Bioaccumulation of Contaminants in Crabs and Clams in Bellingham Bay

Prepared for
Puget Sound Estuary Program
US Environmental Protection Agency
Region 10, Seattle WA

anđ

Fran Solomon and Lucy Pebles
Northwest Regional Office
Washington State Department of Ecology

by

James Cubbage

Washington State Department of Ecology
Environmental Investigations and Laboratory Services
Toxics, Compliance, and Ground Water Investigations Section
Olympia, WA 98504-6814

Waterbody No. WA-01-0040 (Segment No. 01-01-02)

September 1991

ABSTRACT

Bellingham Bay supports commercial and recreational shellfish harvest. Industrial and municipal discharges into the bay have contributed to high sediment concentrations of mercury and PCBs. To investigate potential bioaccumulation of contaminants in shellfish, crab (Cancer magister) muscle was collected from eight sites and littleneck clams (Tapes japonica, Protothaca staminea) from four sites and tested for concentrations of PCBs, other organochlorine compounds including chlorpyrifos and pentachlorophenol, cadmium, arsenic, lead, and mercury. Clams were also tested for polycyclic aromatic hydrocarbons (PAH). In crabs, metals ranged as follows: (Cd:0.002-0.005; As:1.9-5.6; Pb:0.05-0.29; Hg:0.06-0.15; in mg/kg wet weight). Metals in whole clams ranged as follows: (Cd:0.18-0.23; As:1.1-2.0; Pb:0.02-0.15; Hg:not detected-0.02; all mg/kg wet weight). Low concentrations of PAH were found in clams (<2-20 ppb). No pesticides or PCB's were found above detection limit in crabs or clams. A concurrent study conducted by Department of Natural Resources that examined crabs caught from the center of the bay found equivalent concentrations of mercury, arsenic and lead, higher concentrations of cadmium and detections of DDE in 2 of 7 samples (1.5, 0.6 ppb) and chlordane in 1 of 7 samples (3.7 ppb). These metals and PAH concentrations are comparable to concentrations found in Puget Sound reference areas with presumably low levels of contamination. Concentrations of mercury in Bellingham Bay crabs have declined over the last 15 years and reflect the decreased discharge of mercury into the bay.

ACKNOWLEDGEMENTS

Several people and agencies contributed to this study. This project was conducted cooperatively with a Department of Natural Resources (DNR) study to determine chemical concentrations in biota at Puget Sound Dredge Disposal Analysis (PSDDA) sites within Bellingham Bay. This cooperation saved logistic costs and provided greater spacial coverage. Mike MacKay of the Lummi Tribe collected crabs with crab pots and assisted in study design. Michael Cochrane of the Lummi Tribe assisted in collecting crabs. SAIC under contract to DNR provided assistance in the field and the use of the R.V. Kittiwake. Charlie Eaton provided and piloted the R.V. Kittiwake. Sample analysis was supervised by Dick Huntamer, Bob Rieck, Stuart Magoon and Craig Smith of the Manchester Environmental Laboratory. Advice and review of the sampling plan was provided by Betsy Striplin of DNR, Quality Assurance section of the Environmental Protection Agency (EPA) and the Department of Ecology, and Dr. Jacques Faigenblum of U.S. EPA. Project oversight was provided by Dr. Fran Solomon and Lucy Pebles of Department of Ecology. This report was critically reviewed by Art Johnson, Betsy Striplin, and Dr. Fran Solomon. Kelly Carruth and Gayla Diamond typeset and proofread this manuscript. Funding was provided by the U. S. EPA, Puget Sound Estuary Program. Dave Smith administered the contract. I would like to thank all these people and organizations.

INTRODUCTION

Evidence suggests several kinds of contaminants that bioaccumulate occur or could occur in Bellingham Bay biota. Mercury and PCBs have been found in Bellingham Bay sediments (PTI, 1989) at concentrations that exceed sediment quality criteria and thus may be harming marine biota. Pentachlorophenol (PCP) has been found in sediments in Whatcom Creek, a stream that empties into Bellingham Bay (Kendra, 1987). These chemicals can bioaccumulate. Chlorpyrifos is a pesticide of concern in Puget Sound due to its patterns of use and persistence through trophic levels (Tetra Tech, 1988). The Nooksack River, which drains a large agricultural area, may convey pesticide-laden water or sediments into the bay. Arsenic, cadmium, and lead often bioaccumulate and are associated with urban areas. Polycyclic aromatic hydrocarbons (PAH) are potentially harmful compounds often found in relatively high concentrations in urban sediments. They also bioaccumulate in some species. Bellingham Bay supports commercial and recreational crab and clam fisheries.

