Water Column Concentrations of Metals In South Puget Sound and Grays Harbor

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Quality Assurance Project Plan

by
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Washington State Department of Ecology
Environmental Investigations and Laboratory Services Program
Watershed Ecology Section

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Project Description

Budget reductions at the state and federal level over the last decade have reduced or eliminated programs that collect data on metals concentrations in the marine waters of Puget Sound. The only low-level metals data for Sound Puget Sound are for a NOAA station in Nisqually Reach, occupied during the 1980s (Paulson et al., 1991a,b,c).

Because of the lack of South Sound data, needed to determine compliance with state water quality standards and for use in setting discharge permit limits, the Washington State Department of Ecology (Ecology) Environmental Assessment Program (EAP) will survey metal concentrations at selected sites in South Puget Sound. Similar data will also be collected for Grays Harbor, another area where no low-level metals data exist. Ultra-clean sampling techniques and low-level analytical methods will be used to measure concentrations of cadmium, copper, lead, zinc, and mercury.

Historically, these metals have been the focus of water quality studies in Puget Sound and are the metals most frequently limited in discharge permits. For copper and mercury, relatively modest increases in ambient concentrations can approach or exceed marine water quality standards (Table 1).

Table 1. Marine Water Quality Standards (WAC 173-201A) Compared to Puget Sound Background (ug/L, dissolved metal)

Metal	Acute	Chronic	Background*
Cadmium	42	9.3	0.04 - 0.09
Copper	4.8	3.1	0.1 - 0.4
Lead	210	8.1	0.02
Zinc	90	81	0.2 - 1.0
Mercury	1.8	0.025**	0.0002 - 0.001

*from Johnson and Summers (1999)
** chronic standard is for total mercury

Survey objectives will be to:

- Quantify concentrations of the metals of interest in the surface and subsurface waters of Budd Inlet, Shelton Harbor, Nisqually Reach, and Grays Harbor

- Evaluate compliance with state surface water quality standards for protection of marine life (WAC173-201A-040).

- Measure dissolved:total recoverable metals ratios for use in calculating discharge limits for NPDES and stormwater permits.

Four sampling sites are proposed as shown in Table 2 and Figure 1. The Budd Inlet, Shelton Harbor, and Grays Harbor stations were selected as being inner waterway sites in comparable depths of water, outside effluent mixing zones, and removed from the immediate vicinity of other potential metals sources. The Nisqually station will serve as a reference and allow comparison to the historical NOAA data.

Table 2. Stations Proposed for Metals Sampling

Location	Description	Latitude x Longitude	Depth @ MLLW (ft.)
Budd Inlet	Center of Turning Basin off N "14"	47 03 14 x 122 54 24	30
Shelton Harbor	Oakland Bay north of Eagle Point	47 12 41 x 123 04 41	33
Grays Harbor	Cow Point off R "2"	46 57 35 x 123 50 29	29
Nisqually Reach	Center Channel off G "1"	47 07 07 x 122 42 08	186

