
MSL-M-034	APDC Extraction for Trace Metals in Water
MSL-M-035	Arsenic Speciation in Aqueous Samples
MSL-M-043	Identification and Quantification of Polynuclear Aromatic Hydrocarbons by Gas Chromatography/Mass Spectrometry
MSL-M-044	Analysis of Polychlorinated Biphenyls and Chlorinated Pesticides by Gas Chromatography with Electron Capture Detection
MSL-M-047	Calibration and Use of Thermometers
MSL-M-056	Stock and Standard Solution Preparation
MSL-M-071	Operation and Maintenance of Hewlett-Packard 5970B Gas Chromatograph/Mass Selective Detector (GC/MS)
MSL-M-079	Extraction and Clean-up of Sediments and Tissues for Semivolatile Organics following the Surrogate Internal Standard Method
MSL-M-080	Extraction and Clean-up of Waters for Semivolatile Organics following the Surrogate Internal Standard Method
Battelle Pacific Northwest Laboratory, Richland, Washington	
7-40.48	Procedures and Quality Control for Energy Dispersive X-Ray Fluorescence Spectroscopy Using the BFP Approach with the Kevex 0810A System.

APPENDIX B

DATA DELIVERABLE

QUALITY ASSURANCE PROJECT PLAN (QAPjP)

ANALYTICAL CHEMISTRY FOR THE
ESTUARINE ECOLOGICAL RISK ASSESSMENT
AT NAVAL SHIPYARD PORTSMOUTH, MAINE

DATA DELIVERABLE

1. INTRODUCTION

This specification identifies the data deliverable required for reporting the results of routine chemical analysis conducted according to the QA/QC specifications of NRaD TD 2296.

2. DATA REPORT -- HARDCOPY

The Data Report contains a hardcopy documentation of the final results and appropriate flags for each sample analyzed, along with all supporting data validation information. Data validation information includes instrument tuning and calibration, blank and spike recoveries, and all other quality control data, developed on a batch-by-batch basis. A narrative will be prepared for each batch which describes the key performance criteria evaluated to validate the batch as well and any discrepancies or deviations from the QA/QC plan. Any corrective measures taken during the analysis will also be documented in the narrative. The data report will also contain hardcopies of the contents of the Data Diskettes.

3. DATA DUMP -- DATA DISKETTE

The Data Dump will consist of information provided on a 3.5 inch, PC-compatible diskette. The following information will be contained on the diskette:

A. Data Files (*.DAT). ASCII text files with column or comma delimited fields. Data files should not contain any tabs or other control characters. Missing values should be entered as blanks for column delimited files, or null values for comma delimited files.

(1) DATA RECORD. A data record, which provides all the information for one sample, shall consist of an explicitly defined number of rows and columns in the file and shall be consistent through out the data file. The minimum information required per record includes:

(a) All pertinent sample identification and tracking information (e.g. field sample ID, lab sample ID, batch ID number, sample replicate or duplicate number, date sampled and received, etc.) and should be cross-referenced to the appropriate chain-of-custody information;

(b) Sample information (sample matrix, weight/volume, moisture/solid content, units of measure, color, texture, etc.);

(c) Analytical results (in concentration per dry weight or volume) and analytical flag (if applicable). Nondetected results should be reported as values and flagged according to the QA/QC plan.

(2) DATA FILES may be arranged according to the analysis type (e.g. metals, PAHs, PCBs, Pesticides, etc.)

(3) DATA FILES must contain unique identifier, or combination of identifiers, to uniquely identify each record.

(4) DATA FILES must be fully documented with a corresponding VARIABLE FILE (see below).

(5) DATA FILES prepared shall include the following:

(a) SAMPLE RESULTS. A data file which contains the validated results of all field and duplicate samples. Each record should contain the concentration and QA/QC flag obtained for each analyte measured for the analysis type being reported.

(b) BLANK RESULTS. A data file which contains the validated concentrations obtained from analysis of blanks. Nondetected values should be reported as either background or zero, which ever is more appropriate for the analyte of the analysis type being reported. Each record for the blanks must be cross-referenced to the sample results for which the blank results apply (eg. by batch ID number).

(c) REFERENCE STANDARD RESULTS. A data file which contains the validated concentrations obtained from the analysis of SRM or CRMs. The first record of the file should contain the ID and certified and noncertified concentrations of the SRM/CRM used for the analytes of the analysis type being reported. Nondetected values should be reported as either the instrument detection limit (IDL) or method detection limit (MDL) and flagged accordingly. Each record for the blanks must be cross-referenced to the sample results for which the blank results apply (eg. by batch ID number).

matrix spike

(d) SPIKE RECOVERIES. A data file which contains the validated concentrations obtained from analysis of spiked matrices. The first record of the file should contain identification of the spike and

(e) surrogate internal standards

the know concentrations of the spike used. Nondetected values should be reported as IDL or MDL concentrations and flagged accordingly. Each record for the blanks must be cross-referenced to the sample results for which the blank results apply (eg. by batch ID number).

