N00102.AR.001808
NSY PORTSMOUTH
5090.3a

WORK PLAN IN SUPPORT OF THE PHASE 2 ESTUARINE ECOLOGICAL RISK ASSESSMENT CASE STUDY NSY PORTSMOUTH ME

8/1/1993

U S EPA REGION I

1106

ENVIRONMENTAL RESEARCH LABORATORY NARRAGANSETT WORK PLAN

In Support of the Estuarine Ecological Risk Assessment Case Study for Portsmouth Naval Shipard, Kittery Maine

PHASE II

AUGUST 1993

Prepared By

Environmental Research Laboratory Narragansett
US Environmental Protection Agency
27 Tarzwell Dr., Narragansett, RI 02882

ERLN WORKPLAN IN SUPPORT OF
THE ESTUARINE ECOLOGICAL RISK ASSESSMENT CASE STUDY FOR
PORTSMOUTH NAVAL SHIPYARD, KITTERY MAINE

PHASE II

1.0 INTRODUCTION

The Ecological Risk Assessment (ERA) Case Study Project involves the development and implementation of risk assessment methods using site-specific data. The project, developed cooperatively with the Navy, employs marine case study sites associated with Naval facilities, i.e., Naval Construction Battalion Center, Davisville (NCBC, Allen Harbor), RI, and Portsmouth Naval Shipyard (NSP), Kittery, Maine. The Allen Harbor Project, begun in 1988, used a phased approach to characterize the site (field sampling) chemically and biologically and test hypotheses (laboratory experiments) concerning potential impact sources. In the final phase, the evolving EPA ERA framework is being employed to organize site data into a model describing ecological risks associated with the NCBC embayment. The Portsmouth Project, begun in 1991, follows and refines the NCBC model. Phase I (field sampling/exposure characterization) was completed in 1992 and reported on in 1993.

This work plan has three technical components (1) development of exposure/response information, (2) analysis of chemical markers, and (3) marine analytical chemistry. The contents of each technical component and the technical and analytical procedures to be employed are described. The quality control/quality assurance protocals to be used are also presented.

2. 0 TECHNICAL APPROACH

2.1 DEVELOPMENT OF EXPOSURE/RESPONSE INFORMATION

APPROACH

This work plan focusses on the development of stressor-biological response models (through laboratory and field studies), specific to a potentially impacting toxicant of concern (i.e., lead). Biological responses of concern include toxicity, bioaccumulation and trophic transfer. Toxic responses, as reduced reproductive success, will be used to develop a model projecting population effects based on short-term toxicity measurements made following exposure of fertile sea urchins, *Arbacia punctulata*. Exposure models will be developed using

bioaccumulation from sediment contaminants (of the blue mussel, Mytilus edulis) and trophic transfer (using the sea urchin). Comparisons between laboratory and field exposures to will be used to predict environmental risks based on laboratory-observed biological effects.

Several parallel laboratory experiments were designed to demonstrate a range of biological responses associated with exposure to lead-contaminated marine sediments (FIGURE 1, EXPERIMENTAL APPROACH). For these purposes, exposures of test species, plant and animal, will be conducted for approximately 10-30 days using naturally- and artificially-contaminated sediment and biota (as food source). Artificially-contaminated sediment and diets will be amended with lead (sulfate). Sediment exposures will be simulated as bedded and suspended media. To characterize exposures, media will be sampled for chemical analyses and toxicity testing. Selected systems will be used to assess exposure as bioaccumulation of toxicant and effects as survival, growth, fecundity, and/or gamete and larval viability (TABLES 1a,b).

EXPOSURE SEDIMENTS

Sediments were collected by divers during the week of 6 August, 1993, at NSP sites (FIGURE 2, PORTSMOUTH MAP) identified as station 100 (reference site, REF) and station 7 (Clark Cove, CC). The sediments were press-sieved, homogenized using paddles and packed for storage in 1-gallon glass jars. Immediately following homogenization, sediment samples were taken and analyzed for acid volatile sulfide (AVS) content. This value was used to calculate additions required to amend ("spike") sediments with lead to concentrations intended to produce biological effects. Sediments were used in exposure systems as stored or amended with lead as per ERLN SOP "Spiking Sediments with Metals for Sediment Bioassays" (ATTACHMENT 1). Sediments were stored at 4 C until use in exposure systems, i.e., between two and six weeks following collection. Specific calculations for additions of lead are included in APPENDIX 1. Sediment samples were taken for characterization as to total organic carbon (TOC), grain size, organic and metal contaminants.

Sediments were amended based on Water and Sediment Quality Criteria guidelines for lead. Specifically, lead concentrations were designed to approach those predicted to produce biological effects in water (40 - 2000 ug Pb/L, acute values) and bedded sediment (0.3 - 1.0 simultaneously extracted metal (SEM)/AVS molar ratios) exposures. There were four sediment types: REF (station 100), Clark Cove (station 7), and reference sediment amended with low (7000 ppm, nominal) or high (22000 ppm, nominal) lead. These spiked sediments were expected to produce SEM/AVS ratios of about 0.3 and 1.0, approximately 100 and 300 times estimated lead concentrations in sediment samples from Clark Cove. These sediments were used in the suspended sediment exposure systems. In addition, smaller batches of sediment were

EXPERIMENTAL APPROACH

- **Characterize Sediment Toxicity**
  - Collect sediment from reference and contaminated sites
  - Amend reference sediment with lead
  - Distribute sediments to suspended and bedded exposure systems
  - Expose juvenile mussels and adult sea urchins to suspended sediments for 30 days
    - » Measure bioaccumulation, growth and reproductive (urchin) effects
  - Expose amphipods and rooted plants to bedded sediments for 10 days
    - » Measure bioaccumulation, growth (plants) and mortality (amphipods)
- **Characterize Contaminant Trophic Transfer**
  - Collect mussels from reference and contaminated sites
  - Amend reference mussels with lead
  - Formulate artificial diet from mussel meat; feed to adult sea urchins for 30 days
    - » Measure bioaccumulation, growth and reproductive effects
- **Develop Exposure-Response Models for Measured Toxic Effects**
- **Extrapolate Measured Effects to Higher Level Ecological Effects**

FIGURE 1: EXPERIMENTAL APPROACH

Table 1a: PNSY II Biological test systems

TEST SPECIES	*Arbacia punctulata*	*Arbacia punctulata*	*Mytilus edulis*	*Ampelisca abdita*	*Ruppia maritima*
COMMON NAME	Purple sea urchin	Purple sea urchin	Blue mussel	Amphipod	Widgeon grass
EXPOSURE LIFESTAGE	Adult	Gametes	Juvenile	Subadult	Shoot
ENDPOINTS	Survival Fecundity Gamete viability	Fertilization Larval development	Survival Growth	Survival	Root growth Leaf growth
EXPOSURE DURATION	30 days	1 hour (fertilization) 48 hours (larval development)	30 days	10 days	10 days 30 days
EXPOSURE MEDIA	Suspended sediment (SS) Trophic transfer (TT)	Interstitial waters (IW) Exposure waters (EW)	Suspended sediment (SS)	Bedded sediment (BS)	Bedded sediment (BS)

Table 1b: PNSY II Biological exposure systems

SEDIMENT EXPOSURES

TEST SPECIES	*Arbacia punctulata*	*Arbacia punctulata*	*Mytilus edulis*	*Ampelisca abdita*	*Ruppia maritima*
LIFESTAGE	Adult	Gametes	Juvenile	Subadult	Shoot
NONE	SS	IW,EW			BS
REFERENCE (STA100)	SS	IW,EW	SS	BS	BS
0.3 LEAD (100x)	SS	IW,EW	SS	BS	BS
0.5 LEAD (150x)		IW,EW		BS	BS
0.8 LEAD (200x)		IW,EW		BS	BS
1.0 LEAD (300x)	SS	IW,EW		BS	BS
CLARK COVE (STA 7)	SS	IW,EW	SS	BS	BS

DIETARY EXPOSURES

NATURAL FOOD	TT
REFERENCE (STA100)	TT
10x LEAD	TT
100x LEAD	TT
CLARK COVE (STA 7)	TT

MAP OF PORTSMOUTH

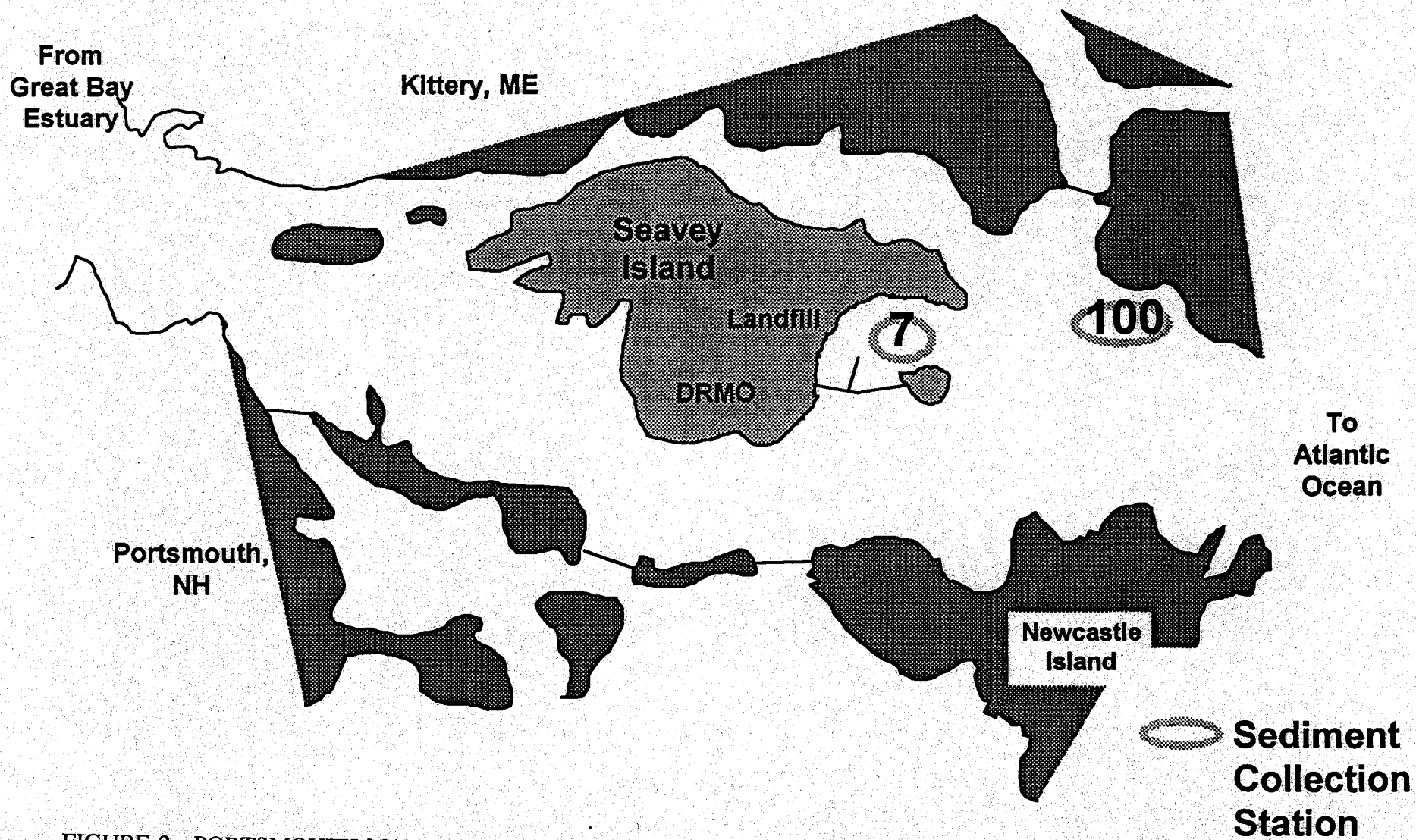


FIGURE 2: PORTSMOUTH MAP

amended to produce sediments with predicted SEM/AVS ratios of 0.5 and 0.8 for use in the bedded sediment studies using amphipods and rooted plants.

