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Bioaccumulation of Contaminants in Crabs and Clams in Bellingham Bay

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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

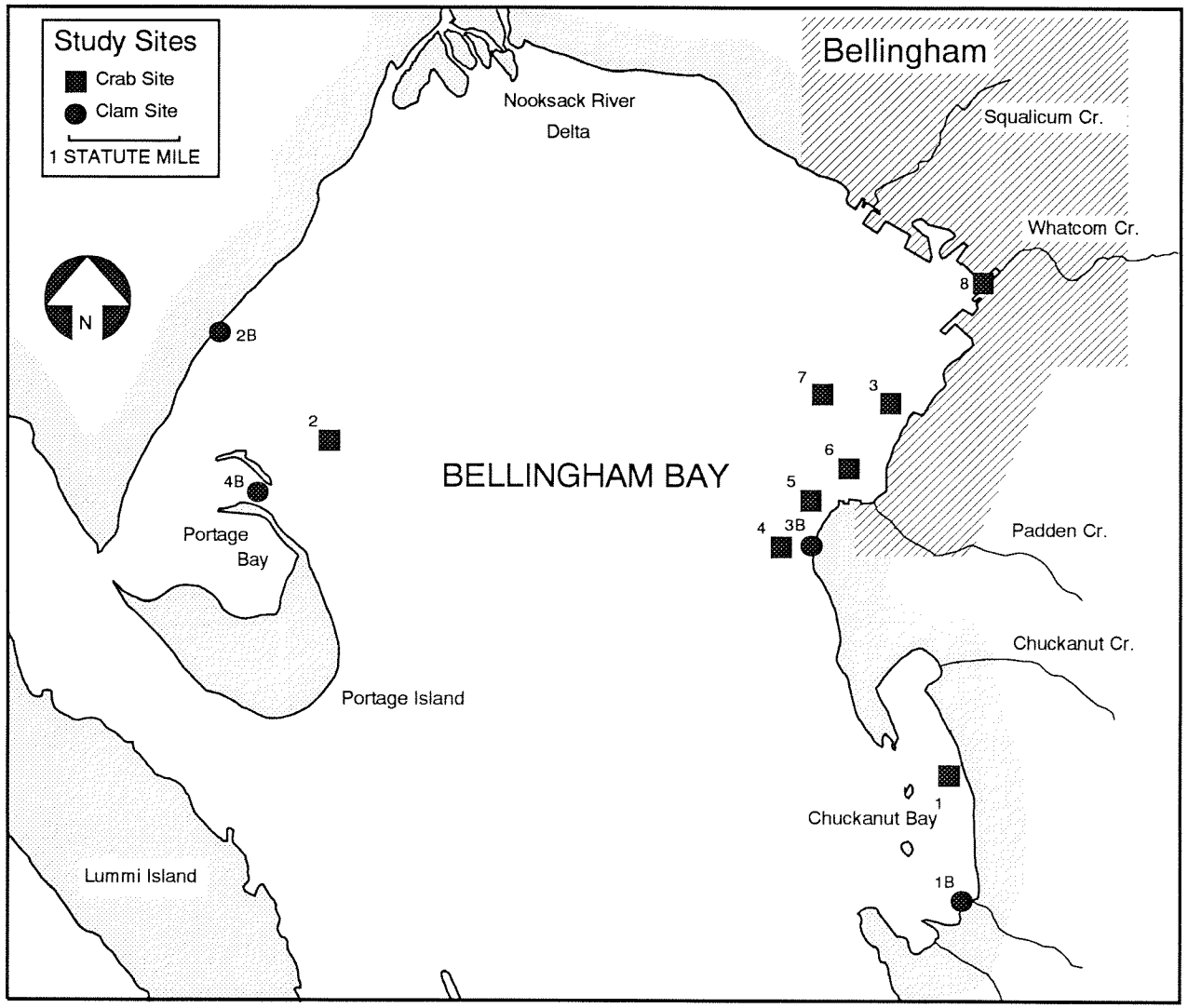

Figure 1. Study area and sampling sites.

Table 1. Sampling sites for Bellingham Bay bioaccumulation study.