B. VARIABLE FILES (*.VAR). An ASCII text file created for each data file (*.DAT) which documents the contents of the data file. The variable file contains the following minimum number fields:

1. HEADER:
   FILENAME - variable file name (*.VAR)
   DATA FILENAME - data filename (*.DAT)
   AUTHOR/PI - author or principal investigator who created the file, affiliation, address and phone number.
   COMMENT - describes the nature of the data and identified the performing laboratory
   QA Check: Identifies person (and date) who verified the accuracy of the information contained in both the data and variable files.

2. DATA TYPES and RECORD LENGTH: Documents record length and data types (integer, character, fixed decimal, etc.) used in the file.

3. VARIABLE LIST. Presents the variable names, column positions, data type, and descriptions in a tabular format. The description should include units of measure, allowable ranges, and any other information necessary to understand the data values.

4. DATA FLAGS. Documents data qualifier codes used to flag variables.

5. META DATA: As identified in Federal Register 48 (191): 30503

   (a) INTENDED USE: The intended use of the data and the associated acceptance criteria for data quality (precision, accuracy, representativeness, completeness, comparability)

   (b) CORRECTNESS: Project requirements for precision, accuracy, representativeness, completeness, comparability, and how these will be determined.

   (c) SAMPLE COLLECTION/PREPARATION: Procedures for selection of samples or sampling sites and collection or preparation of samples.

(d) SAMPLE HANDLING AND STORAGE: Procedures for sample handling, identification, preservation, transportation, and storage.

(e) MEASUREMENT METHOD AND PERFORMANCE CHARACTERISTICS: description of measurement methods or test procedures with a statement of performance characteristics if methods are nonstandard.

(f) QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES: Standard quality assurance / quality control procedures (e.g. American Society for Testing Materials, American Public Health Association standard procedures) to be followed. Non-standard procedures must be documented.

(g) DATA REDUCTION AND REPORTING: Data reduction and reporting procedures, including description of statistical analyses to be used.

6. OTHER. Other information deemed appropriate by the investigator. (Could include ASCII text versions of the hardcopy case narratives, if appropriate).

