PUGET SOUND AMBIENT MONITORING PROGRAM
MARINE SEDIMENT MONITORING COMPONENT

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# FINAL QUALITY ASSURANCE PROJECT & IMPLEMENTATION PLAN

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# MEASURES OF BIOEFFECTS ASSOCIATED WITH TOXICANTS IN PUGET SOUND: SURVEY OF SEDIMENT CONTAMINATION, TOXICITY, AND BENTHIC MACROINFAUNAL COMMUNITY STRUCTURE

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by
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# INTRODUCTION AND BACKGROUND INFORMATION

Since 1989, the Washington State Department of Ecology (Ecology) Marine Sediment Monitoring Unit has conducted the Marine Sediment Monitoring Task (now referred to as the Sediment Monitoring Component) of the Puget Sound Ambient Monitoring Program (PSAMP). Annual monitoring of Puget Sound sediments has occurred through 1996 and has included assessment of physical and chemical sediment parameters, sediment toxicity (measured with bioassays), and benthic macroinvertebrate assemblage structure in bays and deep basins, away from the influence of single point sources of pollution. The goals, objectives, and methodology of the Sediment Component have been, with modifications, described in the Puget Sound Ambient Monitoring Program, Monitoring Management Committee, Final Report (Puget Sound Water Quality Authority, 1988) and in the Puget Sound Ambient Monitoring Program: Marine Sediment Quality Implementation Plan (Striplin,1988). These data were to be used, in part, to establish baseline and long-term sediment quality conditions throughout Puget Sound, identify areas that are accumulating toxic chemicals, and determine the effects of contaminants on biological communities through use of the Sediment Quality Triad approach (Chapman and Long, 1983). Limitations of the past sampling design have prevented fulfillment of all objectives. The Marine Sediment Monitoring Unit is currently preparing a summary report, including analysis of data from 1989 through 1995.

In 1995, PSAMP underwent a comprehensive review. The findings called for revision of program and component goals, objectives, and methodology (Shen, 1995). In 1996, Ecology was approached by representative's of the National Oceanic and Atmospheric Administration (NOAA) National Status and Trends (NS&T) Program wishing to enter into a partnership with PSAMP to conduct joint sediment monitoring in Puget Sound. The NS&T Bioeffects Monitoring Program performs regional intensive studies of the magnitude and extent of toxicant-associated bioeffects in selected coastal embayments and estuaries. With objectives that overlap those of PSAMP, more than 20 large estuaries have been studied nationwide in this program to determine the presence, spatial extent, and severity of adverse bioeffects (Long et. al., in press).

A partnership between Ecology's Marine Sediment Monitoring Unit (i.e., the PSAMP Sediment Monitoring Component) and NOAA's NS&T program was developed, and will be implemented through an Ecology/NOAA Cooperative Agreement. This partnership will address the common goals of the two programs, including the determination and evaluation of the spatial extent of anthropogenic contamination and toxicity in Puget Sound sediments, and assessment of sediment toxicity and it's effect on benthic macroinvertebrate communities through use of the "sediment quality triad" approach (Chapman and Long, 1983). This partnership also includes cooperation with the Washington Department of Fish and Wildlife's Fisheries Unit (i.e., the PSAMP Fishery

Component; see WDFW, 1997) to facilitate better coordination and integration of PSAMP components (as recommended by the PSAMP review panel).

This partnership involves a three year monitoring effort to conduct focused studies throughout Puget Sound (north sound - year 1, central sound - year 2, south sound - year 3), with discrete areas of the Sound being assessed using a stratified random sampling approach. The chemical parameter list, bioassay design, and use of benthic macroinfauna data, as described in this document, are closely aligned with those of the ongoing NS&T program, and are updated from PSAMP's original Marine Sediment Quality Implementation Plan (Striplin, 1988). Standardized methods taken from the Puget Sound Estuary Program (PSEP) protocols (PSEP, 1996a) will be followed for the majority of this work. Any deviations from these protocols are noted below. General methods and procedures for all three years of this project will be recorded in this document. Project changes (e.g., station locations, stratum boundaries, etc.) made in years 2 and 3 will be included in supplements to this report, published prior to the commencement of field work during each year of the project.

# PROBLEM STATEMENT

Toxic contaminants introduced into aquatic ecosystems can bind to particles and collect in deposited sediments. They are found in a wide range of concentrations in surficial (recently deposited) sediments around Puget Sound. Although contaminant levels in some areas have decreased since pollution controls were established in the last few decades, contamination levels in the deep central Puget Sound basin are still significantly higher than estimated pre-industrial levels. Near urban areas, present levels of contamination are much higher -- up to 100 times the levels in the cleanest rural bays in Puget Sound. As a result, accumulation of toxicants in sediments and the resulting damage to natural populations are recognized as serious threats to the Puget Sound marine and estuarine ecosystems (Puget Sound Water Quality Authority, 1994).

Considerable information has been generated on the presence and concentrations of toxicants and their associated adverse effects in Puget Sound. Studies performed by NOAA through the MESA (Marine Ecosystems Analysis) Puget Sound Project determined the concentrations of toxic substances in sediment, resident demersal fishes, marine birds, and marine mammals; the presence of toxicants and toxicity in sea surface microlayers; historical trends in chemical contamination; and the physical processes that influence the fate and transport of toxicants in Puget Sound. Additional work by the Puget Sound National Estuary Program identified spatial patterns in sediment contamination, toxicity, and benthic effects in selected urban embayments and reference areas. Other programs and studies, including the Puget Sound Ambient Monitoring Program, the Puget Sound Dredged Disposal Analysis Program, and marine water and sediment assessments by the King County Department of Natural Resources (formerly METRO), further identified sediment contamination problems in portions of the Sound. Most information on toxic effects in Puget Sound has been collected for the incidence of

abnormalities and diseases in fish, the incidence of toxic sediment samples, the composition of benthic communities, and to a lesser extent, the presence of effects among resident marine birds and mammals.

Ecology, through its Sediment Management Standards (SMS) rule process (Chapter 173-204, WAC, adopted in April 1991), has mapped sites of sediment contamination in the most industrialized urban embayments. Data were derived from numerous regulatory based actions such as sediment quality monitoring for permitted discharges or Superfund cleanup studies rather than from probabilistic, stratified-random sampling designs. While not statistically based, contaminated site characterization is conducted by comparing sediment chemistry and toxicity data to criteria and subsequently ranking contaminated sites for regulatory action.

None of these programs or studies, however, have determined the spatial extent of contamination and biological effects for all of Puget Sound, nor have they made use of a probabilistic, stratified-random sampling design to do so. The spatial extent of sediment degradation will be determined using the probabilistic, stratified-random sampling design developed by NOAA for the NS&T program. Use of this method will enable comparisons to be made among different embayments within Puget Sound, and with different estuaries nationwide, which have been studied by NOAA and the USEPA.

# Regulatory Mandates

The federal and Washington State regulatory mandates that promote and support this work are summarized below:

## Federal

The National Oceanic and Atmospheric Administration (NOAA), U.S. Department of Commerce, has been given authority under Title II of the Marine Protection, Research, and Sanctuaries Act (MPRSA) to develop and implement a continuing program of research with respect to possible long-range effects of pollution, overfishing, and man-induced changes of ocean ecosystems. The authorized activities include monitoring programs to assess the health of the marine environment by measurement of contaminant levels in biota, sediment, and the water column; diseases in fish and shellfish; and changes in types and abundance of indicator species. Title V of the MPRSA authorizes a comprehensive national program for consistent monitoring of the nation's coastal environments and ecosystems, as well as intensive monitoring programs for coastal environmental quality and ecosystem health in designated coastal regions. The purpose of regional programs is to enhance the ability of federal, state, and local authorities to develop and implement effective resource use and pollution abatement programs in order to improve or restore the environmental quality and health of coastal ecosystems. NOAA's National Status and Trends (NS&T) Program, primarily funded under authority of the MPRSA, monitors spatial distribution and temporal trends of contaminant

concentrations in coastal and estuarine regions of the United States. The program also monitors and evaluates biological effects in relation to environmental pollution based on the spatial extent of sediment toxicity, *in situ* changes in benthic biological community structure, and incidence of disease, pathological conditions or physiological dysfunction in fish and shellfish.

The NS&T Program performs regional intensive studies of the magnitude and extent of toxicant-associated bioeffects in selected coastal embayments and estuaries. The areas chosen for these regional studies are those in which the contaminant concentrations indicate the greatest potential for biological effects and where there is a need for toxicant bioeffects information. More than 20 large estuaries have been studied nationwide in this program to determine the presence, spatial extent, and severity of adverse bioeffects. The joint work described in this document is funded, in part, through the NS&T program.

