

# **PTI**

**ENVIRONMENTAL SERVICES**

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## **Puget Sound Dredged Disposal Analysis**

### **BASELINE SURVEY OF PHASE II DISPOSAL SITES**

**APPENDIX D  
Quality Assurance/  
Quality Control Reports**

For

**Washington Department of Ecology  
Olympia, Washington**

June 1989

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**PTI** Environmental Services  
15375 SE 30th Place  
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**PUGET SOUND DREDGED DISPOSAL ANALYSIS  
BASELINE SURVEY OF PHASE II DISPOSAL SITES**

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For  
Washington Department of Ecology  
Olympia, Washington 98504-8711

Ecology Contract C0089128  
PTI Contract C878-04

June 1989

**APPENDIX D**

**QUALITY ASSURANCE/QUALITY  
CONTROL REPORTS**



## CONTENTS

	<u>Page</u>
LIST OF TABLES	D-vi
ANALYSIS OF ACID/BASE/NEUTRAL ORGANIC COMPOUNDS IN SEDIMENTS	D-1
SUMMARY	D-1
SAMPLE COLLECTION: ACCEPTABLE	D-1
SHIPPING AND HOLDING TIMES: ACCEPTABLE	D-1
COMPLETENESS: ACCEPTABLE	D-2
ANALYTICAL METHODS: ACCEPTABLE	D-2
Calibration	D-2
Detection Limits	D-3
Compound Confirmation	D-3
ACCURACY: ACCEPTABLE	D-3
Sediment Reference Materials	D-4
Surrogate Recoveries	D-4
PRECISION: ACCEPTABLE	D-4
BLANKS: ACCEPTABLE	D-9
DATA REPORTING: ACCEPTABLE	D-9
ANALYSIS OF ACID/BASE/NEUTRAL ORGANIC COMPOUNDS IN TISSUE	D-11
SUMMARY	D-11
SAMPLE COLLECTION: ACCEPTABLE	D-11
SHIPPING AND HOLDING TIMES: ACCEPTABLE	D-11
COMPLETENESS: ACCEPTABLE	D-11
ANALYTICAL METHODS: ACCEPTABLE	D-12
Calibration	D-12
Detection Limits	D-13
Compound Confirmation	D-13
ACCURACY: ACCEPTABLE	D-13
Internal Standard Recoveries	D-13
PRECISION: ACCEPTABLE	D-15
BLANKS: ACCEPTABLE	D-15

	<u>Page</u>
ANALYSIS OF PCB/PESTICIDES IN SEDIMENTS	D-16
SUMMARY	D-16
SAMPLE COLLECTION: ACCEPTABLE	D-16
SAMPLE TRANSPORT AND HOLDING TIMES: ACCEPTABLE	D-16
COMPLETENESS: ACCEPTABLE	D-16
ANALYTICAL METHODS: ACCEPTABLE	D-17
Calibration	D-17
Detection Limits	D-17
Compound Confirmation	D-18
ACCURACY: ACCEPTABLE	D-18
Sediment Reference Material	D-18
Pesticide Matrix Spikes	D-18
Surrogate Recoveries	D-20
PRECISION: ACCEPTABLE	D-20
BLANKS: ACCEPTABLE	D-20
ANALYSIS OF PCB/PESTICIDES IN TISSUE	D-22
SUMMARY	D-22
SAMPLE COLLECTION: ACCEPTABLE	D-22
SAMPLE TRANSPORT AND HOLDING TIMES: ACCEPTABLE	D-22
COMPLETENESS: ACCEPTABLE	D-22
ANALYTICAL METHODS: ACCEPTABLE	D-23
Calibration	D-23
Detection Limits	D-23
ACCURACY: ACCEPTABLE	D-24
Pesticide Matrix Spike	D-24
Internal Standard Recoveries	D-24
PRECISION: ACCEPTABLE	D-24
BLANKS: ACCEPTABLE	D-24
ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN SEDIMENTS	D-26
SUMMARY	D-26
SAMPLE COLLECTION: ACCEPTABLE	D-26
SHIPPING AND HOLDING TIMES: ACCEPTABLE	D-26

	<u>Page</u>
COMPLETENESS: ACCEPTABLE	D-26
ANALYTICAL METHODS: ACCEPTABLE	D-26
Detection Limits	D-27
Calibration	D-27
Compound Confirmation	D-27
ACCURACY: ACCEPTABLE	D-27
Surrogate Compounds	D-27
Matrix Spikes	D-27
PRECISION: ACCEPTABLE	D-30
BLANKS: ACCEPTABLE	D-30
ANALYSIS OF TRACE METALS IN SEDIMENTS AND TISSUE	D-31
SUMMARY	D-31
Sediment	D-31
Tissue	D-31
SAMPLE COLLECTION AND TRANSPORT	D-31
Sediment	D-31
Tissue	D-31
COMPLETENESS: ACCEPTABLE	D-32
DATA REPORTING	D-32
Sediment	D-32
Tissue	D-32
ANALYTICAL METHODS: ACCEPTABLE	D-32
Sediment	D-32
Tissue	D-33
CALIBRATION	D-33
Sediment	D-33
Tissue	D-34
DETECTION LIMITS	D-34
Sediment	D-34
Tissue	D-34
ACCURACY	D-35
Sediment	D-35
Tissue	D-35
PRECISION	D-35
Sediment	D-35
Tissue	D-39

	<u>Page</u>
BLANKS	D-39
Sediment	D-39
Tissue	D-39
ANALYSIS OF TRIBUTYLTIN IN SEDIMENTS	D-42
SUMMARY	D-42
SAMPLE COLLECTION: ACCEPTABLE	D-42
SHIPPING AND HOLDING TIMES: ACCEPTABLE	D-42
COMPLETENESS: ACCEPTABLE	D-42
ANALYTICAL METHODS: ACCEPTABLE	D-43
Calibration	D-43
Detection Limits	D-43
Compound Confirmation	D-43
ACCURACY: ACCEPTABLE	D-45
Sediment Reference Material	D-45
Matrix Spikes	D-45
Surrogate Recoveries	D-45
PRECISION: ACCEPTABLE	D-46
BLANKS: ACCEPTABLE	D-46
ANALYSIS OF CONVENTIONAL VARIABLES IN SEDIMENTS	D-48
SUMMARY	D-48
SAMPLE COLLECTION AND TRANSPORT	D-48
COMPLETENESS: ACCEPTABLE	D-48
DATA REPORTING	D-48
ANALYTICAL METHODS: ACCEPTABLE	D-49
CALIBRATION: ACCEPTABLE	D-49
DETECTION LIMITS: ACCEPTABLE	D-49
ACCURACY: ACCEPTABLE	D-50
PRECISION: ACCEPTABLE	D-50
BLANKS: ACCEPTABLE	D-50
ANALYSIS OF PARTICLE SIZE DISTRIBUTION IN SEDIMENTS	D-52
SUMMARY	D-52
SAMPLE COLLECTION AND TRANSPORT	D-52

	<u>Page</u>
COMPLETENESS	D-52
DATA REPORTING	D-52
ANALYTICAL METHODS	D-52
ACCURACY	D-52
PRECISION	D-53
AMPHIPOD MORTALITY BIOASSAY	D-55
NEGATIVE CONTROL	D-55
POSITIVE CONTROL	D-55
WATER QUALITY CONDITIONS	D-55
RESPONSE VARIABILITY	D-56
BIVALVE LARVAE ABNORMALITY BIOASSAY	D-57
NEGATIVE CONTROL	D-57
POSITIVE CONTROL	D-57
WATER QUALITY CONDITIONS	D-57
MICROTOX BIOASSAY	D-58
NEGATIVE CONTROL	D-58
POSITIVE CONTROL	D-58
BENTHIC MACROINVERTEBRATES	D-59
SORTING EFFICIENCY	D-59
TOTAL COUNTS	D-59
REFERENCES	D-62



## LIST OF TABLES

	<u>Page</u>
Table D-1. Results for sediment reference material	D-5
Table D-2. Recoveries for selected A/B/N surrogates	D-6
Table D-3. Precision for A/B/N compounds in sediments (without correction for surrogate recovery)	D-7
Table D-4. Precision for A/B/N compounds in sediments (with correction for surrogate recovery)	D-8
Table D-5. Concentrations of A/B/N compounds found in method blanks	D-10
Table D-6. Recoveries for selected A/B/N internal standard	D-14
Table D-7. Pesticide matrix spike recoveries in sediments	D-19
Table D-8. PCB/pesticide surrogate recoveries	D-21
Table D-9. PCB/pesticide internal standard recoveries	D-25
Table D-10. Volatile organic surrogate recoveries	D-28
Table D-11. Results for matrix spikes of volatile organic compounds	D-29
Table D-12. Metals recovery results for sediment digests	D-36
Table D-13. Metals recovery results for tissue digests	D-37
Table D-14. Results of sediment replicate analyses	D-38
Table D-15. Results of tissue replicate analyses	D-40
Table D-16. Averages, standard deviations, and ranges of TBT ions in standards and sediments	D-44
Table D-17. TPT surrogate recoveries	D-47
Table D-18. Replicate results for conventional analyses	D-51
Table D-19. Replicate results for particle size analyses	D-54
Table D-20. Coefficients of variation for abundances of major taxa	D-61



## ANALYSIS OF ACID/BASE/NEUTRAL ORGANIC COMPOUNDS IN SEDIMENTS

### SUMMARY

Overall, these data were acceptable as qualified. However, some data for hexachloroethane was rejected due to zero surrogate recovery. Estimate (*E*) qualifiers were assigned to data for one or more of the following reasons: 1) values were reported at levels below the lower range of the calibration standards (1 ng on-column), 2) Puget Sound Estuary Program (PSEP) control limits for calibration were exceeded (such exceedances applied primarily to benzoic acid and the benzo-fluoranthenes), and 3) mass spectral interferences or absence of some of the secondary ions for compounds reported at relatively low concentrations were judged to produce some uncertainty in the quantified result. The data were blank-corrected and qualified with either *B* or *Z* (i.e., blank-corrected down to the detection limit and blank-corrected still above the detection limit, respectively).

### SAMPLE COLLECTION: ACCEPTABLE

Details of sediment sampling are given in Appendix A and are summarized in this section. Sediment samples were collected between April 11 and May 4, 1989 with a dual 0.1-m<sup>2</sup> van Veen grab sampler. Sample depths were 10 cm at the disposal zone and 2 cm at all other stations (i.e., perimeter, benchmark, and reference). Each sample was formed of material composited from a minimum of six grabs.

Acceptability of grab samples was evaluated in accordance with criteria specified by PSEP (1986). Grab samples failing to meet PSEP criteria were excluded from compositing. After a grab sample was judged to be acceptable, the overlying water was siphoned off and the sample was collected with stainless steel spatulas according to PSEP recommendations. Grab samples for each station were homogenized in a stainless steel bowl with stainless steel spoons until uniform color and texture were apparent. Sediment was then transferred to the appropriate sample container (discussed in detail in Appendix A) and stored on ice. Cleaning of sampling equipment is described in Appendix A. Chain-of-custody records were completed at the end of each day.

### SHIPPING AND HOLDING TIMES: ACCEPTABLE

Samples were shipped on ice to Analytical Resources, Inc. (ARI) (Seattle, Washington). Sample holding times were well within the PSEP control limit of 1 year for frozen sediments (PSEP 1986). Instrumental gas chromatography/mass spectrometry (GC/MS) analyses were conducted between May 15 and June 29, 1988; the PSEP extract holding time control limit of 40 days was not exceeded for any samples.

## COMPLETENESS: ACCEPTABLE

Results for all 15 samples submitted to the laboratory were provided, as well as results for 1 duplicate, 3 method blanks, and 2 sediment reference materials. Additional materials were requested from the laboratory (e.g., revised calculations, 5-point initial calibration) and were provided.

## ANALYTICAL METHODS: ACCEPTABLE

Samples were analyzed by a modified version of U.S. Environmental Protection Agency Contract Laboratory Program (EPA/CLP) procedures for low-level analysis of sediments/soils. Modifications of routine CLP procedures included the following:

- Larger sample size was used to improve detection limits (i.e., 100 grams wet weight when sufficient material was available, instead of 30 grams as specified by the CLP).
- Gel permeation chromatography (GPC) was required to reduce interferences and improve detection limits (GPC is optional under the CLP).
- Final extract volume of 500  $\mu\text{L}$  was required to improve detection limits (1.0 L is required under CLP).
- Stable isotope-labeled surrogates of all but five target compounds were added to all samples to provide extensive quality assurance (QA) information on analytical recovery and to allow for compound-specific recovery corrections.

Sediment samples were mixed with anhydrous sodium sulfate, spiked with 35 stable isotope-labeled surrogates of acid/base/neutral (A/B/N) target compounds, and sonicated in a 1:1 mixture of methylene chloride/acetone. Extracts were subjected to GPC cleanup and concentrated to a final volume of 500  $\mu\text{L}$ . Extracts were analyzed by GC/MS with a fused silica capillary column (DB-5, 30 meter, 0.25 mm i.d., manufactured by J & W Scientific) with the following temperature programming: 40° C (held 4 minutes), heated at 8° C/minute to 310° C. The injector and detector temperatures were 270° C and 375° C, respectively.

### Calibration

An initial 5-point calibration was performed with solutions of 1, 10, 40, 80, and 120 ng/ $\mu\text{L}$  (except for benzyl alcohol and benzoic acid, which were not calibrated at 1 ng/ $\mu\text{L}$ ). Under CLP, the lowest calibration concentration is 20 ng/ $\mu\text{L}$ . Initial results provided by the laboratory were based on a 4-point calibration that excluded the 1 ng/ $\mu\text{L}$  standard. The percent relative standard deviation (percent RSD) for this 4-point calibration exceeded the  $\pm 20$  percent PSEP control limit for benzoic acid (30.5 percent RSD) only. Upon request the laboratory provided a 5-point initial calibration including the 1 ng/ $\mu\text{L}$  standard (except for benzyl alcohol and benzoic acid), which was also analyzed at the same time as the 10, 40, 80, and 120 ng/ $\mu\text{L}$  standards. The addition of the 1 ng/ $\mu\text{L}$  standard caused all of the high molecular weight polycyclic aromatic hydrocarbons (PAH) to exceed the  $\pm 20$  percent PSEP control limit (and the less stringent  $\pm 30$  percent control limit of EPA/CLP). Hence, the range between 1 and 10 ng/ $\mu\text{L}$  was not considered co-linear with the 4-point calibration for these compounds.