4 EXAMPLES. Examples of properly formatted and documented data deliverables are appended to this document.

110100	B	1	"910547-01"	22	" York Harbor"					44.0 f	3.0 u	2.0 u	2.0 f	6.0 u	3.0 u	59.0 f	0.04 u	4.0 f	10.0 u	1.0 f	3.0 f
110101	B	1	"910547-02"	23	"York River"	91	9	13	31.9	45.2 f	3.0 u	1.6 f	4.0 u	6.0 u	3.0 u	30.5 f	0.04 u	4.0 f	5.3 f	1.0 u	5.0 u
110102	B	1	"910547-03"	2	" C. G. Cove"	91	9	17	30.0	69.2 b	3.0 u	2.3 f	4.0 u	6.0 u	2.8 f	79.4 f	0.04 u	5.7 f	10.0 u	1.3 f	10.8 f
110103	B	1	"910547-04"	3	" Clark Cove"	91	9	16	29.5	23.7 f	3.0 u	2.0 f	4.0 u	6.0 u	3.0 u	3.0 f	0.04 u	5.5 f	10.0 u	0.5 f	17.6 f
110104	B	1	"910547-05"	5	" Clark Cove"	91	9	16	30.0	45.5 f	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	30.6 f	0.04 u	6.0 f	3.4 f	1.0 u	5.5 f
110105	B	1	"910547-06"	7	" Clark Cove"	91	9	16	30.2	35.4 f	3.0 u	2.4 f	4.0 u	6.0 u	3.0 u	26.7 f	0.04 u	6.2 f	2.4 f	1.0 u	1.3 f
110106	B	1	"910547-07"	8	" Clark Cove"	91	9	16	30.2	30.8 f	3.0 u	4.0 f	4.0 u	6.0 u	3.0 u	40.5 f	0.04 u	6.6 f	10.0 u	1.0 u	5.0 u
110106	B	2	"910547-07"	8	" Clark Cove Dup"	91	9	16	30.2	65.5 b	3.0 u	3.8 f	4.0 u	6.0 u	3.0 u	34.6 f	0.04 u	7.1 f	2.4 f	1.0 u	5.0 u
110107	B	1	"910547-08"	6	" Clark Cove"	91	9	16	30.2	20.3 f	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	37.0 u	0.04 u	6.6 f	1.3 f	1.0 u	2.3 f
110108	B	1	"910547-09"	4	" Clark Cove"	91	9	16	30.5	31.8 f	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	25.9 f	0.04 u	6.9 f	3.4 f	1.0 u	1.0 f
110109	B	1	"910547-10"	21	" Spruce Creek"	91	9	16	30.0	57.2 f	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	62.6 f	0.04 u	9.7 f	10.0 u	1.0 u	1.0 f
110110	B	1	"910547-11"	20	"Spruce Creek"	91	9	16	30.0	37.2 f	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	38.3 f	0.04 u	7.1 f	7.7 f	1.0 u	5.0 u
110111	B	1	"910547-12"	19	" Back Channel"	91	9	16	30.0	42.0 f	3.0 u	2.0 u	4.0 u	6.0 u	2.2 f	34.2 f	0.04 u	6.9 f	16.8 f	1.0 u	5.0 u
110112	B	1	"910547-13"	18	" Back Channel"	91	9	16	30.0	42.3 f	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	41.0 f	0.04 u	6.3 f	10.0 u	1.0 u	5.0 u
110113	B	1	"910547-14"	17	" Squash Island"	91	9	16	29.2	16.1 f	3.0 u	1.6 f	4.0 u	6.0 u	3.0 u	24.0 f	0.04 u	9.1 f	3.6 f	1.0 u	5.0 u
110114	B	1	"910547-15"	14	" Pierce Island"	91	9	16	30.0	62.8 b	3.0 u	1.2 f	4.0 u	6.0 u	2.2 f	47.2 f	0.04 u	8.2 f	10.0 u	1.0 u	5.0 u
110115	B	1	"910547-16"	10	" Dry Dock #2"	91	9	16	29.0	32.5 f	3.0 u	1.2 f	4.0 u	6.0 u	3.0 u	25.2 f	0.04 u	5.7 f	10.0 u	1.0 u	1.2 f
110116	B	1	"910547-17"	12	" Dry Dock #1"	91	9	17	29.2	27.0 f	3.0 u	2.0 u	1.0 f	6.0 u	3.0 u	39.0 f	0.04 u	5.0 f	10.0 u	1.0 u	5.0 u
110117	B	1	"910547-18"	13	" Dry Dock #3"	91	9	16	29.5	31.0 f	3.0 u	2.0 u	1.0 f	6.0 u	3.0 u	43.0 f	0.04 u	6.0 f	10.0 u	1.0 u	5.0 u
110118	B	1	"910547-19"	9	" Navy Yard Blue"	91	9	16	29.5	33.0 f	3.0 u	2.0 u	1.0 f	6.0 u	3.0 u	41.0 f	0.04 u	6.0 f	10.0 u	1.0 u	5.0 u
110119	B	1	"910547-20"	15	" Cutts Cove*"	91	9	16	29.2	36.0 f	3.0 u	2.0 u	1.0 f	6.0 u	3.0 u	51.0 f	0.04 u	10.0 f	10.0 u	1.0 u	1.0 f
110119	B	2	"910547-20"	15	" Cutts Cove-Dup"	91	9	16	29.2	27.0 f	3.0 u	2.0 u	2.0 f	6.0 u	3.0 u	51.0 f	0.04 u	10.0 f	10.0 u	1.0 u	5.0 u
110120	B	1	"910547-21"	16	"Interstate Bridge"	91	9	17	26.8	49.0 f	3.0 u	2.0 u	3.0 f	6.0 u	1.0 f	70.0 f	0.04 u	11.0 f	10.0 u	1.0 u	5.0 u
110121	B	1	"910547-22"	11	" Pierce Island"	91	9	17	29.0	19.0 f	3.0 u	2.0 u	1.0 f	2.0 b	1.0 f	52.0 f	0.04 u	9.0 f	10.0 u	1.0 u	1.0 f
110122	B	1	"910547-23"	1	" Gooseberry Islan"	91	9	17	28.9	64.0 f	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	61.0 f	0.04 u	7.0 f	10.0 u	1.1 f	5.0 u
110123	B	1	"910630-01"	22	" York Harbor ME"	92	11	13	28.0	188.0 b	3.0 u	2.0 u	3.0 f	6.0 u	3.0 u	298.0 b	0.04 u	14.0 f	10.0 u	1.8 b	4.0 f