SUSPENDED SEDIMENT EXPOSURE SYSTEM

The exposure system, modified from that described by Daniels (1993), (FIGURE 3, SUSPENDED SEDIMENT EXPOSURE SYSTEM), was designed to provide uniform suspended particulate exposures. There were eight exposure systems: two replicate systems for each of four sediment types. Each system delivered to a mixing chamber ("splitter") which divided the stream of suspended sediment into paired tanks.

For this purpose, sediment slurries (1 part sediment to 9 parts sea water, by volume), were pumped through computer-controlled solenoid valves into streams of filtered sea water (nominally, 300 ml/minute). Targeted particulate load was 20 mg/L, nominally reflecting site conditions as described in the Phase I report. Particulate loading, controlled by length and interval of sediment pulse, was measured on alternate days. Measurements were made using a transmissometer or a whole water sample was taken for direct measurements of total suspended solids (as per ERLN SOP 1.02.004 "Suspended Solids Determinations in Water Samples"). The exposure systems were closed and aquaria overflowed directly into contaminated disposal drains.

ARTIFICIAL DIET EXPOSURE SYSTEM

Artificial diets were provided to sea urchins during an approximately 30-day period. The diets were formulated based on a modification of a used successfully to maintain fertile urchins (Dr. William Sunda, personal communication). This agar-based diet, containing ground kelp and mussel meat, with or without lead amendment, was formulated in large batches and dispensed into feeding units, i.e., plastic trays (about 50 ml volume). Each exposure tank of ten urchins of the same sex was fed 1 plate twice per week. Food was generally consumed before the addition of new plates. While no attempts were made to determine consumption rates by diet type, feeding activity was observed for all food types. Each urchin had access to about a 10 ml volume (about 10 g wet weight) of food per week.

There were four diet types created: one containing mussels from Clark Cove (archived from Phase I collection) and three containing mussels from a reference site (Cape Cod). The three types containing uncontaminated mussels were amended with zero, an intermediate or a high amount of lead, added as lead nitrate solution. The feed levels spiked with lead, intermediate and high, were intended to (very) roughly approximate 10x (about 60 ug Pb/g dry weight) or 100x (about 600 ug/g Pb dry weight) lead levels in Clark Cove biota, respectively. Complete diet formulation are provided in APPENDIX 2.

SUSPENDED SEDIMENT EXPOSURE SYSTEM

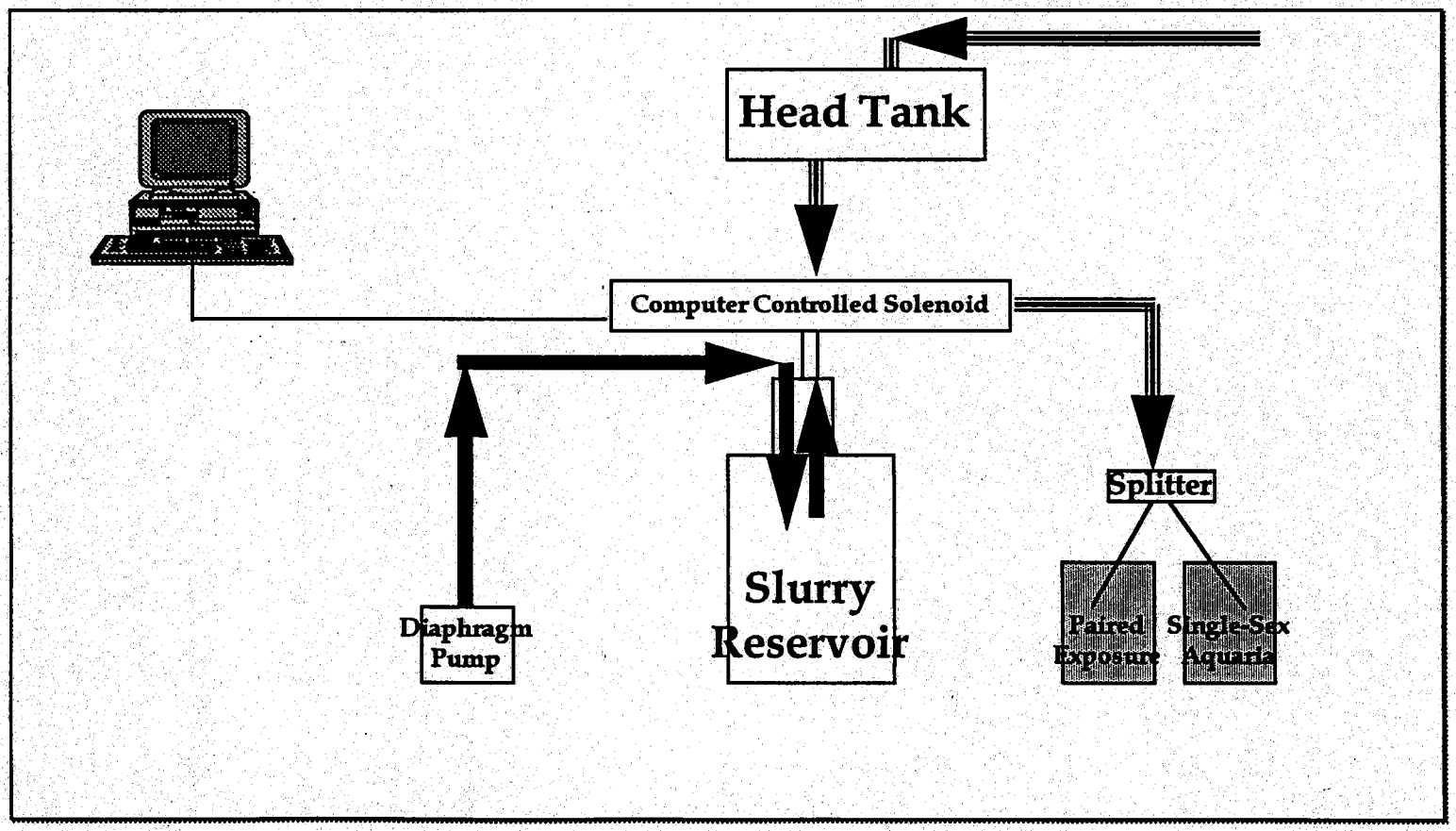


FIGURE 3: SUSPENDED SEDIMENT EXPOSURE SYSTEM

BIOACCUMULATION BY BLUE MUSSELS

Mussels were collected during the week of August 6, 1993, from uncontaminated tidal flats, Sandwich, MA, a site historically used by this lab for "clean" test organisms. Subadult blue mussels of size range, 3.0 $\pm$ 0.1 cm, were selected from the collection and maintained in flowing sea water troughs for about 2 weeks prior to use in the laboratory exposure systems. (Larger mussels were shucked, ground, cooked and frozen for use in diet studies, see above).

These mussels were exposed to naturally- and artificially-contaminated sediment via a suspended sediment exposure system. Mussels were contained in chambers within aquaria flushed with a sediment slurry diluted with filtered sea water (15 C, FIGURE 4, MUSSEL EXPOSURE CHAMBERS). Chambers were open to the surrounding tank or were covered using nylon mesh to restrict particulate entrainment within chambers. Algae (Isochrysis sp) stocks were fed into inflow ports of chambers while peristaltic pumps were employed to draw water and algae through chambers. Monitoring and maintenance procedures were conducted regularly during the 30 days of exposure. Following exposures, mussels were measured for length, segregated by treatment into labelled, plastic storage bags and frozen for future chemical analyses as part of a study focusing on BIOACCUMULATION.

SUSPENDED SEDIMENT TOXICITY AND TROPHIC TRANSFER TO PURPLE URCHINS

Approximately 500 adult purple sea urchins (Arbacia punctulata) were collected by divers during the week of 6 August, 1993, from Narragansett Bay, RI. Urchins were sized for test (shell) diameter using calipers and sexed using electrical stimulation (US EPA, 1987). Urchins were maintained in separate-sex tanks of flowing 15 C sea water prior to exposures. Approximately one-half of these urchins were distributed in units of ten into paired single-sex aquaria containing suspended sediment (SEDIMENT TOXICITY). These urchins were fed freshly collected kelp, Laminaria sp., twice weekly. The remaining urchins were distributed in units of ten into paired single-sex aquaria containing flowing (approximately 300 ml/min), filtered sea water and fed naturally or artificially-contaminated diet as part of a TROPHIC TRANSFER study.

Following exposures of about 30 days, surviving urchins were counted, measured for size (test diameter and wet weight) and qualitatively assessed for gamete production. For a subsample of urchins from each exposure tank (up to four), gamete production was quantified and viability of gametes and larvae were assessed using modifications of the sea urchin fertilization and larval development assays (ERLN SOP "Conducting the Sea Urchin, Arbacia punctulata, Reproductive Success Bioassay", ATTACHMENT 2). Samples of gametes and soft body parts were packaged in labelled

Suspended Sediment Exposure Aquarium

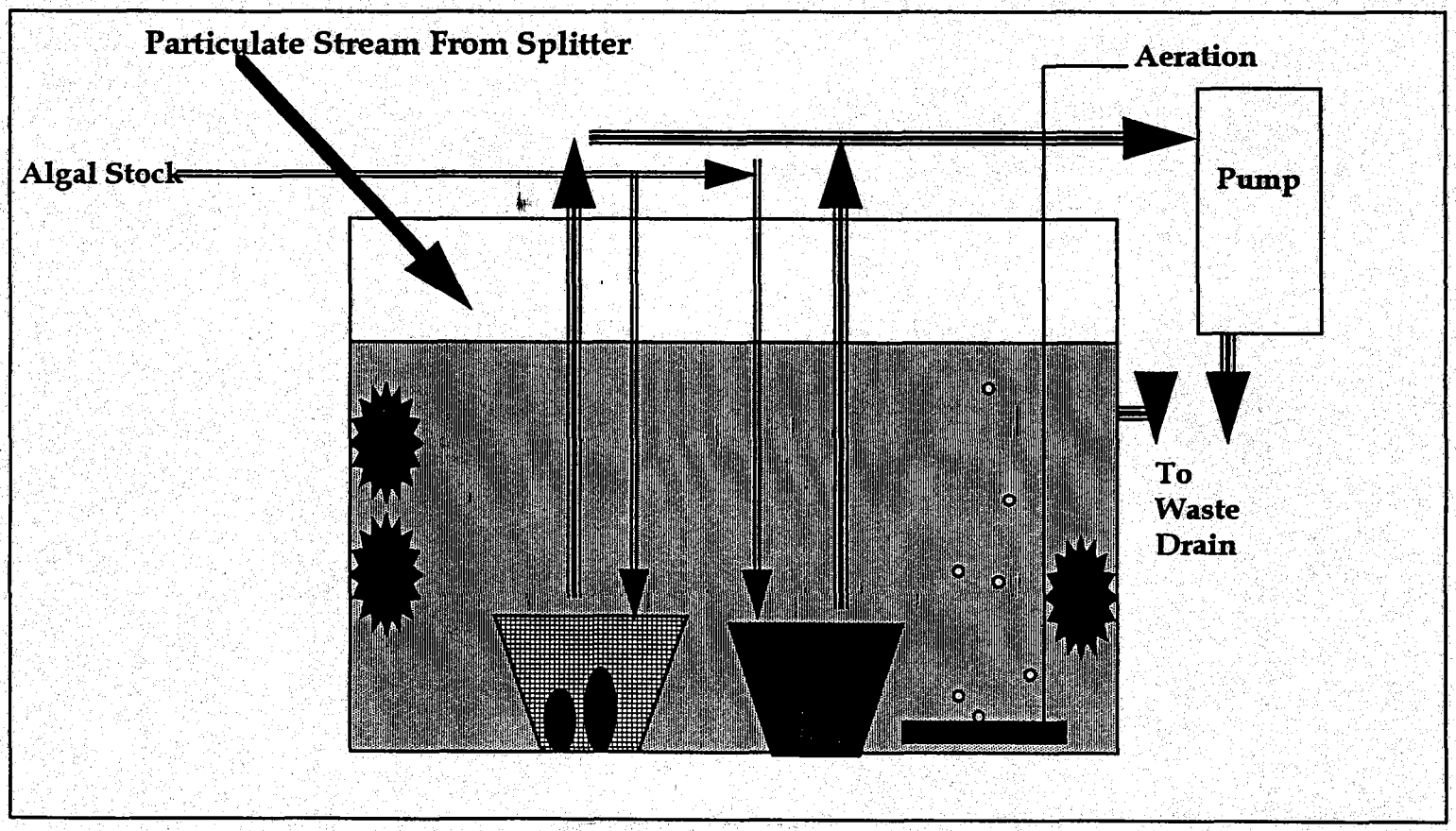


FIGURE 4: SUSPENDED SEDIMENT EXPOSURE AQUARIUM

vials and stored frozen at -70 C for future chemical and biochemical analysis. As part of system characterization, additional sea urchin fertilization and larval development assays were conducted using tank water, sediment interstitial waters and lead-spiked sea water.