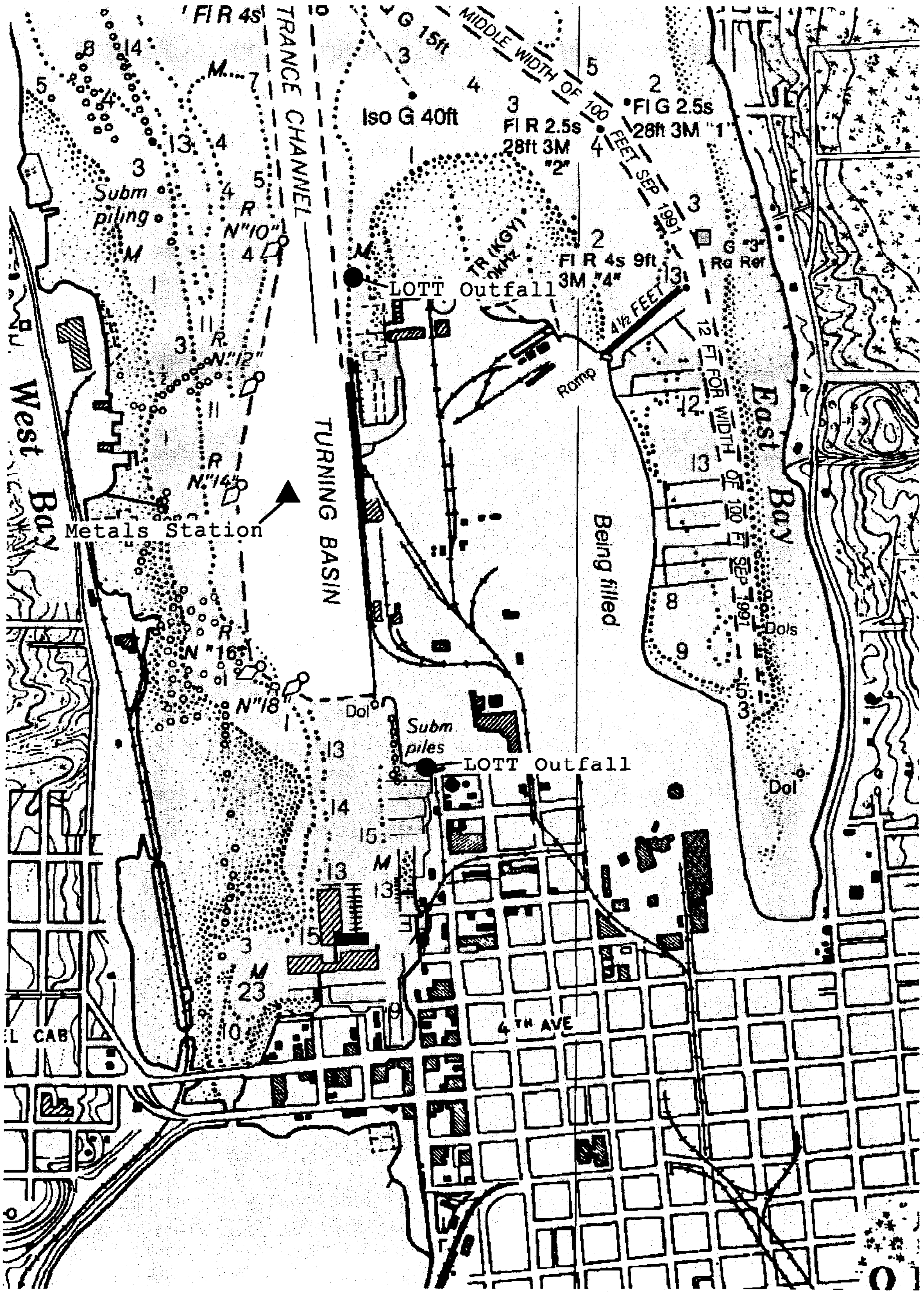

Figure 1a. Budd Inlet Station

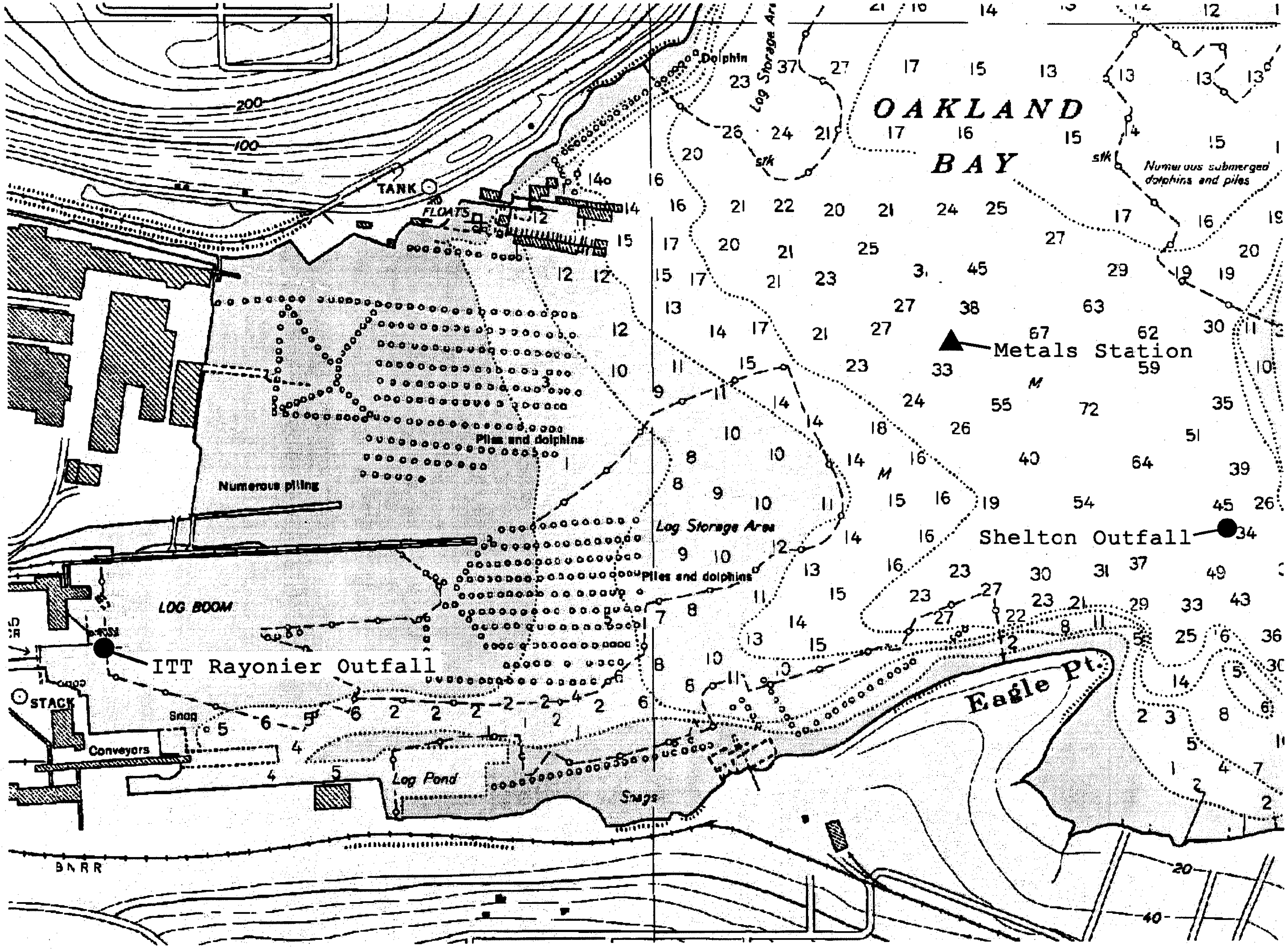

Figure 1b. Shelton Harbor Station

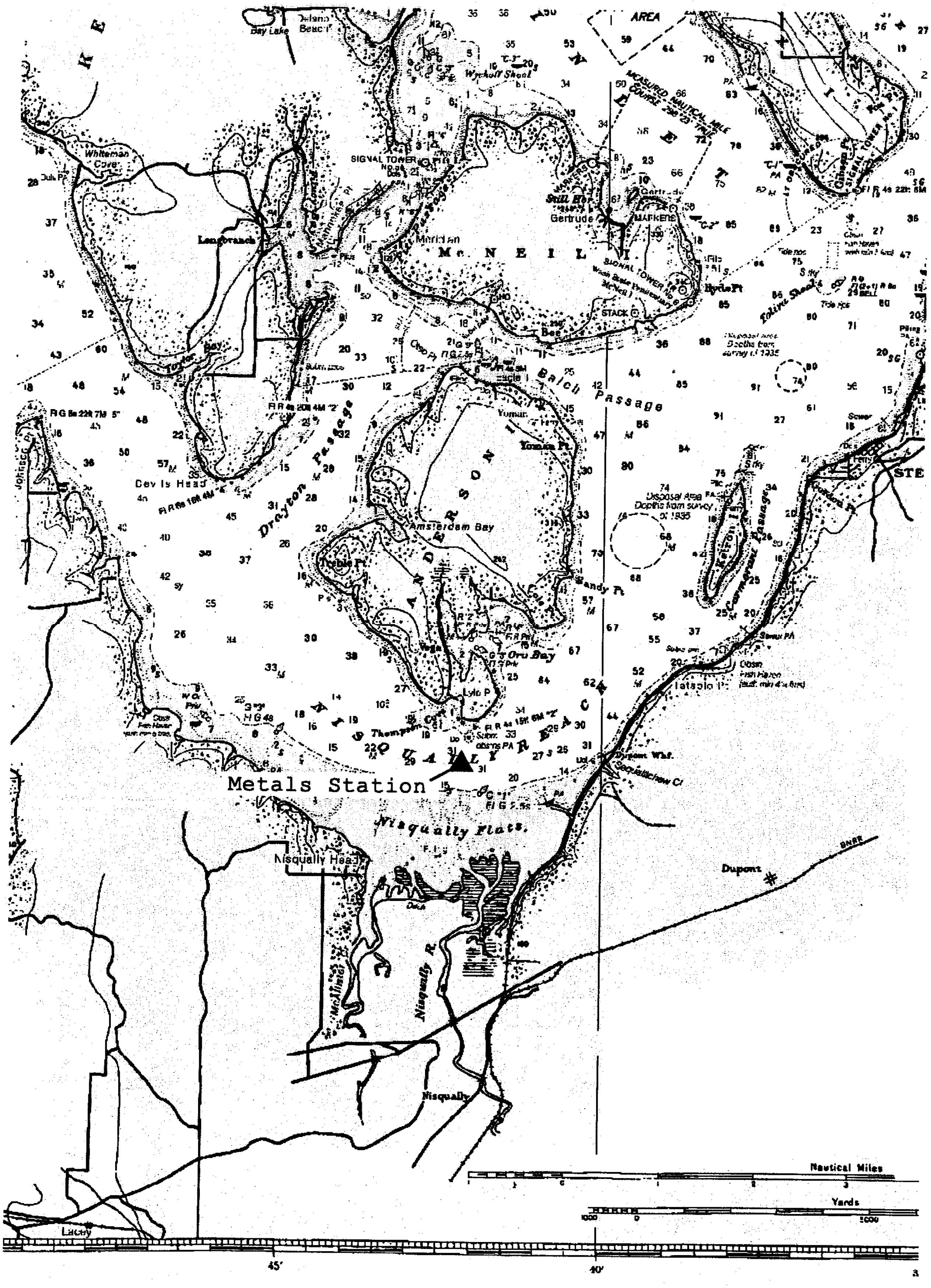

Figure 1c. Nisqually Reach Station

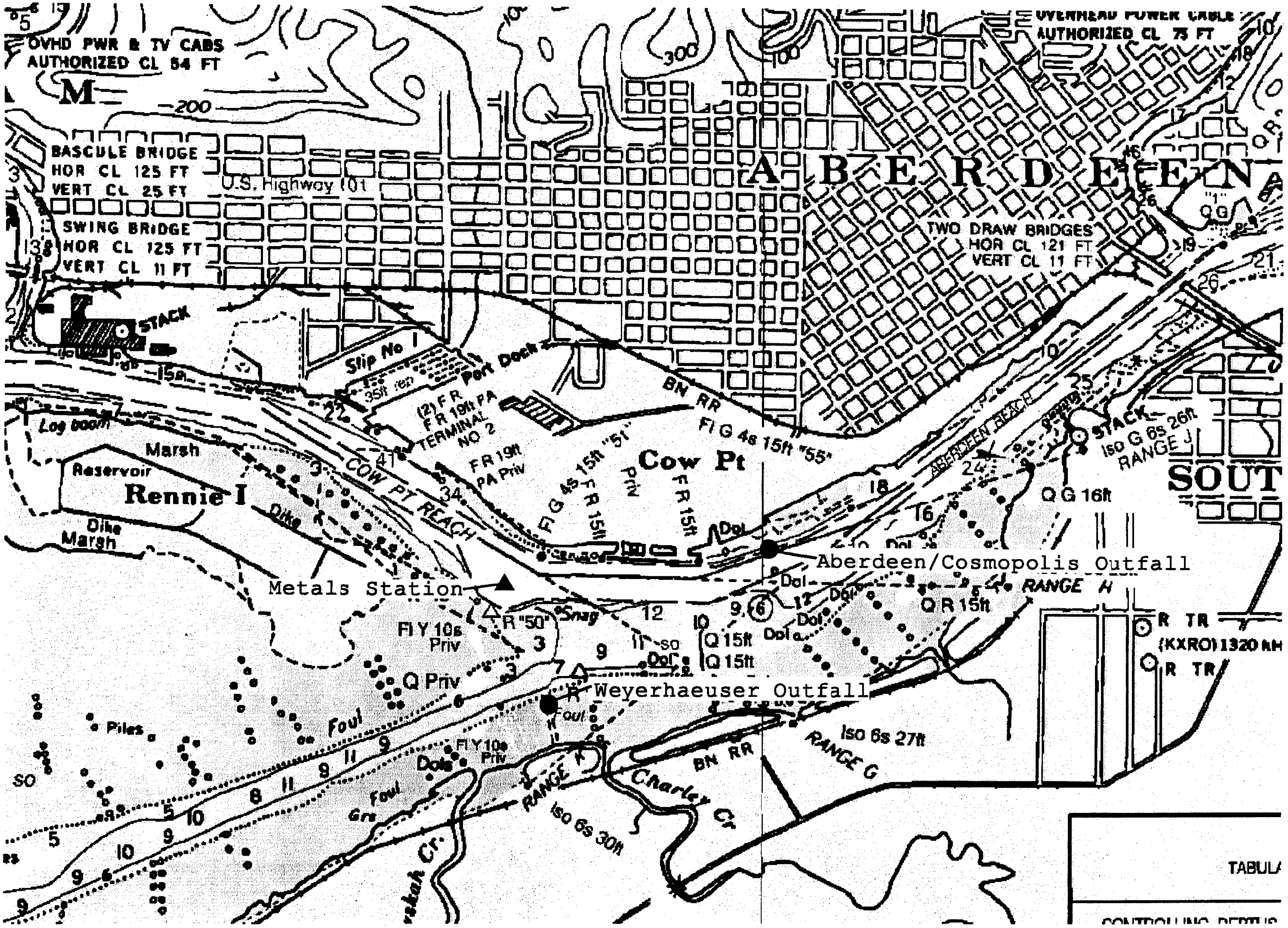

Figure 1d. Grays Harbor Station

To obtain data that represent a range of seasonal conditions, sampling will be conducted on five occasions between July 2000 and April 2001. In an effort to minimize variability due to tidal exchange, all sampling will be done during ebb, avoiding extremes in tide ranges (both spring and neap). Large storm events will also be avoided.

Surface and subsurface samples will be collected at all sites. Subsurface samples will be taken at a depth of approximately 25 feet (limit of pumping system). All samples will be analyzed for dissolved (0.45 micron filtered) and total recoverable cadmium, copper, lead, and zinc, and for total mercury. Ancillary parameters will include temperature, secchi depth, salinity, and total suspended solids (TSS).