### Washington State

In 1996, Washington State enacted legislation (chapter 90.71 RCW) that specifically requires the Puget Sound Water Quality Action Team to ensure continued implementation and coordination of the Puget Sound Ambient Monitoring Program. Through PSAMP, which was previously implemented through the Puget Sound Water Quality Authority, the state has been monitoring ambient sediment quality, fish health, and fish and shellfish contaminant burdens since 1989.

In addition to PSAMP, Washington State also has an active sediment management program. Washington State's sediment quality standards (WAC 173-204-100) are promulgated under the authority of chapter 90.48 RCW, the Water Pollution Control Act; chapter 70.105D RCW, the Model Toxics Control Act; chapter 90.70 RCW, the Puget Sound Water Quality Authority Act; chapter 90.52 RCW, the Pollution Disclosure Act of 1971; and chapter 90.54 RCW, the Water Policy Act, to establish marine, low salinity, and freshwater surface sediment management standards for the state of Washington. Under these standards, Ecology is required to identify contaminated sediment sites in Puget Sound. In response to this mandate, Ecology maintains a database of quality assured sediment contaminant data to allow annual updates of a list of contaminated sites. In addition, the data are used to periodically revise the state's ecological sediment criteria, as well as to support development of future human health sediment criteria. The data are also used to evaluate ongoing and proposed wastewater and storm water discharges, proposed dredging and dredged material disposal activities, and proposed aquatic construction projects. Data generated by the joint PSAMP/NOAA project would be useful for all of these activities.

# SITE DESCRIPTION

The assessment of contamination and associated biological effects in Puget Sound in 1997 will be focused in the northern waters of the Sound (i.e., from Everett Harbor north

to Boundary Bay at the Canadian border). Thirty-three sampling strata were chosen for northern Puget Sound by personnel from Ecology, WDFW, and NOAA. Strata were delineated using a compilation of information available regarding sediment contamination (e.g., known contaminated sites, current and historic sources of anthropogenic contaminants), as well as available information on natural conditions (e.g., bathymetry, geology, currents, etc.) for these waters. The strata chosen are listed in Table 1 and outlined in Figure 1. One hundred stations will be distributed among the 33 strata (three within each stratum and one extra) using a computer program designed to randomly select latitude/longitude coordinates. Detailed area maps and a listing of station coordinates, including a list of alternate locations, will be developed prior to sampling. A final list of station locations will be published after the field sampling is complete.

# PROJECT DESCRIPTION

As indicated above, each year of this three year project will utilize a probabilistic, stratified-random sampling design to sample sediment in bays and inlets of Puget Sound. This sampling designed is patterned after EPA Environmental Monitoring and Assessment Program (EMAP) protocols (Schimmel et al., 1994). This approach combines the strengths of a stratified design with the random-probabilistic selection of sampling locations. Data collected within each stratum can be attributed to the dimensions of the stratum, and used to estimate the spatial extent of toxicity with a quantifiable degree of confidence (Long, E.R. et al., 1996). Sampling of 100 stations in north Puget Sound will occur in June of 1997, with sediment analyses to include three monitoring elements. Toxicity testing will be conducted using four independent tests of sediment toxicity including: 10-day solid phase tests of amphipod survival (*Ampelisca abdita*); pore water tests of sea urchin egg fertilization and embryological development (*Strongylocentrotus purpuratus*); microbial bioluminescence (Microtox) tests of an organic solvent sediment extract; and Cytochrome P-450 RGS tests of sediment extracts. Chemical analyses will quantify one hundred sixty nine (169) parameters and chemical compounds in the sediments (Table 2). Analysis of the benthic infaunal macroinvertebrates will determine the composition of assemblages present in the sediment samples collected. Details of these three monitoring elements are provided in the Analytical Methods section, below. The type of data and reports generated include the following from both Ecology's Marine Sediment Monitoring Unit and from NOAA:

Table 1. North Puget Sound sampling strata for the PSAMP/NOAA bioeffects survey

1. Drayton Harbor
2. Mouth of Drayton Harbor to west boundary of Semiahmoo Bay
3. Boundary Bay - west of Semiahmoo Bay
4. Boundary Bay - southern part
5. Birch Bay - from Birch Point to Whitehorn Point
6. Cherry Point - Whitehorn Point to Sandy Point
7. Bellingham Bay - northern tide flats
8. Bellingham Bay - west downtown Bellingham, including waterways and marinas
9. a. Bellingham Bay - east downtown Bellingham, including waterways and marinas
   b. Bellingham Bay - just south of stratum 9a
10. Bellingham Bay - just south of stratum 9b, along the South Bellingham shoreline
11. Bellingham Bay - shallow northern subtidal
12. Bellingham Bay - to south end of Lummi Island
13. Bellingham Bay - southern end to Samish Island
14. Padilla Bay - shallow eastern boundary
15. Padilla Bay
16. March Point
17. Fidalgo Bay - inner 48°30'north down to tressle
18. Fidalgo Bay - outer, to entrance of Anacortez
19. March Point - north of the point to east end of Guemes Channel
20. Guemes Channel - this stratum was eliminated during the course of sampling due to the rocky nature of the substratum
21. Skagit Bay
22. Saratoga Passage
23. Oak Harbor
24. Penn Cove
25. Saratoga Passage
26. Saratoga Passage
27. Port Susan
28. Possession Sound
29. Everett Harbor
30. Everett Harbor
31. Everett Harbor
32. Possession Sound
33. Steamboat and Ebey Slough

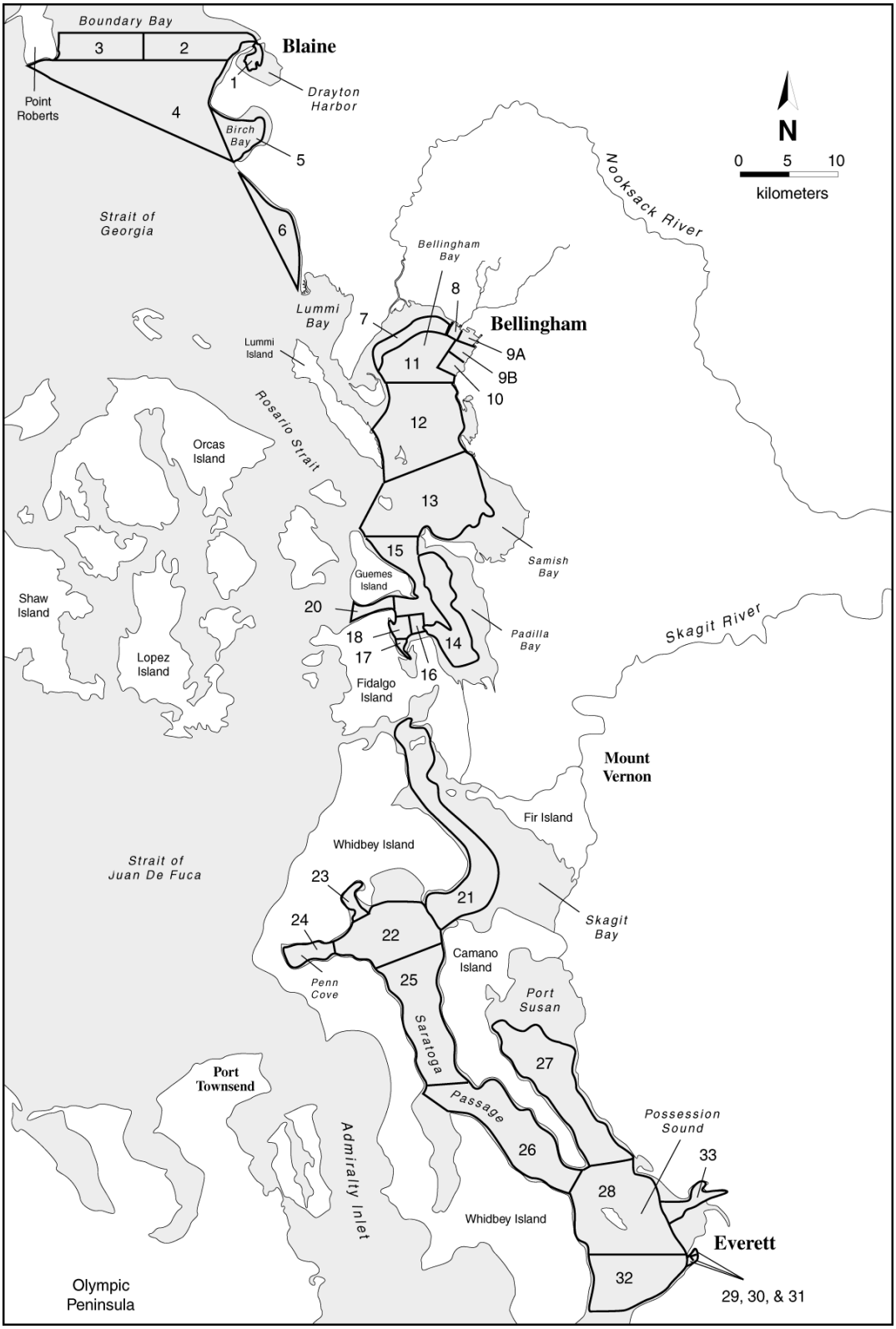


Figure 1. Northern Puget Sound sampling strata for the NOAA/Washington Cooperative Agreement Bioeffects Survey.