BEDDED SEDIMENT TOXICITY TO AMPHIPODS AND ROOTED PLANTS

Standard (static) acute amphipod toxicity tests were conducted using Ampelisca abdita (ERLN SOP 1.03.002 "Conducting Acute Toxicity Tests using Ampelisca abdita") collected from Narragansett, RI. Concurrent, replicate exposure systems were used for the rooted aquatic plants, Ruppia maritima and Zostera marina, collected from an uncontaminated pond in Charlestown, RI.

Plant exposures were conducted as described in ERLN SOP "Conducting Chronic Toxicity Tests using Ruppia maritima", ATTACHMENT 3) with slight modification. Briefly, following ten day static exposures, shoot length (but not root length, as indicated in the protocol) was measured for Ruppia and plants were segregated by treatment and stored frozen in labelled plastic bags for future chemical analysis. As part of system characterization, additional Ruppia tests were conducted using lead-spiked sea water.

DEVELOPMENT OF SEA URCHIN POPULATION MODEL

A sea urchin population model was developed using data from these studies and studies conducted by EPA ERL-N's Complex Effluent Testing Program (George Morrison, personal communication), through which toxicity testing methods were developed using the sea urchin, Arbacia punctulata. While these earlier studies quantified urchin survivorship through early life stages, i.e., from gametes through metamorphosis, current studies contributed information concerning adult survivorship, fecundity and gamete quantification. These data were used to develop parameters for population growth model using the software, RAMAS. Analyses were conducted to evaluate the contribution of lifestage-specific treatment effects, measured during the Phase II laboratory studies, on population growth rate.

2.2 CHEMICAL MARKER DEVELOPMENT

APPROACH

Develop fingerprints of contaminant sources by screening for chemical markers. Applying the results of Phase I chemical marker determinations to the distribution of marker compounds in the estuary will be very useful for validating dispersion models. Chemical marker information will also be very useful for determining the relative sources of chemical impact in the estuary.

1. Shipyard Markers

A portion of what was done during the first phase of this work was to screen sediment samples for a chemical marker or fingerprint specific to the shipyard. This work did not definitively identify a fingerprint of the shipyard. Additional work will be done during this phase in attempting to identify a chemical marker specific to the shipyard. Samples analyzed using gas chromatography - mass spectrometry (GC/MS) with an electron ionization source will be reanalyzed using a GC/LC/MS with a negative ion chemical ionization (NICI) source. This new capability will enable both a quantitative and qualitative analysis of classes of chemicals that are not presently being evaluated with existing instrumentation. This analysis will include additional work on cutting oils. Chlorinated paraffins are potential components of cutting oils previously in use at the shipyard. The analysis of these compounds, at environmental levels, requires the use of a GC/MS system with NICI. This analysis will be applied to existing sediment sample extracts as well as new samples collected as part of the phase II effort.

Water samples were collected from survey wells drilled on the shipyard by McLaren/Hart and analyzed as part of the onshore study. The results of these analyses showed a group of samples to contain a distribution of polycyclic aromatic hydrocarbons. This data will be examined in conjunction with the offshore data to evaluate potential seepage of onshore chemicals from the landfill to the estuary.

2. Seep Samples

New sampling efforts will be specifically directed toward the seeps located on the east and north east shorelines of Seavey Island surrounding the Jamaica Island Landfill. Samples of sediments directly impacted by these seeps, and the seep water itself, will be examined for compounds that may prove to be specific to the shipyard. Techniques used for the qualitative screening of the phase I sediment samples for a shipyard specific source will be applied to the seep samples. This analytical method allows for the analysis of compounds with a greater range of polarity than is typically employed in an environmental analysis. These samples will also be analyzed for the suite of chemical markers used in the first phase of this work and chemicals that were identified in the survey wells.

3. Sediment Cores

Deep sediment cores were collected from several low energy depositional areas in the lower Piscataqua River Estuary. Additional sediment core sampling efforts are being directed toward a marsh on Seavey Island and a marsh on Spruce Creek. An additional site is under investigation that is not directly impacted by the estuary. This core would be used to characterize

the input of eolian material to the immediate area. These cores are being dated using the radionuclides ^{210}Pb and ^{137}Cs. In addition, they are being characterized for grain size and organic carbon. The work proposed for this phase is to subsample a group of these sediment core sections and analyze them for chemical markers of pollution sources. This work would make use the analytical methodology worked out during the first phase of this study. Preliminary results suggest that sediment cores in some locations contain material dating back to the 1880's. These cores will be analyzed with the goal of evaluating the onset and changing patterns of pollutant sources impacting the lower Piscataqua River estuary.

4. Water Samples

As a result of the dynamic nature of the Lower Piscataqua River Estuary the chemicals found in the analysis of sediment samples from this system may have entered from locations all along the waterway. Water samples will be collected in conjunction with University of Rhode Island personnel from several sites in the estuary. Particulate and dissolved phase samples will be collected using a teflon pump and a filter and foam plug system. Sampling stations will be chosen with regard to the stations occupied during the first years efforts. These samples will be analyzed for the suite of chemical markers used in the first phase of this study. In conjunction with the surface sediment data obtained in the first phase, data from the water column samples will enable estimates of the source strengths presently entering the estuary.

2.3 MARINE ANALYTICAL CHEMISTRY

APPROACH

The data quality objectives for conducting ecological risk assessments requires the use of field and laboratory methods that are capable of measuring parts-per-billion levels of organic and inorganic contaminants in marine and estuarine sediments and tissue (fish, invertebrates, and plants). The recommended analytical methods and QA/QC procedures needed to meet the ecological risk data quality objectives are identified in NRaD Technical Document 2296 (Mueller et al. 1992). These procedures have been used to meet the data quality objectives for a variety of federal programs including NOAA's National Status and Trends Program, EPA's Puget Sound Estuary Program, and the Navy's CERCLA assessment for NCBC Davisville and RCRA assessment for Portsmouth Naval Shipyard. The procedures do not specifically require that particular analytical methods always be followed, but rather that the performing laboratory demonstrates its proficiency through routine analysis of standard or certified reference materials (SRMs or CRMs) or similar types of accuracy-based materials. Through the application of this concept, the analytical laboratory participates in on-going performance evaluation exercises conducted throughout the study, both to demonstrate initial capability (i.e., prior to the analysis of actual samples) and on a continuous basis throughout the project. The laboratory will be required to initiate corrective actions if their performance falls below certain predetermined minimal standards.

OBJECTIVE

Provide trace-level analysis of marine sediment, tissue, and elutriate samples for the target analytes identified in the scope of work. Provide data validation and analytical performance information in accordance with the QA/QC requirements identified in this work plan. Document results and technical procedures in the technical data report and data deliverable in accordance with this work plan.

QA/QC SPECIFICATIONS

The QA/QC specifications to be used for this project are documented in detail in the accompany section entitled <u>Quality Assurance Project Plan: Marine Analytical Chemistry Support for the Estuarine Ecological Risk Assessment Case Study at the Portsmouth Naval Shipyard, Kittery, Maine.</u> The QA/QC requirements for the analysis of contaminants in marine sediments and tissues provides special emphasis on a performance-based program, involving continuous laboratory evaluation through the use of accuracy-based materials. Each batch must contain a minimum number of QA/QC samples which includes certified standard

reference materials and/or laboratory control materials, laboratory fortified sample matrices, laboratory reagent blanks, calibration standards, and laboratory and field replicates. The ecological risk QA/QC plan also provides specific control limits or numerical data criteria that, when exceeded, requires specific corrective action by the laboratory before the analyses may proceed. Warning and control limits are specified as is the recommended frequency of analysis for each QA/QC element or sample type. The conceptual basis for the use of these quality control samples is presented in detail in the document. In all other areas, not explicitly addressed by the ecological risk QA/QC plan (instrument tuning, chain-of-custody, data validation, etc.), standard Contract Laboratory Program (CLP) protocols, or equivalent laboratory developed SOPs will apply.

TECHNICAL WORK PLAN:

Conduct marine analytical chemistry research and development for the target analytes in the sample matrices. Before technical analysis can begin, method detection limits (MDLs) and analytical standard operating procedures (SOPs) must be documented to confirm that the methods to be used will acheive the target detection limits identified in Attachment (1). Technical sample analysis should proceed in accordance with the QA/QC plan identified in NRaD TD 2296. Any deviations from the proscribed SOP and QA/QC plan should be documented and approved by the Technical Coordinator of this work plan, prior to sample analysis (or as soon as possible after technical problems are encountered).

3.0 QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES

ORGANISM COLLECTION AND MAINTENANCE

Organisms to be collected for subsequent experimental work in this project include: the benthic amphipod, Ampelisca abdita, for sediment toxicity assessments; the sea urchin, Arbacia punctulata, for water toxicity assessments; and the blue mussel, Mytilus edulis, for laboratory bioaccumulation studies. All animals will be collected and maintained following protocols described in SAIC's Environmental Testing Center (SAIC-ETC) SOPs AMP-01 - AMP-10, and ERLN SOPs 1.01.003 and 1.02.001 (Appendix D). The plants, Zostera marina and Ruppia maritima, will be collected according to JEL SOP 1.01 and ERLN SOP "Development of a Short-Term Marine Sediment Toxicity Assessment Method with the Rooted Aquatic Plant, Ruppia maritima", respectively.

SAMPLE COLLECTION AND PREPARATION

Field sediments will be collected according to procedures employed at ERLN for the Sediment Quality Criteria Program. Specifically, samples will be collected with a Van Veen grab, by divers, or with a shovel. The samples will be kept cold until their arrival at ERLN. Sediments will be press-sieved through a 2mm stainless steel screen and homogenized. The processed sediments will be Stored in 4L glass jars or in covered plastic buckets until used. Sediment spiking will be accomplished according to ERLN SOP "Spiking Sediments with Metals for Sediment Bioassays".

Sediment interstitial waters will be collected from sediments available at ERL-Narragansett using the procedures described in the standard operating procedure (SOP): Extraction of Interstitial Water from Marine Sediments (1991).

MONITORING PARAMETERS AND FREQUENCY OF COLLECTION

Parameters for bioassay methods employed by ERLN are indicated in Table 2 for the Ampelisca assay, Table 3 for the Arbacia assays, Table 4 for the Microtox assay and Table 5 for the Ruppia assay.

TABLE 2. AMPELISCA TOXICITY TEST PARAMETERS

Parameter	Sampling Frequency	Test Replicate Sample	Immediate Processing or Measurement
Survival	Daily	All chambers	Record number of dead amphipods and remove
Molting	Daily	All chambers	Record number of molts and remove
Temperature	Daily	Water bath	Record thermometer measurement to 0.5°C
	Continuous	Water bath	Observe temperature recorder chart for variation
Salinity	Twice/test	All chambers	Record refractometer measurement to 1 ppt
Dissolved Oxygen	Twice/test	All chambers	Record meter reading to 0.1 ppm
pH	Twice/test	All chambers	Record meter reading to 0.1 Ph unit
Emergence	Daily	All chambers	Record number of amphipods on sediment or water surface
Tube	Daily	All chambers	Record unusual formation appearance or lack of tubes

TABLE 3. ARBACIA BIOASSAYS MONITORING PARAMETERS

Parameter	Sampling frequency	Sample identity	Limits[1]
Fertilization endpoint	Termination	All reps	
Larval endpoint	Termination	All reps	
Salinity	Initiation	Sample	30ppt±2ppt
Temperature	Initiation	Sample	20±1°C

[1] Values indicate ideal conditions for performance of tests. If ambient sample parameters differ the sample will be adjusted per ERLN SOP 1.03.006.