Sampling techniques will follow the guidance in EPA (1995) *Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Levels.* Water samples will be collected with an all plastic/Teflon pumping system and in-line filter. The samples will be analyzed at the Ecology Manchester Environmental Laboratory by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Cold Vapor Atomic Adsorption (CVAA). Detection limits will be appropriate for quantifying background metals concentrations in Puget Sound.

Table 3 shows the number and type of samples to be collected and an estimate of the laboratory costs.

Table 3. Number of Samples and Laboratory Cost Estimate

Sample Type	Analysis	Stations or Samples	Sampling Events	Total Samples	Cost per Sample	Cost Subtotals
Field Samples*	Diss. Cd,Cu,Pb,Zn	8	5	40	170	6800
"	T.R. Cd,Cu,Pb,Zn	8	5	40	170	6800
"	Total Hg	8	5	40	48	1920
"	Salinity	8	5	40	10	400
"	TSS	8	5	40	10	400
Replicate Samples	Diss. Cd,Cu,Pb,Zn	1	5	5	170	850
"	T.R. Cd,Cu,Pb,Zn	1	5	5	170	850
"	Total Hg	1	5	5	48	240
"	Salinity	1	5	5	10	50
"	TSS	1	5	5	10	50
Filter/Pump Blanks	Cd,Cu,Pb,Zn	1	2	2	170	340
Bottle Blanks	Cd,Cu,Pb,Zn,Hg	1	2	2	218	436
Dup. Matrix Spikes	Cd,Cu,Pb,Zn,Hg	2	5	10	no charge	0
Std. Ref. Material	Cd,Cu,Pb,Zn,Hg	1	5	5	no charge	0
Method Blank	Dissolved Cd,Cu,Pb,Zn	1	5	5	no charge	0
Method Blank	T.R. Cd,Cu,Pb,Zn	1	5	5	no charge	0
Method Blank	Hg	1	5	5	no charge	0

+0.45 um capsule filters @$35 ea = 1645
+500 mL teflon bottles @$14 ea = 1316
+pump/tubing rental/cleaning @ $100 ea = 500

TOTAL LAB COST = 22597

*4 stations, 2 depths

Schedule

(exact sampling dates to be determined)

July 6-7, 2000............First sample collection
September 2000.........Second sample collection
November 2000.........Third sample collection
February 2001..........Fourth sample collection
April 2001...............Fifth sample collection
June 2001...............Laboratory analyses completed
August 2001............Draft project report
October 2001...........Final project report
December 2001.........Data entered into EIM

Project Organization

Lead - Art Johnson (360/407-6766)
Field Assistance - John Summers (360/407-7548)
Contaminant Studies Unit Supervisor - Dale Norton (360/6765)
Watershed Ecology Section Manager - Will Kendra (360/407-6698)
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Data Quality Objectives

Precision and Bias

Manchester's only previous experience in low-level metals analysis of seawater samples was for a 1997-98 EAP project in Commencement Bay (Johnson and Summers, 1999). The precision and bias Manchester achieved for copper, cadmium, lead, and zinc in these samples is shown in Table 4. The samples for the present project will be analyzed using an SOP prepared by Metro (see below). This SOP is more rigorous and should produce better data (Jim Ross, personal communication).

Mercury will be done by Manchester's standard low level procedure. Spike recovery is +/- 25%. Duplicate precision and LCS accuracy are +/-20% (Jim Ross, personal communication).