This study, conducted under EPA's Puget Sound Estuary Program, examined edible crab and clam tissue to determine concentrations of these potential contaminants in the food chain. Concurrent to this effort was a study conducted by SAIC (1991) for the Washington State Department of Natural Resources to collect and analyze crab tissues for contaminants. This work was designed to determine concentrations of contaminants in crabs at the Puget Sound Dredged Disposal Analysis (PSDDA) disposal site in the middle of Bellingham Bay as well as near industrial and rural areas of the bay. The work was also designed to monitor the relative distribution of crabs within the bay and near the disposal sites.

METHODS

Locations

Figure 1 shows sample collection sites for this study. Table 1 shows the sampling dates, number of individuals collected, and location of samples. These sites were chosen to both reflect areas of recreational use and potential areas of contamination. Adult Dungeness crabs (Cancer magister) were collected at eight sites near the shores of Bellingham Bay. Native littleneck clams (Protothaca staminea) and Japanese littleneck clams (Tapes japonica) were collected at four sites.

Collection Methods

In cooperation with the Lummi Tribe, crabs were collected at all sites except Site 4 with commercial crab pots. These pots were set for 10-18 hours before being hauled and checked. At Site 4, crabs were captured with a 3 meter beam trawl towed behind the research vessel *Kittiwake* at 1.5 kts. Other sites were sampled with the beam trawl, but inadequate numbers of adult male crabs were recovered. Only crabs legal for commercial and recreational harvest were

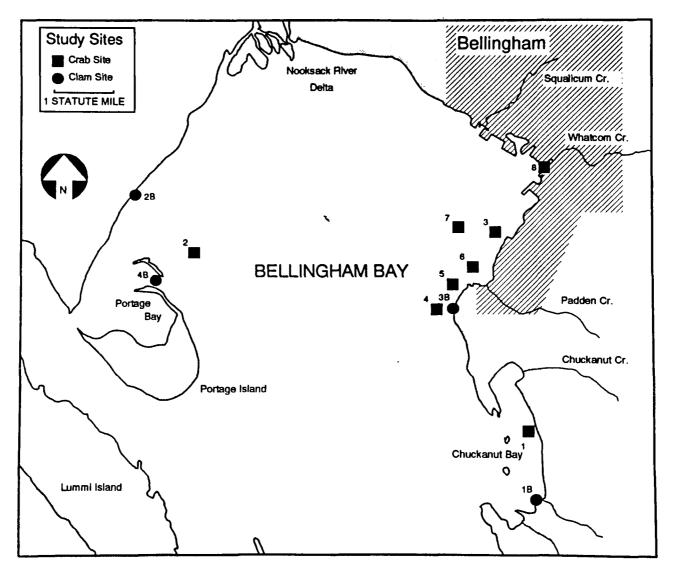


Figure 1. Study area and sampling sites.

Table 1. Sampling sites for Bellingham Bay bioaccumulation study.

	Date	Sample	s Reco	vered(l)				Lo	cation					
Site	Collected	Collected Female Males		ales		Males		les		Latitude		Longitude eptl		epth	Sampling site description
			>6.25in	<6.25in C	ollecte	4	i		· · · · · · · · · · · · · · · · · · ·		(m)				
Dun	geness crab	Cancer	magis	ter											
1	8/20-21/90	9	6	6	5		48	41.3	122	29.4	33	Chuckanut Bay			
2	9/05/90	2	6	3	5		48	43.9	122	36.7	8	East side Lummi Penninsula near Brandt Island			
3	8/20-21/90	1	5	2	5		48	44.0	122	30.1	13	Off dock in Boulevard Park			
4	8/20/90	40	4	1	4		48	42.5	122	31.2	20	Off Post Point marine park (caught with trawls)			
5	9/05/90	18	3	2	3		48	43.2	122	31.3	21	Post Point near municipal outfall diffuser			
6	8/20-21/90	7	8	5	5		48	43.5	122	30.5	16	Padden Creek mouth near Fairhaven boat launch			
7	9/05/90	8	7	4	7		48	44.1	122	31.0	15	Buoy at Georgia Pacific diffuser outfall			
8	8/22/90	-	5	-	5		48	44.5	122	29.5	9	Mouth of Whatcom Waterway			
			:	Size (m	m)										
		Num	Av	Rang	e	Specie	8								
Littl	leneck clams														
1B	9/05/90	22	51.4	45-58	3	Ps	48	40.3	122	29.3		Chuckanut Bay (South side near Yacht Club bay)			
2B	8/20/90	30	37.1	32-48	3	Tj	48	44.0	122	36.7		East side of Lummi Peninsula			
3B	12/14/90	20	47.0	40-58	3	Ps	48	43.7	122	31.0		Post Point marine park			
4B	8/20/90	28	45.3	36-54	ļ	Tj	48	43.5	122	37.0		Brandt Island			