Site	Date Collected	Samples Recovered(1) Female	Males >6.25in	Males <6.25in	Collected	Location Latitude		Longitude		epth (m)	Sampling site description
Dungeness crab	*Cancer magister*										
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

		Num	Size (mm) Av	Range	Species					
Littleneck clams										
1B	9/05/90	22	51.4	45-58	Ps	48	40.3	122	29.3	Chuckanut Bay (South side near Yacht Club bay)
2B	8/20/90	30	37.1	32-48	Tj	48	44.0	122	36.7	East side of Lummi Peninsula
3B	12/14/90	20	47.0	40-58	Ps	48	43.7	122	31.0	Post Point marine park
4B	8/20/90	28	45.3	36-54	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.

(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 penta-chlorophenol 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 3. Times and dates of sample extractions and analysis

Site #	Lab No	Date Collected	Date Prepared	BNA Extract	BNA Analysis	PCBs Extract	PCBs Analysis	PCP Extract	PCP Analysis	Metals Extract	Metals Analysis
Dungeness crab											
1	39-8090	8/21/90	9/28/90	10/16/90	11/19/90	10/16/90	11/16/90	10/16/90	11/20/90	11/1/90	11/2/90
2	39-8081	9/05/90	9/28/90	10/12/90	11/15/90	10/12/90	11/20/90	10/12/90	11/20/90	11/1/90	11/2/90
3	39-8082	8/21/90	9/28/90	10/12/90	11/15/90	10/12/90	11/20/90	10/12/90	11/20/90	11/1/90	11/2/90
4	39-8083	8/20/90	9/28/90	10/12/90	11/15/90	10/12/90	11/16/90	10/12/90	11/20/90	11/1/90	11/2/90
5	39-8080	9/05/90	9/28/90	10/12/90	11/15/90	10/12/90	11/20/90	10/12/90	11/20/90	11/1/90	11/2/90
6	39-8085	8/21/90	9/28/90	10/12/90	11/15/90	10/12/90	11/16/90	10/12/90	11/20/90	11/1/90	11/2/90
7	39-8086	9/05/90	9/28/90	10/12/90	11/15/90	10/12/90	11/16/90	10/12/90	11/20/90	11/1/90	11/2/90
8	39-8087	8/22/90	9/28/90	10/16/90	11/19/90	10/16/90	11/16/90	10/16/90	11/20/90	11/1/90	11/2/90
8*	39-8091	8/22/90	9/28/90	10/16/90	11/19/90	10/16/90	11/16/90	10/16/90	11/20/90	11/1/90	11/2/90
Littleneck clams											
1B	39-8093	9/05/90	9/28/90	10/12/90	11/15/90	10/12/90	11/16/90	--	--	11/1/90	11/2/90
2B	39-8094	8/20/90	9/28/90	10/16/90	11/19/90	10/16/90	11/16/90	--	--	11/1/90	11/2/90
3B	03-8215	12/14/90	1/18/91	02/04/91	03/01/91	02/04/91	03/04/91	--	--	1/24/91	2/15/91
4B	39-8096	8/20/90	9/28/90	10/16/90	11/19/90	10/16/90	11/16/90	--	--	11/1/90	11/2/90
1B*	39-8097	9/05/90	9/28/90	10/12/90	11/15/90	10/12/90	11/16/90	--	--	11/1/90	11/2/90

* Split sample submitted to the laboratory with new number.

1) To analyze for chlorpyrifos, the standards in the pesticide analysis were supplemented with chlorpyrifos. This pesticide is usually analyzed with an organophosphorus pesticide scan, but because of its chlorinated structure, it is possible to analyze for this pesticide with the 8080 method.

2) To analyze for pentachlorophenol and its metabolites, the phenoxy herbicide method 8150 was used. This method relies on derivatization of chlorinated phenols and analysis on a gas chromatograph with an electron capture detector (Ni 63). Pentachloroanisole, a derivatized form as well as a metabolite of pentachlorophenol was evaluated. This method is sensitive to pentachlorophenol and has a far lower detection limit than the base neutral acids GC-MS method 8270.

3) For metals analyses, tissues were digested with nitric acid and hydrogen peroxide. The Puget Sound Protocols (PSEP 1986) call for digestion with nitric and perchloric acid, but they also allow nitric acid/peroxide digestion. The peroxide digestion has produced acceptable recoveries in other studies.