110124	A	1	"910630-02"	15	" Interstate Brid"	91	11	13	22.2	82.8 b	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	99.0 b	0.04 u	9.0 f	10.0 u	1.0 u	3.0 f
110125	A	1	"910630-03"	10	" PNSY Dry Dock #"	91	11	13	24.0	51.0 f	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	98.0 b	0.04 u	7.0 f	10.0 u	3.4 b	6.0 f
110126	A	1	"910630-04"	8	" PNSY Clark Cove"	91	11	13	23.5	57.0 f	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	99.0 b	0.04 u	6.0 f	10.0 u	1.0 u	2.0 f
110127	A	1	"910630-05"	1	" Gooseberry Islan"	91	11	13	24.0	22.0 f	3.0 u	2.0 u	4.0 u	3.0 f	2.0 f	95.0 b	0.04 u	7.0 f	46.0 b	1.0 u	4.0 f
110431	A	1	"910710-02"	1	" Gooseberry Islan"	91	12	17	19.0	163.0 b	3.0 u	2.0 u	1.0 f	2.0 f	3.0 f	88.0 f	0.04 u	7.0 f	3.0 f	1.0 u	7.0 f
110432	A	1	"910710-03"	10	" PNSY Dry Dock #"	91	12	17	19.9	41.0 f	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	47.0 f	0.04 u	1.0 f	10.0 u	1.0 u	3.0 f
110432	A	1	"910710-03D"	10	" PNSY Dry Dock #"	91	12	17	19.9	41.0 f	3.0 u	2.0 u	2.0 f	6.0 u	3.0 u	57.0 f	0.04 u	3.0 f	10.0 u	1.0 u	3.0 f
110433	A	1	"910710-04"	8	" Clark Cove"	91	12	17	23.5	82.0 b	3.0 u	2.0 u	4.0 u	13.0 f	6.0 f	86.0 f	0.04 u	4.0 f	7.0 f	1.0 u	3.0 f
110434	A	1	"910710-05"	15	" Cutts Cove*"	91	12	17	20.0	153.0 b	3.0 u	2.0 u	4.0 u	5.0 f	3.0 f	194.0 b	0.04 u	11.0 f	10.0 u	1.0 u	5.0 f
110435	A	1	"920710-01"	23	" York Harbor ME"	91	12	31	28.0	165.0 b	3.0 u	2.0 u	4.0 u	5.0 f	4.0 f	184.0 b	0.04 u	8.0 f	3.0 f	1.0 u	2.0 f
110436	A	1	"920023-01"	23	" York River"	92	1	15	21.0	171.0 b	3.0 u	2.0 u	3.0 f	6.0 u	3.0 u	189.0 b	0.04 u	6.0 f	10.0 u	1.0 u	5.0 u
110437	A	1	"920023-02"	1	" Gooseberry Islan"	92	1	15	24.0	44.0 f	3.0 u	2.0 u	1.0 f	6.0 u	2.0 f	89.0 f	0.04 u	6.0 f	10.0 u	1.5 b	3.0 f
110438	A	1	"920023-03"	8	" Clark Cove PNSY"	92	1	16	31.0	13.0 f	3.0 u	1.6 f	1.0 f	6.0 u	3.0 u	90.0 b	0.04 u	4.0 f	10.0 u	1.0 u	4.0 f
110439	A	1	"920023-04"	10	" Dry Dock #2 PN"	92	1	16	30.0	24.0 f	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	79.0 f	0.04 u	2.0 f	10.0 u	1.3 f	6.0 f
110440	A	1	"920023-05"	16	"Interstate Bridge"	92	1	15	23.0	79.0 b	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	94.0 b	0.04 u	2.0 f	10.0 u	1.0 u	5.0 u
110441	A	1	"920023-06"	15	"Interstate Bridge"	92	1	15	22.0	91.0 b	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	133.0 b	0.04 u	7.0 f	10.0 u	1.0 u	3.0 f
110442	A	1	"920080-01"	1	" Gooseberry Islan"	92	2	14	26.0	12.0 f	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	72.0 f	0.04 u	5.0 f	10.0 u	1.0 u	2.0 f
110443	A	1	"920080-02"	8	" Clark Cove PNSY"	92	2	17	28.0	46.0 f	3.0 u	2.0 u	1.0 f	6.0 u	2.0 f	109.0 b	0.04 u	3.0 f	10.0 u	1.1 f	6.0 f
110444	A	1	"920080-03"	10	" Dry Dock # 2 PN"	92	2	17	28.2	40.0 f	3.0 u	2.0 u	2.0 f	6.0 u	1.0 f	89.0 f	0.04 u	3.0 f	10.0 u	1.7 b	4.0 f
110445	A	1	"920080-04"	15	"Interstate Bridge"	92	2	17	28.5	26.0 f	3.0 u	1.1 f	4.0 u	6.0 u	12.0 f	81.0 f	0.04 u	2.0 f	10.0 u	1.0 u	5.0 u
110446	A	1	"920080-05"	16	"Interstate Bridge"	92	2	17	28.2	54.0 f	3.0 u	2.0 u	2.0 f	6.0 u	3.0 u	89.0 f	0.04 u	5.0 f	10.0 u	1.0 f	2.0 f
110447	A	1	"920080-06"	23	" York River"	92	2	18	28.2	135.0 f	3.0 u	2.0 u	3.0 f	6.0 u	3.0 u	136.0 b	0.04 u	4.0 f	10.0 u	1.0 u	5.0 u
110448	A	1	"920104-01"	1	" Gooseberry Islan"	92	3	5	25.9	84.0 u	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	31.0 f	0.04 u	6.0 f	10.0 u	1.0 u	5.0 u
110449	A	1	"920104-02"	8	" Clark Cove"	92	3	5	26.5	84.0 u	3.0 u	1.3 f	4.0 u	2.0 f	3.0 f	50.0 f	0.04 u	8.0 f	5.0 f	1.0 u	3.0 f
110450	A	1	"920104-03"	10	" Dry Dock #2 PN"	92	3	5	27.1	84.0 u	3.0 u	1.7 f	4.0 u	6.0 u	3.0 u	33.0 f	0.04 u	3.0 f	10.0 u	1.0 u	5.0 u
110451	A	1	"920104-04"	15	" Cutts Cove (N)*"	92	3	5	24.9	19.0 f	3.0 u	2.0 u	1.0 f	13.0 f	3.0 u	52.0 f	0.04 u	7.0 f	10.0 u	1.0 u	2.0 f