TABLE 4. MICROTOX BIOASSAY MONITORING PARAMETERS

Parameter	Sampling frequency	Sample identity	Limits[1]
Luminescence endpoint	Termination	All reps	
Salinity	Initiation	Sample	30ppt±2ppt
Temperature	Initiation	Sample	20±1°C

[1] Values indicate ideal conditions for performance of tests. If ambient sample parameters differ the sample will be adjusted per ERLN SOP 1.03.006.

TABLE 5. RUPPIA BIOASSAY MONITORING PARAMETERS

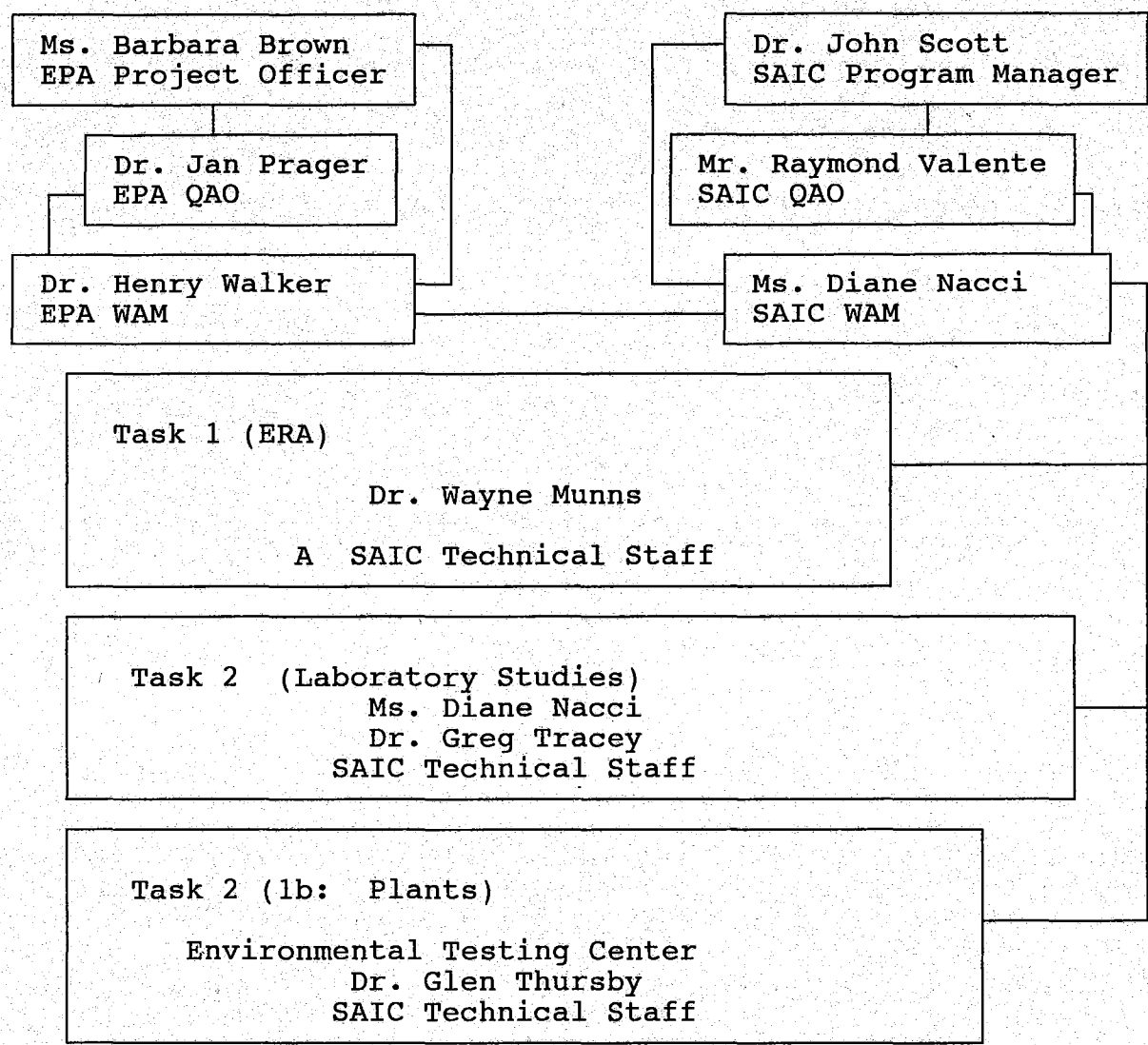
Parameter	Sampling frequency	Sample identity	Limits[1]
Root growth endpoint	Termination	All reps	
Shoot growth endpoint	Termination	All reps	
Salinity	Initiation	Sample	30ppt±2ppt
Temperature	Initiation	Sample	20±1°C

[1] Values indicate ideal conditions for performance of tests. If ambient sample parameters differ the sample will be adjusted per ERLN SOP 1.03.006.

PROJECT ORGANIZATION AND RESPONSIBILITY

The organizational structure and the accompanying responsibilities for this project will be divided into two basic categories. The first is the manager level, from which all work and QA functions will be coordinated. The second, or technical level consists of the personnel who will perform and evaluate the toxicity tests. The technical personnel will also have responsibility over the quality control of their specific technical component. The organization structure is presented in Figure 5. Ms. Barbara Brown will serve as EPA's Project Officer and Dr. John Scott will serve as SAIC's Program Manager. Quality Assurance Officers (QAO) for this project will be Dr. Jan Prager and Mr. Raymond Valente for EPA and SAIC, respectively. Ms. Diane Nacci serve as SAIC Work Assignment Manager (WAM). The SAIC WAM will be in direct contact with EPA's Work Assignment Manager, Dr. Henry Walker.

FIGURE 5. Project Personnel Organization Structure for Work Assignment #2-39-2



The SAIC WAM will be responsible for coordinating all main activities and reviewing all data generated during this project for scientific value and quality. The compilation and production of interim and final technical reports, safety plans and quality assurance documents.

Responsibilities of the SAIC technical staff include the maintenance of organisms and conduct of toxicity tests. Specific responsibilities include maintenance of healthy organisms, as appropriate, and the supplies and equipment necessary for successful testing, actual performance of toxicity tests and analysis of data, and the evaluation and generation of summary reports in memo format (including raw data sheets). Technical personnel also will be responsible for performing all quality assurance/quality control procedures associated with their individual toxicity testing activities.

Technical activity in Task 2.1.b includes testing of submerged aquatic plants. This testing will be coordinated and conducted by personnel at the SAIC Environmental Testing Center (ETC). The subtask manager, Dr. Glen Thursby, will supervise this activity and will be responsible for the generation of all associated record keeping, reporting, implementation of safety procedures and maintenance of quality assurance and quality control protocols.

DATA QUALITY REQUIREMENTS AND ASSESSMENTS

Data quality objectives (DQOs) imposed by the intended use of data discussed in Section 7.3 will be required to ensure that information collected in this project will be of known and acceptable quality. The remainder of this section provides information regarding the representativeness, comparability, completeness, accuracy, and precision of data obtained in project activities at ERLN.

REPRESENTATIVENESS, COMPLETENESS, AND COMPARABILITY

Over the course of methods development and subsequent use in numerous ERLN projects, the Ampelisca and Arbacia bioassays have been shown to produce toxicity information which is representative of benthic and water column organism responses to environmental contaminants. Species used in both tests are sensitive to the suite of contaminants suspected to be associated with the SHIPYARD. Although these bioassays are considered to be "acute" or "rapid", the results of these bioassays may be indicative of the longer-term, chronic effects of introduced compounds. Although few biomonitoring approaches to assessing chronic water quality problems exist, data obtained from this test are considered to be representative of long-term responses of pelagic marine species.

The procedures to be employed in biological assessments of sediment and water quality follow protocols identical to those of numerous ERLN studies, including the marine ecological risk assessment for NCBC. Comparability of assay and test results with these and other studies should therefore be high.

ACCURACY (BIAS) AND PRECISION

Of particular concern in this study are data accuracy and precision. Although both attributes are easily quantified in chemical assessments, the accuracy of a toxicity test is not measurable because the true toxicity of any given environmental sample is unknown. Further, toxicity is a relative property dependent upon exposure conditions (test duration, bioavailability of contaminants) and the species being tested. Fortunately, precision can be addressed in the context of toxicity evaluations.

Generally, the precision of bioassay results can be evaluated in two, conceptually similar, ways: by repeating individual tests (test precision) and through replication of treatments within a single test (treatment precision). The first approach addresses error associated with test conditions and variation in individual organism response, whereas the second primarily addresses variation in response. Test precision of the toxicity bioassays has been measured using a standard toxicant in a systematic fashion (SAIC-ETC unpublished data; Morrison et al. 1990). Such results provide a basis for setting criteria for acceptable test performance. Levels of test precision, expressed as the coefficient of variation (CV) of endpoints associated with exposures to cadmium chloride (Cd) for Ampelisca, and copper sulfate (Cu) and sodium dodecyl sulfate (SDS) for Arbacia, are presented in Table 7. Based upon this information, precision data control charts will be generated and successive standard toxicant toxicity test results plotted on the chart to ensure that the data fall within the limits of quantified variability. Ampelisca test acceptability also is determined based on control response. The acceptable control response level for this bioassay is <10% mortality.

TABLE 7. TEST PRECISION OF AMPELISCA AND ARBACIA BIOASSAYS

Bioassay	Toxicant	CV (%)
Ampelisca	Cd	40
Arbacia	Cu	46
	SDS	33

TOXICITY TESTING PROCEDURES

HEALTH AND SAFETY

Health and safety protocols will be followed during this project. Protocols will be based on guidance supplied by U.S. EPA (1988) and Valente et al. (1990). Specific safety plans will be generated as required to accomplish work assignment goals. In addition, each potentially hazardous chemical and environmental sample that project personnel may be exposed to will have a Materials Safety Data Sheet (MSDS) associated with it to document possible safety concerns. Personnel may require specific safety training such small boat handling, used in the collection of samples and test organisms. Health monitoring of all staff will occur on a biannual basis.

TOXICITY TESTING

Testing organisms, equipment and facilities will be maintained in good condition based on the guidance provided by US EPA (1988), Conducting Acute Toxicity Tests Using Ampelisca abdita (SOP:1990) and Valente et al. (1990).

Toxicity testing procedures used during this project are described in a general fashion by U.S. EPA (1988) and the EMAP Laboratory Methods Document (1990). Specific descriptions of each method are provided in the following SOPs: Conducting the Sea Urchin, Arbacia punctulata, Fertilization Test (1991); Conducting Acute Toxicity Tests Using Ampelisca abdita (1990).

STATISTICAL ANALYSIS

Approaches for performing statistical analyses on the results of the above toxicity tests are presented in the SOPs referenced in the preceding section.

SAMPLE CUSTODY PROCEDURES

All samples will receive a unique sample number generated and tracked by ERLN. This number will be affixed to sampling containers, and pertinent collection information (station, date, time, depth, etc.) will be entered into sampling logs by field personnel. Duplicate logs will be maintained to minimize loss of information.

Because different individuals may be involved in the collection and distribution of individual samples, chain-of-custody forms will be maintained for each set of samples transferred. These forms will follow each set of samples from collection through sample archiving. Duplicate forms will be maintained to minimize loss of information.

Samples for physical and biological analysis will be stored prior to analysis as described in relevant SOPs. Shipment of chemistry and toxicity samples will be effected by overnight carrier, or by transport by project personnel. Sample condition will be evaluated by the appropriate project staff at time of receipt.

CALIBRATION PROCEDURES AND PREVENTIVE MAINTENANCE

All commonly used equipment, such as Ph meters, balances and ovens, will be calibrated and maintained as recommended by the manufacturers. Records of calibration for Ph meters and balances will be kept in notebooks in the area adjacent to the equipment.

DOCUMENTATION, DATA REDUCTION AND REPORTING

Raw biological assessment data collected by ERLN personnel will be entered directly onto test-specific standardized data sheets and log books. Duplicate copies will be maintained to minimize loss of information. The raw data also will be entered into computerized data bases (described in the Data Management Plan). Transcription errors will be minimized by a two level check: personnel responsible for data entry will review each record for errors, and a second individual will check 10% of all entries. Identified errors will be corrected immediately. If transcriptions errors are observed at a rate greater than 2%, all data entered will be rechecked.