4) Tissues were extracted with a 50:50 mixture of methylene chloride and acetone using the Manchester modification of the EPA CLP and method 8270 procedure. Since polycyclic aromatic hydrocarbons (PAH) were the primary target analytes and low detection limits were desired, samples were cleaned up using gel permeation chromatography (GPC) at both 2000 and 1000 molecular weight cutoffs (method 3640) followed by silica gel cleanup method 3630. The extraction was optimized for low detection limits for PAH and thus the phenols and other semivolatile compounds usually searched for in this procedure were not found.

Laboratory Quality Assurance

Several tests were used to assess laboratory accuracy and precision. Overall, the data are usable (see Appendix and Appendix Tables A-1 and A-2 for a quality assurance review.).

RESULTS

Metals

Table 4 presents concentrations of metals found in tissues. In all tissues, cadmium, lead, mercury and arsenic concentrations were relatively low. All concentrations are reported in wet weight basis. Arsenic ranged from 1.9 to 5.6 ppm in crab and 1.1 to 2.1 in clams. The highest concentrations of arsenic occurred from shellfish on the west side of the bay, away from Bellingham. Mercury ranged from 0.06 to 0.15 ppm in crabs and non-detected to 0.02 ppm in clams. A slight pattern appears in the mercury concentrations in crab. Figure 2 shows higher concentrations of mercury in crabs closer to the Whatcom waterway. Cadmium ranged from

Table 4. Metals concentrations found in crabs and clams (ug/g wet weight).

Site #	As	Cd	Pb	Hg	Solids
Crab					
1	4.13	0.003	0.15	0.06	14%
2	5.62	0.003	0.09	0.09	16%
3	2.74	0.003	0.16	0.10	16%
4	1.86	0.003	0.11	0.11	11%
5	5.11	<0.01	0.05	0.08	17%
6	3.30	0.006	0.26	0.10	16%
7	2.85	0.005	0.29	0.12	16%
8	4.19	<0.01	<0.2	0.15	19%
Split 8	4.27	0.002	<0.2	0.16	19%
Clam					
1B	1.62	0.229	0.15	<0.1	12%
2B	2.06	0.214	0.06	0.01	14%
3B	1.11	0.216	0.02	0.01	11%
4B	1.82	0.183	0.09	0.02	16%
Split 1B	1.50	0.232	0.14	<0.1	13%