110452	A	1	"920104-05"	16	"Interstate Bridge"	92	3	5	26.2	84.0 u	3.0 u	1.9 f	4.0 u	6.0 u	3.0 u	43.0 f	0.04 u	7.0 f	10.0 u	1.0 u	5.0 u
110453	A	1	"920104-06"	23	" York Harbor ME"	92	3	5	29.1	45.0 f	3.0 u	2.0 u	7.0 f	6.0 u	3.0 u	26.0 f	0.04 u	4.0 f	10.0 u	1.0 u	10.0 f
110454	A	1	"920209-01"	23	" York River"	92	4	22	20.5	102.0 b	3.0 u	1.0 f	4.0 u	6.0 u	3.0 u	122.0 b	0.04 u	8.0 f	4.0 f	1.0 u	5.0 u
110455	A	1	"920209-02"	1	" Gooseberry Islan"	92	4	23	26.0	130.0 b	3.0 u	1.1 f	4.0 u	6.0 u	3.0 u	220.0 b	0.04 u	9.0 f	10.0 u	1.0 u	5.0 u
110456	A	1	"920209-03"	8	" Clark Cove"	92	4	23	26.2	35.0 f	3.0 u	2.0 u	4.0 u	5.0 f	6.0 f	45.0 f	0.04 u	5.0 f	10.0 u	1.0 u	3.0 f
110457	A	1	"920209-04"	10	" Dry Dock #2 PN"	92	4	23	23.5	62.0 b	3.0 u	2.0 u	4.0 u	6.0 u	6.0 f	107.0 b	0.04 u	9.0 f	10.0 u	1.0 u	4.0 f
110457	A	2	"920209-04D"	10	" Dry Dock #2 PN"	92	4	23	23.5	145.0 b	3.0 u	1.2 f	2.0 f	6.0 u	8.0 f	109.0 b	0.04 u	9.0 f	11.0 f	1.2 f	5.0 f
110458	A	1	"920209-05"	15	" Cutts Cove*"	92	4	23	22.5	115.0 b	3.0 u	2.0 u	4.0 u	6.0 f	9.0 f	143.0 b	0.04 u	12.0 f	5.0 f	1.0 u	2.0 f
110459	A	1	"920209-06"	16	"Interstate Bridge"	92	4	23	22.9	108.0 b	3.0 u	2.0 u	4.0 u	8.0 f	6.0 f	125.0 b	0.04 u	10.0 f	10.0 f	1.0 u	1.0 f
110460	A	1	"900259-01"	15	" Cutts Cove*"	92	5	20	25.5	82.0 b	3.0 u	1.2 f	2.0 f	6.0 u	3.0 u	174.0 b	0.04 u	17.0 b	10.0 u	1.0 u	2.0 f
110461	A	1	"900259-02"	16	"Interstate Bridge"	92	5	20	25.2	55.0 f	3.0 u	2.0 u	4.0 u	4.0 f	3.0 f	141.0 b	0.04 u	13.0 f	10.0 u	1.3 f	3.0 f
110462	A	1	"900259-03"	8	" Clark Cove"	92	5	20	24.2	39.0 f	3.0 u	2.0 u	4.0 u	6.0 u	4.0 f	78.0 f	0.04 u	10.0 f	3.0 f	1.0 u	1.0 f
110463	A	1	"900259-04"	10	" Dry Dock #2 PN"	92	5	20	23.7	28.0 f	3.0 u	2.0 u	4.0 u	6.0 u	2.0 f	97.0 b	0.04 u	12.0 f	10.0 u	1.0 u	2.0 f
110464	A	1	"920259-05"	1	" Gooseberry Islan"	92	5	20	23.7	59.0 f	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	59.0 f	0.04 u	8.0 f	10.0 u	1.0 u	2.0 f
110465	A	1	"920259-06"	23	" York River"	92	5	21	25.1	72.0 f	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	77.0 f	0.04 u	7.0 f	10.0 u	1.0 u	5.0 u
110466	A	1	"920322-01"	23	" York River"	92	6	15	25.5	85.0 b	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	70.0 f	0.04 u	10.0 f	10.0 u	1.0 u	5.0 u
110467	A	1	"920322-02"	15	" Cutts Cove*"	92	6	16	24.0	87.0 b	3.0 u	2.0 u	4.0 u	6.0 u	16.0 f	95.0 b	0.04 u	17.0 b	10.0 u	1.0 u	6.0 f
110467	A	2	"920322-02D"	15	" Cutts Cove Du"	92	6	16	24.0	85.0 b	3.0 u	2.0 u	4.0 u	6.0 u	15.0 f	92.0 b	0.04 u	17.0 b	10.0 u	1.0 u	4.0 f
110468	A	1	"920322-03"	16	"Interstate Bridge"	92	6	16	23.8	79.0 b	3.0 u	2.0 u	4.0 u	6.0 u	4.0 f	88.0 f	0.04 u	18.0 b	10.0 u	1.0 u	2.0 f
110469	A	1	"920322-04"	10	" PNSY Dry Dock #"	92	6	16	25.0	97.0 b	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	105.0 b	0.04 u	16.0 f	10.0 u	1.0 u	2.0 f
110470	A	1	"920322-05"	8	" PNSY Clark Cove"	92	6	16	27.0	41.0 f	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	39.0 f	0.04 u	10.0 f	10.0 u	1.0 u	5.0 u
110471	A	1	"920322-06"	1	" Gooseberry Islan"	92	6	16	29.0	48.0 f	3.0 u	2.0 u	4.0 u	6.0 u	3.0 u	34.0 f	0.04 u	10.0 f	10.0 u	1.0 u	2.0 f
112325	A	1	"920076"	S1	"JL-01-05"	92	2	13		38.0 f	3.0 u	2.0 u	3.0 f	6.0 u	3.0 u	436.0	0.06 f	313.0	3.0 f	1.0 u	4.0 f
112325	B	1	"920076"	S1	"JL-01I-05"	92	2	13		43.0 f	3.0 u	2.0 u	4.0 f	6.0 u	3.0 u	465.0	0.06 f	320.0	9.0 f	1.0 u	5.0 f
112326	A	1	"920076"	S2	"JL-02-05"	92	2	13		2143.0	3.0 u	1.4 f	2.0 f	8.0 f	310.0 b	3013.0	0.88 b	115.0	16.0 f	972.0	216.0
112326	A	2	"920076"	S2	"JL-02-05D"	92	2	13		2161.0	3.0 u	2.6 f	2.0 f	9.0 f	313.0 b	3071.0	0.90 b	116.0	13.0 f	1034.0	219.0
112327	A	1	"920076"	S3	"JL-03-05"	92	2	13		476.0	3.0 u	2.0 u	4.0 f	2.0 f	7.0 f	447.0	0.07 f	6.0 f	6.0 f	8.0 f	54.0 f