Table 2. Parameters and chemical compounds to be analyzed for in sediments collected from Puget Sound.

**Related Parameters**
Grain Size
Total organic carbon
Acid volatile sulfides/simultaneously extracted metals

**Ancillary Metals**
Aluminum
Barium
Calcium
Cobalt
Iron
Magnesium
Manganese
Potassium
Sodium
Vanadium

**Priority Pollutant Metals**
Antimony
Arsenic
Beryllium
Cadmium
Chromium
Copper
Lead
Mercury
Nickel
Selenium
Silver
Thallium
Zinc

**Major Elements**
Silicon

**Trace Elements**
Tin

**Organotins**
Butyl tins: Mono-, Di-, Tri-butyltin

**Chlorinated Aromatic Compounds**
1,2,4-trichlorobenzene
1,2-dichlorobenzene
1,3-dichlorobenzene
1,4-dichlorobenzene
2-chloronaphthalene
Hexachlorobenzene

**Chlorinated Alkanes**
Hexachlorobutadiene
Hexachloroethane
Hexachlorocyclopentadiene

**Chlorinated and Nitro-Substituted Phenols**
2,4,5-trichlorophenol
2,4,6-trichlorophenol
2,4-dichlorophenol
2,4-dinitrophenol
2-chlorophenol
2-nitrophenol
4,6-dinitro 2-methylphenol (=4,6-dinitro-o-cresol)
4-chloro 3-methylphenol
4-nitrophenol
Pentachlorophenol

**Ethers**
4-bromophenyl-phenyl ether
4-chlorophenyl-phenyl ether
Bis(2-chloroethyl)ether
Bis(2-chloroisopropyl)-ether

**HPAHs**
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(g,h,i)perylene
Benzo(k)fluoranthene
Chrysene
Dibenzo(a,h)anthracene
Fluoranthene
Indeno(1,2,3-c,d)pyrene
Pyrene
C1 - C4 Chrysene
Benzo(e)pyrene
Perylene
**calculated values:**
total Benzofluoranthenes
HPAH

**LPAHs**
2-methylnapthalene
Acenaphthene
Acenaphtylene
Anthracene
Fluorene
Napthalene
Phenanthrene
Retene
Biphenyl
1-Methylnaphthalene
2,6-Dimethylnaphthalene
1,6,7-Trimethylnaphthalene
C1 - C4 naphthalenes
1-Methylphenanthrene
Dibenzothiophene
C1 - C2 Fluorenes
C1 - C4 Phenanthrenes
C1 - C3 Dibenzothiophenes
**calculated value:**
LPAH

**Miscellaneous Extractable Compounds**
Benzoic acid
Benzyl alcohol
Beta-coprostanol
Isophorone
Dibenzofuran

**Organonitrogen Compounds**
2,4-dinitrotoluene
2,6-dinitrotoluene
2-nitroaniline
3,3'-dichlorobenzidine
3-nitroaniline
4-chloroaniline
4-nitroaniline
9(H)carbazol
Caffeine
N-nitroso-di-n-propylamine
Nitrobenzene
N-nitrosodiphenylamine

**Phenols**
2,4-dimethylphenol
2-methylphenol
4-methylphenol
Bis(2-chloroethoxy)-methane
Phenol
P-nonylphenol

**Phthalate Esters**
Bis(2-ethylhexyl)phthalate
Butyl benzyl phthalte
Di-n-butyl phthalate
Di-n-octyl phthalate
Diethyl phthalate
Dimethyl phthalate

Table 2. Continued.

**Chlorinated Pesticides**
Aldrin
Alpha-chlordane
Alpha-HCH
Beta-HCH
Delta-HCH
Dieldrin
Endo-sulfansulfate
Endrin
Endrin ketone
Endrin-aldehyde
Gamma-chlordane
Gamma-HCH
Heptachlor
Heptachlor epoxide
Methoxychlor
2,4'-DDD
4,4'-DDD
2,4'-DDE
4,4'-DDE
2,4'-DDT
4-4'DDT
Cis-nonachlor
Trans-nonachlor
Oxychlordane
Mirex
Endosulfan I (Alpha-endosulfan)
Endosulfan II (Beta-endosulfan)
Chlorpyrifos
Toxaphene
Diazinon

**Polycyclic Chlorinated Biphenyls**
PCB Arochlors:
1016
1221
1232
1242
1248
1254
1260

PCB Congeners:
8
18
28
44
52
66
77
101
105
118
126
128
138
153
170
180
187
195
206
209

**Miscellaneous Oxygenated Compounds (may be done at selected stations):**
Polychlorinated dibenzo-p-dioxins:
- 2,3,7,8-Tetrachlordioxin (TCDD)
- Other tetrachlorinated dioxins
- Pentachlorinated dioxins
- Hexachlorinated dioxins
- Heptachlorinated dioxins
- Octachlorinated dioxins

Polychlorinated dibenzofurans:
- Tetrachlorinated furans
- Pentachlorinated furans
- Hexachlorinated furans
- Heptachlorinated furans
- Octachlorinated furans

Responsibilities and products to be generated by the Sediment Monitoring Unit:

- post-cruise reports which shall consist of station coordinates, charts indicating the actual sampling locations of all stations, and field notes including visual conditions of the samples;

- a data report for the sediment analyses which shall include descriptions of field and analytical methods, raw data in tabular form, and a narrative case summary of the chemical and benthic data (including a discussion of data quality); and

- data reports for any other tests Ecology (i.e., Sediment Management Unit, etc.) chooses to fund (e.g., bulk-sediment larval mortality/abnormality toxicity test, etc.) which shall include descriptions of field and analytical methods, raw data in tabular form, and a narrative case summary of the data (including a discussion of data quality).

Responsibilities and products to be generated by NOAA:

- latitude/longitude coordinates for sediment collection stations;

- base maps of each survey area showing strata boundaries, station locations, and spatial patterns in sediment toxicity;

- a data report for the toxicity tests which shall include descriptions of analytical methods, raw data in a tabular format, the results of the data evaluations (including, at a minimum, sample averages, control-normalized sample means, and statistical significance for each station), and a narrative case summary of the data (including a discussion of data quality);

- calculations of the spatial extent of sediment toxicity for each bioassay (with data weighted to the size of the sampling stratum); and

- assistance and advice during data analyses.

Sediment Monitoring Unit personnel, in collaboration with NOAA personnel, will be responsible for producing a final sediment analyses project report for northern Puget Sound, which includes analysis of the data to determine:

- the statistical significance of toxicity data (NOAA lead),

- spatial patterns in toxicity (NOAA lead),

- relative degree of toxicity among the stations (NOAA and Ecology collaboration),

- spatial patterns in chemical concentrations (Ecology lead),
- relationships between toxicity and chemical concentrations (NOAA and Ecology collaboration),
- spatial extent of toxicity (NOAA and Ecology collaboration),
- structure and relative health of benthic communities and populations (Ecology lead), and
- relationships between benthic structure and chemical concentrations and toxicity (Ecology lead).

A schedule for performance of this work is indicated in Figure 2.

# PROJECT OBJECTIVES

The objectives of the assessment of bioeffects in Puget Sound are to:

- estimate the spatial extent of chemical contamination, toxicity, and benthic community alterations in surficial (upper 2-4 cm) sediments;
- identify spatial patterns in chemical concentrations, toxicity, and benthic community alterations (possibly leading to the identification of hot spots);
- determine the incidence and severity of sediment toxicity;
- estimate the apparent relationships between toxicant concentrations and measures of sediment toxicity; and
- compare and rank the quality of sediment among different regions of Puget Sound.