ND=none detected

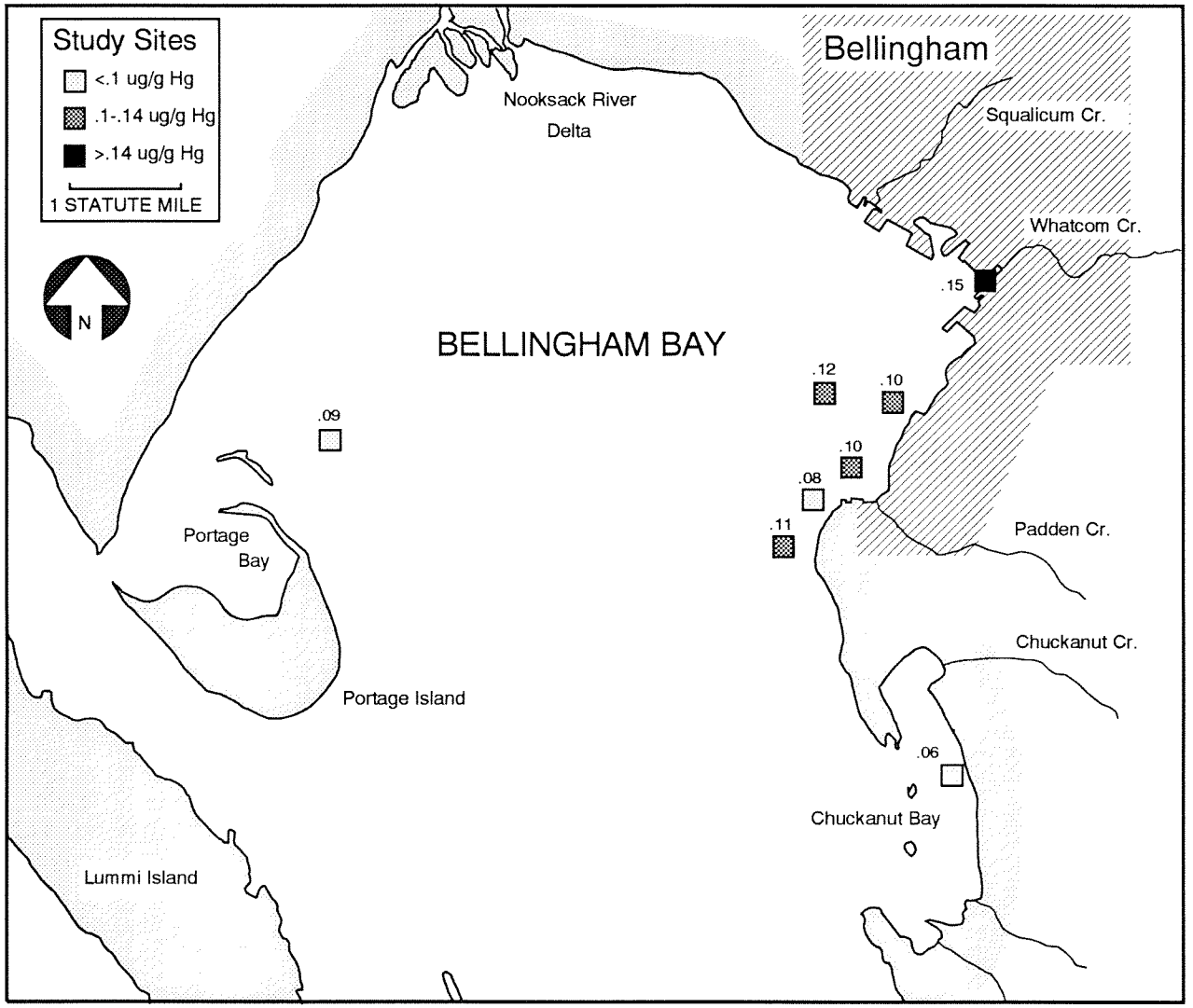

Figure 2. Mercury concentration in crab muscle. (ug/g wet weight)

non-detected to 0.006 ppm in crabs and 0.18 to 0.23 ppm in clams. In crabs, lead ranged from non-detected to 0.29 ppm. Equivalent concentrations of lead were found in clams which ranged from 0.02 to 0.15 ppm.

Chlorinated Pesticides

Table 5 shows results of chlorinated hydrocarbons analysis for tissues. No chlorinated hydrocarbon compounds were found at or above the quantitation limits reported by the laboratory. No pentachlorophenol was found at the low detection limit of 0.5 ppb. No chlorpyrifos was found in any tissue.

Polycyclic aromatic hydrocarbons

Table 6 lists concentrations of polycyclic aromatic hydrocarbons found in clam tissues. The concentrations found are low. Total PAH ranged from 2 to 26 ppb in clams with highest concentrations found at site 3B at Post Point Marine Park, a park near the outfall diffuser for the municipal waste water treatment plant for Bellingham. As noted earlier, the analysis was optimized for PAH, thus few other semivolatile compounds were detected in these tissues.

DISCUSSION

Comparison to other studies - Crab

Few studies have examined metals and pesticides in crab muscle tissue. Table 7 compares contaminants concentrations in crabs from this study with results from other studies in urban bays and a reference area in Discovery Bay.

Metals: Concentrations of all four metals examined ranged lower in this study than in Elliott and Commencement Bays. Arsenic and lead concentrations were lower in this study than in Discovery Bay. Mercury concentrations were equivalent between Everett Harbor and Bellingham Bay. Crab tissues taken off Post Point in 1974 had mercury concentrations of 0.23 ppm (wet weight) (Rasmussen and Williams 1975), a higher concentration than found in this study.