Concentrations of analytes that were below the linear range of the 4-point calibration were slightly overestimated. This overestimation resulted from the mass selective detector exhibiting a higher sensitivity for the 1 ng/ $\mu$ L standard. It is not known why the detector response was higher at lower concentrations of analytes (i.e., a proportionately higher peak height). The data reported below the linear range of the 4-point calibration (without the 1 ng/ $\mu$ L standard) were recalculated using the response factor from the line determined by the 1 and 10 ng/ $\mu$ L standards. The recalculated value was generally <10 percent coefficient of variation (CV); therefore the data were accepted.

Ongoing calibration was performed daily with a 50 ng/ $\mu$ L standard. The PSEP control limit for ongoing calibration, a relative percent difference (RPD) of 25 percent, was exceeded occasionally (i.e., for phenol, benzyl alcohol, benzoic acid, 2-methylnaphthalene, and dimethyl phthalate). Data for which the ongoing calibration exceeded this control limit was qualified with *E*.

GC/MS tuning with decafluorotriphenylphosphine (DFTPP) was conducted according to EPA/CLP and PSEP guidelines.

### Detection Limits

Reported detection limits were based on an extrapolation of instrumental response for a 1 ng/ $\mu$ L standard on-column except for benzyl alcohol and benzoic acid, which were based on injection of a 10 ng/ $\mu$ L standard. Sample detection limits were then calculated by accounting for sample weight, final extract volume, and injection volume. Detection limits ranged from 5 to 17  $\mu$ g/kg dry weight (and approximately 10 times higher for benzyl alcohol and benzoic acid). Detection limits were considered acceptable as reported by the laboratory. The ultimate sensitivity of the instrument was likely better than 1 ng/ $\mu$ L for many compounds, but the analytical recovery of most compounds was also generally <100 percent.

### Compound Confirmation

Mass spectra for all detected compounds were examined during QA review. In some cases, compounds reported as detected by the laboratory were reclassified as undetected because of inconclusive spectra. In particular, butyl benzyl phthalate originally reported at concentrations in the range of detection limits was reclassified as undetected. In addition, *E* qualifiers were assigned to some A/B/N compounds reported at relatively low concentrations when mass spectral interferences were judged to produce some uncertainty in the quantified result, although the interferences were not sufficient to cause rejection of the data.

### ACCURACY: ACCEPTABLE

Accuracy was assessed with sediment reference materials and recoveries of stable isotope-labeled surrogates. As noted in the PSEP protocols, matrix spike samples are not required when the isotope dilution technique is used.

## Sediment Reference Materials

There are no certified reference materials available for organic compounds in marine sediments. However, a locally available reference material was analyzed, which contained low to moderate concentrations of PAH and other compounds [i.e., Sequim-1, developed by National Oceanic and Atmospheric Administration/National Marine Fisheries Service (NOAA/NMFS)]. Because the reference material is not certified, PSEP control limits (the 95 percent confidence interval of certified values) are not strictly applicable to the results. Therefore, reference material data were assessed relative to the 50 percent control limit applicable to surrogate and matrix spike recoveries.

Results of the two sediment reference materials are shown in Table D-1 along with the values reported by NOAA. Only compounds reported as detected by NOAA are included in Table D-1. The data have been recovery-corrected. The 50 percent control limit is exceeded by 2-methylnaphthalene, benzo(a)pyrene, benzo(b+k)fluoranthene, indeno(1,2,3-cd)pyrene, phenol, 4-methylphenol, and bis(2-ethylhexyl)phthalate. As noted in Table D-1, except for the results for 2-methylnaphthalene and benzo(a)pyrene, the NOAA results were based on analysis of one sample only. The laboratory results for the sediment reference material are considered acceptable because the results for 2-methylnaphthalene and benzo(a)pyrene were near the 50 percent control limit (49 and 47 percent, respectively) and the material is not certified.

## Surrogate Recoveries

Stable isotope surrogates were added for all but four of the target A/B/N compounds (2-methylnaphthalene, dibenzofuran, benzyl alcohol, and benzoic acid). Recoveries of 11 of the 35 added surrogates are summarized in Table D-2. These compounds were chosen because they represent a wide range of compound classes (e.g., phenols, low and high molecular weight PAH, chlorinated benzenes, phthalates, organonitrogen compounds).

PSEP control limits for surrogate recoveries are 50 percent (when the isotope dilution technique is not used) and 10 percent (when the isotope dilution technique is used). Surrogate recoveries were typically >50 percent in Puget Sound Dredged Disposal Analysis (PSDDA) samples. Hexachloroethane was the only compound exhibiting surrogate recoveries below the 10 percent control limit (7 samples <10 percent; 5 samples with zero recovery). Samples with zero recovery were rejected, while the detection limits of the other two hexachloroethane results were qualified as *E* and are likely underestimates.

## PRECISION: ACCEPTABLE

One analytical duplicate was analyzed with this data set to assess precision. The results are shown in Table D-3 (data that has not been recovery-corrected) and Table D-4 (data that has been recovery-corrected). The sample analyzed in duplicate was not a PSDDA sample, but it was analyzed at the same time as the PSDDA samples.

Based on data without recovery-corrections, the PSEP control limit of  $\pm 100$  percent RPD was exceeded in one case. For data with recovery-corrections applied, the PSEP control limit was not exceeded. In general, comparison of Tables D-3 and D-4 reveals better precision for recovery-corrected data, except when the concentrations are near the detection limits.

TABLE D-1. RESULTS FOR SEDIMENT REFERENCE MATERIAL  
(concentrations in  $\mu\text{g}/\text{kg}$  dry weight)

Compound	PSDDA 2		NOAA Value <sup>c</sup>	Recovery (%)
	$\bar{x}(n=2)^a$	RPD <sup>b</sup>		
Naphthalene	60	0	98	61
2-Methylnaphthalene	63	-14	130	49
Acenaphthene	73	-5.5	120	61
Fluorene	66	-4.6	120	55
Phenanthrene	90	4.5	130	69
Anthracene	74	5.4	100	74
Fluoranthene	84	1.2	130	65
Pyrene	72	-1.4	110	66
Benz(a)anthracene	62	-9.7	110	56
Chrysene	85	-2.4	150	57
Benzo(a)pyrene	61	1.7	130	47
Dibenz(a,h)anthracene	66	-6.1	74	89
Acenaphthylene <sup>d</sup>	38	-19	40	95
Benzo(a)fluoranthene <sup>d</sup>	68	29	150	45
Indeno(1,2,3-cd)pyrene <sup>d</sup>	12	-8.7	7.0	171
Benzo(g,h,i)perylene <sup>d</sup>	58	-3.4	94	62
Phenol <sup>d</sup>	120	-17	270	44
4-Methylphenol <sup>d</sup>	120	-33	440	27
Diethyl phthalate <sup>d</sup>	L3.4 <sup>e</sup>	L9.0	2	--
Butyl benzyl phthalate <sup>d</sup>	L3.4 <sup>e</sup>	L9.0	3	--
Bis(2-ethylhexyl)phthalate <sup>d</sup>	56	5.4	150	37
Di-n-octyl phthalate <sup>d</sup>	L3.4 <sup>e</sup>	L9.0	0.5	--

<sup>a</sup> Mean based on duplicate analyses.

<sup>b</sup> Relative percent difference for duplicate analysis.

<sup>c</sup> Value reported by NOAA based on 12 analyses unless otherwise noted.

<sup>d</sup> Results of only one analysis were reported by NOAA. Phthalate values were not blank-corrected by NOAA.

<sup>e</sup> L = Less than; (the average included detection limits).

TABLE D-2. RECOVERIES FOR SELECTED A/B/N SURROGATES

	Stations																	SQ1 Duplicate
	AKB02	AKP01	AKP02	AKP03	AKP04	AKZ01	CRR01	BBB01	BBB02	BBB04	BBP01	BBP02	BBP03	BBP04	BBZ01	SQ1		
Phenol	45	79	55	60	52	51	56	76	79	80	77	58	58	60	50	81	75	
1,4-Dichlorobenzene	36	52	39	50	41	42	42	69	54	37	57	31	44	39	36	44	26	
4-Methylphenol	57	76	56	60	62	56	66	80	87	91	82	66	69	77	68	77	75	
Naphthalene	47	72	50	60	54	51	54	83	73	67	70	52	60	74	52	72	61	
Dimethylphthalate	69	71	81	65	77	68	71	101	121	102	99	96	105	118	104	103	108	
Fluorene	72	70	67	68	75	69	71	90	98	98	97	91	89	108	97	102	107	
N-nitrosodiphenylamine	71	70	68	68	78	72	75	89	85	96	97	98	91	132	100	97	107	
Pentachlorophenol	48	41	37	43	66	32	48	98	45	83	88	92	82	78	100	106	123	
Phenanthrene	82	73	74	67	90	49	67	92	93	86	102	75	69	123	93	101	111	
Bis(2-ethylhexyl)phthalate	82	72	53	60	56	60	63	94	85	68	70	786	82	106	95	60	60	
Chrysene	75	79	55	62	70	59	69	83	79	70	74	82	90	109	93	78	79	

TABLE D-3. PRECISION FOR A/B/N COMPOUNDS IN SEDIMENT  
(WITHOUT CORRECTION FOR SURROGATE RECOVERY)

CAS Number	Compound	Sample Number <sup>a</sup>				%RSD <sup>b</sup>
		BBD NR (Uncorrected)		BBD NR Duplicate (Uncorrected)		
		µg/kg	Recovery (%)	µg/kg	Recovery (%)	
108-95-2	Phenol	21U	52.9	19U	88.0	--
541-73-1	1,3-Dichlorobenzene	10U	46.0	9.3U	55.3	--
106-46-7	1,4-Dichlorobenzene	10U	48.1	9.3U	59.5	--
100-51-6	Benzyl alcohol	51U	IS	47U	IS	--
95-50-1	1,1-Dichlorobenzene	10U	49.5	9.3U	58.9	--
95-48-7	2-Methylphenol	10U	73.3	9.3U	82.3	--
106-44-5	4-Methylphenol	27E	73.3	25E	82.3	7.7
67-72-1	Hexachloroethane	21UC	11.4	19UC	13.0	--
105-67-9	2,4-Dimethylphenol	21UC	77.0	19UC	88.6	--
65-85-0	Benzoic acid	100U	IS	90U	IS	--
120-82-1	1,2,4-Trichlorobenzene	10U	65.4	9.3U	65.2	--
91-20-3	Naphthalene	20	66.1	24	73.2	-18
87-68-3	Hexachlorobutadiene	11U	74.0	10U	73.7	--
91-57-6	2-Methylnaphthalene	6.4E	IS	9.2E	IS	-36
131-11-3	Dimethylphthalate	10U	81	9.3U	101	--
208-96-8	Acenaphthylene	2.9E	73.5	7.0E	91.8	-83
83-32-9	Acenaphthene	10U	77.1	9.3U	91.4	--
132-64-9	Dibenzofuran	10U	IS	9.3U	IS	--
84-66-2	Diethylphthalate	8.2E	76.3	8.8E	97.1	-7.1
86-73-7	Fluorene	3.1E	78.3	6.5E	90.0	-71
86-30-6	N-Nitrosodiphenylamine(1)	10U	81.2	9.3U	96.6	--
118-74-1	Hexachlorobenzene	10U	87.5	9.3U	100	--
87-86-5	Pentachlorophenol	17U	68.8	15U	90.1	--
85-01-8	Phenanthrene	36	76.4	65	86.1	-57
120-12-7	Anthracene	10	65.3	21	72.3	-71
84-74-2	Di-n-butylphthalate	10U	75.6	9.3U	80.2	--
206-44-0	Fluoranthene	170	208	51	59.9	110
129-00-0	Pyrene	180	204	68	61.4	90
85-68-7	Butylbenzylphthalate	10U	183	9.3U	67.0	--
56-55-3	Benzo(a)anthracene	59	161	37	79.2	46
117-81-7	Bis(2-ethylhexyl)phthalate	40B	151	19B	63.6	71
218-01-9	Chrysene	65	183	37	65.4	55
117-84-0	Di-n-octyl phthalate	10U	93.4	9.3U	70.2	--
205-99-2	Benzo(b)fluoranthene					
207-08-9	Benzo(k)fluoranthene	46	99.2	84	106	-59
50-32-8	Benzo(a)pyrene	16	84.1	43	121	-92
193-39-5	Indeno(1,2,3,-cd)pyrene	10U	43.4	25E	177	--
53-70-3	Dibenz(a,h)anthracene	10U	43.4	9.3U	177	--
191-24-2	Benzo(ghi)perylene	10U	24.7	23E	136	--

<sup>a</sup> Qualifiers:

- U - undetected at detection limit shown
- E - estimated value
- B - blank-corrected down to detection limit
- C - combined with unresolved substances.

<sup>b</sup> Relative standard deviation.

TABLE D-4. PRECISION FOR A/B/N COMPOUNDS IN SEDIMENTS  
(WITH CORRECTION FOR SURROGATE RECOVERY)

CAS Number	Compound	Sample Number <sup>a</sup>				%RSD <sup>b</sup>
		BBD NR (Uncorrected)		BBD NR Duplicate (Uncorrected)		
		µg/kg	Recovery (%)	µg/kg	Recovery (%)	
108-95-2	Phenol	21U	52.9	19U	88.0	--
541-73-1	1,3-Dichlorobenzene	10U	46.0	9.3U	55.3	--
106-46-7	1,4-Dichlorobenzene	10U	48.1	9.3U	59.5	--
100-51-6	Benzyl alcohol	100U	IS	90U	IS	11
95-50-1	1,1-Dichlorobenzene	10U	49.5	9.3U	58.9	--
95-48-7	2-Methylphenol	10U	73.3	9.3U	82.3	--
106-44-5	4-Methylphenol	37E	73.3	31E	82.3	18
67-72-1	Hexachloroethane	21UC	11.4	19UC	13.0	--
105-67-9	2,4-Dimethylphenol	21UC	77.0	19UC	88.6	--
65-85-0	Benzoic acid	100U	IS	90U	IS	--
120-82-1	1,2,4-Trichlorobenzene	10U	65.4	9.3U	65.2	--
91-20-3	Naphthalene	30	66.1	32	73.2	6.5
87-68-3	Hexachlorobutadiene	11U	74.0	10U	73.7	--
91-57-6	2-Methylnaphthalene	10E	IS	13E	IS	-26
131-11-3	Dimethylphthalate	10U	81	9.3U	101	--
208-96-8	Acenaphthylene	4E	73.5	8E	91.8	-67
83-32-9	Acenaphthene	10U	77.1	9.3U	91.4	--
132-64-9	Dibenzofuran	10U	IS	9.3U	IS	--
84-66-2	Diethylphthalate	11E	76.3	9E	97.1	20
86-73-7	Fluorene	4E	78.3	7E	90.0	-55
86-30-6	N-Nitrosodiphenylamine(1)	10U	81.2	9.3U	96.6	--
118-74-1	Hexachlorobenzene	10U	87.5	9.3U	100	--
87-86-5	Pentachlorophenol	17U	68.8	15U	90.1	--
85-01-8	Phenanthrene	47	76.4	75	86.1	-46
120-12-7	Anthracene	16E	65.3	29	72.3	-58
84-74-2	Di-n-butylphthalate	10U	75.6	9.3U	80.2	--
206-44-0	Fluoranthene	82	208	86	59.9	-4.8
129-00-0	Pyrene	90L	204	110L	61.4	-20
85-68-7	Butylbenzylphthalate	10U	183	9.3U	67.0	--
56-55-3	Benzo(a)anthracene	36L	161	47L	79.2	-27
117-81-7	Bis(2-ethylhexyl)phthalate	23Z	151	24Z	63.6	-4.3
218-01-9	Chrysene	36L	183	57L	65.4	-45
117-84-0	Di-n-octyl phthalate	10U	93.4	9.3U	70.2	--
205-99-2	Benzo(b)fluoranthene			80EL		
207-08-9	Benzo(k)fluoranthene	47L	99.2		106	-52
50-32-8	Benzo(a)pyrene	19EL	84.1	36L	121	-62
193-39-5	Indeno(1,2,3,-cd)pyrene	10U	43.4	14EL	177	--
53-70-3	Dibenz(a,h)anthracene	10U	43.4	9.3U	177	--
191-24-2	Benzo(ghi)perylene	10U	24.7	17EL	136	--

<sup>a</sup> Qualifiers:

- U - undetected at detection limit shown
- E - estimated value
- L - value is less than the maximum shown
- Z - blank-corrected, still above detection limit.