⁽¹⁾ For crabs: number of animals caught in traps. Collected refers to number taken for analysis. For crabs, only males 76.25 inches were analyzed.

w

⁽²⁾ Species: Ps = Protothaca staminea
Tj = Tapes japonica

sampled (males with carapaces wider than 6.25 inches). For all trapped crabs, sampled animals were killed with a blow to the ventral surface, wrapped in aluminum foil and frozen up side down to minimize contamination of muscle by hepato-pancreas fluids. For the trawled crabs, animals were wrapped alive in foil and frozen upside down.

Clams were collected with shovels and rakes off the beach at low tide. Clams were sampled from at least two areas at least 20 meters apart. A sample of at least 20 clams was collected, rinsed with site water, and frozen at the earliest opportunity. The clams were not allowed to depurate in order to provide a potential worst case exposure to recreational users.

Sample Preparation

All stainless steel sample tools (forceps, scalpel, and knives) and blenders were decontaminated with the following procedure:

- 1) Wash in hot water and Alconox detergent;
- 2) rinse in tap water;
- 3) rinse in 10% nitric acid;
- 4) rinse with deionized water;
- 5) rinse with pesticide analysis grade acetone; and
- 6) air dried.

Clam sizes and crab carapace widths were measured. Samples from each site were shelled separately. Muscle from crabs was collected while still partially frozen by breaking off the legs and claws from the body, cutting the shell with scissors and scooping out the muscle with stainless steel scalpels. All tissue and fluid from whole shelled clams and fluid were scooped out with stainless steel spoons. Tissues from 4-7 crabs and 20-30 clams from each site were homogenized in a decontaminated Waring blender and poured into pollutant-free glass jars with teflon-lined lids (ICHEM series 300) and frozen. Samples were frozen within 48 hours of collection and extracted within 35 days of dissection, or, within 60 days of original collection.

Sample Analysis

Samples were analyzed for percent solids, percent lipids, mercury, arsenic, lead, cadmium, PCBs, chlorinated pesticides and chlorpyrifos. Crab samples were also analyzed for pentachlorophenol and its breakdown products. Table 2 presents sample analyses. Clam samples were also analyzed for PAH. Table 3 reviews the schedule of analyses. Due to field collection problems, sample 3B was collected three months later than the other samples. It was analyzed with a batch of shellfish samples collected from Sinclair Inlet. All organic analyses were conducted by the Department of Ecology/EPA Manchester Laboratory. Metals analyses were conducted by Columbia Analytical Laboratory. The methods used were standard methods with the following exceptions:

Table 2. Analytical methods for Bellingham Bay investigation.

Analysis	Method	Reference	Laboratory
Metals	Atomic Absorption 7000	EPA 1986a	Columbia Analytical
As	GFAA method 7060	EPA 1986a	Columbia Analytical
Cd	GFAA method 7420	EPA 1986a	Columbia Analytical
Hg	CVAA method 7471	EPA 1986a	Columbia Analytical
Pb	GFAA method 7420	EPA 1986a	Columbia Analytical
Base Neutral Acids	GC/MS method 8270	EPA 1986a	Ecology/EPA (Man.)
Pest/PCB	GC/EC method 8080*	EPA 1986a	Ecology/EPA (Man.)
Pentachlorophenol	GC/EC method 8150**	EPA 1986a	Ecology/EPA (Man.)
% Moisture	Dry @ 105°C	APHA 1985	Ecology/EPA (Man.)
% Lipids	Gravimetric	EPA 1980	Ecology/EPA (Man.)