Test-specific data reduction practices and statistical analyses are described in SOPs. Generally, data reduction and statistical analyses will be performed by computerized utilities (e.g., SAS). All statistical analysis approaches have been reviewed and approved by the ERLN statistician.

Final data reports will contain descriptions of test conditions, results, and ancillary observations, and may contain preliminary interpretations. Additionally, raw data will be accessible through centralized data bases and data sheets.

DATA VALIDATION

As described above, all raw and computerized data reported by ERLN in this project will be subjected to a 100% review by the personnel responsible for each assessment. An additional review will be performed by a second individual to identify errors in recording, transcription, and reporting. Raw data sheets and laboratory notebooks will be reviewed in this process. Data that do not meet the standards described in this document will be reported with an explanatory notation. The Project Officers and Principal Investigators will make the final determination as to data validity. Descriptions of interpretation and synthesis

activities utilizing suspect data will be prefaced with an explanation of data quality.

PERFORMANCE AND SYSTEMS AUDITS

Audits for all aspects of this work assignment may be performed by the ERL-N and SAIC QA Officers at any time over the course of the project.

CORRECTIVE ACTION

TECHNICAL ACTION

Corrective technical action in this project has two components. The first is related to failure to meet minor test requirements, for example in one of the physical parameters. If a physical parameter is exceeded the technical personnel involved and the SAIC Work Assignment Manager will discuss the potential impacts on the quality of the test results. Using professional judgement on an individual incident basis, a decision will be made as to how to report the infraction and its significance.

The second component of corrective technical action involves more serious infractions. The standard operating procedures cited define specific acceptability criteria for each toxicity test. If any one of these acceptability criteria are not met during the performance of a test, the test will be rejected and repeated if possible. This rule also holds true for standard toxicant(s) tested during a routine toxicity test that fall outside the range of acceptability on the control chart.

MANAGEMENT ACTION

Infractions will be reported to the SAIC Work Assignment Manager as soon as possible by involved personnel, verbally or via memo, and the SAIC Work Assignment Manager will notify the EPA Work Assignment Manager. Generally, this notification will occur only to maintain lines of communications. However, if the infractions are sufficiently severe (e.g. repeated problems with the same procedure) decisions may be made to cancel or revise project research.

The SAIC Work Assignment Manager will describe specific infractions in interim and final technical reports.

REPORTS

Technical personnel will report to the work assignment manager via memo. The SAIC Work Assignment Manager delivers to the EPA Work Assignment Manager all required reports and any SOPs developed during the course of this project.

4.0 REFERENCES

Daniels, T, D. Cartier, D. Sleczkowski, A. Russel Malcolm, 1993. A Computer Controlled Dosing System for Sediment Particle Suspensions. ERLN Report.

EMAP Laboratory Manual 1990. Environmental Monitoring and Assessment Program: Near Coastal. U.S. Environmental Protection Agency, Office of Research and Development, Narragansett, Rhode Island (draft)

Morrison, G., E. Torello, R. Comeleo, R. Walsh, A. Kuhn, R. Burgess, M. Tagliabue and W. Greene 1989. Intralaboratory precision of saltwater short-term chronic toxicity tests. Res. J. Wat. Pollut. Contr. Fed. 61:1707-1710

Mueller C., W.R. Munns, Jr., D.J. Cobb, E.A. Petrocelli, G.G. Pesch, W.G. Nelson, D.M. Burdick, F.T. Short and R.K. Johnston (eds.) 1992. Standard Operating Procedures and Field Methods Used of 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, 484pp.

U.S. EPA 1988. Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms. U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH EPA/600/4-87/028

Valente, R. 1990. Environmental Monitoring and Assessment Program: Near Coastal Component. Quality Assurance/Quality Control Manual. U.S. Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, Narragansett, Rhode Island (draft)

APPENDIX 1: SEDIMENT AMENDMENT

Station identification = PNSY100

Wet volume	=	100 ml
Wet weight	=	126 g
Dry weight	=	60 g
Sediment density	=	1.26 g/ml wet
Fraction solids	=	0.48 g dry weight/g wet weight
AVS	=	55 - 88 uM/g
Chemical formula	=	$PbNO_3$
Molecular weight of salt	=	331.20
Molecular weight of Pb	=	207.20
Fraction of metal/salt	=	0.63

Actual concentrations of lead added to 1 gallon of sediment, HIGH LEAD treatment:

Spiking stock	=	174.87 g salt/L
Volume stock	=	500 ml
Amount of Pb added	=	174.87 * 0.5 * 0.63
	=	55.06 g Pb
Sediment volume	=	4000 ml wet
Sediment dry	=	4000 * 1.26 * 0.48
	=	2419 g dry weight
Lead concentration	=	55060000 ug Pb/2419 g dry sediment
	=	22,800 ug/g
SEM/AVS	=	22,800 ug/g /207.2 ug/uM
	=	110.04 uM PB
	=	1.25 uM/g(assuming 88 uM AVS)

Nominal concentrations of lead per sediment treatments: presumed effect concentration = 1.0 SEM/AVS

Treatment Common name	SEM/AVS*	Lead, ppm Bnominal	Increase Factor
REF	0.001	30	
CC (Clark Cove)	0.003	70 - 100	1
LL (Low Lead)	0.3	6,840	100
	0.5	11,400	150
	0.8	18,240	250
HL (Low Lead)	1.0	22,800	300

* approximations assuming AVS = 100 uM/g dry sediment

Nominal concentrations of lead in suspended sediment treatments: presumed effect concentrations = 2000 ug/L WQC acute value; acute/chronic = 500:1; 40 ug/L chronic value

Treatment = HL		
Lead in sediment	=	22,800 ug Pb/g dry sediment
	=	22.8 ug Pb/mg dry sediment
Tank particulate load	=	35 mg/L
Pb from particulates	=	22.8 ug Pb * 35 mg/L
	=	800 ug/L Pb (HL)*

* assumes all lead from particulates are dissolved in water column

Treatment Common name	Lead, ppb nominal	Increase Factor
REF	1 ?	
CC (Clark Cove)	2.5 ?	1
LL (Low Lead)	250	100
HL (High Lead)	800	300

APPENDIX 2: ARTIFICIAL DIET

Recipe for 12 plates of urchin food:

150 ml	Ground cooked mussels (including liquid)
300 ml	Chopped laminaria (including liquid)
50 ml	Crushed tetramin flakes
37 g	Marine agar
220 ml	Sea water (/deionized water spiked with lead)

Lead content in Reference (STA 100) Biota (guess based on other reference site measurements):

Mussels: 2.5 ug/g dry, 15% solids, or about 0.4 ug Pb/g wet weight

Mussel proportion of artificial diet = 22%,
or about 0.1 ug/Pb/g wet weight

Lead content in Clark Cove (STA 7) Biota (estimated from NSP Phase I report):

Mussels: 25 ug/g dry, 15% solids, or about 4 ug Pb/g wet weight

Mussel proportion of artificial diet = 22%,
or about 1 ug/Pb/g wet weight

Lead additions:

Intermediate lead spiked food:

Stock= 17.4 g/l $Pb(NO3)2$ = 10940 mg/l Pb
Volume stock/food= 0.667 ml/667 ml= 10.940 ug/ml Pb,
approximately 10 ug Pb/g wet weight
(about 60 ug/g dry)

High lead spiked food:

Stock= 17.4 g/l $Pb(NO3)2$ = 10940 mg/l Pb
Volume stock/food= 6.67 ml/667 ml= 109.40 ug/ml Pb,
approximately 100 ug Pb/g wet weight
(about 600 ug/g dry)

QUALITY ASSURANCE PROJECT PLAN
ESTUARINE ECOLOGICAL RISK ASSESSMENT
AT THE PORTSMOUTH NAVAL SHIPYARD
KITTERY, MAINE

U.S. ENVIRONMENTAL PROTECTION AGENCY
Environmental Research Laboratory
27 Tarzwell Drive
Narragansett, Rhode Island 02882

July, 1993

TABLE OF CONTENTS

Section	Section Title	Page
1	TITLE PAGE	1
2	TABLE OF CONTENTS	2
3	INTRODUCTION	3
4	PROJECT ORGANIZATION	3
5	QUALITY ASSURANCE REQUIREMENTS	5
6	ANALYTICAL PROCEDURES	14
7	DOCUMENTATION AND DATA VALIDATION	17
8	REFERENCES	18

3.0 INTRODUCTION

This Quality Assurance Project Plan (QAPjP) provides Quality Control / Quality Assurance guidelines to be followed during the analysis of routine sediment, tissue and seep samples collected as part of the Estuarine Ecological Risk Assessment at the Portsmouth Naval Shipyard, Kittery, ME.

3.1. PROJECT DESCRIPTION

The project includes a sampling program to assess the bioaccumulation potential of contaminants in lobster and winter flounder collected in the vicinity of the Portsmouth Naval Shipyard in Portsmouth Harbor. Muscle tissue from tail and claw as well as the hepatopancreas of adult and juvenile lobsters will be analyzed for selected organic and inorganic contaminants. The flesh and liver of winter flounder will be analyzed and data ultimately used to assess the bioaccumulation potential of contaminants. In addition, seep samples and sediment cores will be collected and analyzed for Acid Volatile Sulfides (AVS) / Simultaneously Extractable Metals (SEM), with the data generated being used to evaluate contaminant specific geochemical assimilation / availability . Sediment cores, as well as other sample sources, will also be examined for the possible presence of contaminants that may be used as chemical markers.

3.2 OBJECTIVES

The objective of this project is to perform chemical analysis of sediments, tissues and seep samples collected as part of the Estuarine Ecological Risk Assessment at the Portsmouth Naval Shipyard, Kittery, ME.

4.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

The Work Assignment Organization Chart (Figure 1) shows key personnel associated with this work assignment. Responsibilities of the key personnel are outlined below.

Dr. John Scott will function as the overall Program Manager. He will be directly responsible to EPA, through the Project Officer Ms. Barbara Brown, for the overall conduct of the program and for the quality and timely submission of all deliverables.

Mr. Richard McKinney will be the SAIC Work Assignment Manager (WAM). Working in conjunction with Dr. Richard Pruell, the EPA WAM, he will oversee and coordinate the activities of the chemistry laboratory personnel, and all subcontractors, as required. Mr. McKinney will serve as the single point of contact for technical direction from the EPA WAM relating to this work assignment. He will be responsible for data synthesis, interpretation and QA/QC, and for preparation and submission of reports to EPA. He will also be responsible for submitting the final QAPjP (this document) to the ERLN QAO for inclusion in the laboratory's computerized QA documentation system.