<sup>b</sup> Relative standard deviation.

**BLANKS: ACCEPTABLE**

Laboratory contaminants for certain A/B/N compounds occurred at relatively low levels (less than 3-8  $\mu\text{g}/\text{kg}$  based on 100-gram sample dry weight) in the three method blanks analyzed (Table D-5). These were within the PSEP control limit of 2.5  $\mu\text{g}$  total/blank (absolute concentration). During QA review, all data were blank-corrected using the blank extracted concurrently with each sample batch.

**DATA REPORTING: ACCEPTABLE**

The few errors found during QA review were confirmed with the laboratory and were corrected.

**TABLE D-5. CONCENTRATIONS OF A/B/N COMPOUNDS  
FOUND IN METHOD BLANKS**

Compound	Concentrations	
	$\mu\text{g}/\text{Blank}^{\text{a}}$	$\mu\text{g}/\text{kg DW}^{\text{b}}$
<b>Method Blank I</b>		
Bis(2-ethylhexyl)phthalate	0.59	5.9
<b>Method Blank II</b>		
Phenanthrene	0.25	2.5
Anthracene	0.32	3.2
Fluoranthene	0.53	5.3
Pyrene	0.53	5.2
Benzo(a)anthracene	0.49	4.9
Bis(2-ethylhexyl)phthalate	0.83	8.3
Chrysene	0.38	3.8
<b>Method Blank III</b>		
Bis(2-ethylhexyl)phthalate	0.38	3.8

<sup>a</sup> Concentrations in blanks are based on a 100-gram (dry weight) sediment sample.

<sup>b</sup> DW - dry weight, values are recovery corrected.

## ANALYSIS OF ACID/BASE/NEUTRAL ORGANIC COMPOUNDS IN TISSUE

### SUMMARY

Few A/B/N compounds were detected in tissue samples analyzed from the PSDDA Phase II survey. Benzoic acid was detected in 20/21 samples, bis(2-ethylhexyl)phthalate was detected in 2/21 samples, and 2-methylphenol was detected in 1/21 samples. All of the benzoic acid data were qualified as *E* because the ongoing calibration values were all outside the control limit of 25 percent difference relative to the initial calibration (in addition, benzoic acid for three samples was above the upper limit of calibration). The 2-methylphenol value was also qualified, as mass spectral interferences produced some uncertainty in the quantified result.

### SAMPLE COLLECTION: ACCEPTABLE

In Bellingham Bay and at the Anderson/Ketron site, the bivalve *Compsomyax subdiaphana* was selected for bioaccumulation analysis based on abundance and biomass of organisms in benthic infauna samples. Sample collection procedures are described in detail in Appendix A and are summarized in this section. Samples were collected between April 11 and May 4, 1989 with a dual 0.1-m<sup>2</sup> van Veen grab sampler. One sample was collected at each sampling station. This sample was composited from up to 24 grabs (12 deployments of the van Veen sampler). A bioaccumulation sample was not successfully collected at Station AKB02. Neither *C. subdiaphana* nor any other suitable organisms were found in the 24 grabs taken at this station. For all other stations, a minimum of 5 grams (wet weight) of tissue was collected for analysis (total sample sizes ranged from 5 to 173 grams wet weight). Cleaning procedures used during sample collection and handling are described in Appendix A. Organisms were kept on ice after collection and during storage and transport. Chain-of-custody records were prepared at the end of each day.

### SHIPPING AND HOLDING TIMES: ACCEPTABLE

Intact samples were hand-delivered to EcoChem Inc. (Seattle, Washington). The clams were opened, rinsed with seawater to remove adhering sediment and debris, drained, and the tissue was shucked into solvent-rinsed jars. Their intestines were removed to eliminate interference from ingested sediment. Samples were then hand-carried to ARI (Seattle, Washington) for organic analyses, and a subsample was shipped to Columbia Analytical Services, Inc. (CAS) (Longview, Washington) for metals analyses. Chain-of-custody records and packing lists (including a list of analyses to be performed) accompanied each group of samples.

### COMPLETENESS: ACCEPTABLE

Twenty tissue samples were analyzed for A/B/N organic compounds. There was insufficient tissue for Samples BBT12A and AKT06A; Sample BBB03A was substituted for Sample BBB02A; and an extra Sample (BBZ01A) was collected and analyzed. In addition, one laboratory duplicate

and two method blanks were analyzed for A/B/N compounds. No tissue reference material could be obtained for analysis.

## **ANALYTICAL METHODS: ACCEPTABLE**

Samples were analyzed by a modified version of EPA/CLP procedures for low level analysis of sediments/soils. Modifications from routine EPA/CLP procedures included:

- GPC was required to reduce interferences from biological macromolecules and to improve detection limits (GPC is optional for sediment/soil extracts under the CLP).
- To improve detection limits, the final extract volume (0.5 mL) was smaller than the 1.0 mL volume specified under the CLP for sediment/soil extracts.
- Thirty-five stable isotope labeled surrogates were added to four samples to provide extensive QA information on analytical recovery; the six surrogate compounds routinely used for the EPA/CLP protocol were added to the remaining samples.

Details of sample treatment are discussed in Appendix A. The tissue sample was blended with anhydrous sodium sulfate, spiked with surrogate compounds, and homogenized with 1:1 methylene chloride/acetone in a tissue homogenizer. The tissue/solvent mixture was centrifuged to separate the emulsion produced by homogenization. Extracts were dried by elution through a sodium sulfate column and concentrated to 2 mL using a Kuderna-Danish apparatus and nitrogen blowdown. A 3 percent (by volume) portion of the extract was taken for gravimetric determination of total lipids (i.e., total extractable organic matter), and the remainder of the extract was subjected to GPC cleanup. After GPC cleanup, a 90 percent (by volume) portion of the extract was concentrated to 0.45 mL [for samples treated with CLP surrogate compounds, the remaining 10 percent was used for gas chromatography/electron capture detection (GC/ECD) analysis of polychlorinated biphenyls (PCB)/pesticides]. For the four samples treated with 35 stable isotope labeled surrogate compounds, different tissue subsamples were used for GC/MS and GC/ECD analysis and the final A/B/N extract was concentrated to 0.5 mL. Extracts were analyzed by GC/MS with a fused silica capillary column (DB-5, 30 m, 0.25 mm i.d., J & W Scientific) with the following temperature programming: 40° C (held 4 minutes) heated at 8° C/minute to 310° C. The injector temperature was 270° C.

## **Calibration**

An initial 5-point calibration was performed with solutions of 1, 10, 40, 80, and 120 ng/ $\mu$ L except for benzyl alcohol, which was calibrated at 10, 40, 80, and 120 ng/ $\mu$ L. Under CLP, the lowest calibration concentration is 20 ng/ $\mu$ L. The laboratory initially provided a 4-point calibration summary that did not include the 1 ng/ $\mu$ L standard. The percent RSD exceeded the  $\pm$ 20 percent control limit for benzoic acid, fluoranthene, pyrene, benz(a)anthracene, benzo(b)fluoranthene, and benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, and benzo(g,h,i)perylene. The CLP control limit of  $\pm$ 30 percent, however, was exceeded only by benzoic acid, benzo(k)fluoranthene, and benzo(g,h,i)perylene. Upon request, the laboratory provided a 5-point initial calibration including the 1 ng/ $\mu$ L standard, which was also analyzed at the same time as the 10, 40, 80, and 120 ng/ $\mu$ L standards. The addition of the 1 ng/ $\mu$ L standard caused all of the high molecular weight PAH to exceed the  $\pm$ 30 percent CLP control limit for linearity. The data reported below the range of the 4-point calibration (without the 1 ng/ $\mu$ L standard) were recalculated using the response factor from the line determined by the 1 and 10 ng/ $\mu$ L standards.

Because the difference was generally <10 percent CV and within expected analytical variations, the data were accepted as unqualified.

Ongoing calibration was performed at least every 12 hours with a 50 ng/ $\mu$ L standard. The PSEP control limit of 25 percent difference for ongoing calibration was exceeded by benzoic acid in all cases. This exceedance caused all of the benzoic acid data to be qualified with an *E*. Phenol and acenaphthylene exceeded PSEP control limits for ongoing calibration twice and once, respectively. Because neither of these compounds was detected, no action was taken.

GC/MS tuning with DFIPP was conducted according to EPA/CLP and PSEP guidelines.

### Detection Limits

Reported detection limits were based on an extrapolation of instrumental response for a 1 ng/ $\mu$ L standard on-column except for benzyl alcohol, which was based on injection of a 10 ng/ $\mu$ L standard. Sample detection limits were then calculated by accounting for sample weight, final extract volume (including dilution factors), and injection volume. Detection limits ranged from 13 to 1,200  $\mu$ g/kg wet weight. High detection limits were due to small sample size and dilution of the sample (i.e., equivalent to increasing final extract volume).

### Compound Confirmation

Mass spectra for all detected compounds were examined during QA review. An *E* qualifier was assigned to the value for 4-methylphenol in Sample BBB01A because mass spectral interferences were judged to produce some uncertainty in the quantified result, although the interferences were not sufficient to cause rejection of the data.

### ACCURACY: ACCEPTABLE

Accuracy was assessed with recoveries of stable isotope-labeled internal standards, as there was no tissue reference material available for analysis. Matrix spike samples were not required because the isotope dilution technique was used (PSEP 1986).

### Internal Standard Recoveries

Stable isotope labeled internal standards were added for prior to extraction all but four of the target A/B/N compounds (2-methylnaphthalene, dibenzofuran, benzyl alcohol, and benzoic acid). Recoveries of 11 of the 35 added internal standards are summarized in Table D-6. These compounds were chosen because they represent a wide range of compound classes (e.g., phenols, low and high molecular weight PAH, chlorinated benzenes, phthalates, organonitrogen compounds).

PSEP control limits for internal standards are 50 percent (when the isotope dilution technique is not used) and 10 percent (when the isotope dilution technique is used). Recoveries of stable isotope-labeled internal standards were typically >50 percent (231/798 were <50 percent, 45/798 were <10 percent, and 37/798 were zero recovery) Sample data for internal standards with zero

TABLE D-6. RECOVERIES FOR SELECTED A/B/N INTERNAL STANDARDS<sup>a</sup>

	Stations														BBT01A DUP
	AKT01A	AKT02A	AKT03A	AKT04A	AKT05A	BBB01A	BBB03A	BBB04A	BBZ01A	BBT01A	BBT09A	BBT10A	BBT11A		
d <sub>5</sub> -Phenol	49	70	43	46	59	40	83	72	56	19	56	19	26		
d <sub>4</sub> -1,4-Dichlorobenzene	37	45	38	32	40	31	54	38	31	16	31	16	23		
2,3,5,6-d <sub>4</sub> -p-cresol	76	63	62	64	76	61	89	58	62	47	62	47	60		
d <sub>8</sub> -Naphthalene	70	59	63	59	68	53	74	53	54	43	54	43	55		
d <sub>4</sub> -Dimethylphthalate	94	60	58	55	73	64	76	60	71	61	71	61	72		
d <sub>10</sub> -Fluorene	79	52	56	55	60	55	73	53	60	57	60	57	69		
d <sub>6</sub> -N-nitrosodiphenylamine	76	53	56	53	43	43	81	49	44	58	44	58	72		
d <sub>6</sub> -Pentachlorophenol	34	17	0	0	0	31	66	22	21	21	21	21	33		
d <sub>10</sub> -Phenanthrene	31	62	63	65	61	68	64	55	55	84	55	84	88		
d <sub>4</sub> -Bis(2-ethylhexyl)phthalate	93	76	55	46	52	72	89	57	44	80	44	80	101		
d <sub>10</sub> -Chrysene	48	54	54	53	53	55	100	52	59	71	59	71	81		

  

	Stations													
	BBT02A	BBT03A	BBT04A	BBT05A	BBT06A	BBT07A	BBT08A	BBT09A	BBT10A	BBT11A				
d <sub>5</sub> -Phenol	35	49	41	27	44	22	33	36	24	70				
d <sub>4</sub> -1,4-Dichlorobenzene	7	36	20	27	24	9	25	6	4	43				
2,3,5,6-d <sub>4</sub> -p-cresol	56	70	56	49	54	60	60	55	47	63				
d <sub>8</sub> -Naphthalene	48	58	45	48	50	55	51	45	36	51				
d <sub>4</sub> -Dimethylphthalate	50	70	57	56	57	67	55	57	56	62				
d <sub>10</sub> -Fluorene	42	61	50	52	51	63	55	50	50	60				
d <sub>6</sub> -N-nitrosodiphenylamine	40	45	33	27	30	0	0	25	45	29				
d <sub>6</sub> -Pentachlorophenol	0	19	23	25	23	0	0	0	25	31				
d <sub>10</sub> -Phenanthrene	49	56	55	69	54	72	64	55	62	70				
d <sub>4</sub> -Bis(2-ethylhexyl)phthalate	46	45	65	96	62	83	94	39	63	62				
d <sub>10</sub> -Chrysene	53	62	53	67	70	69	60	53	67	54				

<sup>a</sup> Expressed as percent of amount added.

recovery were rejected. The most commonly data rejected for zero recovery were for hexachloroethane, pentachlorophenol, and hexachlorobutadiene.