^{*} Chlorpyrifos added to standards and measured in samples.

^{**} Phenoxy herbicide method.

Table 8. Comparison of metals concentrations in clams with other studies in Puget Sound. All results ug/g wet weight basis.

	-		Non-Refer	rence Area	•		Reference /	Bellingham Bay		
		Elliott Bay	Puget Sound	Eagle Harbor	McNeil Island	Birch Bay	Point Blakely	Horsehead Bay	Post Point	This study 4 sites
Metal	Species code	5 sites	8 sites	1	2	2		2	2	2
	Study:	Romberg et al. 1984	Faigenblum 1988	Yako et al. 1984	Nonon 1988	Faigenblum 1988	Yako et al. 1984	Norton 1988	СН2МНШ 1984	
As										
	Mean	2.4	2.70	2.9	1.3	2.6	3.7	1.4		1.82
	Range	1.8-3.5	1.3-4.1	1.5-4.4	1.1-1.4	2.1-3.2				1.1-2.1
	N	?	27	8	3	5	1	1		4
Cd										
	Mean	0.13	0.32	0.16	0.31	% 0.3	0.11	0.35		0.21
	Range	.1019	.1054	.0829	.2934	.2236				.18~.23
	N	?	39	8	3	6	1	1		4
Pb										
	Mean	0.40	0.09	0.84		<.04	0.38			0.08
	Range	.1050	.0418	.43-2.0		<.04-<.04				.0215
	N	?	25	8		4	1			4
Hg										
	Mean	0.020	0.02	0.33	0.011	<.02	0.012	0.012		0.01
	Range	.1128	<.0203	.0107	.010011	<.02-<.02			<.1028	<.0102
	N	?	25	8	3	3	1	1	3	4

^{*} Presumption within study that area may exceed background concentrations.

^{**} Used within studies as reference or control site.

***	Species codes:	1	2	3
	•	Saxidomus giganteus	Protothaca staminea	Protothaca staminea
				Saxidomus giganteus
				Tapes japonica
				Tresus capax
				(first two predominated)

Non-Reference area*			area+		Reference	Area**	Bell. Bay	Selected Foods	
	Eagle		Industrial	Point	N. Budd	Case	This study	Smoked	Smoked
Chemical	Harbor	Inlet	Waterway	Blakely	Inlet	Inlet	4 sites	Ham	Fish
Species code**** Study:	1 Yako et al. 1984	2 Norton 1986	3 Mailine et al 1980	1 Yako et al. 1984	2 Norton 1986	3 Malins et al 1980		Puckent 1981	Puckest 1981
LPAH(1)									
Mean	126	67	47	21	<10	<1	3		
Range	14-690	16-159	6-96				<2-6		9.2-145
N	8	3	4	1	1	1	4	ř	
HPAH(2)							ŀ		
Mean	403	373	386	76	<10	<1	3.7		
Range	45-1575	72-938	138-701				<2-20	10-496	3-30
N	8	3	4	1	x 1	1	4		

^{*} Presumption within study that area may exceed background concentrations.

^{***} Duwamish, Commencement Bay, and Hylebos Waterways, Seattle Waterfront

****	Species	codes:
------	---------	--------

17

1	2	. 3
Protothaca staminea	Protothaca staminea	Macoma nasuta
Tapes japonica	Tapes japonica	Macoma carlottensis
Saxidomus giganteus	Mya arenaria	Acila castrensis
<u></u>		

⁽¹⁾ LPAH = Low molecular weight Polycyclic Aromatic Hydrocarbons. (2 and 3 ring compounds)

^{**} Used within study as reference or control site.

⁽²⁾ HPAH = High molecular weight Polycyclic Aromatic Hydrocarbons. (4,5 and 6 ring compounds)

not found in the samples. DDE was found in low concentrations in a concurrent study in 2 out of 7 samples and chlordane in 1 out of 7 samples. PAH's were found at low concentrations in clam samples. Overall, the levels of contaminants examined were low compared with areas with known sediment contamination and were equivalent to concentrations found at reference areas.