9111

WATERDA2.VAR

A. HEADER
FILENAME: waterda2.var
DATAFILE: waterda2.dat
AUTHOR: Robert K. Johnston,
Marine Environmental Support Office
Naval Command Control and Ocean
Surveillance Center, Code 522
c/o USEPA Environmental Research Laboratory Narragansett
27 Tarzwell Dr.
Narragansett, RI 02882
(401)295-5462 FAX: 401-295-5462
ERLN: (401)782-3088 GSO:(401)792-6273
COMMENT: CEIMIC marine water chemistry data (raw data)

QA Check: RKJ Jan. 17, 1993

B. DATA TYPES
DATA TYPES: I = integer
A = character string
D = fixed decimal with explicit decimal point
One Sample per Record; Record size = 1 row by 193 cols.

C. VARIABLE LIST

variable	column position beg-end	type	Description
EPAID	1- 8	I	EPA id number, identifies unique sampling event
REP	10	A	Replicate assigned on chain-of-custody
DUP	14	I	Duplicate number which identifies repeated analytical measurements: e.g. 1 = first analysis; 2 = duplicate analysis; 3 = tripicate analyssi, etc.
CID	16- 27	A	Ceimic id number (sample ID)
STA	29- 30	A	Station location recorded on chain-of-custody
COMMNET	32- 55	A	Comment from chain-of-custody (includes Hart ID number used for seep samples)
YEAR	57- 58	I	Year sample was taken (91 or 92)
MON	60- 61	I	Month sample was taken (1 - 12)
DAY	63- 64	I	Day sample was taken (1 - 31)
SALINITY	69- 73	D	Salinity recorded for the water sample in parts per thousand (o/oo)
AL	76- 80	D	Aluminum concentration ug/L (ppb)
ALF	82	A	Data flag for Al
AG	88- 91	D	Silver concentration ug/L (ppb)
AGF	93	A	Data Flag for Ag
AS	98-101	D	Arsenic concentration ug/L (ppb)
ASF	103	A	Data Flag for As
CD	108-111	D	Cadmium concentration ug/L (ppb)
CDF	113	A	Data flag for Cd
CR	118-121	D	Chromium concentration ug/L (ppb)
CRF	123	A	Data flag for Cr
CU	127-131	D	Copper concentration ug/L (ppb)
CUF	133	A	Data flag for Cu
FE	136-141	D	Iron concentration ug/L (ppb)
FEF	143	A	Data flag for Fe
HG	147-151	D	Mercury concentration ug/L (ppb)
HGF	153	A	Data flag for Hg