A major source of mercury for the bay has been the chlor-alkali plant owned by Georgia Pacific to produce caustic soda (sodium chlorate) at their pulp mill on the Whatcom Waterway. The history of this plant's operation is reviewed by Tetra Tech (1988). This plant started operation in 1965 and by 1970 a discharge of 0.5 pounds of mercury per day was allowed. The allowed discharge was decreased to 0.07 pounds per day by 1979. However, in 1979, discharge from the whole facility was calculated at 0.82 pounds per day. By 1988 the discharge was 0.016 pounds per day (Ecology 1988). The current discharge averages 0.01 pounds per day. The decreasing trend of discharge rates of mercury corresponds well to the decreased mercury

Table 5. Results of pesticide scan of crab muscle and whole shucked clams. All values ug/kg wet weight.

	Crab								Clam			
Site	1	2	3	4	5	6	7	8	1B	2B	3B	4B
Aldrin	4 U	2 U	2 U	2 U	2 U	4 U	4 U	4 U	4 U	4 U	1.9 U	4 U
Chlordane	20 U	20 U	20 U	20 U	20 U	40 U	20 U	20 U	20 U	20 U	1.9 U	20 U
Dieldrin	4 U	2 U	2 U	2 U	2 U	4 U	4 U	4 U	4 U	4 U	1.9 U	4 U
4,4'-DDT	4 U	2 U	2 U	2 U	2 U	4 U	4 U	4 U	4 U	4 U	1.9 U	4 U
4,4'-DDE	4 U	2 U	2 U	2 U	2 U	4 U	4 U	4 U	4 U	4 U	1.9 U	4 U
4,4'-DDD	4 U	2 U	2 U	2 U	2 U	4 U	4 U	4 U	4 U	4 U	1.9 U	4 U
alpha Endosulfan	4 U	2 U	2 U	2 U	2 U	4 U	4 U	4 U	4 U	4 U	1.9 U	4 U
beta Endosulfan	4 U	2 U	2 U	2 U	2 U	4 U	4 U	4 U	4 U	4 U	1.9 U	4 U
Endosulfan sulfate	4 U	2 U	2 U	2 U	2 U	4 U	4 U	4 U	4 U	4 U	1.9 U	4 U
Endrin	4 U	2 U	2 U	2 U	2 U	4 U	4 U	4 U	4 U	4 U	1.9 U	4 U
Endrin aldehyde	4 U	2 U	2 U	2 U	2 U	4 U	4 U	4 U	4 U	4 U	1.9 U	4 U
Heptachlor	4 U	2 U	2 U	2 U	2 U	4 U	4 U	4 U	4 U	4 U	1.9 U	4 U
Heptachlor epoxide	4 U	2 U	2 U	2 U	2 U	4 U	4 U	4 U	4 U	4 U	1.9 U	4 U
alpha-BHC	4 U	2 U	2 U	2 U	2 U	4 U	4 U	4 U	4 U	4 U	1.9 U	4 U
beta-BHC	4 U	2 U	2 U	2 U	2 U	4 U	4 U	4 U	4 U	4 U	1.9 U	4 U
gamma-BHC	4 U	2 U	2 U	2 U	2 U	4 U	4 U	4 U	4 U	4 U	1.9 U	4 U
delta-BHC	4 U	2 U	2 U	2 U	2 U	4 U	4 U	4 U	4 U	4 U	1.9 U	4 U
Toxaphene	120 U	60 U	60 U	60 U	60 U	120 U	120 U	120 U	120 U	120 U	120 U	120 U
Aroclor-1016	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	19 U	20 U
Aroclor-1221	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	19 U	20 U
Aroclor-1232	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	19 U	20 U
Aroclor-1242	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	19 U	20 U
Aroclor-1248	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	19 U	20 U
Aroclor-1254	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	19 U	20 U
Aroclor-1260	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	19 U	20 U
Methoxychlor	4 U	2 U	2 U	2 U	2 U	4 U	4 U	4 U	4 U	4 U	1.9 U	4 U
Chlorpyrifos	8 U	4 U	4 U	4 U	4 U	8 U	8 U	8 U	8 U	8 U	NA	8 U
Pentachlorophenol	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	1 U	1 U	NA	2 U
Percent lipid	0.10%	0.09%	0.00%	0.09%	0.00%	0.00%	0.00%	0.00%	0.30%	0.39%	0.25%	0.68%

U=Quantitation limit, no analyte found at this concentration

Table 6. Results of PAH scan of whole shucked clams. All values ug/kg wet weight basis.