REFERENCES CITED

- APHA. Standard methods for the examination of water and wastewater. 16th edition. 1985.
- CH2M Hill. Final report of Bellingham Bay water quality monitoring program. Prepared for City of Bellingham and Georgia-Pacific Corporation. CH2M Hill, Bellevue, WA, 1976.
- Ecology. Report of findings of the annual wastewater NPDES inspection at Georgia Pacific, Bellingham, WA. Washington State Department of Ecology, Industrial Section, Olympia, WA, 1988.
- EPA. Manual of analytical methods for the analyses of pesticides in humans and environmental samples. EPA 600/18-80-038, 1980.
- EPA. 1986a. Test methods for evaluating solid waste. EPA Environmental monitoring and support laboratory, Cincinnati, OH, 1986.
- EPA. Recommended guidelines for measuring organic compounds in Puget Sound sediment and tissue samples. Puget Sound Estuary Program. EPA Region 10, Office of Puget Sound, Seattle, WA, 1989.
- Faigenblum, J. Chemicals and bacteriological organisms in recreational shellfish. Final Report. Prepared for U.S. Environmental Protection Agency Region 10, Office of Puget Sound, Seattle, WA, 1988.
- FDA. Polychlorinated biphenyls (PCBs) in fish and shellfish; reduction of tolerances; final decision. Food and Drug Administration. Fed. Reg. V. 49(100); 21514-21520, 1984.
- FDA. Action levels for poisonous or deleterious substances in human food and animal feed. Center for Food Safety and Applied Nutrition, Industry Programs Branch, Food and Drug Administration. 200 C Street SW, Washington D.C., 1985.
- Gahler, A.R., J.M Cummins, J.N. Blazevich, R.H. Rieck, R. Arp, C.E. Gangmark, S.V.W. Pope, S. Filip. Chemical contaminants in edible, non-salmonid fish and crabs from Commencement Bay, Washington. USEPA Environmental Services Division, Region X, Seattle, WA, 1982.
- Kendra, W. Investigation of recurrent coho salmon mortality at the Maritime Heritage fish hatchery in Bellingham WA. Washington State Department of Ecology, Olympia, WA, 1988. 49 pp.

- Malins, D.C., B.B. McLain, D.W. Brown, et al. Chemical contaminants and biological abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum OMPA-2, 1980, 295 pp.
- Norton, D. Results of priority pollutant analyses on water, sediment and clam samples collected in lower Budd Inlet near McFarland Cascade, Olympia, WA. Washington State Department of Ecology, Memorandum to Tom Eaton. Olympia, WA, 1986.
- Norton, D. McNeil Island: Intertidal screening survey for toxic chemicals in water, sediment and clam tissue. Washington Department of Ecology, Olympia, WA, 1988.
- PSEP. Puget Sound Estuary Program: 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, 1986.
- PSDDA. Management plan report: Unconfined, open-water disposal of dredged material Phase 1 (Central Puget Sound). Puget Sound Dredged Disposal Analysis. U.S. Army Corps of Engineers, Seattle District; U.S. Environmental Protection Agency, Region 10; Washington State Department of Natural Resources; Washington State Department of Ecology, 1988.
- Pucknat, A.W. Health impacts of polynuclear aromatic hydrocarbons. Noyes Data Corporation, Park Ridge, NJ, 1981.
- PTI. Everett Harbor Action Program: Analysis of toxic problem areas. Final Report. Prepared for U.S. Environmental Protection Agency Region 10, Office of Puget Sound, Seattle, WA, 1988.
- PTI. Bellingham Bay Action Program: Initial data summaries and problem identification. Prepared for US Environmental Protection Agency Region 10, Office of Puget Sound, Seattle, WA, 1989.
- Rasmussen, L.F., and D.C. Williams. The occurrence and distribution of mercury in marine organisms in Bellingham Bay. Northwest Science, 49, 87-94. 1975.
- Romberg, G.P., S.P. Pavlou, R.F. Shokes, W. Horn, E.A. Crecelius, P. Hamilton, J.T. Gunn, R.D. Muench and J. Vinelli. Toxicant pretreatment planning study technical report: Presence, distribution and fate of toxicants in Puget Sound and Lake Washington. Metro, Seattle, WA, 1984.
- SAIC. PSDDA 1990 Crab bioaccumulation survey of Bellingham Bay. Report to Washington State Department of Natural Resources, Division of Aquatic Lands. Olympia, WA, 1991.