MN	157-161	D	Manganese concentration ug/L (ppb)
MNF	163	A	Data flag for Mn
NI	168-171	D	Nickel concentration ug/L (ppb)
NIF	173	A	Data Flag for Ni
PB	176-181	D	Lead concentration ug/L (ppb)
PBF	183	A	Data flag for Pb
ZN	186-191	D	Zinc concentration ug/L (ppb)
ZNF	193	A	Data flag for Zn

D. Data Flags:

DATA QUALIFIER CODES USED BY THE ERA-NSYP PROJECT

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

E. METADATA:

(1) USE:
Data usage and acceptability is documented in "Work/Quality Assurance Project Plan for the NOSC/ERLN Case Study of Estuarine Ecological Risk Assessment at Naval Shipyard Portsmouth, Kittery, Maine", September 1991. Prepared by EPA-ERLN and Marine Environmental Support Office of NOSC, W.G. Nelson and R.K. Johnston, Project Officers.

(2) PROJECT REQUIREMENTS FOR PRECISION, ACCURACY, REPRESENTATIVENESS, COMPLETENESS, AND COMPARABILITY.
See: "Work/Quality Assurance Project Plan for the NOSC/ERLN Case Study of Estuarine Ecological Risk Assessment at Naval Shipyard Portsmouth, Kittery, Maine", September 1991. Prepared by EPA-ERLN and Marine Environmental Support Office of NOSC, W.G. Nelson and R.K. Johnston, Project Officers.

(3) SAMPLING SITES AND COLLECTION/PREPARATION PROCDURES:

The sampling plan is documented in "Work/Quality Assurance Project Plan for the NOSC/ERLN Case Study of Estuarine Ecological Risk Assessment at Naval Shipyard Portsmouth, Kittery, Maine", September 1991. Prepared by EPA-ERLN and Marine Environmental Support Office of NOSC, W.G. Nelson and R.K. Johnston, Project Officers.

Standard Operating Procedures (SOPS) used for sample collection and preparation are documented in: Mueller, Munns, Cobb, Petrocelli, Pesch, Nelson, Burdick, Short and Johnston (eds), 1992. "Standard Operating Procedures and Field Methods Used for Conducting Ecological Risk Assessment Case Studies: Naval Construction Battalion Center Davisville, RI, and Naval Shipyard Portsmouth, Kittery, ME", Naval Command, Control and Ocean Surveillance Center RDT&E Division Technical Document 2296.

Evaluation of method performance and results is contained within: Johnston, Munns, Mills, Short, and Nelson (eds) 1992. "An Estuarine Ecological Risk Assessment Case Study for Naval Shipyard Portsmouth, Kittery, Maine: DRAFT Peliminary Phase I Report", prepared by Naval Command Control and Ocean Surveillance Center and EPA-ERLN (Nov. 1992).

(4) SAMPLE HANDILING AND STORAGE:

See: "Work/Quality Assurance Project Plan for the NOSC/ERLN Case Study of Estuarine Ecological Risk Assessment at Naval Shipyard Portsmouth, Kittery, Maine", September 1991. Prepared by EPA-ERLN and Marine Environmental Support Office of NOSC, W.G. Nelson and R.K. Johnston, Project Officers.

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(5) MEASUREMENT METHOD AND PERFORMANCE CHARACTERISTICS:

Water sample were analyzed using a standard drinking water analysis technique modified for marine water chemistry. This deviation in the workplan was approved by the Project Officer (Memo from R.K. Johnston (NRaD) to John F. McGarry (Ceimic Corp.) of June 30, 1992)

Quality Control of Estuarine Ecological Risk Assesment Seawater Metal Analysis: (Provided by Ceimic Corp.)