# DATA QUALITY OBJECTIVES

## Program Requirements

The type of data to be collected for this joint project were chosen after consideration of the intersecting needs of the established monitoring and regulatory programs described in

Figure 2. Timeline of activities

| | 1997 | | | | | | | | | | | 1998 | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Activity | M | A | M | J | J | A | S | O | N | D | J | F | M | A | M | J | J | A | S | O |
| Planning (NOAA, Ecology, WDFW, PSAMP) | X | X | X | | | | | | | X | X | X | X | X | X | | | | | |
| Task 1 | | | | | | | | | | | | | | | | | | | | |
| Field Sampling (Ecology) | | | | X | X | | | | | | | | | | | X | X | | | |
| Sediment Toxicity Lab Analysis (NOAA) | | | | X | X | X | X | X | X | X | X | | | | | X | X | X | X | X |
| Sediment Chemistry Lab Analysis (MEL) | | | | X | X | X | X | X | X | X | X | | | | | X | X | X | X | X |
| Benthic Community Analysis (Ecology) | | | | | | X | X | X | X | X | X | X | X | X | | | | X | X | X |
| Deliverables | | | | | | | | | | | | | | | | | | | | |
| Post-Cruise Reports | | | | | X | | | | | | | | | | | | X | | | |
| Quarterly Reports (Ecology) | | | | X | | | X | | | X | | | X | | | X | | | X | |
| Data Report: sediment toxicity data | | | | | | | | | | | | X | | | | | | | | |
| Data Report: sediment chemistry | | | | | | | | | | | | X | | | | | | | | |
| Data Report: benthic invertebrate data | | | | | | | | | | | | | | | X | | | | | |
| 1997 Final Report | | | | | | | | | | | | | | | | | | | X | |

the Problem Statement section, above. Each of the three monitoring elements (toxicity, chemical, and benthic infaunal analyses) is required by the NOAA NS&T program and has been revised for the PSAMP Sediment Component. Analysis of the data collected will serve to address the project objectives, listed above, and will be compared with historical data from both of these programs. The sediment chemistry data will also be available for correlation with both historical and current fish tissue chemistry and histopathology data generated by the PSAMP Fish Component. The toxicity testing data is useful in the development of regulatory standards for contaminated sediments by Ecology's Sediment Management Unit, responsible for administration of the state's Sediment Management Standards (SMS) rule.

## Parameter Lists

### *Toxicity Tests*

All toxicity testing is being funded by NOAA and conducted by their contractors. Results will be provided to Ecology, as indicated in the Project Description section, above.

### *Chemical Analyses*

The laboratory analytical methods and reporting limits for quantification of the 169 chemistry parameters to be analyzed for are summarized in Table 3. These methods are described in detail in the Analytical Methods section, below. Methods and resolution levels for field collection of temperature and salinity are included in Table 4.

### *Benthic Community Analyses*

The laboratory analytical methods and resolution levels for the benthic infauna data collected are summarized in Table 5. These methods are described in detail in the Analytical Methods section, below.

## Precision, Bias, and Accuracy

The degree of precision, bias, and accuracy routinely achieved with the methods selected for the toxicity, chemical, and benthic community analyses will be adequate for the purposes of this project. As described in the Experimental Design section, below, three replicate sediment samples per strata will be taken and analyzed for each component of this project for determination of the degree of precision of the data. In addition, five

Table 3: Chemistry Parameters: Laboratory analytical methods and reporting limits

| PARAMETER | METHOD | REFERENCE | REPORTING LIMIT |
|---|---|---|---|
| Grain Size | Sieve-pipette method | PSEP, 1986b | >2000 to <3.9 microns |
| Total Organic Carbon | Conversion to $CO_2$ measured by nondispersive infra-red spectroscopy | PSEP, 1986b | 1 mg/L |
| Acid Volatile Sulfides/ Simult. Extracted Metals | AVS - EPA method<br>SEM - ICP-MS | AVS - EPA, 1991<br>SEM - EPA 200.7AV | AVS - n/a<br>SEM - 1-10 ppm |
| Metals (Partial digestion) | Strong acid (aqua regia) digestion and analyzed via ICP, ICP-MS, or GFAA, depending upon the analyte | - digestion - EPA 3050<br>- analysis - PSEP, 1996d (EPA 200.7, 200.8, 206.2, 245.5, 270.2) | 1-10 ppm |
| Metals (Total digestion) | Hydrofluoric acid-based digestion and analyzed via ICP or GFAA, depending upon the analyte | - digestion - EPA 3052<br>- analysis - PSEP, 1996d (EPA 200.7, 204.2, 206.2, 239.2, 270.2, 279.2, 282.2) | 1-10 ppm |
| Mercury | Cold Vapor Atomic Absorption | PSEP, 1996d<br>EPA 245.5 | 1-10 ppm |
| Butyl Tins | Solvent Extraction, Derivitization,Gas Chromatography/Mass Spectrometry in selected ion mode | Manchester Method (Manchester Environmental Laboratory, 1997) | 40 ug/kg |
| Base/Neutral/Acid Organic Compounds | Capillary column Gas Chromatography/ Mass Spectrometry | PSEP 1996e, EPA 8270 | 1-5 ppb |
| Chlorinated Pesticides and PCB (Arochlors) | Gas Chromatography Electron Capture Detection | PSEP 1996e, EPA 8081 | 1-5 ppb |
| PCB Congeners | | NOAA, 1993a | 1-5 ppb |

Table 4: Chemistry Parameters: Field analytical methods and resolution

| PARAMETER | METHOD | RESOLUTION |
|---|---|---|
| Temperature | Mercury Thermometer | 1.0 °C |
| Surface salinity | Refractometer | 1.0 ppt |

Table 5: Benthic Infaunal Parameters: Laboratory analytical methods and resolution

| PARAMETER | METHOD | RESOLUTION |
|---|---|---|
| Taxonomic Identification | Identification with dissection and compound microscopes | species level |
| Taxon Enumeration | Count | count all organisms |

percent (5%) of all sediment samples will be analyzed in duplicate (a single sample homogenized and split into two aliquots) to provide an estimate of variability in the data generated by the ship-board sample handling and chemistry laboratory's analytical procedures. Other QA/QC measures to be used during this project are described in the Quality Control Procedures section, below.

Expectations of achievable precision and bias, including acceptable ranges of results of quality control samples will be determined in accordance with standard operating procedures set forth by the toxicity and chemistry laboratories. Data considered imprecise, biased, or of compromised usability may be qualified by the laboratory or during subsequent data assessment by NOAA or Marine Sediment Monitoring Unit personnel.

## Representativeness

The probabilistic, stratified-random sampling design chosen for this project is described in the Experimental Design section, below. This sampling design was used to gain representative spatial distribution of stations in strata of high potential toxicity, moderate potential toxicity, and in potential reference (non-toxic) areas.

## Completeness

The completeness of the data, or number of useable data points with respect to the number of data points targeted for collection (PSEP, 1996c), will be maximized by employing all appropriate sample handling techniques, as described in the Sample Collection and Analytical Methods sections, below. A double volume of homogenized sediment from each station will be sent to the toxicity testing contractors, and one 16 oz jar of homogenized sediment from each station will be archived at Manchester Laboratory until all toxicity and chemistry analysis results can be reviewed by the project lead. The goal for generation of usable data will be 95%.

## Comparability

Sample collection and analytical methods were selected to be appropriate for comparison with historical PSAMP sediment data and with data generated by NOAA's NS&T Bioeffects Monitoring Program. These methods, in general, follow the PSEP protocols (1987a), and should therefore produce data that are comparable with any historical data sets that have been generated in adherence with these guidelines developed for sediment monitoring in Puget Sound.

# PROJECT ORGANIZATION

The cooperative agreement between NOAA and Ecology will serve to coordinate the otherwise potentially separate environmental monitoring activities of NOAA, Ecology, and WDFW. This coordination will significantly increase the total benefit of the separate efforts by assuring synoptic collection of data, providing a common and shared sampling design, and by coordinating logistics and other expenses.

NOAA, Ecology, and WDFW will designate agency-level liaisons to discuss and resolve issues involving the cooperative agreement. All will designate technical managers to discuss and resolve issues involving methods and analyses and provide technical staff support for program planning, determination of technical scope and methods, logistics planning and facilitation, data evaluation, and report review. Agency contacts are indicated in Figure 3. Table 6 identifies personnel from each agency who will be working on this project, along with a description of their duties and telephone numbers.