**PRECISION: ACCEPTABLE**

One analytical duplicate was analyzed to assess precision. Benzoic acid was the only target compound detected. Benzoic acid values of 2,600 and 2,900  $\mu\text{g}/\text{kg}$  wet weight were within the PSEP control limits of  $\pm 100$  percent RPD (i.e., 11 percent in this case).

**BLANKS: ACCEPTABLE**

Several high molecular weight PAH [i.e., fluoranthene, pyrene, benz(a)anthracene, benzo(b+k)fluoranthene, and benzo(a)pyrene] were reported at concentrations below their nominal detection limits in one of the two method blank analyses. No correction was performed on the associated data due to the uncertainty of values below the nominal detection limit. No other A/B/N compounds were detected in either blank.



## ANALYSIS OF PCB/PESTICIDES IN SEDIMENTS

### SUMMARY

PCB and pesticide data are acceptable as qualified. All of the data are reported below the limits of detection. Accuracy and precision data for PCB and pesticides were favorable. Several PCB reported as detected below the detection limit were reclassified as undetected because too few peaks matched those of Aroclor mixtures.

### SAMPLE COLLECTION: ACCEPTABLE

Details of sediment sampling are given in Appendix A and are summarized in this section. Sediment samples were collected between April 5 and May 4, 1989 with a dual 0.1-m<sup>2</sup> van Veen grab sampler. Sample depths were 10 cm at the disposal zone and other site stations and 2 cm at all other stations (i.e., perimeter, benchmark, and reference). Each sample was formed of material composited from a minimum of six grabs.

Acceptability of grab samples was evaluated in accordance with criteria specified by PSEP (1986). Grab samples failing to meet PSEP criteria were excluded from compositing. After a grab sample was judged to be acceptable, the overlying water was siphoned off and the sample was collected with stainless steel spatulas according to PSEP recommendations. Grab samples for each station were homogenized in a stainless steel bowl with stainless steel spoons until uniform color and texture were apparent. Sediment was then transferred to the appropriate sample container (discussed in detail in Appendix A) and stored on ice. Cleaning of sampling equipment is described in Appendix A. Chain-of-custody records were completed at the end of each day.

### SAMPLE TRANSPORT AND HOLDING TIMES: ACCEPTABLE

Samples were shipped on ice to ARI (Seattle, Washington). Sample holding times were well within the PSEP control limit of 1 year for frozen sediments (PSEP 1986). Instrumental GC/MS analyses were conducted between May 15 and June 29, 1988; the PSEP extract holding time control limit of 40 days was not exceeded for any samples.

### COMPLETENESS: ACCEPTABLE

Results for all 15 samples submitted to the laboratory were provided, as well as results for a matrix spike sample plus a matrix spike duplicate, two method blanks, and two sediment reference materials. Additional materials were requested from the laboratory (e.g., revised calculations) and were provided.

## **ANALYTICAL METHODS: ACCEPTABLE**

Samples were analyzed by a modified version of EPA/CLP procedures for low level analysis of sediments/soils. Modifications from routine EPA/CLP procedures included the following:

- Larger sample size was used to improve detection limits (approximately 75 grams wet weight).
- Extracts for PCB/pesticide analysis were not aliquots of the extracts used for analysis of A/B/N compounds as under the EPA/CLP protocol; to preclude GC/ECD interferences from the 35 isotope labeled surrogate compounds added to sediment samples prior to A/B/N analysis, separate sediment subsamples were extracted for PCB/pesticide and A/B/N analysis.
- 4,4'-Dibromooctafluorobiphenyl (DBOFB) was used as a surrogate compound in addition to the EPA/CLP surrogate [dibutylchlorodate (DBC)], which has been reported as being susceptible to degradation during analysis.
- To enhance GC/ECD resolution and reduce the potential for interferences, fused silica capillary column analyses were performed for compound quantification and confirmation rather than packed column analyses as specified in the EPA/CLP.
- A three-point PCB calibration was performed (in addition to a three-point calibration for selected pesticides) to document linearity of the GC/ECD response for PCB; the EPA/CLP procedure used by the laboratory relies only on the pesticide calibration to verify linearity.

Sediment samples were mixed with anhydrous sodium sulfate, spiked with recovery surrogates, and extracted by sonication with 1:1 methylene chloride/acetone. Extracts were subjected to alumina column cleanup as described in the EPA/CLP and were concentrated to a final volume of 10 mL. Extracts were analyzed using a Hewlett-Packard 5890 GC system equipped with two 15-meter fused silica capillary columns and two detectors. A DB-5 column (0.53 mm i.d., J & W Scientific) was used for quantification and a DB-608 column (0.53 mm i.d., J & W Scientific) was used for confirmation. Temperature programming was as follows: 150° C (held 1 minute) heated at 2.5° C/minute to 235° C (followed by a "bake out" at 275° C for 5 minutes). Injector and detector temperatures were 225° C and 375° C, respectively.

### **Calibration**

The laboratory performed calibrations according to PSEP protocols using three standard concentrations and target compounds (including Aroclor 1254). Both the pesticide and PCB calibrations were within the PSEP control limits of 20 percent CV (all were less than 10 percent CV). Pesticide and Aroclor 1254 standards were injected at the beginning, during, and at the end of each GC run to verify calibration. Initial calibration was repeated every 72 hours.

### **Detection Limits**

Instrument detection limits (IDL) were based on an assessment of signal/noise ratios in GC/ECD chromatograms and a determination of the minimum peak height that could be

distinguished from noise. IDL ranged from 0.002 to 0.006 ng/ $\mu$ L for the target compounds. The laboratory considered their estimates of IDL to be conservatively high. Based on IDL, sample weight, final extract volume, and injection volume, the sample detection limits for PCB ranged from 20 to 60  $\mu$ g/kg dry weight. Detection limits for target pesticides ranged from 1 to 6  $\mu$ g/kg dry weight.

### **Compound Confirmation**

GC/ECD chromatograms (from both the DB-5 and DB-608 columns) were reviewed to assess compound confirmation for PCB. For certain samples in which PCB were reported well below the detection limits, only a few peaks suggesting the presence of PCB assemblages were actually present on both columns. These samples were reclassified as undetected. Chromatograms were also checked to preclude the possibility of false negatives (i.e., failure to report a compound that is actually present).

### **ACCURACY: ACCEPTABLE**

Accuracy was assessed with two sediment reference materials (for PCB), a matrix spike sample (for pesticides), and surrogate recoveries.

### **Sediment Reference Material**

There are no certified reference materials available for organic compounds in marine sediments. However, a locally available reference material containing low to moderate concentrations of PCB and other compounds (Sequim-1, developed by NOAA/NMFS) was analyzed in duplicate. Because this reference material is not certified, PSEP control limits (the 95 percent confidence interval of certified values) are not strictly applicable to the results. Reference material data were assessed relative to the 50 percent recovery control limit applicable to surrogate and matrix spike recoveries under PSEP.

The laboratory reported concentrations of 110  $\mu$ g/kg and 120  $\mu$ g/kg dry weight of PCB in the reference sediment (Sequim-1). No recovery-corrections have been applied to these data, but such corrections based on surrogate recoveries would not significantly change these values. Based on 12 analyses, NOAA/NMFS reported 110  $\mu$ g/kg dry weight for the Sequim-1 reference sediment. The recoveries of PCB from the reference sediment in this study (100 percent and 110 percent) were well within the control limit of 50 percent for non-certified reference materials.

### **Pesticide Matrix Spikes**

A matrix spike and a matrix spike duplicate were performed for the six pesticides routinely spiked under the EPA/CLP program (Table D-7). All recoveries met the 50 percent control limit specified by PSEP. Average recoveries ranged from 62 to 105 percent (Table D-7) and are considered acceptable.

**TABLE D-7. PESTICIDE MATRIX SPIKE  
RECOVERIES IN SEDIMENTS  
(as percent of amount spiked)**

Compound	CRR01	CRR01 Duplicate	Mean % Recovery	Relative Percent Difference
Lindane	102	105	104	1.9
Heptachlor	101	101	101	0
Aldrin	60	70	65	15
Dieldrin	105	105	105	0
Endrin	95	95	95	0
p,p'-DDT	67	57	62	16

### **Surrogate Recoveries**

Recoveries of DBOFB and DBC are presented for all samples in Table D-8. Recoveries averaged 105 percent and 94 percent for DBC and DBOFB, respectively, with a coefficient of variation (CV) of approximately 6 percent (Table D-8). All surrogate recoveries were above the PSEP control limit of 50 percent.

### **PRECISION: ACCEPTABLE**

One reference material duplicate (for PCB) and one matrix spike duplicate (for select pesticides) were analyzed to assess precision. The PCB concentrations for the duplicate reference sediment were 110  $\mu\text{g}/\text{kg}$  and 120  $\mu\text{g}/\text{kg}$  dry weight (8.7 RPD). The matrix spike duplicate results are shown in Table D-7. The RPD of the matrix spike samples ranged from 0 to 16 percent. All duplicate analyses were within the PSEP control limit of  $\pm 100$  percent RPD.

### **BLANKS: ACCEPTABLE**

PCB and target pesticides were not found in either of the method blanks analyzed.

**TABLE D-8. PCB/PESTICIDE SURROGATE RECOVERIES  
(as percent)**

Station	DBC <sup>a</sup>	DBOFB <sup>b</sup>
AKB02	105	99
AKP01	103	93
AKP02	107	97
AKP03	111	96
AKP04	106	96
AKZ01	103	93
BBB01	103	93
BBB02	116	99
BBB04	102	88
BBP01	43	87
BBP02	107	96
BBP03	114	100
BBP04	102	95
BBZ01	116	101
CRR01	98	80
SQ1	96	92
SQ1 Duplicate	95	91
<b>Mean</b>	<b>105</b>	<b>94</b>
<b>Coefficient of variation (%)</b>	<b>6.6</b>	<b>5.7</b>
<b>Range</b>	<b>93-116</b>	<b>80-101</b>

<sup>a</sup> DBC - dibutylchlorodate.

<sup>b</sup> DBOFB - dibromooctafluorobiphenyl.

## ANALYSIS OF PCB/PESTICIDES IN TISSUE

### SUMMARY

PCB and pesticides were reported as undetected in all tissue samples analyzed from the PSDDA Phase II survey. QA data indicated overall acceptability of the data as reported.

### SAMPLE COLLECTION: ACCEPTABLE

In Bellingham Bay and at the Anderson/Ketron site, the bivalve *C. subdiaphana* was selected for bioaccumulation analysis based on abundance and biomass of organisms in benthic infauna samples. Sample collection procedures are described in detail in Appendix A and are summarized in this section. Samples were collected between April 11 and May 4, 1989 with a dual 0.1-m<sup>2</sup> van Veen grab sampler. One sample was collected at each sampling station. This sample was composited from up to 24 grabs (12 deployments of the van Veen sampler). A bioaccumulation sample was not successfully collected at Station AKB02. Neither *C. subdiaphana* nor any other suitable organisms were found in the 24 grabs taken at this station. For all other stations, a minimum of 5 grams (wet weight) of tissue was collected for analysis (total sample sizes ranged from 5 to 173 grams wet weight). Cleaning procedures used during sample collection and handling are described in Appendix A. Organisms were kept on ice after collection and during storage and transport. Chain-of-custody records were prepared at the end of each day.

### SAMPLE TRANSPORT AND HOLDING TIMES: ACCEPTABLE

Intact samples were hand-delivered to EcoChem Inc. (Seattle, Washington). The clams were opened, rinsed with seawater to remove adhering sediment and debris, drained, and the tissue shucked into solvent-rinsed jars. Their intestines were removed to eliminate interference from ingested sediment. Samples were then hand-carried to ARI (Seattle, Washington) for organic analyses, and a subsample was shipped to CAS (Longview, Washington) for metals analyses. Chain-of-custody records and packing lists (including a list of analyses to be performed) accompanied each group of samples.

### COMPLETENESS: ACCEPTABLE

Twenty tissue samples were analyzed for PCB and pesticides. There was insufficient tissue for Samples BBT12A and AKT06A, Sample BBB03A was substituted for Sample BBB02A, and an extra sample (BB01A) was collected and analyzed. In addition, one PCB matrix spike sample, one analytical duplicate, and two method blanks. No reference materials could be obtained for analysis.

## **ANALYTICAL METHODS: ACCEPTABLE**

The tissue sample extracts were analyzed for five Aroclor (PCB) mixtures and eight priority pollutant pesticides using a modified version of the EPA/CLP method for low-level analysis of sediment/soil. Modifications of the method included the following:

- Extracts for PCB/pesticide analysis were not aliquots of the extracts used for analysis of A/B/N compounds as under the EPA/CLP protocol; to preclude GC/ECD interferences from the 35 isotope labeled surrogate compounds added to tissue samples prior to A/B/N analysis, separate tissue subsamples were extracted for PCB/pesticide and A/B/N analysis.
- 4,4'-DBOFB was used as a surrogate compound in addition to the EPA/CLP surrogate, DBC, which has been reported as being susceptible to degradation during analysis.
- Sample analysis was performed by fused silica capillary column GC/ECD to enhance resolution and reduce the potential for interferences. EPA/CLP uses packed columns analysis.
- Multipoint calibration of GC/ECD for PCB and pesticides (EPA/CLP requires multipoint calibration for pesticides only).
- A modification requested by not performed was the use of GPC on all tissue samples to remove interferences resulting from the presence of biological macromolecules (alumina columns were used for sample cleanup, as per EPA/CLP).

The tissue sample was blended with anhydrous sodium sulfate, spiked with surrogate compounds, and homogenized with 1:1 methylene chloride/acetone in a tissue homogenizer. The tissue/solvent mixture was centrifuged to separate the emulsion produced by homogenization. The extracts were subjected to alumina chromatography and concentrated to 10 mL. Extracts were analyzed using a Hewlett Packard 5890 GC system equipped with two 15-meter fused silica capillary columns and two detectors. A DB-5 capillary column (0.53 mm i.d., J & W Scientific) was used for quantification and a DB-608 column (0.53 mm i.d., J & W Scientific) was used for confirmation. Temperature programming was as follows: 150° C (held 1 minute) heated at 2.5° C/minute to 235 °C (followed by a "bake-out" at 275° C for 5 minutes). Injector and detector temperatures were 225° C and 375° C, respectively.