Table 4. Manchester 1997-98 Results on Seawater SRMs (ug/L)

	Copper	Cadmium	Lead	Zinc
		CASS-3		
Manchester Result	0.47	0.025	0.016	1.1
" "	0.44	0.023	0.019	2.3
" "	0.45	0.024	0.020	2.0
" "	0.53	0.026	0.060	1.5
Certified Value and	0.517	0.030	0.012	1.24
Range	+/-0.062	+/-0.005	+/-0.004	+/-0.25
Mean Recovery	92%	82%	240%	140%
		SLEW-1		
Manchester Result	1.42	0.016	0.030	0.92
" "	1.15	0.016	0.042	1.25
Certified Value and	1.76	0.018	0.028	0.86
Range	+/-0.09	+/-0.003	+/-0.007	+/-0.15
Mean Recovery	73%	89%	128%	126%

Sources of bias will be minimized by adherence to Method 1669 procedures for collection, preservation, transport, and storage of samples.

Representativeness

The sampling design is intended to give results that are representative of metals concentrations in the areas studied, within the limits of the available funding. Measures taken in the interest of obtaining representative data include locating sampling sites away from the immediate vicinity of sources, sampling at two depths five times during the year, and avoiding extremes in tidal conditions and runoff. The data may not be representative of water quality conditions during flooding or high tides.

Completeness

The amount of useable data obtained will be maximized by careful planning of field work, following EPA sampling guidance, and taking care in packaging and transport of samples. Manchester will save excess sample for 60 days from the time the data is sent to the project lead to give time for its review.

Comparability

Sampling, quality assurance, and analytical methods were selected to be consistent with other low-level metals studies on Puget Sound (Paulson et al., 1991a,b,c; Crecelius, 1998; Johnson and Summers, 1999).

Sampling Methods

Sampling methods will follow EPA Method 1669 and will be consistent with PSEP protocols (EPA, 1996). Chain of custody will be maintained.

Water samples will be collected using pre-cleaned Teflon tubing, a battery-operated peristaltic pump with pre-cleaned C-flex tubing for the pump head, and in-line 0.45 μm Gelman Aqua Prep 250 capsule filters. The intake will be weighted with a Teflon bottle filled with sand. Before samples are taken, the pumping system will be flushed with five volumes of site water. After the dissolved sample is taken, the filter will be removed for collecting a total recoverable metals and total mercury sample (two separate samples). Separate tubing will be used for surface and subsurface samples. Between stations, the system will be rinsed with a solution of 1-2% high-purity nitric acid.

Sampling will begin at the Nisqually Reach station, which is expected to have the lowest metals concentrations. Non-talc nitrile gloves will be worn by personnel collecting and filtering the samples. Sample containers for metals will be 500 mL Teflon bottles. Salinity and TSS samples will be collected in polyethylene bottles. Temperature will be measured with a long-line thermometer. Station positions will be recorded from a differentially-corrected GPS.

Each metals sample will be placed in double polyethylene bags and all samples will be held on blue ice for transport to Manchester Laboratory. The metals samples will be acidified to pH 2 at Manchester on receipt (within one day of collection), using high-purity nitric acid in a class 100 clean hood.

Teflon sample bottles will be supplied by Manchester, cleaned as described in Kammin et al. (1995) and sealed in plastic bags. The pumping system and filters will be obtained from the Battelle Marine Sciences Laboratory, cleaned and sealed in plastic bags as described in Method 1669.

Laboratory Methods

Metals analysis will be conducted by Manchester Laboratory. The samples will be held for at least two days following acidification before being analyzed.

Cadmium, copper, lead, and zinc will be preconcentrated by reductive co-precipitation following King County Environmental Laboratory SOP #06-03-006-000 *Preparation of Water Samples using Reductive Precipitation Preconcentration Technique for ICP-MS Analysis of Trace Metals in Seawate*r. Analysis will be by ICP-MS following EPA Method 200.8. Mercury will be analyzed by CVAA, EPA Method 245.7, modified for AA by Manchester. The addition of a chelating agent (DPPA) in the reductive co-precipitation procedure is the primary difference between the King County SOP and earlier methods used by Manchester for EAP's Commencement Bay study (Johnson and Summers, 1999).