# EXPERIMENTAL DESIGN

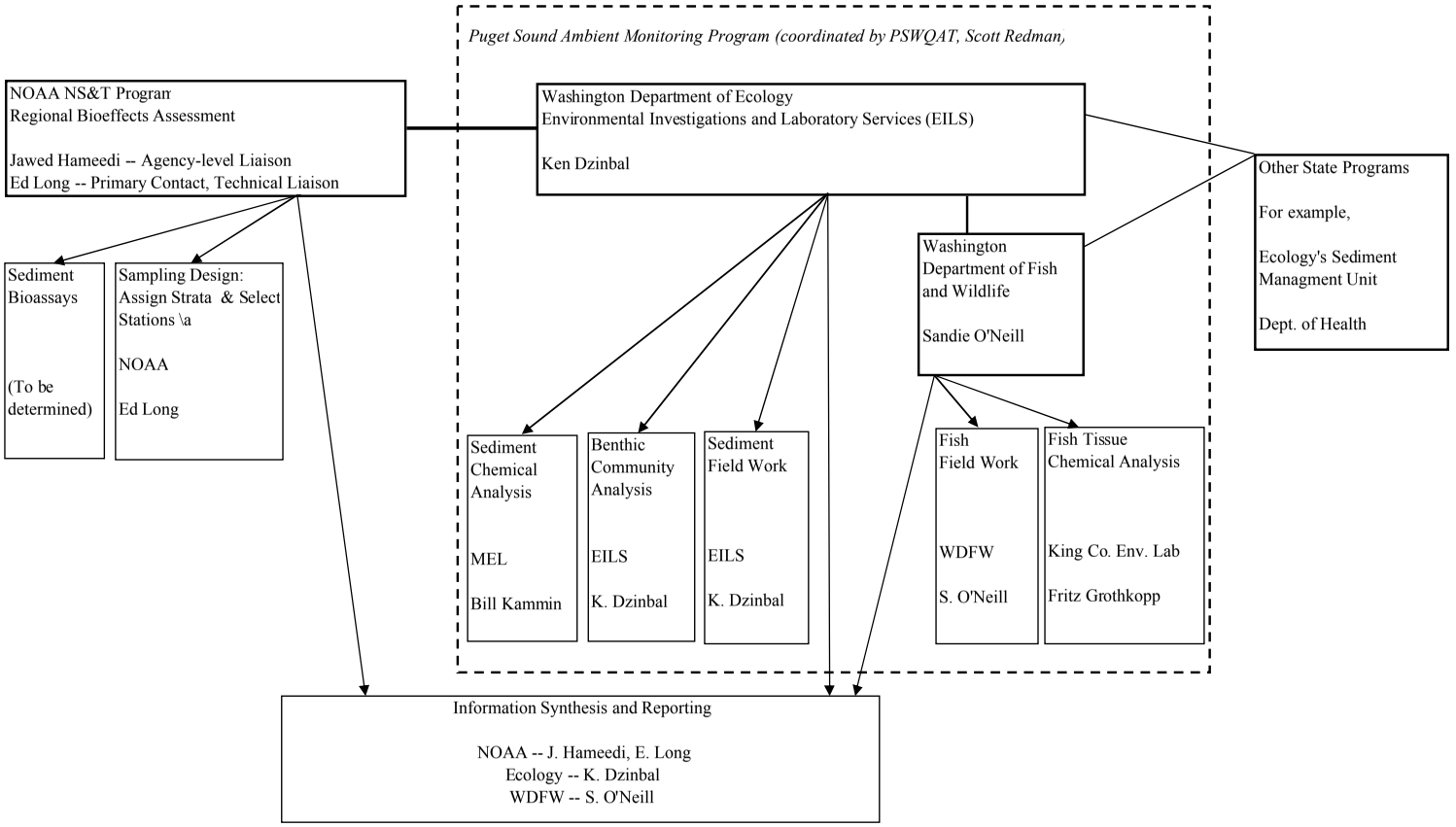
Station locations for this project were selected with a probabilistic, stratified-random sampling design similar to that previously used by NOAA in other bioeffects surveys (Long, in press). As described in the Site Description section above, 33 discrete strata were selected in 1997 from various regions throughout northern Puget Sound. The strata were identified jointly by Ecology, NOAA, WDFW, and PSWQAT using toxicity and oceanographic data available for the northern region. One hundred stations will be randomly selected (three within each strata and one extra) and sampled once each in June of 1997. This sampling design was used to ensure representative spatial distribution of stations in locations of high potential toxicity, moderate potential toxicity, and in potential reference (non-toxic) areas.

# SAMPLE COLLECTION

Collection of sediment for chemistry, bioassay and infaunal analyses will be led by personnel from Ecology's Marine Sediment Monitoring Unit. Sampling methods will, in general, follow those described in PSEP (1996b). A summary of these methods follows below.

A marine research vessel of adequate size and speed, and suitably equipped for deployment of sample collection equipment and shipboard sample processing will be contracted by Ecology for this work. From this platform, station-positioning protocols will follow PSEP (1986a). Positioning will rely on Differential Global Positioning

Figure 3. NOAA/Washington Cooperative Agreement Management Structure, including agency-level and technic




NOTES:
Proposed interagency agreement is between NOAA and Washington Department of Ecology. The state team also includes key contributions by WDFW and PSWQAT. PIs are responsible for deliverables for their tasks and subtasks.

a/ With assistance of and approval by state of Washington.

Table 6. NOAA/Washington Cooperative Agreement project personnel and areas of responsibility.

| PERSONNEL | DUTIES | PHONE |
|---|---|---|
| **Ecology:** | | |
| Ken Dzinbal | Manager, Ambient Monitoring Section - project coordination and oversight | 360-407-6672 |
| **- Marine Sediment Monitoring Unit:** | | |
| Sandra Aasen | All Marine Sediment Monitoring Unit members share responsibilities for conducting field work, processing benthic infaunal samples, analysis of chemistry, toxicity, and benthic community data, and production of annual summary report. | 360-407-6980 |
| Margaret Dutch | | 360-407-6021 |
| Christina Ricci | | 360-407-6027 |
| Kathy Welch | | 360-407-6035 |
| **WDFW:** | | |
| Sandra O'Neill | Principal Investigator, Fish Component of PSAMP - coordination and oversight of PSAMP fish component | 360-902-2843<br>206-784-2836 |
| **Manchester Lab:** | | |
| Bill Kammin | Laboratory Manager - coordination and oversight of all chemistry analyses conducted for this project at Manchester Laboratory | 360-871-8801 |
| **NOAA:** | | |
| Ed Long | NOAA Project Manager - coordination and oversight of Cooperative Agreement requirements; responsible for all deliverables from NOAA to Ecology, as outlined in the Project Description, including subcontracting and data report production for all toxicity testing. | 206-526-6338 |

System (DGPS) with expected accuracy of better than 5 meters. Variable radar ranging, water depth, and line-of-site fixes on land objects may supplement the DGPS if necessary.

Prior to sampling, all sampling equipment will be washed with Alconox soap and rinsed with fresh water. Sediment samples will be collected using a double 0.1 $m^2$ stainless steel modified van Veen grab sampler, which allows the chemistry and bioassay samples to be collected simultaneously with the benthic infaunal samples. Upon collection by the grab, the sample will be visually inspected. Any station lacking fine-grained particles in its samples (e.g., all cobble, shell hash, etc.) will be rejected and replaced with a station from the list of randomly selected alternate sites. As each grab sample is collected, station information and a number of visually descriptive assessments and measurements will be made and recorded on field logs which have been copied onto water-resistant paper (Figure 4).

From one side of the sampler, the top two to three centimeters of sediment from three to six replicate grab samples per station (i.e., grabs will be taken until enough sediment is collected to fill all sample containers for a station) will be collected with a disposable plastic scoop, composited in a high density polyethylene (HDPE) bucket, and homogenized for chemistry and bioassay samples by stirring until textural and color homogeneity are achieved. The bucket will have an inner HDPE lid that is placed on the sediment surface, as well as a top lid, to minimize oxidation and photo-activation between grabs (Long, E.R., personal communication).

From the other side of the sampler, one grab sample per station (= three replicates per strata) will be collected for benthic infaunal analyses. All infaunal samples will be rinsed through, and organisms retained from, nested 1.0 and 0.5mm screens. Organisms will be preserved in the field with a 10% aqueous solution of borax-buffered formalin. Ecology personnel will conduct further processing (i.e., rescreening, sorting, taxonomic identification, data compilation and analysis) of the 1.0mm infaunal fraction. Techniques will follow PSEP (1987a). The 0.5mm fraction will be rescreened and transferred to 95% ethanol by Ecology, then archived by Ecology or NOAA until further funding sources are allocated by NOAA for sample processing by NOAA.