	Clam							
Site	1B		2B		3B		4B	
Napthalene	82	U	82	U	94	U	82	U
2-Methylnapthalene	82	U	82	U	94	U	82	U
1-Methylnapthalene	82	U	82	U	94	U	82	U
2-Chloronaphthalene	82	U	82	U	94	U	82	U
Acenaphthylene	82	U	82	U	94	U	82	U
Acenapthene	82	U	82	U	94	U	82	U
Dibenzofuran	82	U	82	U	94	U	82	U
Fluorene	82	U	82	U	94	U	82	U
Phenanthrene	4	J	82	U	6	J	2	J
Anthracene	82	U	82	U	94	U	82	U
Carbazole	82	U	82	U	490	U	82	U
Fluoranthene	2	J	3	J	10	J	82	U
Pyrene	82	U	82	U	10	J	82	U
Retene	82	U	82	U	94	U	82	U
Benzo(a)Anthracene	82	U	82	U	94	U	82	U
Chrysene	82	U	82	U	94	U	82	U
Benzo(b)Fluoranthene	82	U	82	U	94	U	82	U
Benzo(k)Fluoranthene	82	U	82	U	94	U	82	U
Benzo(a)pyrene	82	U	82	U	94	U	82	U
Ideno(1,2,3-cd)Pyrene	82	U	82	U	94	U	82	U
Dibenz(a,h)Anthracene	82	U	82	U	240	U	82	U
Benzo(g,h,i)Perylene	82	U	82	U	94	U	82	U

U=Quantitation limit, no analyte found at this concentration
J=Quantification estimate due to low signal to noise ratio.

Table 7. Comparison of contaminant concentrations in crab (Cancer magister) with other studies. All results ug/g wet weight.

Site	N		As	Cd	Pb	Hg	Sum PCBs	DDE		Source
Commencement Bay										
Hylebos	2	Avg	2.8		0.82	0.080	0.052	0.002		Gahler et al. 1982
City Waterway	2	Avg	5.8		0.69	0.080	0.068	0.004		Gahler et al. 1982
Elliott Bay										
Denny Way	-	Avg	5.8	0.09	0.17	0.140	0.086	0.005		Romberg et al. 1984
Alki Point	-	Avg	4.2	0.03	0.07	0.038	0.023	0.002		Romberg et al. 1984
Carkeek Park	-	Avg	5.5	0.20	0.07	0.087	0.020	0.002		Romberg et al. 1984
Richmond Beach	-	Avg	3.6	0.02	0.09	0.090	0.049	0.003		Romberg et al. 1984
Westpoint	-	Avg	6.3	0.17	0.08	0.252	0.054	0.002		Romberg et al. 1984
Everett Harbor	11	Min				0.042	0.003	<.0008	**	PTI 1988
		Max				0.130	0.024	<.0008	**	
Above studies	-	Min	2.8	0.02	0.07	0.038	0.003	0.002		
		Max	6.3	0.20	0.82	0.252	0.086	0.005		
Discovery Bay	2	Avg	7.2		0.36	0.070	0.010	0.005		Gahler et al. 1982
Bellingham Bay	7	Min	0.9	0.06	0.00	0.03	0.005	0.0004	U	SAIC 1991
		Max	1.9	0.11	0.32	0.09	0.005	0.0015		
Bellingham Bay (This Study)	8	Min	1.9	0.00	0.00	0.06	0.02	0.0020	U	This study
		Max	5.6	0.01	0.29	0.15	0.02	0.0020	U	

U No contaminants detected at detection limit.
* Sum of PCBs detected; Does not include detection limits in calculations.
** Range of detection limits (.0001-.0008 ppm)

contamination found in crabs in this study compared to 1975. The slight geographic trend found of increasing contamination with decreasing distance from Whatcom Waterway is consistent with the waterway being the location of a major historic source of mercury.

