Results of Sampling to Verify 303(d) Listings for Chemical Contaminants in Shellfish from Dyes Inlet and Port Washington Narrows

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Results of Sampling to Verify 303(d) Listings for Chemical Contaminants in Shellfish from Dyes Inlet and Port Washington Narrows

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March 2002

Waterbody No. WA-15-0050
303(d) Segments: 47122F6I8, 47122F6G7, 47122F6H2

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Abstract

Ostrich Bay, Oyster Bay, and Port Washington Narrows were placed on Washington State's 1998 303(d) list of impaired waterbodies, based on two studies reporting exceedances of EPA human health criteria for various metals and organic contaminants in the edible tissues of crabs and clams. In formulating an approach for addressing these listings, the Washington State Department of Ecology concluded that data from those studies for antimony, bis(2-ethylhexyl)phthalate, and several polynuclear aromatic hydrocarbons may not describe current conditions and that sampling should be conducted to confirm the need for these 303(d) designations. Verification sampling was conducted during July, August, and September of 2001.

Results of the 2001 sampling showed that crab from Ostrich Bay do not contain detectable levels of antimony, bis(2-ethylhexly)phthalate, or the polynuclear aromatic hydrocarbons of interest. Clam samples from Oyster Bay had detectable levels of several PAHs, but the concentrations were at or below the human health criteria. With four parameters exceeding the human health criteria, concentrations of PAHs in Port Washington Narrows clams were much higher than Oyster Bay.

Based on these results, it is recommended that:

1. Ostrich Bay be de-listed for antimony, bis(2-ethylhexyl)phthalate, benzo(a)anthracene, chrysene, and benzo(b)fluoranthene in crab tissue.

2. Oyster Bay be de-listed for benzo(b)fluoranthene in clam tissue.

3. Port Washington Narrows be retained on the list for benzo(b)fluoranthene in clam tissue, and be added to the list for benzo(a)anthracene and chrysene in clam tissue.

Acknowledgements

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- Dale Norton for helping to collect crab samples and for donating salmon carcasses and traps.

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- Joan LeTourneau for formatting and editing the final report.

Introduction

Background

The Washington State Department of Ecology (Ecology) placed Dyes Inlet and Port Washington Narrows on Washington State's 1998 303(d) list of impaired waterbodies based on excursions for various metal and organic contaminants in the edible tissues of crabs and clams. The contaminants include antimony, arsenic, mercury, bis(2-ethylhexyl)phthalate (BEHP), 3,3'-dichlorobenzidine (DCB), pentachlorophenol (PCP), and several polyaromatic hydrocarbons (PAHs) (benzo(a)anthracene, benzo(b)fluoranthene, and chrysene).

The listings are based on data reported in two studies:

1. A remedial investigation of the Jackson Park Housing Complex/Naval Hospital, located on Ostrich Bay at the southern end of Dyes Inlet (EA Engineering, 1995).

2. A study of chemical contaminants in Sinclair and Dyes inlet fish and clams conducted by Ecology (Cubbage, 1992). Cubbage's sampling sites included Port Washington Narrows which connects Sinclair and Dyes inlets, and Oyster Bay at the southern end of Dyes Inlet (see Figures 1 and 2).

The studies reported one or more tissue samples with concentrations exceeding the EPA National Toxics Rule (NTR) for human health criteria. The 303(d) listing criteria require at least two excursions of single-fish samples or one excursion of a composite of at least five separate fish (Ecology, 2001). Table 1 is a summary of the findings from these two studies.

Ecology reviewed the 1998 303(d) list to determine the best approach for addressing the toxics listings (Johnson, 2001). The following recommendations were made as a result of this review.

- PCP should be removed from the list for Ostrich Bay crab, because the supporting data show the listing was an error.

- DCB should be removed from the list for Ostrich Bay clam, because recent data show standards being met (Johnson, 1998).

- Arsenic and mercury in Ostrich and Oyster bays should not be included in this verification study, because the listings appeared reasonable.

- Antimony, BEHP, and PAHs in Ostrich Bay, Oyster Bay, and Port Washington Narrows should be included in this verification sampling (Table 2).