Field decontamination of sampling equipment and associated utensils will be conducted between sampling stations by scrubbing with a soft brush and *in situ* seawater to remove excess sample material. All equipment will be thoroughly rinsed with *in situ* seawater, solvents and/or acids (if sediment is heavily contaminated), followed by a final rinse with *in situ* seawater.

Recommended sample sizes, containers, preservation techniques, and holding times for all sediment samples are those listed for the PSEP (1996b) and the Manchester Environmental Laboratory Lab User's Manual (Manchester Environmental Laboratory, 1994) and are summarized in Table 7. In the field, samples for chemical and bioassay

Figure 4. Field Sampling Log Sheet

**WASHINGTON STATE DEPARTMENT OF ECOLOGY**
**PUGET SOUND SEDIMENT MONITORING PROGRAM/NOAA BIOEFFECTS MONITORING**

# 1997 FIELD LOG

## STRATUM NO: _____ STATION NO: _____

SAMPLING DATE: ___/___/1997 TIME ON: _____AM/PM TIME OFF: _____ AM/PM

WEATHER: _____

CREW: _____

_____

LOCATION: _____

DGPS LATITUDE: _____ DGPS LONGITUDE: _____

STATION DESCRIPTION:
(URBAN/RURAL/OTHER)_____

_____

WATER DEPTH: _____m SURFACE SALINITY: _____ppt TEMP: _____ºC

CHEMISTRY SPLIT: _____

SEDIMENT TYPE: COBBLE GRAVEL SAND SILT/CLAY WOOD SHELL FRAG

SEDIMENT COLOR: BLACK OLIVE GRAY BROWN BROWN SURFACE

SEDIMENT ODOR: $H_2S$ PETROLEUM (SLIGHT MODERATE STRONG) OTHER: _____

PENETRATION DEPTH: _____cm RPD: _____cm

NUMBER OF GRABS TAKEN: _____ REJECTED: _____

FAUNA OBSERVED:

_____
_____
_____

COMMENTS:

_____
_____
_____
_____
_____

Table 7. Sample container and collection information

| PARAMETER | CONTAINER NO. & TYPE | MINIMUM SAMPLE REQUIRED | PRESERVATION | HOLDING TIME |
|---|---|---|---|---|
| Grain Size | 1 - Polyethylene Whirlpak Bag | 200 g, fill bag | Refrigerate at 4ºC | 6 months |
| Total Organic Carbon | 1 - 2 oz wide mouth glass jar with Teflon-lined lid | 2 oz, fill , but leave head space for expansion during freezing | Refrigerate at 4ºC, freeze at -18°C | 14 days |
| Acid Volatile Sulfides/Simult. Extracted Metals | 1 - 4 oz wide mouth glass jar with Teflon-lined lid | 4 oz, fill jar to top | Refrigerate at 4ºC | 14 days |
| Metals (both partial and total digestion) | 1 - 4 oz wide mouth glass jar with Teflon-lined lid | 4 oz, fill jar to top | Refrigerate at 4ºC | 6 months, 28 days for mercury |
| Butyl Tins | 1 - 8 oz wide mouth glass jar with Teflon-lined lid | 8 oz, fill, but leave head space for expansion during freezing | Refrigerate at 4ºC, freeze at -18°C | 14 days |
| Base/Neutral/Acid Organic Compounds, Chlorinated Pesticides and PCB (Arochlors), & PCB Congeners | 2 - 16 oz wide mouth glass jar with Teflon-lined lids | 16 oz each jar, fill, but leave head space for expansion during freezing | Refrigerate at 4ºC, freeze at -18°C | 1 year |
| Chemistry Archive Sample | 1 - 16 oz wide mouth glass jar with Teflon-lined lid | 16 oz, fill, but leave head space for expansion during freezing | Refrigerate at 4ºC, freeze at -18°C | 1 year |
| Amphipod Survival - solid phase | 1 gallon HDPE jar | fill to top | Refrigerate at 4ºC | 10 days |
| Urchin Fertilization and Embryonic development - pore water | 1 gallon HDPE jar | fill to top | Refrigerate at 4ºC | --- |
| Urchin Embryo Mortality/Abnormality - solid phase | 1 - 8 oz wide mouth glass jar with Teflon-lined lid | 8 oz, fill jar to top | Refrigerate at 4ºC | 14 days |
| Microtox - organic solvent extract and Cytochrome P450 RGS Toxicity | 1 - 16 oz wide mouth glass jar with Teflon-lined lid | fill to top | Refrigerate at 4ºC | --- |
| Microtox - solid phase | 1 - 50 gram test tube | fill to top | Refrigerate at 4ºC | --- |
| Benthic Macro Fauna | 1 or 2 gallon zip-lock bags | 0.1 $m^2$ screened through 0.5 and 1.0mm mesh | 10% aqueous solution of borax-buffered formalin | 48 hours to 14 days |
| Foraminiferans* | zip-lock bag | 1 pint | Refrigerate at 4ºC | unspecified |

* collected upon request by Dr. Doris Sloan, U.C. Berkeley

analyses will be stored in sealed containers placed in insulated chests filled with ice. Chemistry samples will be off-loaded from the research vessel and transferred to the walk-in refrigerator at Ecology's headquarters building in Olympia. There, they will be held at 4°C until they are transported to Ecology's Manchester Environmental Laboratory (Manchester), located in Manchester, Washington. Samples collected for toxicity testing will be shipped to NOAA bioassay contractors by the state. The formalin-fixed sediment samples collected for infaunal analyses will be transported to the benthic laboratory at Ecology's headquarters building in Olympia to await rescreening. All appropriate sample holding times will be observed.

Chain-of-custody procedures will follow those recommended by the PSEP (1996c). They will be initiated when the first sample is collected and will be followed until all samples are relinquished to the analytical laboratory. Chemistry, bioassay, and infaunal chain-of custody forms designed for this project are depicted in Figures 5, 6, and 7. These procedures will provide an unbroken trail of accountability that ensures the physical security of samples, data, and records.

# ANALYTICAL METHODS

## Toxicity Tests

Through separate contracts funded and managed by NOAA, four independent tests of sediment toxicity will be performed with each sample: 10-day solid phase tests of amphipod survival (*Ampelisca abdita*); pore water tests of sea urchin egg fertilization and embryological development (*Strongylocentrotus purpuratus*); microbial bioluminescence (Microtox) tests of an organic solvent sediment extract; and Cytochrome P-450 RGS tests of sediment extracts. The sediment from each station will be tested in quintuplicate in the laboratory. Each test will be accompanied with equivalent tests of a positive control chemical (e.g., cadmium chloride) and negative, non-toxic controls. Protocols equivalent to the PSEP bioassay protocols (1995) will be used by NOAA contractors to perform the amphipod and Microtox tests. Other published, widely recognized protocols familiar to NOAA contractors will be used to perform the pore water and RGS tests. A list of NOAA contractors selected each year will be provided in the post-cruise report generated at the end of each field season.

For comparability with the sea urchin (*Arbacia punctata*) tests performed elsewhere, NOAA will also support an intercomparison study for the two species of sea urchins, with approximately 10 known toxicants that are also pertinent to Puget Sound. NOAA may also support a comparative study between solid-phase and organic solvent extract Microtox tests. Similarly, Ecology's Sediment Management Unit will also separately fund and manage an additional sediment toxicity test. A 48-hour bulk-sediment larval

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# CHAIN OF CUSTODY/CHEMICAL ANALYSIS REQUIRED

| Station Number | Lab Number | Date Sampled | Grain Size | Total Organic Carbon | Acid Volatile Sulfides/ SEM | Metals (Partial Digestion) | Metals (Hydrofluoric Digestion) | Butyl Tins | Acids/Base/ Neutrals | Chlorinated Pesticides/ PCBs (Archlors) | PCB (Congeners) | Other |
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Comments:

**WASHINGTON STATE DEPARTMENT OF ECOLOGY**
**PUGET SOUND SEDIMENT MONITORING PROGRAM/NOAA BIOEFFECTS MONITORING PARTNERSHIP**

# CHAIN OF CUSTODY/BIOASSAY ANALYSIS REQUIRED

| Enter number of sample containers under each analysis | | | | | | | |
|---|---|---|---|---|---|---|---|
| Station Number | Date Sampled | Amphipod Survival (solid phase) | Urchin fertilization and development (pore water) | Urchin fertilization. and development (solid phase) | Microtox (organic solvent extract) | Cytochrome P-450 RGS | Comments |
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Figure 7. Infaunal Analysis Chain-of-Custody Form

## WASHINGTON STATE DEPARTMENT OF ECOLOGY
## PUGET SOUND SEDIMENT MONITORING PROGRAM

# INFAUNAL CHAIN OF CUSTODY

| Station Number | Replicate | Date Sampled | Sieve size | Number of containers | Comments |
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mortality/abnormality bioassay , required under Washington's Sediment Management Standards, will be conducted with *Strongylocentrotus purpuratus* on samples from a selected subset of the stations. Stations chosen will correspond to known or suspected contaminated sediment sites, or be located in near shore areas of urban embayments. These data may provide useful information to Ecology's Sediment Management Unit regarding the differences in the sensitivity of the pore water and bulk-sediment urchin tests and their relative ability to predict deleterious effects of toxicants in the environment.