Comparisons with the concurrent study conducted in support of the PSDDA program (SAIC, 1991) showed equivalent concentrations of lead in crab muscle. Arsenic levels were considerably higher in this study and mercury somewhat higher, but cadmium concentrations were higher in the SAIC study. To compare analysis between laboratories in these concurrent studies, one sample (site 7 crabs), was homogenized split and sent to both laboratories. The comparisons between the two studies of the same split follow with SAIC (AmTest Labs) first followed by this study (Columbia Analytical): As 0.9, 2.8; Cd 0.1, 0.005; Pb 0.32, 0.29; Hg 0.06, 0.12.

Mercury concentrations in crab muscle found by the PSDDA study (SAIC 1991) ranged from 0.03 to 0.09 mg/kg wet weight. Most of these samples were taken from the center of the bay at the dredged material disposal site located between site 4 of this study and Portage Bay. These values were lower than those found in this study. The difference may have been caused by different ages of crabs (the PSDDA samples were smaller) or by differences in laboratories. The low concentrations found in the PSDDA samples are consistent with the geographic pattern of decreasing mercury concentration with increasing distance from the historic source of mercury in Whatcom Waterway.

No clear explanation exists for the discrepancy between laboratories. The homogenizing method for the splits was effective (split samples sent to the same lab showed essentially no difference, (see Appendix: Replicate analysis). The analytical methods were the same. The difference between the cadmium values, though great, is probably inconsequential because both values are comparatively low. In the mercury analyses, the quality assurance reports from both studies are complete except the SAIC study does not report an analysis of standard reference material for mercury. The arsenic variation is also without a clear explanation.

Pesticides: No pesticide residues were found in the crab muscle collected in this study. The SAIC study found DDE in two of seven crab samples, one of which was the interlaboratory split. The split value was 0.6 ppb DDE (this study had a detection limit of 2 ppb). An additional crab muscle sample had 1.5 ppb DDE (SAIC, 1991). These are low concentrations. SAIC also found chlordane at 1.0 ppb in crab muscle. No PCB's were found in either study. The lack of pesticide residues may partially be a reflection of low lipid weight of these muscle tissues. Organochlorine contaminants are non-polar and tend to accumulate primarily in lipids. All of 6 crab hepatopancreas tissues tested for pesticides in the SAIC study had DDE residues varying from 22 to 62 ppb. One of these samples also contained chlordane. The hepatopancreas tissue had comparatively higher lipid weights than the muscle tissue (3.4-20.5% lipid). No PCB's were found in the hepatopancreas tissue.

Comparison to other studies - Clams

Metals: Table 8 reviews comparisons of metals found in clams in Puget Sound. Mean concentrations of the four metals examined in this study are comparable to concentrations in clams from "Reference areas" (areas presumed to have little contamination and used as a control in other studies). For these metals, only mercury appears higher in the non-reference compared to the reference areas. Mercury concentrations in clams examined 16 years ago (CH2M Hill, 1974) from Bellingham Bay are considerably higher than current concentrations found in this study. This trend reflects the trend found in crabs and is probably due to reduced mercury discharge at the Georgia Pacific plant. Concentrations of metals in Bellingham Bay clams do not appear elevated above reference areas.

Pesticides: The low concentrations of lipids found in the clams may contribute to the lack of pesticides and PCB's found in these tissues.

Polycyclic Aromatic Hydrocarbons: Table 9 shows PAH concentrations found in clams at other sites in Puget Sound. The total PAH concentration in the clams from this study is comparatively low and equivalent to reference areas. PAH concentrations are well below those found in smoked foods.

Comparisons to Standards

The U.S. Food and Drug Administration issues guidelines for contaminants in food called Action Levels (FDA, 1984 and 1985). When these levels are exceeded in food, the product cannot be commercially traded. FDA ascribes no risk assessment data to these concentrations. The limit for mercury is 1 ppm. The limit for total PCB's is 2 ppm. The pesticide limits for DDE is 5 ppm and for chlordane it is 0.3 ppm. All samples were well below these limits.

As part of the PSDDA monitoring program, guidelines have been developed based upon an exposure analysis that calculates potential transfer of chemicals of concern from a dredged spoils disposal site to humans via seafood consumption (PSDDA, 1988). The estimated low potential for this transfer results in relatively high tissue values for interpretation of lab tests. These values are as follows (all in ppm): As=10.1; Hg=300; Total DDT=41; chlordane=8.7; Total PCBs=3.2; fluoranthene=8,400; and benzo(a)pyrene=1.2. With the exception of arsenic, these concentrations found in this study are from 2 to 5 orders of magnitude less than these guidelines. Arsenic concentrations found in this study varied from 1/10 to 1/2 of the guidelines.