### **Calibration**

The laboratory performed three-point calibrations according to PSEP protocols for both PCB and target pesticides. Both the pesticide and PCB calibrations were within the PSEP control limits of 20 percent RSD. Standards were injected at the beginning, during, and at the end of each GC/ECD run to verify calibration. Recalibration of the instrument was performed every 72 hours.

### **Detection Limits**

IDL were based on an assessment of signal/noise ratios in GC/ECD chromatograms and a determination of the minimum peak height that could be distinguished from noise. The laboratory

considered their estimates of IDL to be conservatively high. Sample detection limits for single compounds ranged from 0.3 to 4.5  $\mu\text{g}/\text{kg}$  wet weight for individual pesticides and from 10 to 80  $\mu\text{g}/\text{kg}$  wet weight for PCB mixtures.

#### **ACCURACY: ACCEPTABLE**

Accuracy was assessed with one PCB matrix spike and surrogate recoveries. No tissue reference material was available for analysis.

#### **Pesticide Matrix Spike**

A matrix spike of Aroclor 1242 was performed. The recovery was 65 percent of the amount added to the sample. This is within the PSEP control limit of 50 percent.

#### **Internal Standard Recoveries**

DBC and DBOFB were added to all samples as internal standards for PCB/pesticide. Table D-9 summarizes the internal standard recoveries for the PCB/pesticide analyses. Internal standard recoveries were within PSEP guidelines (>50 percent recovery) with the exception of one blank, which exhibited a DBOFB recovery of 46 percent. This result was qualified as *E*.

#### **PRECISION: UNDEFINED**

A replicate analysis was performed on 5 percent of the samples (one sample). All variables were undetected in both of the samples, so the degree of precision attained in the analyses cannot be interpreted from these data.

#### **BLANKS: ACCEPTABLE**

Two method blanks were run. No target compounds were detected in either blank.

**TABLE D-9. PCB/PESTICIDE INTERNAL STANDARD RECOVERIES  
(as percent)**

Station	DBC <sup>a</sup>	DBOFB <sup>b</sup>
AKT01A	81	81
AKT02A	96	78
AKT03A	70	78
AKT04A	78	78
AKT05A	78	78
BBZ01A	68	79
BBB01A	76	78
BBB03A	88	85
BBB04A	72	81
BBT01A	88	83
BBT02A	54	56
BBT03A	82	78
BBT03A matrix spike	79	83
BBT04A	83	76
BBYT04 duplicate	76	72
BBT05A	80	75
BBT06A	67	71
BBT07A	53	54
BBT08A	76	73
BBT09A	64	72
BBT10A	84	79
BBT11A	96	80
Blank 1	92	46
Blank 2	93	70
<b>Mean</b>	<b>78</b>	<b>74</b>
<b>Coefficient of Variation (%)</b>	<b>15</b>	<b>13</b>
<b>Range</b>	<b>53-96</b>	<b>46-85</b>

<sup>a</sup> DBC - dibutylchloroendate.

<sup>b</sup> DBOFB - dibromoctafluorobiphenyl.

## ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN SEDIMENTS

### SUMMARY

Volatile organic compounds were undetected in all samples. Available QA information (holding times, surrogate and matrix spike recoveries, detection limits, and calibration) indicate that these data were otherwise acceptable as received from the laboratory.

### SAMPLE COLLECTION: ACCEPTABLE

Details of sediment sampling are given in Appendix A and are summarized in this section. Sediment samples were collected between April 5 and May 4, 1989 with a dual 0.1-m<sup>2</sup> van Veen grab sampler. Sample depths were 10 cm at the disposal zone and other site stations and 2 cm at all other stations (i.e., perimeter, benchmark, and reference). Each sample was formed of material composited from a minimum of six grabs.

Acceptability of grab samples was evaluated in accordance with criteria specified by PSEP (1986). Grab samples failing to meet PSEP criteria were excluded from compositing. After a grab sample was judged to be acceptable, the overlying water was siphoned off and the sample was collected with stainless steel spatulas according to PSEP recommendations. Grab samples for each station were homogenized in a stainless steel bowl with stainless steel spoons until uniform color and texture were apparent. Sediment was then transferred to the appropriate sample container (discussed in detail in Appendix A) and stored on ice. Cleaning of sampling equipment is described in Appendix A. Chain-of-custody records were completed at the end of each day.

### SHIPPING AND HOLDING TIMES: ACCEPTABLE

Samples were shipped on ice to ARI (Seattle, Washington). Sample holding times were all within the PSEP control limit of 14 days.

### COMPLETENESS: ACCEPTABLE

Data for all 15 samples submitted for analysis were reported, as well as results for 1 analytical duplicate, 1 matrix spike and matrix spike duplicate, and 6 method blanks.

### ANALYTICAL METHODS: ACCEPTABLE

Samples were analyzed for trichloroethene, tetrachloroethene, ethylbenzene, and total xylenes using heated (40° C) purge-and-trap GC/MS, as specified by EPA/CLP. The adsorption trap for volatile organic compounds contained 1 cm of 3 percent OV-1 on Chromosorb W, 15 cm of Tenax-GC, and 8 cm of silica gel in a 0.1 inch x 25 cm long stainless steel tube. Desorbed compounds were analyzed on a 0.1 inch x 6 foot glass column packed with 1 percent SP-1000 on

Carbopak B (60/80 mesh). The GC oven was held at 45° C for 3 minutes and heated at 8°/minute to 230° C, where it was held for 5 minutes.

### **Detection Limits**

Detection limits for all target compounds ranged from 0.4 to 5.2 µg/kg dry weight. These values are well within the guidelines for detection limits recommended by PSEP (1986). IDL defined according to EPA/CLP procedures were used along with sample sizes to determine sample detection limits.

### **Calibration**

A six-point initial calibration was performed with concentrations ranging from 20 to 200 ng/mL. A single point ongoing calibration check (50 ng/mL) was run on a daily basis. All results for initial and ongoing calibration met PSEP control limits (PSEP 1986). GC/MS tuning with bromofluorobenzene (BFB) was performed within EPA/CLP and PSEP guidelines.

### **Compound Confirmation**

No compounds were reported above the detection limit for any of the samples.

### **ACCURACY: ACCEPTABLE**

Accuracy was assessed with surrogate recoveries and matrix spike results. No standard reference materials (SRM) are available for volatile organic compounds in a sediment or soil matrix.

### **Surrogate Compounds**

Prior to analysis, all samples were spiked with the three surrogate compounds specified by the EPA/CLP; recoveries are reported in Table D-10. Average recoveries were 100, 89, and 96 percent for d<sub>8</sub>-toluene, BFB, and d<sub>4</sub>-1,2-dichloroethane, respectively, with CV of less than 6 percent (Table D-10).

### **Matrix Spikes**

A matrix spike and matrix spike duplicate were analyzed for the five volatile organic chemicals required by EPA/CLP matrix spike samples. The results are summarized in Table D-11. All recoveries (81-107 percent) were well within PSEP control limits (≥50 percent recovery; PSEP 1986) as were the RPD values (-6.4-2.4 percent; PSEP control limit is ±100 percent RPD).

**TABLE D-10. VOLATILE ORGANIC SURROGATE RECOVERIES  
(as percent)**

Station	d <sub>8</sub> -Toluene	BFB	d <sub>4</sub> -1,2-Dichloroethane
AKB02	100	87	100
AKP01	100	88	100
AKP01 Duplicate	110	89	98
AKP02	100	88	97
AKP03	97	97	94
AKP04	100	95	95
AKZ01	100	88	99
BBB01	110	81	95
BBB02	99	92	88
BBB04	110	83	94
BBP01	110	86	95
BBP02	100	94	96
BBP03	110	93	96
BBP04	110	83	95
BBZ01	100	98	97
CRR01	100	88	99
<b>Mean</b>	100	89	96
<b>Coefficient of Variation (%)</b>	5.1	5.6	3.1
<b>Range</b>	97-110	81-98	88-100

**TABLE D-11. RESULTS FOR MATRIX SPIKES OF  
VOLATILE ORGANIC COMPOUNDS  
(concentrations in  $\mu\text{g}/\text{kg}$  dry weight)**

Compound	Nominal Spiking Concentration	Sample Result (Unspiked)	MS <sup>a</sup>		MSD <sup>b</sup>		RPD <sup>c</sup>
			Concentration	Recovery (%)	Concentration	Recovery (%)	
1,1-Dichloroethene	102	0	84	83	82	81	2.4
Trichloroethene	102	0	84	83	86	84	-2.4
Benzene	102	0	106	104	109	107	-2.8
Toluene	102	0	96	94	94	92	2.1
Chlorobenzene	102	0	91	90	97	96	-6.4

<sup>a</sup> MS - matrix spike.

<sup>b</sup> MSD - matrix spike duplicate.

<sup>c</sup> RPD - relative percent difference.

**PRECISION: ACCEPTABLE**

One analytical duplicate analysis was performed in addition to the matrix spike duplicate. Volatile organic compounds were not detected in either of these samples, so the replicate data could not be interpreted. However, overall analytical precision was acceptable based on surrogate and matrix spike recoveries (Tables D-8 and D-9).

**BLANKS: ACCEPTABLE**

Method blanks were analyzed at the recommended frequency (PSEP 1986) of at least one per 12-hour shift. No target compounds were detected in any of the blank analyses.



## ANALYSIS OF TRACE METALS IN SEDIMENTS AND TISSUE

### SUMMARY

#### Sediment

The results are acceptable for all metals, except antimony. Antimony was assigned a *G* qualifier because both the SRM and the predigestion matrix spike recovery values were not within PSEP control limits.

#### Tissue

The results are acceptable for all metals, except silver, five samples for arsenic, and one sample for lead. Silver was assigned an *E* qualifier because serial dilution values were outside control limits, precision was poor, and the predigestion matrix spike recovery values were not within PSEP control limits. For arsenic, Samples AKT06A, BBB01A, BBZ01A, BBT03A, and BBT06A had correlation coefficients outside the control limits for methods of standard additions analyses. These five samples were assigned an *E* qualifier. Sample BBB01A for lead was blank-corrected and assigned a *Z* qualifier.

### SAMPLE COLLECTION AND TRANSPORT

#### Sediment

Details of sediment sampling are described in Appendix A and are summarized in this section. Sediment samples were collected between April 11 and May 4, 1989. Samples were shipped on ice via bus with chain-of-custody documentation to CAS (Longview, Washington).

#### Tissue

In Bellingham Bay and between Anderson and Ketron Islands, the clam species *C. subdiaphana* was selected for bioaccumulation analysis based on abundance and biomass of organisms in benthic infauna species. Sample collection procedures are described in detail in Appendix A and are summarized in this section. Organisms were kept on ice after collection, and during storage and transport. Chain-of-custody records were prepared at the end of each day. The clams were dissected from the shell whole and placed in sampling jars after a brief seawater rinse. Samples were frozen until tissues were prepared for analysis. The clam samples were thawed and drained of liquids before weighing. After weighing, both the tissue and liquid fractions were placed in a glass jar and homogenized in a blender fitted with stainless steel blades, and PTFE gaskets. The glass jars were rinsed with acetone and methylene chloride then placed in a drying oven to

evaporate the solvents prior to use. The blender blades and PTFE gaskets were rinsed with distilled water, acetone, and methylene chloride and allowed to air dry between uses. After homogenation the samples were split into laboratory containers and one container was shipped via bus, with chain-of-custody documentation, to CAS (Longview, Washington).

#### **COMPLETENESS: ACCEPTABLE**

Results were received for all sediment and tissue samples submitted for analysis. All samples were analyzed within the recommended holding times.

#### **DATA REPORTING**

##### **Sediment**

The laboratory compiled the data with the use of a CLP deliverables program (SMART LOG, Telecation Associates) with the necessary modifications to meet PSDDA requirements. The data summary sheets are produced by the computer directly from the raw data generated during analyses. Graphite furnace atomic absorption (GFAA) raw data results are stored by the instrument directly on disk and then transferred into the CLP database automatically. Dilution factor, sample aliquot weight, final digestate volume, and flame atomic absorption (FAA) concentration data must be manually entered. The manually entered data were verified 100 percent and no errors were found. The final data summary sheets were spot checked and no calculation errors were found.

##### **Tissue**

The laboratory compiled the data with the use of a CLP deliverables program (SMART LOG, Telecation Associates) with the necessary modifications to meet PSDDA requirements. The data summary sheets are produced by the computer directly from the raw data generated during analyses. GFAA raw data results are stored by the instrument directly on computer disk and then transferred into the CLP database automatically. Dilution factor, sample aliquot weight, final digestate volume data must be manually entered. The manually entered data were verified 100 percent and one error was found. The mercury sample aliquot weight for Sample BBT04A duplicate was entered incorrectly. The corrected value should be 0.04 mg/kg.

#### **ANALYTICAL METHODS: ACCEPTABLE**

##### **Sediment**

PSEP guidelines (PSEP 1986) recommend a strong acid digestion for sediment samples prior to analysis by FAA of GFAA. The laboratory analyzed SRM using several alternate strong acid digestion procedures and compared the analyte recoveries. Results indicated acceptable recoveries (80-120 percent) could be obtained for arsenic, cadmium, copper, nickel, and zinc, for the modified CLP method (Shelton, M., 25 April 1989, personal communication). Results of the PSDDA Phase I archive analyses indicated acceptable recoveries could be obtained for antimony and lead. There is no certified value available for silver. All analytes were analyzed using the strong acid digestate.

Sixteen samples (plus one duplicate, one predigestion matrix spike, and one SRM sample) were digested using the CLP strong acid method, which uses nitric acid and hydrogen peroxide for digestion followed by refluxing with hydrochloric acid prior to instrumental analysis. The digests were analyzed by FAA for copper, nickel, lead, and zinc; and by GFAA for antimony, arsenic, cadmium, and silver.

Mercury samples were digested using nitric and sulfuric acids followed by oxidation using potassium permanganate and potassium persulfate, then analysis of the digestate using cold vapor atomic absorption (CVAA). Analytical methods followed PSEP guidelines (PSEP 1986), except the laboratory used a 1.0-gram sample aliquot to improve detection limits.