- Tetra Tech. Pesticides of Concern in the Puget Sound Basin: A review of contemporary pesticide usage. Final report TC-3338-32 to U.S. Environmental Protection Agency, 1988.
- Yake, B, J. Joy, and A. Johnson. Chemical contaminants in clams and crabs from Eagle Harbor, Washington State, with emphasis on polynuclear aromatic hydrocarbons. Washington State Department of Ecology, Olympia, WA, 1984.

APPENDIX 1: LABORATORY QUALITY ASSURANCE

Several tests were used to assess laboratory accuracy and precision. Overall, the data are usable. Table A-1 presents the results of these different tests for organics. Table A-2 shows results for metals. Following is a review of the tests. These results apply to all samples except clam site 3B. This sample was collected later and was analyzed along with shellfish from another study. This sample also passed quality assurance tests.

Matrix Spike: Matrix spikes were performed for each of the three types of analyses. A known amount of the target compound was added to the matrix (homogenized tissue) and the recovery of the compound was a measure of extraction efficiency and analytical accuracy. Table 4 shows all matrix spike recoveries are within acceptable limits.

Replicate Analysis: Relative percent difference (RPD) was calculated from results of replicate analyses as a measure precision. The formula for RPD is

$$RPD = (S1-S2)/((S1+S2)/2) * 100$$

where S1 and S2 are the duplicate samples. Matrix spike samples were analyzed in duplicate so that there were two RPD measurements. One sample was split after homogenization and submitted to the laboratory blind. Results of this blind replicate analysis of metals showed remarkably similar results, an indication of complete homogenization and high analytical precision. Because no compounds were found above detection limits in the blind replicate analyses of organics and pesticides, no blind RPD is available.

<u>Surrogate recovery:</u> For the GC-EC and GC-MS analyses, recovery of surrogates added before extraction were analyzed. Surrogates have similar chemical structure to the analytes of interest but are not expected to be found in the environment. The surrogate for PCP analysis is tribromophenol. For the pesticides, three surrogates, 4,4 dibromooctafluorobiphenyl, dibutylchlorendate, and octochloronapthalene were used. In the base, neutral and acid extraction, due to the silica gel cleanup and optimization for PAHs, only the non-polar surrogates terphenyl-d14, pyrene-d10, and 2- fluorobiphenyl were recovered. All surrogates recoveries were within EPA CLP guidelines for sediment (there are no CLP guidelines for tissues).

<u>Reference Material:</u> For metals analysis, a standard reference material, oyster tissue, was analyzed. This material is provided by the National Bureau of Standards and is exhaustively analyzed and its metals concentrations certified to be within a narrow range of values. Results showed high accuracy.

Method Blanks: Analysis of method blanks showed no laboratory contamination.

Table A-1. Results of matrix spike recovery tests for organics.

				Percent Spil	ke Reco	verý	
		Crab			Clam		Recommended
Lab number	8081	8090	RPD (1)	8093	8093	RPD	Range for spike(2
PESTICIDES						-	
Aldrin	101%	98%	3 %	108%	96%	12%	50%-150%
Chlordane	85 %	81%	5%	122%	102%	18%	50%-150%
4,4'-DDT	81%	71%	14%	96%	94%	1 %	50%-150%
alpha Endosulfan	84 %	84 %	0%	100%	99%	1%	50%-150%
Endrin	82 %	82%	1%	103 %	94%	9%	50%-150%
Heptachlor	76%	72%	5%	88%	88%	0%	50%-150%
gamma-BHC	75%	80%	6%	95%	94%	1%	50%-150%
Methoxychlor	95%	94%	1%	116%	129%	11%	50%-150%
Pentachiorophenol	99%	105 %	6%				
PAHs							
Napthalene				46%	66%	36%	50%-150%
Acenaphthylene				73 %	85%	15%	50%-150%
Acenapthene				78%	83 %	6%	50%-150%
Fluorene				91%	96%	5%	50%-150%
Phenanthrene				83 %	86%	4%	50%-150%
Anthracene				70%	73 %	4%	50%-150%
Fluoranthene				74%	76%	3 %	50%-150%
Pyrene				120%	138%	14%	50%-150%
Benzo(a) Anthracene			b ^j	103 %	114%	10%	50%-150%
Chrysene				102%	111%	8%	50%-150%
Benzo(b)Fluoranthene				88%	104%	17%	50%-150%
Benzo(k)Fluoranthene				96%	98%	2%	50%-150%
Benzo(a)Pyrene				91%	96%	5%	50%-150%
Ideno(1,2,3-cd)Pyrene				85%	82%	4%	50%-150%
Dibenz(a,h)Anthracene				73 %	75%	3%	50%-150%
Benzo(g,h,i)Perylene				75%	51%	38%	50%-150%