# Chemical Analyses

## Manchester Environmental Laboratory

Manchester personnel will use the PSEP protocols (1995,1996b,c,d,e) whenever possible as the standard for analysis, data validation and review, reporting, and other laboratory activities related to this project. Manchester will also use NOAA NS&T Program quality assurance protocols when required or more stringent. In addition, Manchester will participate in required NOAA quality assurance interlaboratory studies during the course of the project.

## Project Specific Methodology and Procedures

As indicated in the Project Description section, above, one hundred sixty nine (169) parameters and chemical compounds will be analyzed for (Table 2), including ninety two (92) trace metals, pesticides, hydrocarbons and selected normalizers (*i.e.*, grain size, total organic carbon) that are routinely quantified by the NS&T Program, plus simultaneously-extracted metals/acid volatile sulfides. An additional twenty-seven (27) compounds have been added as requested by Ecology's Sediment Monitoring and Management Units, and by the WDFW for the fish component of the PSAMP. Fifty (50) more compounds are automatically quantified by Manchester during analysis for the required compounds.

Analytical procedures will provide performance equivalent to those of the NS&T Program and the PSEP protocols, including those for analyses of blanks and standard reference materials. Information shall be reported on recovery of spiked blanks, analytical precision with standard reference materials, and duplicate analyses of every 20th sample. Method detection limits normally achieved by NOAA contractors shall be achieved by Manchester (1-10 ppm for metals, 1-5 ppb for organic compounds). A portion of all samples collected will be frozen at -18°C (O°F) and archived by Ecology for one year, in case re-extraction or retrospective analysis is needed or required. Details of the analytical methods are provided, below.

### *Grain Size*

Analysis for grain size will be performed according to the PSEP protocols (PSEP, 1986b). The PSEP grain size method is a sieve-pipette method. In this method the sample is passed through a series of progressively smaller sieves, with each fraction being weighed. After this separation, the very fine material remaining is placed into a column of water, and allowed to settle. Aliquots are removed at measured intervals, and the amount of material in each settling fraction is measured. This parameter will be contracted by Manchester to an external laboratory.

### *Total Organic Carbon (TOC) in Sediment*

Total organic carbon analysis will be performed according to PSEP protocols (PSEP, 1986b). The method involves drying sediment material, pretreatment and subsequent oxidation of the dried sediment, and determination of $CO_2$ by infrared spectroscopy.

### *Acid Volatile Sulfides (AVS)/Simultaneously Extracted Metals (SEM)*

Methodology for the determination of AVS follows EPA, 1991. Simultaneously extracted metals will be determined by USEPA Method 200.7AV, the method for ultra-trace metals by inductively coupled plasma mass spectrometry.

### *Metals in Sediment - Preparation and Analysis*

EPA method 3050 is a strong acid (aqua regia) digest, which has been used for the last several years by Ecology for the characterization of sediments for trace metal contamination. Method 3050 is also the recommended digestion technique for digestion of sediments in the recently revised PSEP protocols (PSEP, 1996d). This digestion does not yield geologic (total) recoveries for most analytes including silicon, iron, aluminum and manganese. It does, however, recover quantitatively most anthropogenic metals contamination and deposition. In addition, for comparison with NOAA's national bioeffects survey's existing database, Manchester will simultaneously perform a total (hydrofluoric acid-based) digestion (EPA method 3052) on a second set of sediment samples. Determination of metals values for both sets of samples will be made via ICP, ICP-MS, or GFAA, using a variety of EPA methods (see Table 3) depending upon the appropriateness of the technique for each analyte.

### *Mercury*

Mercury will be determined by USEPA Method 245.5, mercury in sediment by cold vapor atomic absorption (CVAA). The method consists of a strong acid sediment digestion, followed by reduction of ionic mercury to $Hg^0$, and analysis of mercury by cold vapor atomic absorption. This method is recommended by the PSEP protocols (PSEP, 1996d) for the determination of mercury in Puget Sound sediment.

### *Butyl Tins*

Butyl tins in sediments will be analyzed by the Manchester Method (Manchester Environmental Laboratory, 1997). This method consists of solvent extraction of sediment, derivitization of the extract with the Grignard reagent hexylmagnesium bromide, cleanup with silica and alumina, and analysis by GC/MS in selected ion mode (SIM).

### *BNA (extended list)*

USEPA Method 8270, a recommended PSEP method (PSEP, 1996e) will be used for semi-volatile analysis. This is a capillary column, GC/MS method. The extended analyte list will be modified by inclusion of additional PAH compounds on the NOAA target analyte list. Selected ion mode (SIM) may be used to enhance detection capability.

### *Chlorinated Pesticides and PCB (Arochlors)*

EPA Method 8081 for chlorinated pesticides and PCB will be used for the analysis of these compounds. This method is a GC method with dual dissimilar column confirmation. Electron capture detectors are used.

### *PCB Congeners*

PCB methodology will be based on the NOAA congener methods detailed in Volume IV of the NS&T Sampling and Analytical Methods documents (NOAA, 1993). The standard NOAA list of 20 congeners will be determined.

# Benthic Community Analyses

The majority of the work required to process, identify, and analyze the benthic infaunal macroinvertebrate assemblages present in the sediment samples collected for this project will be conducted by Ecology personnel. All methods, procedures, and documentation (chain-of-custody forms, tracking logs, and data sheets) will be similar to those described for the PSEP (1987), and are briefly summarized below. Marine Sediment Monitoring Unit personnel are currently preparing a manual detailing all standard operating procedures to be used in processing these infaunal samples. Laboratory activities include removing infaunal organisms from the sediment samples, sorting them into major taxonomic groups, identification to the lowest taxonomic level possible, and conducting QA/QC on all procedures.

## Sample Processing and Sorting

Upon completion of field collection, benthic infaunal samples will be checked into the benthic laboratory at Ecology's headquarters building and recorded on a sample-tracking log (Figure 8). After a minimum fixation period of 24 hours (and maximum of 7 to 10 days), the samples will be rescreened (1.0mm fraction on a 0.5mm sieve, 0.5mm fraction on a 0.25 sieve) and transferred to 70 percent ethanol. All 0.5mm sample fractions will be archived. After staining with rose bengal, 1.0mm sample fractions will be examined under dissection microscopes, and all macroinfaunal invertebrates and fragments will be removed and sorted into the following major taxonomic groups: Annelida, Arthropoda, Mollusca, Echinodermata, and Miscellaneous Phyla. Meiofaunal organisms such as nematodes and oligochaetes, as well as foraminiferans, will not be removed from samples, although their presence and relative abundance will be recorded. Representative samples of colonial organisms such as hydrozoans, sponges, and bryozoans will be collected, and their relative abundance noted.

## Taxonomic Identification

Personnel in the Marine Sediment Monitoring Unit will conduct portions of the taxonomic identifications in-house, and will contract to recognized specialists the remainder of the taxonomic work. Taxonomic identification will be conducted as follows. Upon completion of sorting, all organisms will be enumerated and identification will be to the lowest taxonomic level possible, generally to species. If possible, at least two pieces of literature (preferably including original descriptions) will be used for each species identification, and identifications will be checked against a reference specimen from a verified reference collection maintained by Ecology. If available, at least three

Figure 8. 1997 Infaunal Sample Tracking Log

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**PUGET SOUND SEDIMENT MONITORING PROGRAM/NOAA BIOEFFECTS MONITORING PARTNERSHIP**

# 1997 INFAUNAL SAMPLE TRACKING LOG

**STRATUM: 1** **SAMPLING DATE:**

| STA | SIEVE SIZE (mm) | RESCREEN By | RESCREEN Date | No. of Jars | Archive yes/no | Sorters init. | DATE Start | DATE End | Sort Time | DISTRIBUTION OF SORTED MATERIAL (# OF VIALS/JARS) POLYCHAETA POLY | POLYCHAETA FRAG | MOLL | CRUST | ECHIN | MISC. | Initial # of orgs | Final # of orgs | QA P/F | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.5 | | | | | | | | | | | | | | | | | | |
| | 1.0 | | | | | | | | | | | | | | | | | | |
| 2 | 0.5 | | | | | | | | | | | | | | | | | | |
| | 1.0 | | | | | | | | | | | | | | | | | | |
| 3 | 0.5 | | | | | | | | | | | | | | | | | | |
| | 1.0 | | | | | | | | | | | | | | | | | | |