## **Tissue**

Twenty-two dissected and blended tissue samples were submitted to CAS for trace metal analysis. Cadmium, copper, silver, and zinc were analyzed by ICP following digestion with nitric acid and hydrogen peroxide. Antimony, arsenic, nickel, lead, and low-level silver were analyzed by GFAA following digestion with nitric acid and hydrogen peroxide. The digestion procedure employed was not the one stated under PSEP protocols (PSEP 1986). The nitric and perchloric acid digestion specified under PSEP protocols produces interferences that make GFAA analyses difficult. The laboratory analyzed a known reference material and demonstrated acceptable recovery using a nitric acid and hydrogen peroxide digestion procedure (Shelton, M., 25 April 1989, personal communication).

Mercury samples were digested using nitric and sulfuric acids followed by oxidation using potassium permanganate and potassium persulfate, then analysis of the digestate using CVAA. Analytical methods followed PSEP guidelines (PSEP 1986).

## **CALIBRATION**

### **Sediment**

The laboratory followed PSEP protocols using a three-point standard curve for instrument calibration prior to analysis. The linear correlation coefficient of the calibration curves for all metals was greater than 0.99. Sample results were bracketed by calibration standards for all unqualified data except silver and cadmium. The laboratory analyzed standards at or near the IDL to verify low-end calibration and the data are acceptable.

Laboratory quality control (QC) included the analysis of initial (ICV) and continuing (CCV) calibration verification standards, initial (ICB) and continuing (CCB) calibration blanks, and laboratory control samples at frequencies specified under the EPA/CLP (U.S. EPA 1987). All results for these QC checks were within CLP requirements.

For GFAA analyses, duplicate injections and post-digestion spikes were run for each sample analyzed, as outlined under CLP requirements. Method of standard additions (MSA) was employed for all samples outside the control limits of 85-115 percent recovery for the post-digestion spike. All MSA criteria were met and the data are acceptable.

## Tissue

For GFAA analyses, calibration followed CLP protocols (U.S. EPA 1987) using a minimum three-point calibration, followed by ICV and CCV as described for sediment analyses. Duplicate injections and post-digestion spikes were performed as described under CLP (U.S. EPA 1987). If post-digestion spikes were not within the control limits of 85-115 percent recovery, then the laboratory used MSA for quantification. All MSA criteria were met, except the correlation coefficients for five samples for arsenic. The laboratory reanalyzed the samples, as required, and the correlation coefficients were still less than 0.995. The five samples are AKT06A, BBB01A, BBZ01A, BBT03A, and BBT06A. It is recommended that arsenic results for these samples be assigned an *E* qualifier and be considered estimates.

For inductively coupled plasma (ICP) spectroscopy, instrument calibration followed CLP protocols (U.S. EPA 1987), allowing the laboratory to calibrate the instrument according to the instrument manufacturer's recommended procedures.

Laboratory QC checks, for both GFAA and ICP, included ICV, CCV, ICB, and CCB. Additional QC checks for ICP included serial dilutions, interference check sample, and the linear range standard. All QA/QC control limits were met except one serial dilution for copper (19 percent variability) and two serial dilutions for silver (12 percent and 14 percent variability). The data will not be qualified for copper because one out of two serial dilution analyses was in compliance. The silver data had both serial dilutions outside the control limits. Silver data are recommended to be qualified as *E*, because of poor serial dilution results as well as poor precision and matrix spike recovery.

## DETECTION LIMITS

### Sediment

Reported detection limits met PSEP (PSEP 1986) contract required detection limits (CRDL). No analytes were reported as undetected in the sediment sample.

### Tissue

Undetected results were reported for antimony that were above the PSEP CRDL. All other results met PSEP CRDL for all samples. Reported detection limits for antimony ranged from 0.02 to 0.10 mg/kg wet weight and the PSEP CRDL for antimony is 0.02 mg/kg wet weight. The elevated detection limits are due to the limited sample size available for analysis. PSEP recommends a sample aliquot size of 5.0 grams. The laboratory used from 1.0 to 5.0 grams of tissue for analysis because sample size available for analysis was limited.

## ACCURACY

### Sediment

The laboratory performed one SRM analysis (U.S. Department of Commerce, National Bureau of Standards, Estuarine Sediment 1646) and one predigestion matrix spike. Results are summarized in Table D-12. All analytes, except antimony and cadmium, were within control limits (80-120 percent recovery) for the SRM. All analytes, except antimony, were within the control limits (75-125 percent recovery) for the matrix spike. For antimony, poor recovery (and poor precision for replicate analyses) indicates that antimony data should be qualified as *E*, and given a *G* qualifier to indicate the sample results may be biased low. The SRM percent recovery for cadmium was slightly outside the control limits (123 percent). The data will not be qualified because all other quality control variables were within the control limits. The matrix spike and SRM results were within guidelines for arsenic, copper, lead, nickel, silver, and zinc.

The matrix spike and SRM results were within control limits for mercury.

### Tissue

The laboratory performed two SRM analyses (National Research Council of Canada, Lobster Hepatopancreas, TORT-1), and two matrix spike analyses. Results are summarized in Table D-13. For both SRM analyses, all analyte recoveries except antimony and silver were within PSEP control limits (80-120 percent recovery). The SRM is not certified for antimony and silver.

Both matrix spike recoveries were outside the control limits (75-125 percent recovery) for silver. Silver values were qualified as *E*. One matrix spike was outside the control limits for antimony. The data will not be qualified because only one matrix spike was outside the control limits, and all the sample results were undetected for antimony.

Arsenic, cadmium, copper, lead, mercury, nickel, and zinc matrix spike and SRM analyses were within the control limits and the data are acceptable.

## PRECISION

### Sediment

No blind field replicates were submitted to the laboratory. One laboratory replicate was analyzed for each metal. The RPD values obtained for the sediment replicate analyses are presented in Table D-14. For all metals, except antimony, the RPD between all replicates was within the  $\pm 20$  percent control limit under PSEP protocols. The RPD value for antimony was outside the CLP (PSEP 1986) sediment control limit of  $\pm 35$  percent. Antimony data were previously qualified for poor SRM and matrix spike percent recovery.

**TABLE D-12. METALS RECOVERY RESULTS FOR SEDIMENT DIGESTS**

	Spike Recoveries (%)	
	Spike Concentration (mg/kg)	Station BBB01
Antimony	7.5	9.7 <sup>a</sup>
Arsenic	24.0	82
Cadmium	2.2	123
Copper	75.0	101
Lead	60.0	90
Mercury <sup>b</sup>	0.158 <sup>c</sup>	94 <sup>c</sup>
Nickel	60.0	99
Silver	2.0	84
Zinc	105.0	101

  

	Standard Reference Material (SRM) Recoveries (%)	
	NBS 1646 True Values (ppm)	NBS 1646 % Recovery
Antimony	0.4	50 <sup>d</sup>
Arsenic	11.6	80
Cadmium	0.36	94
Copper	18	88
Lead	28.2	84
Mercury	12.7	100
Nickel	32	82
Silver	NC <sup>e</sup>	--
Zinc	138	85

<sup>a</sup> Recoveries outside control limits of 75-125 percent recovery.

<sup>b</sup> Mercury analyzed by cold vapor atomic absorption method.

<sup>c</sup> Mercury analyzed on Sample AKB02 for predigestion spike.

<sup>d</sup> Recoveries outside control limits of 80-120 percent recovery.

<sup>e</sup> NC = Not certified.

TABLE D-13. METALS RECOVERY RESULTS FOR TISSUE DIGESTS

	Spike Recoveries (%)		
	Spike Concentration (mg/kg)	Station BBT04A	Station BBT08A
Antimony	2.5	64 <sup>a</sup>	82
Arsenic	20.0	98	91
Cadmium	0.5	108	101
Copper	5.0	97	105
Lead	2.0	102	97
Mercury <sup>b</sup>	0.05	101	124
Nickel	2.5	103	92
Silver	0.4	19 <sup>a</sup>	9.5 <sup>a</sup>
Zinc	25.0	91	91

  

	Standard Reference Material (SRM) Recoveries (%)		
	TORT-1 True Values (ppm)	TORT-1 % Recovery	TORT-1 % Recovery
Antimony	NC <sup>c</sup>	--	--
Arsenic	24.6	88	104
Cadmium	26.3	89	102
Copper	439.0	88	102
Lead	10.4	96	98
Mercury	0.3	100	100
Nickel	2.3	100	100
Silver	NC	--	--
Zinc	177.0	80	94

<sup>a</sup> Recoveries outside control limits of 75-125 percent recovery.

<sup>b</sup> Mercury analyzed by cold vapor atomic absorption method.

<sup>c</sup> NC = Not certified.

**TABLE D-14. RESULTS OF SEDIMENT REPLICATE ANALYSES**

	Station BBB01		
	Rep 1	Rep 2	RPD
Antimony	0.21	0.12	53 <sup>a</sup>
Arsenic	7.7	9.3	18
Cadmium	0.77	0.79	2.3
Copper	49	53	6.5
Lead	18	19	6.2
Mercury	0.076 <sup>b</sup>	0.069 <sup>b</sup>	11 <sup>b</sup>
Nickel	103	109	5.2
Silver	0.32	0.33f	4.6
Zinc	110	127	15

<sup>a</sup> Sample outside PSEP control limit of  $\pm 20$  percent RPD.

<sup>b</sup> Sample AKB02 used for replicate analysis of mercury.

## Tissue

The laboratory performed two replicate tissue analyses. Results are summarized in Table D-15. For both samples, the  $\pm 20$  percent PSEP control limit was exceeded for silver. Silver data are recommended to be qualified as *E*.

Replicate results were within PSEP control limits for arsenic, cadmium, copper, lead, mercury, nickel, and zinc. The antimony replicate concentrations were undetected; therefore, the RPD value could not be calculated.

## BLANKS

### Sediment

Reagent and calibration blanks were analyzed for all metals and accompanied the sediment samples. Reagent and calibration blanks were less than the IDL for all metals, except cadmium. One CCB was reported at the IDL. The data were not qualified or blank-corrected because the blank value was less than 2 times the IDL.

### Tissue

Reagent and calibration blanks were analyzed for all metals and accompanied the tissue analyses. All reagent and calibration blanks were less than the PSEP CRDL and IDL for antimony, arsenic, cadmium, mercury, nickel, and zinc. The reagent blanks for copper and lead were above the PSEP CRDL. PSEP protocols require the samples to be redigested and reanalyzed if any blank exceeds the CRDL. The laboratory had limited amount of sample and reanalysis was not possible. The PSEP CRDL is based on a 5-gram sample aliquot diluted to 25 mL after digestion. Because of the limited sample size, many samples were analyzed using a 1-gram sample aliquot. Therefore, the method detection limit is raised by a factor of 5, to take into account the reduced sample size. Because of the raised method detection limit the blank value was below the limit which would require redigestion and reanalysis by the laboratory. However, the blanks were greater than the IDL, therefore the sample values were evaluated to determine what effect blank contamination had on the final sample values.

Two different criteria have been developed to evaluate blank contamination: 1) high level criteria for ICP blank evaluation, and 2) low level criteria for GFAA blank evaluation (PTI 1989). The two criteria were developed due to the low levels of detection required for PSEP contract analyses. PSEP CRDL can be at or near the IDL for GFAA analyses. Therefore, blank contamination can significantly affect data quality.

Copper was analyzed by ICP and the blank contamination was evaluated using the high level criteria. Under high level criteria, to determine if any action is warranted, the concentration in the highest blank is multiplied by five. This value is considered the action level and any samples less than this value would be blank-corrected and qualified as *E* because of blank contamination. The action level for copper is 0.14 mg/kg and the sample concentrations ranged from 0.73 to 6.2 mg/kg. The samples all had copper concentrations greater than the action level; therefore, no data qualifiers are required.

TABLE D-15. RESULTS OF TISSUE REPLICATE ANALYSES

	Station BBI04A			Station BBT08A		
	Rep 1	Rep 2	RPD	Rep 1	Rep 2	RPD
Antimony	0.02U	0.02U	NC <sup>a</sup>	0.02U	0.02U	NC <sup>a</sup>
Arsenic	1.5	1.7	15	1.3	1.3	0.0
Cadmium	0.46	0.48	3.3	0.49	0.51	3.6
Copper	1.2	1.2	4.8	1.3	1.3	1.5
Lead	0.76	0.87	14	0.82	0.87	6.0
Mercury	0.033	0.037	12	0.034	0.031	8.4
Nickel	0.58	0.62	6.6	0.56	0.56	0.9
Silver	0.31	0.19	49 <sup>b</sup>	0.19	0.36	60 <sup>b</sup>
Zinc	12.0	13.2	10	10.1	10.9	7.7

<sup>a</sup> Not calculated because of undetected values.

<sup>b</sup> Sample outside PSEP control limit of  $\pm 20$  percent RPD.

Lead was analyzed by GFAA and the blank contamination was evaluated using the low-level criteria. The blank contamination is evaluated based on the blank concentration and the sample concentrations. Blank concentrations above 2 times the IDL are to be evaluated and any data qualifiers are assigned based on whether the sample values are significantly or marginally affected. The highest blank value for lead was greater than 2 times the IDL, but all samples, except Sample BBB01A, had sample concentrations greater than 10 times the IDL. For those samples with lead values greater than 10 times the IDL, blank-correction is not necessary and no data qualifiers are assigned. For Sample BBB01A, the blank value was subtracted and the corrected sample result is 0.02 mg/kg and the sample is assigned a Z qualifier.



## ANALYSIS OF TRIBUTYLTIN IN SEDIMENTS

### SUMMARY

Overall, tributyltin (TBT) data are acceptable as qualified. All data reported below the lowest concentration of the calibration curve ( $10 \mu\text{g}/\text{kg}$  dry weight) were qualified as *E*. This affected nearly all of the TBT data. Control limits for TBT analysis are not yet available from PSEP, but TBT data typically met PSEP control limits for organic analyses, and in most cases control limits for metals as well. Based on the method of TBT analysis used in this study (e.g., including organic extraction, extract cleanup, and gas chromatographic analysis), control limits for organic compounds were considered more germane to the analysis than control limits for metals.

### SAMPLE COLLECTION: ACCEPTABLE

Details of sediment sampling are given in Appendix A and are summarized in this section. Sediment samples were collected between April 11 and May 4, 1989 with a dual  $0.1\text{-m}^2$  van Veen grab sampler. Sample depths were 10 cm at the disposal zone and other site stations and 2 cm at all other stations (i.e., perimeter, benchmark, and reference). Each sample was formed of material composited from a minimum of six grabs.

Acceptability of grab samples was evaluated in accordance with criteria specified by PSEP (1986). Grab samples failing to meet PSEP criteria were excluded from compositing. After a grab sample was judged to be acceptable, the overlying water was siphoned off and the sample was collected with stainless steel spatulas according to PSEP recommendations. Grab samples for each station were homogenized in a stainless steel bowl with stainless steel spoons until uniform color and texture were apparent. Sediment was then transferred to the appropriate sample container (discussed in detail in Appendix A) and stored on ice. Cleaning of sampling equipment is described in Appendix A. Chain-of-custody records were completed at the end of each day.