The detection limits Manchester expects to achieve are shown in Table 5 and compared to background levels for Puget Sound. The detection limit for mercury may not be low enough to quantify mercury levels in all samples. An MDL of 0.0002 ug/L or lower may be achieved for mercury by CVAF/ EPA Method 1631, but is not an option at Manchester at this time.

Table 5. Manchester Detection Limits for Seawater Metals Analysis Compared to Puget Sound Background (ug/L)

Metal	MDL	Background*
Cadmium	0.005	0.04 - 0.09
Copper	0.01	0.1 - 0.4
Lead	0.005	0.02
Zinc	0.1 - 0.3	0.2 - 1.0
Mercury	0.002	0.0002 - 0.001

*from Johnson and Summers (1999)

Salinity and TSS will be analyzed at Manchester using routine methods.

Quality Control Procedures

Field QC samples will include bottle blanks, filter blanks, and field replicates.

The field blanks will be used to check for contamination arising from sample containers or the filtration procedure. Bottle blanks will consist of 500 mL Teflon bottles cleaned and filled with de-ionized (DI) water at Manchester Laboratory, as previously described. Filter blanks were prepared by filtering the contents of a DI-filled Teflon bottle. Field blanks will be analyzed for the July and February sample collections.

The total variability (field + laboratory) of the data for this project will be assessed by collecting samples in replicate. The replicates will consist of two separate sets of samples collected approximately five minutes apart. All of the Budd Inlet surface water samples will be collected in replicate.

A certified seawater standard reference material (SRM), CASS-3 or equivalent, will be analyzed with each sample set. CASS-3 is certified for cadmium, copper, lead, zinc, and other metals, not including mercury. Before running any project samples, Manchester will analyze copper, cadmium, lead, and zinc in the SRM they have selected and report the results to the project lead.

If available, a seawater or freshwater SRM for mercury, certified at a low level, will also be analyzed. If not, Manchester will analyze with each sample set a laboratory control sample consisting of a 0.025 ug/L or lower dilution of a second source stock standard.

One pair of matrix spikes and matrix spike duplicates will be analyzed with each sample set. A separate sample will be collected and labeled for that purpose. The concentrations spiked should be within 1-10X the concentrations in the field samples in order to be useful for estimating bias due to interference.

All QC samples (SRMs, MS/MSDs, and blanks) will be taken through the reductive co-precipitation preconcentration procedure to control the accuracy of the entire analysis.

Data Assessment Procedures and Reporting

Manchester's SOP for data reduction, review, and reporting will meet the needs of this project. Each laboratory unit assembles data packages consisting of raw data from the analyses of the samples, copies of the pertinent logbook sheets, QA/QC data, and final reports of data entered into LIMS. These data packages are subjected to a data verification and quality assurance review by another analyst familiar with the procedure. Reviewers use *Laboratory Data Validation National Functional Guidelines for Evaluating Inorganic Analyses* (EPA, 1988).

The following additional information will be reported for the metals data: 1) the name, source, and certified values for SRMs analyzed; 2) the metals concentrations measured in the SRM (in addition to percent recovery); and 3) the spiking levels used in matrix spikes.

The project lead will prepare a draft report of the overall study by August 2001. The report will contain:

- a map of the study area showing sampling sites
- latitude/longitude and other location information for each sampling site
- descriptions of field and laboratory methods
- a discussion of data quality, estimates of precision and bias, and the significance of any problems encountered in the analyses
- summary tables of the metals and ancillary data
- an evaluation of significant findings with respect to exceedances of standards, differences within and between sampling sites, dissolved vs. total recoverable metals, comparison with other data on Puget Sound, and additional data interpretation as appropriate
- recommendations for follow-up work if warranted.

A final report will be prepared after receiving review comments from SWRO and EAP. The goal is to have the revised final report on or before October 2001. The data will be entered into Ecology's Environmental Information Management (EIM) system by December 2001.

References

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