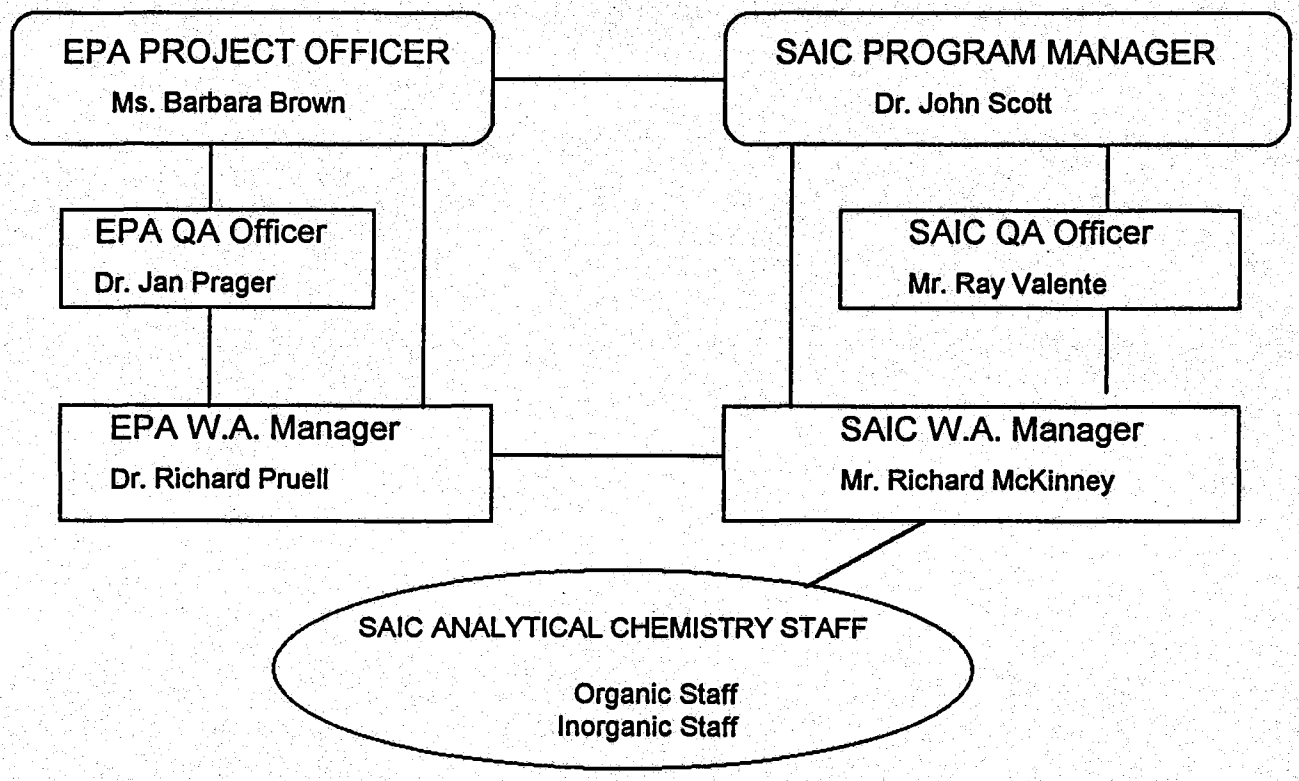
Mr. Raymond Valente will be the SAIC Quality Assurance Officer (QAO). He will work with the EPA QAO, Dr. Jan Prager, as required, to ensure that the data generated under this work assignment are in compliance with the ERLN quality assurance plans and programs.

Dr. Richard Pruell, the EPA WAM, will be responsible for the technical direction of the work. He will have the overall responsibility for approval of all analytical methods employed, experiment planning and

implementation, data quality and interpretation, and for the quality of all EPA technical reports and papers.

Dr. Jan Prager is the EPA Quality Assurance Officer responsible for the auditing of the laboratory for compliance with data and analytical protocols as specified in this QAPjP. He is also responsible for the maintenance of all QA materials in the laboratory's computerized QA system.

FIGURE 1. WORK ASSIGNMENT ORGANIZATION



5.0 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) REQUIREMENTS

The characteristics that define the quality of data are accuracy, precision, completeness, comparability and representativeness and method detection limit. These characteristics are defined below. Key elements for quality control of chemical analysis are given in Table 5.1.

5.1 ACCURACY

Accuracy is the closeness of agreement between an observed and accepted value. Accuracy is verified by the analysis of reference materials, intercalibration samples, internal standards, procedural blanks, initial calibration, calibration checks and matrix spikes.

5.1.1 Reference Materials

Reference Materials (as Standard Reference Materials (SRMs) or Certified Reference Materials (CRMs)) are analyzed to determine the efficiency and accuracy of the method. These Reference Materials have certified for concentrations of the analytes of interest by a recognized authority. Analysis of an SRM or CRM will accompany each batch (20 samples) of sediment samples for organic or metals analysis, and each batch of tissue samples for metals analysis. Percent recovery for analytes of interest is calculated by the following:

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

%R = percent recovery
C_1 = measured value
C_2 = certified value

The Laboratory Control Material (LCM) to be used in this study is similar to the CRM in that it is a homogeneous matrix which closely matches the sample being analyzed. Unlike CRMs, though, there are no certified concentrations of the analytes of interest. As part of the NIST/NOAA National Status and Trends FY91 QA Excercise 1, a Tissue Control Material III (QC90TC) was distributed to participating laboratories and a consensus value was generated for selected organic analytes based on a statistically valid number of replicate analyses by those laboratories. ERL-N has demonstrated an acceptable level of batch-to-batch consistency using this LCM, and percent recoveries previously generated by this laboratory will be used in this study as acceptable values. Control charts will be used to verify that each LCM analysis is within acceptable limits. Analysis of an LCM will accompany each batch of tissue samples for organic analysis.

5.1.2 Intercalibration Exercises

ERL-N participates in intercalibration exercises sponsored in jointly by the NOAA National Status and Trends Program and the EPA's Environmental Monitoring and Assessment Program for the measurement of polychlorinated biphenyls (PCBs), chlorinated pesticides, Polycyclic Aromatic Hydrocarbons (PAHs), and selected metals. These are meant to assess the laboratory's performance on a continuous basis. Each exercise involves the blind analysis of different representative matrices; three or four different NS&T exercises are conducted over the course of a year.

5.1.3 Internal Standards

Internal standards (referred to as surrogate standards by some laboratories) are reference compounds selected to be representative of the various classes of analytes. They are added immediately prior to extraction to each sample and analyte concentrations will be corrected for the recovery of internal standards prior to reporting. Their recovery will also be used as a measure of method performance, and will be monitored by means of control charts.

5.1.4 Procedural Blanks

Procedural blanks are treated identically to samples and carried through the entire extraction procedure. They are used to assess any contamination associated with the extraction and subsequent analysis of samples. A procedural blank will be analyzed with each batch of samples.

5.1.5 Initial Calibration and Calibration Checks

Instruments must be calibrated prior to analysis, after each major equipment disruption, or whenever ongoing calibration checks do not meet recommended control limit criteria. All calibration standards used should be traceable to recognized organizations for the preparation of QA/QC materials. Multiple level analyses are performed using several standards containing different concentrations of the analytes of interest to establish the calibration curve. For organic analyses, a five-point response factor calibration curve is established that brackets the liner range of analysis. A mid-level standard is then analyzed as a calibration check at the beginning of each analysis and after every six samples. For inorganic analyses using the Inductively Coupled Plasma Spectrophotometer (ICP), initial calibration curves are established using ten (for sediment analysis) or eight (for tissue analysis) standards that braket the linear range of analysis. A curve normalization is run before each set of analyses using an automated procedure that requires adherence to documented QA criteria. A check standard at 1 part per million is then analyzed during the course of the run. For inorganic analyses using the Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS), an initial five-point response factor calibration curve is established that brackets the liner range of analysis. A mid-level standard is then analyzed as a calibration check.

5.1.6 Matrix Spikes

Matrix spikes are performed to estimate the overall method recovery and the accuracy of chemical analysis. They may also provide information on any interferences which might affect the analysis. Matrix spikes are performed by adding a known concentration of the analytes of interest (the sample should be spiked no more than four times and no less than two times the sample value) to a previously analyzed sample. The recovery of spike is then calculated and the percent recovery is calculated as follows.

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

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

A matrix spike will be run with each batch of samples, using one of the samples from the batch as a

matrix if appropriate.

5.2 PRECISION

Precision is defined as the degree to which individual measurements converge upon a single value. Precision is determined by the analysis of laboratory duplicates, which are prepared by homogenizing and sub sampling a sample in the laboratory and carrying the sub-samples through the entire the analytical process. Precision will be expressed as the relative percent difference (RPD) for all laboratory duplicates according to the following equation.

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

RPD = Relative Percent Difference
C_1 = larger of the two observed values
C_2 = smaller of the two observed values

A laboratory duplicate will be analyzed for each batch of samples.

5.3 COMPLETENESS

Completeness is 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. An aspect of completeness that can be expressed for all data types is the percentage of valid data obtained from the measurement process. It also may be expressed as the percentage of samples for which valid data are obtained. Reasonable target completeness values are 90% for sample analysis. The inability to complete a sample analysis is documented in the laboratory notebook with an appropriate explanation.

To ensure that all required samples are analyzed, each sample is assigned a unique identity that is tracked electronically through all stages of an experiment: from assignment of ID to calculation of final concentration(s). The analyst conducting the experiment is responsible for ensuring that 100% of the samples have been completed, or, in the event of sample loss, that records are maintained in laboratory notebooks that document a sample loss. The SAIC WAM is responsible for verifying the records of completeness.

5.4 REPRESENTATIVENESS

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 addressed by the proper handling and storage of samples prior to analysis and analysis in a timely manner so that the material analyzed reflects the original material collected as accurately as possible.

5.5 COMPARABILITY

Data comparability depends on the consistency in analytical methodology and the use of standard reporting units for data and reflects the degree to which one data set can be compared to another. Previously demonstrated analytical techniques and the results of laboratory intercomparison exercises will be used to ensure comparability.

5.6 DETECTION LIMIT

Detection Limit is the minimum concentration of a substance that can be measured and reported. the 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. The Instrument Limit of Detection (ILOD) is the lowest concentration level that can be determined statistically from a blank, while the Instrumental Limit of Quantitation (ILOQ) is the level above which quantitative results may be obtained. A triplicate analyses of serial dilutions of standard mixtures is performed, and the standard deviation of the difference between the lowest concentration of each analyte instrumentally detectable and a blank value is used to establish the ILOD (three times the standard deviation) and ILOQ (ten times the standard deviation).

The Method Detection Limits (MDLs) are calculated by spiking a representative sample matrix with target analytes at three to five times the estimated detection limit. A minimum of seven replicates are analyzed and the standard deviation in analyte concentrations are calculated. Method detection limits determined as follows:

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

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

The Method Limit of Quantification (MLOQ) is the concentration above which quantitative results may be obtained with an assumed degree of confidence. The MLOQ is defined as ten times the MDL. Target MDLs for the analytes of interest are given in Table 5.2. Typical MLOQs for PCBs and pesticides will be in the range of 0.01 to 0.1 ng/g for a sample weight of 10 g, 0.01-0.1µg/g for PAHs and for inorganic analyses with similar sample weights.

5.7 CORRECTIVE ACTION FOR SAMPLES

The SAIC WAM will be notified of any samples that fall outside the established criteria listed in Table 5.1 and will initiate corrective action which may include review of data calculations, flagging of suspect data, or reanalysis or reprep of individual or an entire batch of samples.

5.7.1 Chemistry Analysis

An assortment of QC check lists (shown in Appendix A) shall be prepared by the analyst for each batch of analyses. This check list is an identification tool for any QC problems and can be used to determine if any immediate corrective action is required.

5.8 SAMPLE RECEIPT AND STORAGE

Samples received will be handled in such a way to preclude contamination or loss of any of the samples. Sample chain of custody will be maintained by use of the US EPA Chain of Custody Record shown in Appendix B and as instructed by the Project Officer. After receipt of samples at ERLN, all sediment and tissue samples will be held frozen at -20° C until extraction is initiated. Seep samples will be held refrigerated at 4° C until extracted. No holding times apply to any samples to be analyzed for this project.

5.8.1 Sample Archiving

If sufficient sample remains after completing all analyses and sub-sampling, the remaining sample aliquot will be stored frozen at -20° C for a minimum of 6 months after the collection date.