### SHIPPING AND HOLDING TIMES: ACCEPTABLE

Samples were shipped on ice to Battelle Northwest Laboratories (Sequim, Washington). Sample holding times were well within the PSEP control limit of 1 year for frozen sediments (PSEP 1986). Instrumental [gas chromatography/mass selective detection (GC/MSD)] analyses were conducted between June 2 and June 16, 1989; the PSEP extract holding time of 40 days was not exceeded for any samples.

### COMPLETENESS: ACCEPTABLE

Data were received for all 15 samples submitted to the laboratory for analysis, along with data for 1 sediment reference material, 1 matrix spike, 1 analytical replicate, and 2 method blanks.

## **ANALYTICAL METHODS: ACCEPTABLE**

Methods used for TBT analysis in this study were based on procedures and recommendations discussed in the EPA Region 10 memorandum that resulted from a meeting of the Subcommittee on Organotin Analysis Methods (September 25, 1987).

Sediment samples were acidified and mixed with sodium sulfate prior to extraction with tropolone/methylene chloride. The extracts were concentrated, exchanged into hexane, and treated with a Grignard reagent to form hexyl derivatives. Derivatized extracts were subjected to Florisil column chromatography cleanup and were analyzed by GC/MSD (1.0 mL final extract volume). GC/MSD analyses employed a fused silica capillary column (DB-5, 30 m, 0.25 mm i.d., J & W Scientific) and the following temperature program: 75° C initial temperature, heated to 250° C at 30° C/minute (held at 250° C for 20 minutes). The following ions were monitored during analysis: m/z 235, 263, and 319 (TBT) and m/z 249 and 291 [tripropyltin (TPT), the recovery surrogate compound].

### **Calibration**

TBT standards were prepared by derivatizing pure TBT, cleaning the derivatives on a Florisil column, evaporating solvent to a constant dry weight, and then weighing out the solid and dissolving it in hexane. Standards were prepared for 0.1, 0.5, and 1.0 ppm TBT as tin. Assuming a dry weight sample of 10 grams, these standards would correspond to 10, 50, and 100 µg/kg dry weight TBT as tin. Initial calibrations were performed both times the samples were analyzed by GC/MSD. The initial calibrations were within the PSEP guidelines of ±20 percent RSD of the response factors at each concentration.

### **Detection Limits**

IDL were determined analogously to the method specified by the EPA/CLP. The lowest concentration standard (0.1 ppm) was run three times in each of four analytical sessions and the standard deviation was calculated for each analytical session. IDL were calculated as three times these standard deviations. Sample detection limits were then calculated using the IDL, sample weight, and final extract volume. Nominal sample detection limits averaged 2.5 µg/kg dry weight. Data reported below 10 µg/kg dry weight were qualified with an *E* because the calibration range did not encompass (i.e., show linearity) concentrations below 10 µg/kg dry weight.

### **Compound Confirmation**

The use of a mass selective detector allowed for a relatively high degree of reliability in compound confirmation. Compound confirmation was examined during QA review by comparing ion ratios of standards to those in samples. In this study, the alkyl tin species were derivatized by reaction with a Grignard reagent, hexylmagnesium bromide. The resultant hexyl-TBT has predominant mass spectrum peaks at m/z 319 (loss of butyl), m/z 263 (loss of two butyls), and m/z 235 (loss of butyl and hexyl) among others. The average ion ratios (as percent of each peak of the total three peaks) of standards and the samples, along with the standard deviations and ranges are shown in Table D-16. The mean ion percentages for standards and samples are very

**TABLE D-16. AVERAGES, STANDARD DEVIATIONS, AND RANGES OF TBT IONS IN STANDARDS AND SEDIMENTS**

Ion	Mean	Standard Deviation	Range
<b>Standards</b>			
235	36	4.0	32-40
263	26	1.0	25-27
319	38	5.0	33-43
<b>Samples</b>			
235	39	12	0-55
263	26	4.7	18-39
319	36	8.3	29-61

similar. The larger ranges and standard deviations of sample ions is indicative of ion contributions from interferences and ion ratios biased by the absence of TBT in the sample.

#### ACCURACY: ACCEPTABLE

Accuracy was assessed with analysis of one sediment reference material, one matrix spike, and recoveries of the surrogate compound, TPT, which was added to all samples. PSEP protocols do not provide guidance for control limits for the analysis of organometallics such as TBT. In the following discussion, comparisons are made with the QA checks and control limits specified by PSEP for metals and organic compounds. It should be noted that, in general, the control limits for inorganic analyses are more stringent than those for organic analyses, and that the method used in this study (including solvent extraction and analysis by GC/MSD) is more closely aligned to analyses for organic compounds.

#### Sediment Reference Material

The results for the analysis of Sequim-1 (SQ-1) sediment reference material by laboratory was 60  $\mu\text{g}/\text{kg}$  and 67  $\mu\text{g}/\text{kg}$  dry weight. The reported results are duplicate GC/MSD analyses of the same extract. The TBT concentration of  $31 \pm 12 \mu\text{g}/\text{kg}$  dry weight (mean  $\pm$  standard deviation) reported by NOAA for this reference material is based on 13 analyses. PSEP control limits (the 95 percent confidence interval of certified values) for organic compounds are not strictly applicable to the results. The observed results are 194 percent and 216 percent recovery of the NOAA value. These results indicate a high bias for TBT data that is not corroborated by surrogate recoveries (discussed below). Matrix spike recoveries show this bias to a lesser degree (discussed below).

#### Matrix Spikes

One matrix spike analysis was performed on Sample AKP01 and analyzed in duplicate by GC/MSD. The matrix spike results are as follows (concentration units are  $\mu\text{g}/\text{kg}$  dry weight):

Sample	Spike + Sample	Sample	Spike	Recovery (%)
AKP01	261	3.0	208	124
AKP01 (GC duplicate)	224	2.5	208	106

The PSEP control limit for matrix spike recovery is  $\geq 50$  percent recovery for organic compounds and 75-125 percent recovery for metals. The percent recoveries listed above are within both sets of control limits and indicate acceptable accuracy of the TBT data.

#### Surrogate Recoveries

Every sample contained TPT as a surrogate, added along with the methylene chloride/tropolone at the beginning of the extraction. The PSEP control limit for recovery of organic surrogate compounds,  $\geq 50$  percent, was considered appropriate for TBT analyses (surrogates are not

a QA element of the metals analysis under PSEP or EPA/CLP). TPT recovery results for the 15 samples are shown in Table D-17. All of the surrogate recovery results are within the PSEP control limit of  $\geq 50$  percent.

#### PRECISION: ACCEPTABLE

One analytical duplicate analysis was performed on Sample BBP01. Concentrations of the duplicate analysis were 7.2  $\mu\text{g}/\text{kg}$  and 4.0  $\mu\text{g}/\text{kg}$  dry weight (RPD of 57 percent). The PSEP control limit for precision (as RPD) is 20 percent for metals and 100 percent for organic compounds. The control limit for organic compounds is more appropriate for IBT analysis, therefore, the precision is considered acceptable.

#### BLANKS: ACCEPTABLE

Two reagent blanks were analyzed. The results were as follows:

Blank	$\mu\text{g}/\text{kg}$ Tin
1	<2.4
2	<2.4

Blanks were analyzed by adding sodium sulfate and then the methylene chloride/tropolone mixture to an empty sample container. The results assume a 5-gram dry weight sample size in order to be comparable to samples (average sample size was roughly 5 grams dry weight). Blank results are considered acceptable.

**TABLE D-17. TPT SURROGATE RECOVERIES  
(as percent)**

Station	TPT
AKB02	81
AKP01	75
AKP02	53
AKP03	56
AKP04	67
AKZ01	95
BBB01	83
BBB02	83
BBB04	89
BBP01	84
BBP02	68
BBP03	105
BBP04	78
BBZ01	102
CRR01	74
SQ1	96
SQ1 Duplicate	73
<b>Mean</b>	<b>80</b>
<b>Coefficient of Variation (%)</b>	<b>18</b>
<b>Range</b>	<b>53-105</b>

## ANALYSIS OF CONVENTIONAL VARIABLES IN SEDIMENTS

### SUMMARY

The results for conventional analyses, total solids (TS), total volatile solids (TVS), total organic carbon (TOC), total sulfide, and ammonia are acceptable as reported.

### SAMPLE COLLECTION AND TRANSPORT

Details of sediment sampling are described in Appendix A and are summarized in this section. Sediment samples were collected between April 11 and May 4, 1989. Samples were shipped on ice via bus with chain-of-custody documentation to CAS (Longview, Washington).

### COMPLETENESS: ACCEPTABLE

Results were received for all samples submitted to the laboratory. All samples were analyzed within the recommended holding times.

### DATA REPORTING

The raw data sheets were 100 percent verified for TS and TVS, and no calculation errors were revealed. A spot check of the raw data sheets for TOC, total sulfide, and ammonia revealed no calculation errors.

The final report sheets were reviewed for reporting errors and the sample identifications were crossed referenced with laboratory numbers and chain-of-custody records to verify correct identification. The average of the triplicate analyses for TS, TVS, total sulfide, and two TOC samples were reported as the sample value. The sample values should be corrected as follows:

Sample Identification	Parameter	Corrected Value
AKB02	TS5	6.8%
AKP03	TS	48.0%
AKB02	TVS	2.1%
AKP03	TVS	3.8%
BBB01	Total Sulfide	1 mg/kg
BBP01	TOC	2.4 mg/kg
BBP02	TOC	2.6 mg/kg

Review of the raw data sheets revealed the ammonia values had been calculated using the wrong total solids values. The ammonia values should be corrected as follows:

Sample Identification	Corrected Ammonia (mg/Kg)
BBB01	232
BBB02	197
BBB0	471.0
BBP0	195.5
BBP0	2129
BBP0	3150
BBP0	4125
BBZ01	69.1
AKB02	32.6
AKP01	59.3
AKP04	49.6
AKZ01	40.9
CRR01	85.8
AKP02	35.9
AKP03	51.5

#### **ANALYTICAL METHODS: ACCEPTABLE**

Sixteen samples were analyzed for IS, IVS, total sulfide, and ammonia (plus two laboratory triplicates). Thirty-nine samples (plus four laboratory triplicates) were analyzed for TOC. The procedures used for IS, IVS, TOC, and total sulfide analyses were in accordance with PSEP protocols (PSEP 1986). TOC was measured using a combustion technique followed by coulometric detection. Total sulfides were determined by distillation followed by spectrophotometric analysis. PSEP does not specify a procedure for ammonia analysis. Ammonia analyses were performed by methods described in Plumb (1981) (Method 1, using KCl extraction), with analysis of the extract by specific ion probe (EPA Method 350.3).

#### **CALIBRATION: ACCEPTABLE**

For TOC determinations, the laboratory used a urea standard to verify instrument calibration. The laboratory analyzed seven urea standards obtaining a mean recovery of 95 percent with a range of 89-104 percent recovery.

Total sulfide determination used a four- and five-point calibration curve. The samples were analyzed on two separate days and the correlation coefficient ( $r$ ) was 0.999 for both days.

Ammonia determination used a four-point calibration curve. An EPA SRM, WP987 (water matrix), was analyzed to verify the calibration curve with recoveries of 92 percent and 109 percent.

#### **DETECTION LIMITS: ACCEPTABLE**

Except for total sulfides, no undetected values were reported. Detection limits are acceptable.

### **ACCURACY: ACCEPTABLE**

The analysis of sample spikes is not specified under PSEP protocols for TS, TVS, or TOC analyses. For TOC analyses the laboratory analyzed a known amount of a urea standard to verify the instrument's accuracy, obtaining a mean recovery of 95 percent and a range of 89-104 percent.

Two spikes were analyzed for total sulfides. Sulfide spike recoveries were 84 percent and 98 percent, with a mean of 91 percent.

For ammonia analysis, the EPA SRM, WP987 (water matrix), was analyzed. Because the SRM is a water standard, the analysis cannot truly duplicate the recovery for sediment. However, acceptable recovery was obtained (118 percent and 114 percent).

### **PRECISION: ACCEPTABLE**

No blind duplicates were submitted to the laboratory. Results of triplicate analyses performed by the laboratory are presented in Table D-18. The frequency of triplicate analyses met PSEP guidelines for laboratory replication. Coefficients of variation for the triplicate analyses indicated acceptable analytical precision for all analyses. Coefficients of variation ranged from 1.4-2.4 percent for TS, 4.5-6.3 percent for TVS, 0-12 percent for IOC, 9.1 percent for total sulfide, and 4.3-9.7 percent for ammonia.

### **BLANKS: ACCEPTABLE**

Reagent blanks were analyzed for TOC, total sulfide, and ammonia. For IOC and total sulfide, the raw blank value was subtracted from the sample value prior to calculating the sample concentrations. The blank value for ammonia was not subtracted prior to calculating sample concentrations. All blank values were less than one-tenth the sample concentrations, except four samples for TOC. Samples AKT03I, AKT04 I-1, AKB02, and AKP01 should be assigned a Z qualifier because the blank concentration was greater than one-tenth the sample concentrations.

TABLE D-18. REPLICATE RESULTS FOR CONVENTIONAL ANALYSES

Sample Identification	Replicate Results	Mean	Standard Deviation	c.v. <sup>a</sup>
Total Solids (%)				
AKB02	56.8, 59.3, 59.2	58.4	1.42	2.4
AKP03	48.0, 46.0, 47.9	47.3	1.13	2.4
Total Volatile Solids (%)				
AKB02	2.1, 2.2, 2.3	2.2	0.10	4.5
AKP03	3.8, 4.3, 4.2	4.1	0.26	6.3
Total Organic Carbon (%)				
BBP01	2.4, 2.4, 2.4	2.4	0.00	0.0
BBP02	2.6, 2.6, 2.6	2.6	0.00	0.0
BBT01 I-1	2.2, 2.2, 2.2	2.2	0.00	0.0
AKT05 I-1	0.6, 0.5, 0.5	0.5	0.06	12
Total Sulfide (mg/kg)				
AKB02	1 U, 1 U, 1 U <sup>b</sup>	1 U	-- <sup>c</sup>	-- <sup>c</sup>
BBB01	1 U, 1 U, 1 U <sup>b</sup>	1.1	0.10	9.1
Ammonia (mg/kg)				
BBB01	232, 191, 210	211	20.5	9.7
AKZ01	40.9, 40.9, 37.9	39.9	1.73	4.3

<sup>a</sup> c.v. - coefficient of variation (as percent).