⁽¹⁾ Relative Percent Difference

⁽²⁾ From Puget Sound Estuary Program Guidelines (EPA 1989). Due to problems of matrix interference, exceedence of spike recovery limits does not require data qualification.

Table A-2. Results of tests of laboratory accuracy and precision for metals.

	Spike Recovery Precision							of multiple analyses (results=mg/kg)					Standard Reference		
	Crab	Clam		Lab		Blind(2)						Material (3)			
Lab no.	8087	8094	8094	8094	RPD(1)	8087	8091	RPD	8093	8097	RPD	True	Found	%	
Arsenic	58%	100%	14.7	14.1	4%	21.8	22	1%	13.2	11.9	10%	14.0	13.8	99%	
Cadmium	94%	89%	1.53	1.62	6%	<0.01	0.01	NA	1.86	1.84	1%	4.15	4.1	98%	
Lead	103%	94%	0.4	0.4	<1%	<0.2	<0.2	NA	1.2	1.1	9%	0.371	0.40	108%	
Mercury	100%	100%	0.1	0.1	<1%	0.8	0.8	0%	<0.1	<0.1	NA	0.064	0.06	93%	

⁽¹⁾ Relative Percent Difference

⁽²⁾ Homogenized split of sample submitted to laboratory as separate sample (3) National Bureau of Standards oyster tissue #1566a

MANCHESTER ENVIRONMENTAL LABORATORY

7411 Beach Drive SE, Port Orchard Washington 98366

CASE NARRATIVE

December 13, 1990

Subject: Bellingham Bay Bioaccumulation

Samples: 90 - 398080, 398081, 398082, 398083, 398085, 398086, 398087, 398090, 398091, 398093,

398094, 398096, 398097

Case No. DOE-601B

Officer: James Cubbage

By: Dickey D. Huntamer

Robert Carrell Organic Analysis Unit

POLYNUCLEAR AROMATIC HYDROCARBONS

ANALYTICAL METHODS:

No official EPA method exists for semivolatile tissue analysis. The prepared tissue samples were extracted with a 50:50 mixture of methylene chloride and acetone using the Manchester modification of the EPA CLP and SW-846 Method 8270 procedure with capillary GC/MS analysis of the sample extracts. All CLP QA/QC procedures were performed on the samples. Since Polynuclear Aromatic Hydrocarbons (PAH) were the primary target analytes and low detection limits were desired sample cleanup using Gel Permeation Chromatography (GPC) at both 2000 Molecular Weight (MW) and 1000MW cutoff (SW-846 Method 3640) followed by Silica Gel cleanup Method 3630 was done on the samples. Lower Quantitation Limits were also realized by extracting approximately 50 grams of tissue and concentrating the final extract to 1.0 mL for analysis.

HOLDING TIMES:

Under Puget Sound Estuary Program (PSEP) Guidelines for organic compounds tissue samples can be stored frozen for up to one year before extraction. After collection samples were prepared for the laboratory by the field staff and stored frozen until extraction. Since the samples were stored frozen all sample extraction holding times were met. The reporting form for holding times indicates that the sample holding times were exceeded however this is not he case since it is measured from collection date and includes the time the samples were frozen. All analyses were performed within the specified 40 day holding time.

BLANKS:

No significant PAH blank contamination was detected.

SURROGATES:

The samples received all six surrogate compounds normally added to semivolatile analyses. Due to the silica gel cleanup only the non-polar surrogates Terphenyl-d14, Pyrene-d10 and 2-Fluorobiphenyl were recovered. Only one of these compounds, Pyrene-d10 is a true PAH compound and is representative of the PAH target analytes. Surrogate spike recoveries for all three compounds were within normal limits for CLP soil recovery limits. The CLP recovery limits are only advisory since no tissue surrogate spike recovery limits have been established.