**STRATUM: 2** **SAMPLING DATE:**

| STA | SIEVE SIZE (mm) | RESCREEN By | RESCREEN Date | No. of Jars | Archive yes/no | Sorters init. | DATE Start | DATE End | Sort Time | DISTRIBUTION OF SORTED MATERIAL (# OF VIALS/JARS) POLYCHAETA POLY | POLYCHAETA FRAG | MOLL | CRUST | ECHIN | MISC. | Initial # of orgs | Final # of orgs | QA P/F | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4 | 0.5 | | | | | | | | | | | | | | | | | | |
| | 1.0 | | | | | | | | | | | | | | | | | | |
| 5 | 0.5 | | | | | | | | | | | | | | | | | | |
| | 1.0 | | | | | | | | | | | | | | | | | | |
| 6 | 0.5 | | | | | | | | | | | | | | | | | | |
| | 1.0 | | | | | | | | | | | | | | | | | | |

**STRATUM: 3** **SAMPLING DATE:**

representative organisms of each species or taxon will be removed from the samples and placed in a voucher collection.

# QUALITY CONTROL PROCEDURES

In general, the recommended quality assurance/quality control guidelines for the collection of environmental data in Puget Sound will be followed (PSEP, 1996c). Procedures for the different components of this project are detailed, below.

## Field Sampling

Field quality control sampling will include collection of field split samples at 5% of the stations sampled (i.e., 5 of the 100 stations), and sampling of three field replicates (i.e., three stations) per strata. To assess whether diesel exhaust from the boat contributed any measurable contamination to the samples, one field blank will also be collected during the cruise and analyzed for PAH levels.

## Toxicity Tests

All bioassay work conducted by NOAA subcontractors should adhere to general QA/QC procedures that apply to all sediment bioassays, as outlined in the PSEP protocols (1995). These include use of both negative (clean) and positive (toxic) controls as well as reference test sediments; use of healthy test organisms; observance of sediment holding times, proper equipment cleaning procedures, and standard laboratory procedures; measurement and maintenance of water quality; and blind testing. NOAA's contract laboratories will follow QA/QC procedures specific to each of the individual bioassays that differ from these generic guidelines.

## Chemical Analyses

**All chemistry analyses conducted by Manchester Lab and their subcontractors will adhere to analytical quality control methods outlined in the PSEP protocols (1996d,e) and in Manchester Lab's in-house standard operating procedures. Quality control methods for organic analyses include both instrument calibration and analytical quality control procedures (i.e., use of method blanks, surrogate spike compounds, analytical replicates, matrix spikes, spiked method blanks, and reference materials). Quality control for metals analyses also includes both instrument (calibration, etc.) And method (method blank,**

**matrix spike, etc.) Quality control procedures. Manchester will also use NOAA NS&T program quality assurance protocols when required or more stringent. In addition, Manchester will participate in required NOAA quality assurance interlaboratory studies during the course of the project.**

## Sorting of Infaunal Samples

Sorting QA/QC procedures will consist of resorting 20% of each sample to determine whether a sample sorting efficiency of 95% removal has been met.

## Taxonomic Identification of Infaunal Samples

Taxonomic identification quality control for both Ecology and out-of-house taxonomists will include re-identification of 5% of all samples identified by one taxonomist, and review and verification of all voucher specimens generated, by another qualified taxonomist. In-house taxonomists will also generate a series of taxonomic voucher sheets to insure standardized in-house identifications. In addition, Ecology's Marine Sediment Monitoring Unit houses a large collection of marine infaunal invertebrate organisms from Puget Sound. The collection contains over 2400 specimens from 908 taxa, and includes all reference and voucher specimens collected from PSAMP work conducted since 1989, as well as some earlier Puget Sound studies. The collection is an extremely valuable tool that will be used by taxonomists to help insure consistency in taxonomic identifications in future PSAMP work.

In addition to specimen reidentification, Ecology personnel have developed, and have extensive experience applying, a standardization review process for QA/QC of taxonomic data generated by numerous contracted taxonomists. This review process was developed by Ecology personnel while reviewing 5 years of PSAMP data. It is a method of comparing taxa designations between stations and between years of a study to locate nomenclature and identification discrepancies invariably generated when multiple taxonomists work on a project. The process attempts to minimize the unavoidable inconsistencies in taxonomic nomenclature due to changing taxonomic nomenclature in the published literature and to assignment of species names by taxonomists with varying backgrounds and skill levels. An extensive list of previous taxonomic discrepancies was generated during development of this process, which will be helpful in pinpointing and avoiding common discrepancies in future taxonomic work.

This standardization review process will be applied to all taxonomic data to ensure consistency between different taxonomists both within and between years. The process will be applied at regular intervals as data are generated, so that inconsistencies can be resolved and data standardized while the taxonomy is still being conducted.

# DATA REVIEW, VALIDATION AND ASSESSMENT

Upon completion of each phase of this project, data reports will be generated according to the schedule presented in Figure 2. These reports will be examined by appropriate personnel from Ecology's Marine Sediment Monitoring Unit, Manchester Laboratory, and/or NOAA as part of data review, validation and assessment.

## Field Sampling

Throughout the duration of the field sampling, a cruise leader and all crew members will have responsibilities for proper implementation of the station positioning and sample collection procedures, including systematic review of all field documentation generated (e.g., field logs, chain-of-custody sheets, etc.) to ensure accuracy and completeness of entries. Upon completion of field sampling, Marine Sediment Monitoring Unit personnel will complete a post-cruise report which shall consist of station coordinates, charts indicating the actual sampling locations of all stations, and field notes including visual conditions of the samples, and notes which describe any unusual events or alterations of the original sampling plan.

## Toxicity Tests

Upon completion of the toxicity testing, a data report will be submitted to Ecology by NOAA including descriptions of analytical methods, raw data in a tabular format, the results of the data evaluations (including, at a minimum, sample averages, control-normalized sample means, and statistical significance for each station), and a narrative case summary of the data. Calculations of the spatial extent of sediment toxicity for each bioassay (with data weighted to the size of the sampling stratum) will also be included. Marine Sediment Monitoring Unit personnel will review all data received, including all quality assurance results. Any discrepancies noted will be reported to NOAA's project lead for correction and amendment.

## Chemical Analyses

Manchester Laboratory will provide a case narrative and data package generated for the sediment chemistry data to Marine Sediment Monitoring Unit personnel through the Laboratory Information Management System (LIMS). At a minimum, this data package will include the following: a description of analyses performed and any problems encountered; all sample results; all quality assurance sample results; and a description of data qualifiers. All data will have 100% verification and errors corrected by the

laboratory. Marine Sediment Monitoring Unit personnel will review all data received. Any discrepancies noted will be reported to appropriate Manchester Laboratory personnel for correction and amendment.

## Benthic Community Analyses

A data report will be generated by personnel from Ecology's Marine Sediment Monitoring Unit for the benthic infaunal analyses. This report will include information regarding the sample sorting process, including any unusual information regarding sample composition and a summary of the QA/QC activities, as well as all species count data generated by the taxonomic work. All benthic infaunal data will be entered onto EXCEL spreadsheets in a matrix format with the following column headings: Taxon Name, Station Number, Date Collected, Replicate Number (heading for count data for each taxon found in each replicate), and Taxonomist. Taxonomic data, generated by both Ecology and contracted taxonomists, will be examined frequently by Ecology's Marine Sediment Monitoring Unit personnel throughout the duration of this work. As described in the Quality Control Procedures section, above, all QA/QC and standardization procedures will be applied to and completed for these data prior to their entry in the data report. Upon completion of this data report, the infaunal data will be ready for further data reduction and analysis.

## 1997 Final Report

Upon receipt of all intermittent data reports, and subsequent data review, validation, and assessment described above, Marine Sediment Monitoring Unit personnel will generate a comprehensive final report for the 1997 component of this three year project. This report will contain a description of the project methods and procedures, summary tables showing results of all field measurements and sample analyses, a description of all statistical analyses used to integrate, examine, and compare the relationships within and between the toxicity, chemistry, and benthic infaunal data, and a discussion of significant findings. This summary report will be distributed to all appropriate Ecology, PSAMP, and NOAA, and WDFW personnel for review and comment, and will be finalized as a joint Ecology/NOAA publication.

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