Drinking Water Quality Parameters (ppb):

Element	LOQ(ug/L)	MDL(ug/L)*	IDL(ug/L)	Instrument/Method
Aluminum	200	60	84	ICP (plasma)
Arsenic	50	15	2	GFAA (graphite furnace)
Cadmium	10	3	4	ICP
Chromium	50	15	6	ICP
Copper	1000	300	3	ICP
Iron	300	90	37	ICP

Lead	5	1.5	1	GFAA
Manganese	50	15	2	ICP
Mercury	2	0.6	0.2(0.04)+	CV (Cold Vapor)
Nickel	100	30	10	ICP
Silver	50	15	3	GFAA
Zinc	5000	1500	5	ICP

LOQ = limit of quantitation ~= 10s; where s is the standard deviation determined from 6 repeated seawater matrix analysis to determine the MDL.

MDL = method detection limit ~= 3s
* for this table the MDL was estimated by: MDL = (LOQ/10)*3

IDL = instrument detection limit
+ the IDL actually realized for Mercury was 0.04 ug/L

Prepartion:
Seawaters were acidified and then analyzed.
Seeps were prepped by microwave digestion method 3015

1) Insturment Calibration
a) Standards are prepared at thime of analysis
b) Standards are prepared with the same amount of acid as the samples
c) For the Graphite Furnace AA, three standards and the standrd blank are used for the calibration. Resloping is acceptable if a Calibration Check is run before and after the reslope.
2) Calibration Check Samples
a) The calilbration check sample is to be analyzed after the standrad. No more than ten samples (or twenty analytical burns) should be anlyzed between check samples and the analysis run must end witha check sample.
b) Target recovery of the blank sample must be less than the limit of Quantification (LOQ)
3) Calibration Blank Samples
a) The calibration blank sample is analyzed immediatedly after the initial calibration check smaple.
b) The concentration of the blank sample must be less thatn the limit of Quntification (LOQ)
c) Deviations are noted with explaination in the case narrative.

(6) QA/QC PROCEDURES:
Applicable QA/QC procedures are documented in:
"Analytical Chemistry Quality Control, Protocols, Criteria, and Corrective Action for the Estuarine Ecological Risk Assessment at Naval Shipyard Portsmouth, Kittery, ME" found as appendix C in "Work/Quality Assurance Project Plan for the NOSC/ERLN Case Study of Estuarine Ecological Risk Assessment at Naval Shipyard Portsmouth, Kittery, Maine", September 1991. Prepared by EPA-ERLN and Marine Environmental Support Office of NOSC, W.G. Nelson and R.K. Johnston, Project Officers and Mueller, Munns, Cobb, Petrocelli, Pesch, Nelson, Burdick, Short and Johnston (eds), 1992. "Standard Operating Procedures and Field Methods Used for Conducting Ecological Risk Assessment Case Studies: Naval Construction Battalion Center Davisville, RI, and Naval Shipyard Portsmouth, Kittery, ME", Naval Command, Control and Ocean Surveillance Center RDT&E Division Technical Document 2296.

Evaluation of method performance and results is contained within: Johnston, Munns, Mills, Short, and Nelson (eds) 1992. "An Estuarine

Ecological Risk Assessment Case Study for Naval Shipyard Portsmouth, Kittery, Maine: DRAFT Peliminary Phase I Report", prepared by Naval Command Control and Ocean Surveillance Center and EPA-ERLN (Nov. 1992).

(7) DATA REDUCTION AND REPORTING

Applicable data reporting and analysis are contained in: Johnston, Munns, Mills, Short, and Nelson (eds) 1992. "An Estuarine Ecological Risk Assessment Case Study for Naval Shipyard Portsmouth, Kittery, Maine: DRAFT Peliminary Phase I Report", prepared by Naval Command Control and Ocean Surveillance Center and EPA-ERLN (Nov. 1992).

F: OTHER:

Memo from R.K. Johnston (NRaD) to John F. McGarry (Ceimic Corp.) of June 30, 1992:

June 30, 1992

John F. McGarry, Jr.
CEIMIC Corporation
10 Dean Knauss Dr.
Narragansett, RI 02882

SUBJ: INORGANIC ANALYSES OF SEAWATER SAMPLES FOR NAVAL SHIPYARD PORTSMOUTH

Dear John,

This is to notify you that the proposed quality control of estuarine ecological risk assessment seawater metal analysis, outlined in your letter of June 23, 1992, will be acceptable to complete the inorganic analysis of seawater samples for the subject project. As discussed in your letter of June 23, 1992, delivery of the subject data will be within thirty days of your receipt of a signed modification for the contract.

If you have any questions, please contact me at (401) 295-5462.

Sincerely,

/signed/
Robert K. Johnston
Naval Command, Control and Ocean Surveillance Center
c/o Graduate School of Oceanography
University of Rhode Island
Narragansett, RI 02874

cc:
L. Dietz (Northern Divison)
S. Urschel (MacLaren Hart)
S. Nelson, W. Boothman, R. Pruel (ERLN)
J. Grovhoug (NCCOSC)