CONCLUSIONS

Concentrations of metals in Bellingham Bay crabs and clams are low and near background levels. A slight geographic trend appears in mercury concentrations in crabs with high concentrations found closer to Whatcom Waterway. In this study, pesticides and PCB's were

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

		Non-Reference Area*				Reference Area**			Bellingham Bay	
		Elliott Bay	Puget Sound	Eagle Harbor	McNeil Island	Birch Bay	Point Blakely	Horsehead Bay	Post Point	This study
Metal		5 sites	8 sites							4 sites
***	Species code:	1	2	3	2	2	3	2	2	2
	Study:	Romberg et al. 1984	Faigenblum 1988	Yake et al. 1984	Norton 1988	Faigenblum 1988	Yake et al. 1984	Norton 1988	CH2MHill 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	.10-.19	.10-.54	.08-.29	.29-.34	.22-.36				.18-.23
	N	?	39	8	3	6	1	1		4
Pb										
	Mean	0.40	0.09	0.84		<.04	0.38			0.08
	Range	.10-.50	.04-.18	.43-2.0		<.04-<.04				.02-.15
	N	?	25	8		4	1			4
Hg										
	Mean	0.020	0.02	0.33	0.011	<.02	0.012	0.012		0.01
	Range	.11-.28	<.02-.03	.01-.07	.010-.011	<.02-<.02			<.10-.28	<.01-.02
	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)

Table 9. Comparison of PAH concentrations in clams with other studies. All results ug/kg wet weight.

	Non-Reference area*				Reference Area**			Bell. Bay	Selected Foods	
Chemical	Eagle Harbor	S. Budd Inlet	Industrial Waterway ***		Point Blakely	N. Budd Inlet	Case Inlet	This study 4 sites	Smoked Ham	Smoked Fish
Species code****	1	2	3		1	2	3			
Study:	Yake et al. 1984	Norton 1986	Malins et al 1980		Yake et al. 1984	Norton 1986	Malins et al 1980		Pucknat 1981	Pucknat 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		
HPAH(2)										
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	1	1	4		

* Presumption within study that area may exceed background concentrations.

** Used within study as reference or control site.

*** Duwamish, Commencement Bay, and Hylebos Waterways, Seattle Waterfront

**** Species codes:

1	2	3
Protothaca staminea	*Protothaca staminea*	*Macoma nasuta*
Tapes japonica	*Tapes japonica*	*Macoma carlottensis*
Saxidomus giganteus	*Mya arenaria*	*Acila castrensis*

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

(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.

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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.

Surrogate recovery: 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).

Reference Material: 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 Spike Recovery						
	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%
Pentachlorophenol	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	--	--	--	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 Material (3)		
	Crab	Clam	Lab			Blind(2)								
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.

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.

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 Dibromooctafluorobiphenyl (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 limits so 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.

WASHINGTON STATE DEPARTMENT OF ECOLOGY
MANCHESTER ENVIRONMENTAL LABORATORY
Manchester, Washington 98353

DATA REVIEW

By: Craig Smith, Chemist
PROJECT: Bellingham Bioaccumulation
Lab Sample No: 398080 - 398097 **Report Date:** 11-26-90

Metals
Digestion: Total
Matrix: Crab and Clam tissue

Holding time: Analysis for all parameters were performed within the holding time limits.

Reagent Blank: The method blank showed no analyte values above the reporting detection limit.

Matrix Spike: The targeted accuracy of matrix spikes is +/- 25% of the true value. All values were within the targeted limits.

Spike Duplicate: The target limits are +/- 20%, or +/- 1 detection limit for samples less than 5 times the detection limit.

Laboratory Control Sample: The target is a +/- 20% recovery control limit. All values were within the targeted limits.

The data may be used without qualification.

All required criterion were accomplished, as per the QA Plan.

The samples were freeze dried, and then digested., with the exception of Hg.

All metals levels were quite low, with the quite apparent exception of Arsenic.