Table 5.1 KEY ELEMENTS FOR QUALITY CONTROL OF CHEMICAL ANALYSES

QC MEASUREMENT	WARNING LIMIT Criteria	CONTROL LIMIT Criteria	FREQUENCY	CORRECTIVE ACTION(for samples outside the control limit)
1. Initial demonstration of calibration standards. (prior to Analysis of samples)				
A.) Initial Calibration	NA	Organics: < 20% for any one analyte, no more than 2 analytes can be > 20% Inorganics: <15% for any one analyte	To establish calibration curve prior to sample analysis	NA
B.) Method Detection Limits	NA	NA	At least once each sample matrix	NA
2. On-going Demonstration Capability				
A.) Intercalibration Exercises[1]	NA	NA	two or three per year	NA
B.) Continuing Calibration Checks using Calibration Standard Solutions	NA	Organics: < 25% for any one analyte, no more than 2 analytes can be > 25% Inorganics: <25% for Mercury, <15% for all others, no more than 2 analytes can exceed	Calibration standards at the beginning, end, and every ten samples	Reestablish initial calibration curve, batch must be re-analyzed
C.) Analysis of Standard Reference Material (SRM) OR Laboratory Control Material (LCM)[2]	NA	Organics: +/- 40% percent diff., no more than 35% of the recoveries can exceed the limit with an overall average recovery of 35%. Inorganics: +/- 25% percent diff. for Mercury, 20% for all others with no more than 15% of the recoveries exceeding the limit	1 per batch (20 samples)	Note in case narrative and flag analytes involved in final data report. Sample batch may be considered for re-analysis
D.) Laboratory Duplicates[3]	NA	Organics: <30% RPD; Inorganics <50% RPD for Iron and Aluminum, <30% for all others; no more than 35% of the recoveries can exceed the limit	1 per each sample batch	All samples associated with duplicates will be noted in the case narrative; batch may be considered for re-analysis based on other QC criteria

E.) Procedural Blank Analysis	NA	<3 times the MDL	1 per each sample batch	Note affected samples and analytes in the case narrative. Flag corresponding data as contaminated.
F.) Matrix Spike[4]	Recovery should be within the range 50% to 120% for at least 70% of the analytes	NA	1 per each sample batch	Individual analytes flagged and explained in the case narrative. If more than 30% of the analytes fall outside of the control limit, the batch may be considered for re-analysis based on other QC criteria
Internal Standards (Surrogate Internal Standards)	Recovery should be within the range of 30% to 120%	NA	Each Sample	Batch may be considered for re-analysis based on other QC criteria
Internal Injection Standards	Lab develops its own	NA	Each Sample	NA

NOTES:

1. The purpose of the Intercalibration exercise is to assess data comparability. Gross differences between the laboratories will be subject to review by the Project Officer to determine if corrective action is necessary.
2. Reported results from the analysis of SRMs or LCMs which are below the MLOQ are not to be used for computing control limits; however those results will be reported in order to identify possible matrix problems and evaluate method performance.
3. Analyte concentrations in the sample duplicate must be above the MLOQ before the RPD can be calculated. It is understood that there will be a higher amount of variability in RPDs calculated for analytes at or near the MLOQ.
4. No control limit is expressed for Matrix Spikes. If analytes fall outside the warning limits they should be flagged accordingly and explained in the case narrative. The samples should be spiked at a level of not less than 2 times or more than 4 times the sample value.

Table 5.2 TARGET METHOD DETECTION LIMITS

Analyte	Matrix	Target MDL	Typical Marine Minimum Concentration
PAHs	seep water	5.0 ug/L	
PAHs	sediment	5.0 ng/g	
PAHs	tissue	20.0 ng/g	
PCBs	seep water	1.0 ug/L	
PCBs	sediment	0.5 ng/g	
PCBs	tissue	0.5 ng/g	
Pesticides	seep water	0.6 ug/L	
Pesticides	sediment	0.6 ng/g	
Pesticides	tissue	0.6 ng/g	
Aluminum	seep water	75.0 ug/L	2.0 ug/L
Aluminum	sediment	Not Specified	32000.0 ug/g
Aluminum	tissue	Not Specified	26.0 ug/g
Arsenic	seep water	3.1 ug/L	3.7ug/L
Arsenic	sediment	1.1 ug/g	3.5 ug/g
Arsenic	tissue	4.3 ug/g	14.0 ug/g
Cadmium	seep water	0.2 ug/L	0.1 ug/L
Cadmium	sediment	0.35 ug/L	0.15 ug/g
Cadmium	tissue	0.055 ug/L	0.035 ug/g
Chromium	seep water	3.0 ug/L	2.0 ug/L
Chromium	sediment	3.16 ug/g	41.0 ug/g
Chromium	tissue	0.28 ug/g	1.4 ug/g

Table 5.2 TARGET METHOD DETECTION LIMITS(cont'd)

Analyte	Matrix	Target MDL	Typical Marine Minimum Concentration
Copper	seep water	0.7 ug/L	0.1 ug/L
Copper	sediment	1.25 ug/g	6.7 ug/g
Copper	tissue	5.0 ug/g	2.8 ug/g
Iron	seep water	20.0 ug/L	2.0 ug/L
Iron	sediment	Not Specified	18000.0 ug/g
Iron	tissue	Not Specified	15.2ug/g
Lead	seep water	3.0 ug/L	0.0005 ug/L
Lead	sediment	1.2 ug/g	2.7 ug/g
Lead	tissue	0.6 ug/g	0.37 ug/g
Manganese	seep water	0.5 ug/L	0.2 ug/L
Manganese	sediment	Not Specified	266.0 ug/g
Manganese	tissue	Not Specified	0.73 ug/g
Mercury	seep water	5.0 ug/L	0.03 ug/L
Mercury	sediment	0.007 ug/g	
Mercury	tissue	0.036 ug/g	0.064 ug/g
Nickel	seep water	3.0 ug/L	1.7 ug/L
Nickel	sediment	1.08 ug/g	16.0 ug/g
Nickel	tissue	0.73 ug/g	0.72 ug/g
Silver	seep water	75.0 ug/L	0.2 ug/L
Silver	sediment	0.04 ug/g	0.02 ug/g
Silver	tissue	0.037 ug/g	
Tin	seep water	3.0 ug/L	2.0 ug/L
Tin	sediment	1.75 ug/g	0.95 ug/g
Zinc	seep water	0.1 ug/L	0.5 ug/L
Zinc	sediment	2.15 ug/g	62.0 ug/g
Zinc	tissue	11.65 ug/g	21.0 ug/g

NOTES:

1. The target MDLs for organic compounds should be within a factor of two of the target MDL. Final acceptance of MDLs is subject to review by the Project Officer. Specific analytes will be reviewed on a case by case basis.
2. The target MDLs for inorganic compounds should be within a factor of two of the target MDL, or within a factor of two of the "typical" marine minimum concentrations. Final acceptance of MDLs is subject to review by the Project Officer. Specific analytes will be reviewed on a case by case basis.
3. The target MDLs for seep samples were derived from the detection limits reported for the NCBC Davisville risk assessment pilot study (Munns et al. 1991)
4. The target MDLs for inorganic analytes in sediment and tissue samples were obtained by calculating the midpoint of the range of actual MDLs, for each element,

as reported by laboratories participating in the Status and Trends Program (NOAA 1991).

5. Typical marine minimum concentrations were those reported for "typical" samples by laboratories participating in the Status and Trends Program (NOAA 1991) for tissue and sediment, and those found in oceanic sea water (Brown et al. 1989) for seep samples.

6.0 ANALYTICAL PROCEDURES

Sediment, tissue samples and seep samples will be chemically analyzed for routine organic and inorganic analytes using the appropriate ERLN Standard Operating Procedures. For all analyses, sufficient sample size is necessary to obtain the target MDLs listed in Table 5.2. In cases where there appears not to be enough material for analysis, the Project Officer will be consulted and will determine if it is possible to composite samples to obtain enough sample for a valid analysis.

6.1 SAMPLE ANALYSIS SCHEME

A typical batch of samples contain 20 samples. A hypothetical batch should have the following sample analysis scheme:

SAMPLE DESCRIPTION	Sub-batch 1	Sub-batch 2	Sub-batch 3	Sub-batch 4
Extracted Samples	Extracted Samples	Extracted Samples	Extracted Samples	Extracted Samples
S_1, S_2, ... S_5 (Extracted Samples)	5	5	5	5
SRM/LCM	1	0	0	0
Matrix spike	0	1	0	0
Laboratory Blank	0	0	1	0
Duplicate	0	0	0	1

6.1.1 Sequence of analysis for organic analyses

SOLVENT	1	HEXANE
CC_1	1	Calibration check
ES_1, ...ES_6 (F-1)	5	Extracted Samples
CC_2	1	Calibration check
ES_1, ...ES_6 (F-2)	5	Extracted Samples
CC_3	1	Calibration check
Recovery standard	1	to measure surrogate recoveries

A typical sequence has approximately twenty samples. The fractions generated from chemical class separations (PCB and pesticide fractions) are analyzed concurrently. The laboratory blank comes after the calibration standard. The SRM/CRM is placed with the extracted samples. The laboratory duplicates are run sequentially along with the extracted samples in the sequence. For inorganic analyses, the sequence of analysis will depend on the number of samples analyzed and instrument calibration

requirements.

6.2 PROCEDURES FOR CHEMICAL ANALYSIS

Sediment, tissue samples and seep samples will be chemically analyzed for routine organic and inorganic analytes using the appropriate ERLN Standard Operating Procedures. Table 6.1 lists the applicable methods as ERLN Chemistry Group Standard Operating Procedures.

Table 6.1 Standard Operating Procedures for Chemical Analyses

ANALYSIS TYPE	ERLN SOP	MATRIX
PCBs, Pesticides, PAHs	Tissue Extraction of Semivolatile Organic Analytes	Tissue
PCBs, Pesticides, PAHs	Sediment Extraction of Semivolatile Organic Analytes	Sediment
PCBs, Pesticides, PAHs	Column Chromatography of Semivolatile Organic Analytes in Sediment and Tissue Extracts	Tissue/Sediment
PCBs, Pesticides	Gas Chromatographic Analysis of PCBs and Chlorinated Pesticides	Tissue/Sediment
PAHs	Analysis of PAHs by Gas Chromatography/ Mass Spectrometry	Tissue/Sediment
Metals	Digestion of Marine Organism Samples for Metals Analysis	Tissue
Metals	Total Digestion of Sediment Samples	Sediment
Metals	Instrumental Analysis of Metals in Sediment and Tissue Extracts	Tissue/Sediment

6.2.1 Organics in Tissue and Sediment

Details of the extraction of tissue and sediment samples can be found in the appropriate SOPs listed in Table 6.1. In general, samples will be spiked with internal standards and solvent extracted. Following solvent reduction, the extracts undergo clean-up and class fractionation by silica column chromatography. PCB and pesticide analysis is carried out by gas chromatography with electron capture detection (GC/ECD), and PAHs will be analyzed by gas chromatography/mass spectrometry (GC/MS) using selected ion monitoring. A list of organic analytes measured for this project is given in Table 6.2.

Table 6.2 ORGANIC ANALYTES MEASURED IN MARINE SAMPLES BY ERLN

PCBs	PESTICIDES	PAHs
CB008	HCB	FLUORENE
CB018	LINDANE	PHENANTHRENE
CB028	MIREX	ANTHRACENE
CB052	ACHLORDANE	Sum MW178-C1
CB044	TNONACHLOR	Sum MW178-C2
CB066	PPDDE	Sum MW178-C3
CB101	PPDDD	Sum MW178-C4
CB118	PPDDT	FLUORANTHENE
CB153		PYRENE
CB105		BENZ[a]ANTHRACENE
CB138		CHRYSENE
CB187		Sum MW228
CB128		Sum BENZOFLUORANTHENES
CB180		BENZO[e]PYRENE
CB170		BENZO[a]PYRENE
CB195		PERYLENE
CB206		INDENO[123-cd]PYRENE
CB209		DIBENZ[ah]ANTHRACENE
		BENZO[ghi]PERYLENE
		Sum MW276
		Sum MW278
		Sum MW302
		CORONENE

6.2.2 Chemical Markers in Sediments, Seep Samples and Water Samples

Procedures developed during Phase 1 of the project for the qualitative screening of samples for site specific chemical markers will be further developed and applied to selected seep, sediment core, and water samples collected as part of this current project. These procedures will be documented as they become finalized.

6.2.3 Trace metals in Tissues and Sediments

As with organic analyses, details of the extraction of tissue and sediment samples can be found in the appropriate SOPs listed in Table 6.1. Sample aliquots are freeze-dried, weighed, and digested in acid. Both sediment and organism samples are microwave digested. Following digestion, samples are analyzed by either Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS) or by Inductively Coupled Plasma Spectrometer (ICP) depending on the detection limit which is required. The analytical instruments are operated and maintained according to the manufacturer's recommendations or ERLN SOPs.

7.0 DOCUMENTATION AND DATA VALIDATION

ERLN Laboratory notebooks will be used to record information such as sample numbers, chemistry designated identification numbers (ChemIDs), date of sample prep, sample weights, (surrogate) internal standard amounts, method modifications, problems encountered and observations. These notebooks will be maintained by laboratory personnel, and all entries will be made in pen. Raw data such as chromatograms from the GCs will be retained as both hard copy and stored on magnetic tape. Similarly, reduced data generated through computer programs will be retained in both hard copy and electronic form. Logs of data transfers between computer systems, such as the Chemistry Group's computers and the ERLN VAX, will be maintained by the SAIC Work Assignment Manager or his designee.