Å

MATRIX SPIKE AND MATRIX SPIKE DUPLICATE:

Matrix spikes compounds were added at 20 ug, rather than the normal spiking concentration of 50 ug, to more closely approximate the low detection limits requested. No significant problems were encountered with recovering the matrix spike compounds at this level (400 ug/Kg wet weight). Although no matrix spike recovery limits have been established at this low level, spike recoveries were generally within the normal CLP recovery range found at higher matrix spike levels.

Two matrix spike and matrix spike duplicates (MS/MSD) were analyzed with the set. Sample 398093 was used as one matrix source and due to insufficient sample tissue from both 398081 and 398090 had to be used to make the second MS/MSD pair. Matrix spike recoveries ranged from 48% to 103% for 398081/398090 and 46% to 138% for 398093.

SPECIAL ANALYTICAL PROBLEMS:

No analytical problems were encountered in the analysis. The low detection limits were achieved by extracting 50 grams of sample and concentrating the extract after cleanup to 1.0 mL prior to analysis.

PESTICIDES / PCB - CHLORPYRIFOS AND PCP

ANALYTICAL METHODS:

The tissue (clams and crabs) was extracted by the Manchester Laboratory using a Polytron tissue grinder and a 50:50 mixture of methylene chloride and acetone as the solvent. The analyses were done following EPA Method 8080 (chlorinated pesticides, PCB's and chlorpyrifos) and EPA Method 8150 (PCP) using capillary Gas Chromatography/Electron Capture Detector (GC/ECD) analysis.

Page 3
Bellingham Bioaccumulation - Tissue

The percent lipid determination was performed in a similar fashion to the analytical extractions except petroleum ether was used as the solvent. The extract was evaporated and weighed to determine the extractable lipid. Percent solids were also determined on the samples. The results are given in the table below.

Lab Number	Percent Solids	Percent Lipids		
398080	16	0.0		
398081	16	0.09		
398082	16	0.0		
398083	17	0.09		
398085	16 ·	0.0		
398086	15	0.0		
398087	19	0.0		
398090	13	0.10		
398091	19	0.09		
398093	11	0.30		
398094	14	0.39		
398096	14	0.68		
398097	11	0.10		

BLANKS:

No significant blank contamination was found.

HOLDING TIMES:

All samples were analyzed within the 40 day holding time.

SURROGATES:

Surrogate spike recoveries for the Pesticides/PCB's ranged from 70.1% to 117% for Dibromoocta-fluorobiphenyl (DBOB); 73.3% to 108.8% for Dibutylchlorendate (DBC); 63.7% to 118.3% for octachloronaphthalene (OCN) and 71.9% to 115.3% for Decachlorobiphenyl (DCB). These values are well within the advisory limits of 60% to 150% recoveries listed in CLP for soil samples.

For the PCP analysis, excluding the method blanks which experienced low recoveries due to lack of "keeper", the surrogate recoveries for Tribromophenol (TBP) ranged from 75.1% to 99.6%. The method blank surrogate recoveries were 26.7% to 86.1%. There are, however, no advisory limited data qualifiers were not added to the data based on surrogate recoveries.

MATRIX SPIKE AND MATRIX SPIKE DUPLICATE:

Four matrix spikes were analyzed for pesticides to reflect the two different types of tissue (clam and crab) matrix effects. Recoveries of the pesticides ranged from 70.5% to 129.3%. Two matrix spikes were run for PCP with recoveries of PCP ranging from 99.1% to 104.9%.

SPECIAL ANALYTICAL PROBLEMS:

The pesticides were run on the tissue extracts first then the extract was cleaned up with Sulfuric acid treatment. These acid treated extracts were then reanalyzed for PCB's thus allowing lower quantitation limits.

DATA QUALIFIER CODES:

- U The material was analyzed for, but was not detected. The associated numerical value is the sample quantitation limit.
- J The associated numerical value is an estimated quantity.
- R The data are unusable (compound may or may not be present). Resampling and reanalysis is necessary for verification.
- NAR No Analytical Result.
- M The compound was detected and confirmed but was not quantitated.