<sup>b</sup> Qualifiers:

U - undetected at detection limit shown.

<sup>c</sup> -- not calculated because of undetected values.

## ANALYSIS OF PARTICLE SIZE DISTRIBUTION IN SEDIMENTS

### SUMMARY

The data are acceptable as reported for all samples except in Samples AKB01I-1, AKT02I, AKT03I-1, AKT05I-1, AKT06I-1, BBZ01, and BBDNR. These samples are being reanalyzed by the laboratory.

### SAMPLE COLLECTION AND TRANSPORT

Details of sediment sampling are described in Appendix A and are summarized in this section. Sediment samples were collected between April 11 and May 4, 1989. Samples were shipped on ice via bus with chain-of-custody documentation to CAS (Longview, Washington).

### COMPLETENESS

Results were received for all samples submitted. Raw data sheets were submitted for all samples. All samples were analyzed within the 6-month PSEP holding time.

### DATA REPORTING

The laboratory report sheets are generated by computer. The raw data were checked against the data entry sheet to verify that no data entry errors were made. The triplicate analysis of Sample AKP03 had a data entry error and the data were corrected prior to entry into the database. No other calculation or data entry errors were found.

### ANALYTICAL METHODS

Thirty-nine samples (plus two triplicates) were analyzed for particle size. Analytical methods were in accordance with the PSEP protocols (PSEP 1986).

Samples were oxidized with hydrogen peroxide to remove organic materials prior to sieve analysis. Sand fractions were sieved to 1-phi intervals and clay and silt fractions were differentiated by the pipet technique.

### ACCURACY

Analysis of SRM are not specified under PSEP protocols for particle size determinations. Overall sample recovery is assessed by comparing the sum of the fraction weights with the calculated dry weight of the initial sample aliquot. PSEP recommends losses, assessed by this method, should be less than 5 percent (or >95 percent recovery). Of the 41 analyses reported,

95 percent recovery based on the total sample weight was not obtained for Sample BBP02. Review of the data indicates that these slightly low recoveries would not significantly change the size fractions reported, therefore the data were not qualified.

PSEP protocols recommend that the total weight of fine-grained material used in the silt and clay determination be between 5 and 25 grams. A sample size of less than 5 grams was used for the following seven samples: AKB02I-1, AKT02I, AKT03I-1, AKT05I-1, AKT06I-1, AKT06I-1 (duplicate), Sample AKT06I-1 (triplicate). A sample size greater than 25 grams was used for Sample BBZ01. If more material is used, particles may interfere with each other during the settling and the possibility of flocculation may be enhanced. If less material is used, then the experimental error in weighing becomes large relative to the sample size. According to PSEP protocols, total weights outside this range are not acceptable and the aliquot size should be modified to bring the amount of fine-grained material into the acceptable range. The laboratory is reanalyzing those samples outside the acceptable range for the clay and silt fraction.

## PRECISION

Two triplicate analyses were performed. Table D-19 lists the replicate results for the particle size determinations for all fractions. One triplicate analyses is being reanalyzed by the laboratory for the clay and silt fractions. For Sample AKP03, the precision was good for all fractions. The CV for the size fractions ranged from zero to 7.2 percent.

TABLE D-19. REPLICATE RESULTS FOR PARTICLE SIZE ANALYSES

Sample Identification	Replicate Results	Mean	Standard Deviation	c.v. <sup>a</sup>
<b>AKP03</b>				
Gravel	0, 0, 0	0	0.00	0.0
Very coarse sand	0, 0, 0	0	0.00	0.0
Coarse sand	0, 0, 0	0	0.00	0.0
Medium sand	1, 1, 1	1	1.15	4.8
Fine sand	25, 23, 25	24	1.15	4.8
Very fine sand	38, 41, 37	39	2.08	5.3
Silt	20, 20, 19	20	0.58	2.9
Clay	15, 15, 17	16	1.15	7.2
<b>AKT06</b>				
Gravel	0, 0, 0	0	0.00	0.0
Very coarse sand	0, 0, 0	0	0.00	0.0
Coarse sand	0, 0, 0	0	0.00	0.0
Medium sand	31, 36, 32	33	2.64	8.0
Fine sand	49, 45, 49	48	2.31	4.8
Very fine sand	4, 4, 4	4	0.00	0.0
Silt	5, 6, 5	5	0.57	11.5
Clay	10, 9, 10	10	0.57	5.8

<sup>a</sup> c.v. - coefficient of variation (as percent).



## AMPHIPOD MORTALITY BIOASSAY

The amphipod mortality bioassay using *Rhepoxynius abronius* was conducted at seven PSDDA stations, as well as at a control station at West Beach. The protocols were consistent with those recommended by PSEP (1986). The quality assurance/quality control (QA/QC) evaluation consisted of a review of the following information:

- Negative control
- Positive control
- Water quality conditions
- Response variability.

Results of the QA/QC evaluation are presented below.

### NEGATIVE CONTROL

Mean mortality at the West Beach control station was 4 percent. This value is less than the maximum allowable value of 10 percent, indicating that testing conditions were appropriate and the test organisms were not unusually sensitive.

### POSITIVE CONTROL

Positive control testing was conducted using sodium pentachlorophenate (NaPCP) as the reference toxicant. Six test concentrations were used (i.e., 1,000, 560, 320, 180, 100, and 0 ppb), and a dose-responsive relationship was observed. A 96-hour LC<sub>50</sub> (chemical concentration lethal to 50 percent of test organisms) of 382 ppb was found, with 95-percent confidence limits of 180-560 ppb. These results indicate that the test organisms were responsive to chemical contaminants in a dose-responsive manner.

### WATER QUALITY CONDITIONS

In all cases, salinity ranged from 28 to 30 ppt and was within the recommended range of 27-30 ppt. Temperature ranged from 14 to 17° C and exceeded the recommended range of 14-16° C in three cases. A temperature of 17° C was observed on day 5 for the West Beach negative control and Stations CCR01 and AKZ01. However, because these exceedances were relatively small (i.e., 1° C) and because they were only found on one of the 10 test days, it is unlikely that they substantially influenced the test results.

Dissolved oxygen ranged from 6.9 to 8.4 mg/L, and pH ranged from 7.8 to 8.3. Neither of these variables was found at levels that could jeopardize the quality of test results.

## **RESPONSE VARIABILITY**

The standard deviation of percent mortality ranged from 4.0 to 11.5 and was not unusually high (i.e., >15) at any station. Statistical comparisons at all stations should therefore not be influenced by low statistical power.

## BIVALVE LARVAE ABNORMALITY BIOASSAY

The bivalve larvae abnormality bioassay using the Pacific oyster (*Crassostrea gigas*) was conducted at seven PSDDA stations, as well as at a control station at West Beach. The protocols were consistent with those recommended by PSEP (1986). The QA/QC evaluation consisted of a review of the following information:

- Negative control
- Positive control
- Water quality conditions.

Results of the QA/QC evaluation are presented below.

### NEGATIVE CONTROL

Mean mortality and abnormality in the seawater control was 51 percent, exceeding the control performance standard of 50 percent being considered by PSDDA. Performance standards for this bioassay continue to be modified by PSDDA, and the exceedance is considered minor. However, if a reference performance standard is also applied to the data, the bioassay data would be rejected. Mortality and abnormality in Carr Inlet reference sediments was 61 percent above the seawater controls. This exceeds the 20 percent maximum currently being considered by PSDDA. These data suggest that either Carr Inlet sediments are toxic to larvae or the interpretation of this bioassay require further analysis.

### POSITIVE CONTROL

Positive control testing was conducted using sodium lauryl sulfate as the reference toxicant. Three test concentrations were used (i.e., 1, 10, and 100 ppm) and a dose-responsive relationship was found. However, the concentration range did not include the EC<sub>50</sub> (chemical concentration effective in eliciting response in 50 percent of test organisms), so it could only be estimated as <1 ppm. These results indicate that the test organisms were responsive to chemical contaminants in a dose-responsive manner.

### WATER QUALITY CONDITIONS

Salinity ranged from 29 to 32 ppt and exceeded the recommended range of 27-29 ppt in 52 of 54 cases. However, because the test species is sensitive primarily to reduced salinities, it is unlikely that salinities exceeding the maximum value by 1-3 ppt would substantially influence response sensitivity. Temperature was 20° C in all cases and was within the recommended range of 19-21° C.

Dissolved oxygen ranged from 4.0 to 6.4 mg/L, and pH ranged from 7.3 to 7.8. Dissolved oxygen was potentially low enough (i.e., <5.0 mg/L) to influence test results in six samples, all of which were positive controls. No values of pH were found at levels that could jeopardize the quality of test results.



## MICROTOX BIOASSAY

The Microtox bioassay using the bacterium *Photobacterium phosphoreum* and a saline extract was conducted at seven PSDDA stations, as well as at a control station at West Beach. The protocols were consistent with those recommended by PSEP (1986). The QA/QC evaluation consisted of a review of the following information:

- Negative control
- Positive control.

Results of the QA/QC evaluation are presented below.

### NEGATIVE CONTROL

Bacterial luminescence showed no dose-responsive relationships at the West Beach control station and was judged nontoxic. These results indicate that test conditions were appropriate and the test organisms were not unusually sensitive.

### POSITIVE CONTROL

Positive control testing was conducted using phenol as the reference toxicant. Four test concentrations were used (i.e., 16, 32, 64, and 128 ppm), and a dose-responsive relationship was observed. A 15-minute  $EC_{50}$  of 24.8 ppm was found. These results indicate that the test organisms were responsive to chemical contaminants in a dose-responsive manner.



## BENTHIC MACROINVERTEBRATES

Benthic macroinvertebrate assemblages were sampled at 11 PSDDA stations (five replicates per station) using a box corer and a sieve mesh size of 1.0 mm. Collected organisms were identified to the following major taxa levels: Polychaeta, Mollusca, Crustacea, and miscellaneous taxa (e.g., Echinodermata, Nemertea, Sipuncula, Anthozoa, Echiura, Nematoda, and Urochordata). The QA/QC evaluation consisted of a review of the following information:

- Sorting efficiency
- Total counts.

Results of the QA/QC evaluation are presented below.

### SORTING EFFICIENCY

Twenty percent of each sample was resorted by a person other than the one who originally sorted the sample. In 18 of 55 cases (33 percent), the number of organisms found during resorting was greater than 5 percent of the total number of organisms in the sample (i.e., sorting efficiency was less than the desired level of 95 percent). Those samples included:

- Station BBB01I: Replicates 2 (5.8 percent) and 4 (7.3 percent)
- Station BBB02I: Replicates 2 (6.6 percent) and 4 (5.3 percent)
- Station BBB03I: Replicate 2 (16.9 percent)
- Station BBB04I: Replicates 2 (11.5 percent) and 3 (9.0 percent)
- Station BBT01I: Replicates 1 (10.9 percent) and 3 (11.5 percent)
- Station BBT02I: Replicate 1 (7.5 percent)
- Station BBT03I: Replicates 2 (8.5 percent), 3 (8.6 percent), and 5 (5.7 percent)
- Station AKB02I: Replicates 1 (7.5 percent) and 3 (11.2 percent)
- Station AKT01I: Replicates 4 (5.9 percent) and 5 (6.5 percent)
- Station AKT03I: Replicate 1 (6.3 percent).

Each of the above samples was completely sorted and subjected to a second 20 percent QA/QC evaluation. The desired sorting efficiency of  $\geq 95$  percent was achieved for all of these samples after each was sorted a second time.

### TOTAL COUNTS

The total numbers of individuals for the most abundant major taxa (i.e., Polychaeta, Mollusca, and Crustacea) were compared among replicates at each station to determine whether any exhibited

unusually high variation. Coefficients of variation ranged from 17 to 109 percent for Polychaeta, 11 to 55 percent for Mollusca, and 12 to 49 percent for Crustacea (Table D-20). The only sample exhibiting unusually high variability was for polychaetes at Station AKT01I. Excluding that sample, the coefficients of variation for polychaetes ranged from 17 to 38 percent. Although the mean abundance of polychaetes at Station BBB01I was unusually high (i.e., 1,229 individuals), the CV was relatively low (i.e., 36 percent) indicating that the high mean value was the result of all five replicate measurements rather than an anomalously high value for only one or two replicates. Most of the polychaetes at Station BBB01I (i.e., 82-96 percent) were cirratulids, a family that is often very abundant in other parts of Puget Sound (e.g., Commencement Bay). The laboratory noted that high abundances of nematodes in replicate 5 at Stations BBB03I and BBT02I were the result of small individuals (i.e., <1.0 mm in size) being retained in the sample by mucous produced by the sea anemone *Pachycerianthus fimbriatus*. Mucous was also noted in samples from Stations BBB02I, BBB04I, BBT01I, BBT02I, and BBT03I. However, relatively low numbers of nematodes were retained in those samples. The laboratory did not include nematodes in the final counts they reported because these small organisms would not have been retained under normal circumstances.

TABLE D-20. COEFFICIENTS OF VARIATION<sup>a</sup>  
FOR ABUNDANCES OF MAJOR TAXA

Station	Taxon		
	Polychaeta	Mollusca	Crustacea
AKB02I	17	52	12
AKT01I	109	42	22
AKT02I	17	30	27
AKT03I	19	55	25
BBB01I	36	32	47
BBB02I	18	26	40
BBB03I	38	25	49
BBB04I	61	42	48
BBT01I	29	31	32
BBT02I	35	11	43
BBT03I	27	43	23

<sup>a</sup> As percent.



## REFERENCES

Plumb, R.H., Jr. 1981. Procedures for handling and chemical analysis of sediment and water samples. Technical Report EPA/CE-81-1. U.S. Environmental Protection Agency and U.S. Army Corps of Engineers, Waterways Experiment Station, Vicksburg, MS.

PSEP. 1986. Recommended protocols for measuring selected environmental variables in Puget Sound. Final report. Prepared for U.S. Environmental Protection Agency Region 10, Office of Puget Sound, and U.S. Army Corps of Engineers. Tetra Tech, Inc., Bellevue, WA.

PTI. 1989. Data validation guidance manual for selected sediment variables. Draft report. Prepared for Washington Department of Ecology. PTI Environmental Services, Bellevue, WA.

Shelton, M. 25 April 1989. Personal Communication (letter to Mr. Robert Barrick, PTI Environmental Services, Bellevue, WA). Columbia Analytical Services, Inc., Longview, WA.

U.S. EPA. 1987. Contract Laboratory Program statement of work for inorganic analysis. SOW No. 787. U.S. Environmental Protection Agency, Washington, DC.