All data associated with each project will be included in the final reports. These reports include the results of all analyses, including SRMs and performance evaluation samples, the detection limits calculated for each analyte, and information on precision, recoveries, and blanks. Also included in the final reports will be detailed methodologies for all analytical or instrumental procedures. The final reports will also contain discussions on the five data quality indicators (accuracy, precision, completeness, comparability, and representativeness).

7.1 DATA VALIDATION

All data generated under this work assignment will be subject to a multi-step validation process. Each analyst is required to check 100 percent of their data for transcription, calculation, misidentification or computer input errors. A second analyst will then conduct random checks of the data for the same types of errors. The following four QA/QC check lists will be included with each data batch of organic chemistry results:

1) "EPA-ERLN Organic Chemistry Group Final Data Package Check List"
2) "EPA-ERLN Organic Chemistry Group Quality Control Check List for Routine PCB and Pesticide Analysis",
3) "EPA-ERLN Organic Chemistry Group Quality Control Check List for Routine PAH Analysis"
4) "EPA-ERLN Organic Chemistry Group Quality Control Checklist"

List 1.) documents primary and secondary review of all material in the batch data package and catalogs all relevant QA/QC material. Lists 2.) and 3.) indicate that calibration results and sample analysis fall within acceptable limits or that exceptions are noted in the case narrative. List 4.) lists samples included in the data batch, and documents that relevant QA/QC requirements have been met or exceptions noted. The following four QA/QC check lists will be included with each data batch of inorganic chemistry results:

5) "EPA-ERLN Inorganic Chemistry Group Final Data Package Check List For AVS"
6) "EPA-ERLN Inorganic Chemistry Group Final Data Package Check List for Sediments, Tissues, and SEMs"
7) "EPA-ERLN Quality Control Checklist For Inorganic Analysis"

List 5.) documents primary and secondary review of all material in the batch data package and catalogs all relevant QA/QC material for AVS analyses. List 6.) documents primary and secondary review of all material in the batch data package and catalogs all relevant QA/QC material for routine metals analyses and indicates that calibration results and sample analysis fall within acceptable limits or that exceptions are noted in the case narrative. List 7.) lists samples included in the data batch, and documents that

relevant QA/QC requirements have been met or exceptions noted. Examples of each of these list 1.) through 7.) is included in Appendix A.

Only after these checks have been performed will the data packages be presented to the SAIC WAM for review. The SAIC WAM is responsible for checking the final data packages for calculation and identification errors, for checking computer printouts of data transfers for errors, and for the maintenance of the data transfer logs. The SAIC WAM will also review all other quality assurance data, including those which address accuracy, precision, and calibration of instrumentation, to ensure that all requirements have been met. These requirements will be summarized in the appropriate "Quality Control Checklist" that will accompany each batch of data. Data which do not meet all requirements will be reanalyzed, if possible; rejected; or reported with an explanation of the associated problem in the case narrative.

Once all data has been certified final, results in the form of concentrations will be transferred electronically via established ERLN data transfer routines to a database on the ERLN VAX-4500 computer. Records of these data transfers will be maintained by the SAIC WAM or his designee.

8.0 REFERENCES

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

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

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

APPENDIX A

ERLN CHEMISTRY GROUP QUALITY CONTROL CHECKLISTS

EPA - ERLN Organic Chemistry Group
Final Data Package Check List

____ Copy of initial PCB/pesticide calibration data including plots, reports, regression (CFPLOT) for one compound and data sheet

____ Copy of initial PAH calibration data including reports, response factor table, regression (cal. curve) for one compound and data sheet

____ 3 page plot of one of the PCB/pesticide calibration standards to illustrate column performance, resolution and peak identification

____ Copies of any check standard results including reports, plots and data sheet, for standards run in the beginning, middle and at the end of GC or GC/MS runs

____ Any SRM data, triplicates, matrix spikes, etc. generated for this sample set, including plots and reports for each

____ Sample prep information obtained from OPREP

____ Copy of method used to analyze samples in data set and/or method SOP referenced on log page

____ Copy of log book page with Chem Ids and standard information (amounts added)

____ Reports and plots for all samples in the sample set listed on the included log pages

Additional relevant information (reruns, QC problems, ect.) added to back of package

Analyst: _____ Date: _____ Reviewer: _____ Date: _____

EPA - ERLN Organic Chemistry Group
Quality Control Check List for Routine PCB and Pesticide Analysis

Standards

____ All initial and continuing calibration curves meet appropriate criteria

____ Resolution of CB153 to CB105 should be better than 50% (valley between pks should be greater than 50% peak ht)

____ p,p'-DDD/p,p'-DDT peak height ratio is approximately 1

____ p,p'-DDT peak height at least 50% of CB138 peak height

____ p,p'-DDD/ o,p'-DDT peak height ratio at least 50%

____ Doublet before p,p'-DDE (CB087/Dieldrin) resolved approximately 20%

____ Lindane peak height greater than CB018 peak height

____ Peak height ratio of CB028 to first peak in doublet (CB031) should be approximately 1:1

____ Peak heights for standards are same as in previous GC runs (should not drop more than 25% from initial calibration)

____ Check for any negative peaks and remove (use IP event)

Samples

____ Internal standard amount listed on data sheet is confirmed by lab bookactual amount added

____ Sample wt/vol is correct amount from lab book

____ Retention times match up to those in standards

Items having to do with instrument resolution and response do not neccessarily disqualify a calibration if not met but may indicate a need for instrument maintenance. If instrument response drops by more than 25%, maintenance and recalibration are required before continuing.

Analyst: _____ Date: _____ Reviewer: _____ Date: _____

EPA - ERLN Organic Chemistry Group
Quality Control Check List for Routine PAH Analysis

Standards

____ All initial and continuing calibration curves meet appropriate criteria

____ All integrations checked manually to insure proper peak assignment and baseline.

____ All peaks found satisfy peak match criteria based on parent ion / qualifier ion ratio.

____ Scan time windows for Sums (MW 178-C-1 through MW 178-C-4, MW 228, Benzofluoranthenes, MW 276,278,and 302) are appropriate.

____ Peak areas for standards are same as in previous GC/MSD runs (should not drop more than 25% from initial calibration)

____ Check for any negative peaks and remove .

Samples

____ Internal standard amount listed on data sheet is confirmed by lab book actual amount added

____ Sample wt/vol is correct amount from lab book

____ Retention times match up to those in standards

____ All integrations checked manually to insure proper peak assignment and baseline.

____ All peaks found satisfy peak match criteria based on parent ion / qualifier ion ratio.

Items having to do with instrument resolution and response do not neccessarily disqualify a calibration if not met but may indicate a need for instrument maintenance. If instrument response drops by more than 25%, maintenance and recalibration are required before continuing.

Analyst: _____ Date: _____ Reviewer: _____ Date: _____

ENVIRONMENTAL RESEARCH LABORATORY

QUALITY CONTROL CHECK LIST FOR ORGANIC ANALYSIS

PROJECT NAME.....

Analyst..... Date of sample prep.....

KIND CODE						
SAMP #						
CHEM ID						

Analyst..... Date of sample prep.....

KIND CODE						
SAMP #						
CHEM ID						

Analyst..... Date of sample prep.....

KIND CODE						
SAMP #						
CHEM ID						

Analyst..... Date of sample prep.....

KIND CODE						
SAMP #						
CHEM ID						

SAMPLE TYPE	CONTROL LIMIT	PCB	PEST	PAH	COMMENTS
CALIBRATION	± 15% on avg; not to exceed 25%				
LAB BLANKS	<3 MDL				
REPLICATE PRECISION	±30% RPD ; <35% allowed out				
SRM/TCM	±40% , 35% allowed out, ±35% on aveage				
MATRIX SPIKE	± 50%				
IS* RECOVERY (SURROGATE/ INTERNAL STANDARD RECOVERY)	30 - 130% , <50% difference between SRM & and sample recoveries				

INITIAL QA CHECK..... DATE.....

EPA - ERLN Inorganic Chemistry Group
Final Data Package Check List for Sediments, Tissues and SEMs

____ Copy of initial calibration data

____ Copy of any check standard results for standards run during ICP or GFAA runs

____ Any SRM data, replicates, matrix spikes, etc. generated for this sample set

____ Sample prep information obtained from OPREP

____ Copy of method used to analyze samples in data set and/or method SOP referenced on log page

____ Copy of log book page with Chem Ids

____ Reports for all samples in the sample set listed on the included log pages

Additional relevant information (reruns, QC problems, ect.) added to back of package

Analyst: _____ Date: _____ Reviewer: _____ Date: _____

EPA - ERLN Inorganic Chemistry Group
Final Data Package Check List for AVS

____ Copy of initial calibration data

____ Sample prep information obtained from NARVAX

____ Copy of method used to analyze samples in data set and/or method SOP referenced on log page

____ Copy of log book page with Chem Ids

____ Reports for all samples in the sample set listed on the included log pages

Additional relevant information (reruns, QC problems, ect.) added to back of package

Analyst: _____ Date: _____ Reviewer: _____ Date: _____

chcklist.wri

Environmental Research Laboratory

Quality Control Checklist for Inorganic Analysis

Project Name_____

Analyst_____ Date of Sample Prep_____

Kind Code						
Samp #						
Chem ID						

Analyst_____ Date of Sample Prep_____

Kind Code						
Samp #						
Chem ID						

Analyst_____ Date of Sample Prep_____

Kind Code						
Samp #						
Chem ID						

Analyst_____ Date of Sample Prep_____

Kind Code						
Samp #						
Chem ID						

Sample Type	Control Limit	PNSY Metals	Comments
Calibration (Initial and Continuing)	±15% 2 allowed out		
Lab Blanks	<3 MDL		
Replicate Precision	Al, Fe;<50%RPD all others; <35%RPD <35% allowed out		
SRM/TCM	±20%, 15% allowed out		
Matrix Spike	±50%		

APPENDIX B

SAMPLE USEPA CHAIN OF CUSTODY RECORD

Office of Enforcement

CHAIN OF CUSTODY RECORD

JJ. NO.

PROJECT NAME: PNSY Phase II

LERS: (Signature) K. Johnston

NO.	DATE 1993	TIME	COMP.	GRAB	STATION LOCATION	NO. OF CONTAINERS							REMARKS
	6/17/93	1005			Police Dock UNH station 3	1	1	1	2	7	5	1	15 cm AVS Core Sample no scup # Core # 1
	6/17/93	1005			Police Dock UNH station 3	1	1	1	2	7	5	2	AVS Core " no scup # 2
	6/17	1005			Police Dock UNH station 3	1	1	1	2	7	5	3	no scup # 3
7	6/17	1334			Clark Cove UNH 3	1	1	1	2	7	5	4	no scup # 4
9	6/17	1110			Jamaica Island UNH 19	1	1	1	2	7	5	5	5
9	6/17	1110			Jamaica Island UNH 19	1	1	1	2	7	5	6	6
9	6/17	1110			" 19	1	1	1	2	7	5	7	no scup # 7
9	6/17	1110			" 19	1	1	1	2	7	5	8	no scup # 8
3	6/17	1404			Clark Cove UNH 3	1	1	1	2	7	5	9	* no scup # Fine 9
2	6/17	1334			Clark Cove UNH 7	1	1	1	2	7	6	0	10
7	6/17	1334			" " UNH 7	1	1	1	2	7	6	1	no scup # 11
7	6/17	1334			" " UNH 7	1	1	1	2	7	6	2	no scup # 12
3	6/17	1404			Clark Cove UNH 3	1	1	1	2	7	6	3	" " 13
3	6/17	1404			" 3	1	1	1	2	7	6	5	no scup # 15
3	6/17	1404			" 3	1	1	1	2	7	6	6	no scup # 16

Relinquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
nquished by: (Signature)	Date / Time	Received by: (Signature)	Relinquished by: (Signature)	Date / Time	Received by: (Signature)
nquished by: (S)	Date / Time	Received for Laboratory by: (Signature)	Date / Time	Remarks	