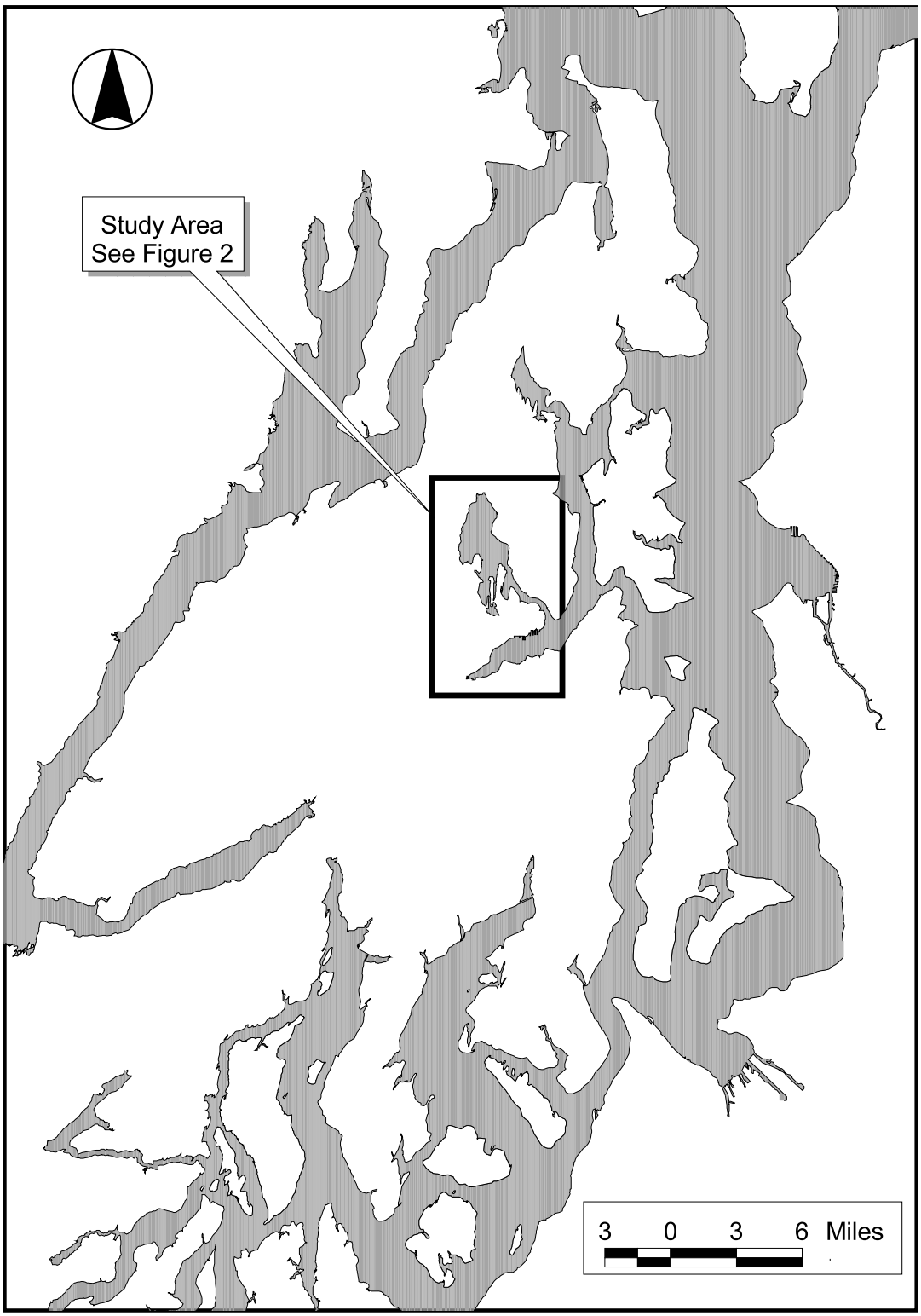

Figure 1. Dyes Inlet/Port Washington Narrows Study Area

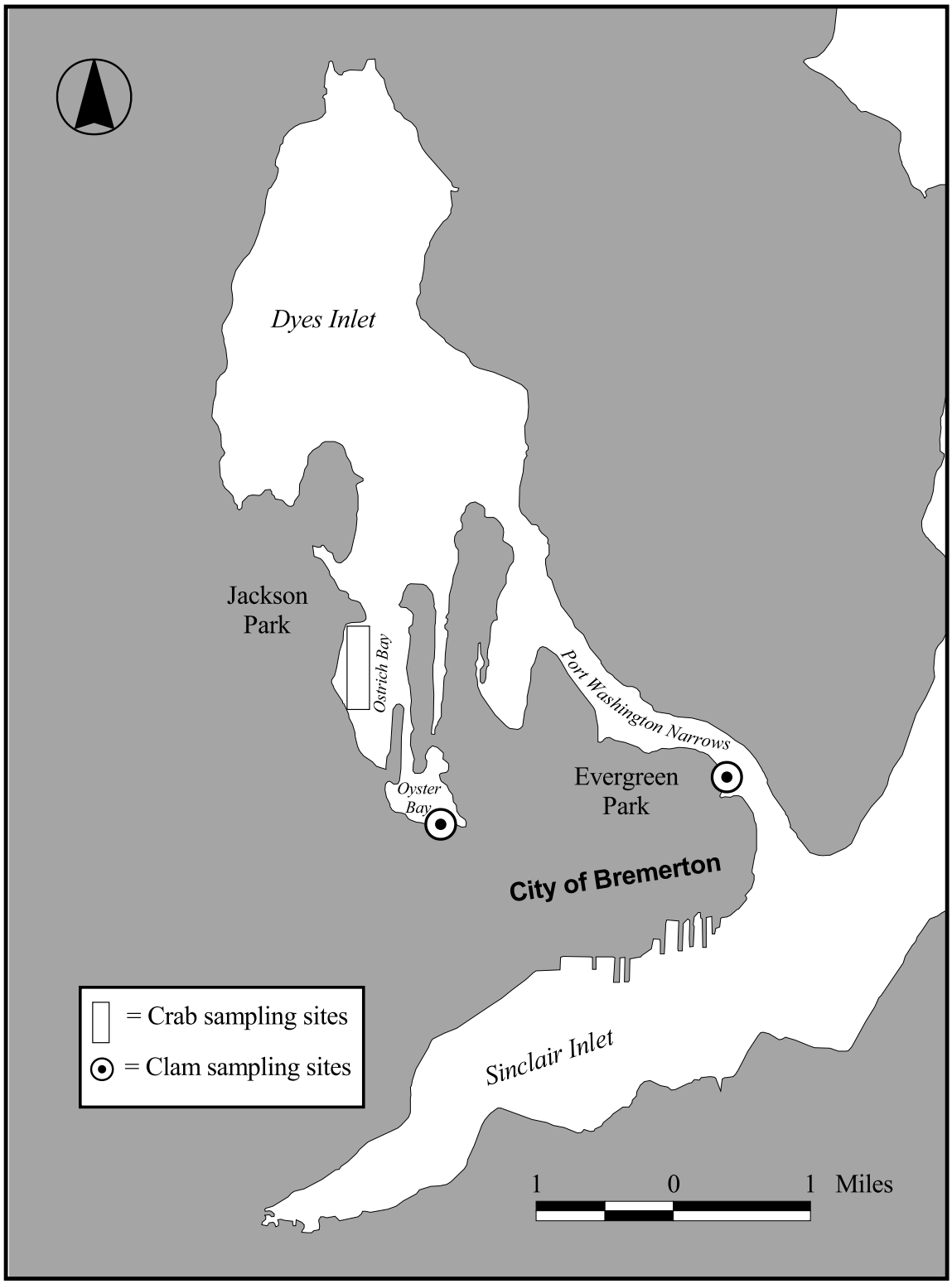

Figure 2. Clam and Crab Sampling Sites in Dyes Inlet and Port Washington Narrows

Table 1. Data Sources for 1998 303(d) Listings.

Parameter	Tissue	Number of Samples Tested	Number of Samples Detected	Average Concentration[a] (ug/kg, wet weight)	303(d) Listing Criterion[b]
EA Engineering (1995)					
Ostrich Bay (Grid # 47122F6I8)					
antimony	Clam soft parts	45	5	10,900	4,300
bis (2-ethylhexyl) phthalate	Clam soft parts	45	7	2,800	767
3,3-dichlorobenzidine	Clam soft parts	27	3	3,800	24
antimony	Crab muscle	24	7	13,500	4,300
bis (2-ethylhexyl) phthalate	Crab muscle	24	2	4,800	767
benzo(a)anthracene	Crab muscle	11	1	180	0.93
benzo(b)fluoranthene	Crab muscle	11	1	210	0.93
chrysene	Crab muscle	11	1	170	0.93
pentachlorophenol[c]	Crab muscle	12	0	nd	90
Cubbage (1992)					
Oyster Bay (Grid # 47122F6G7)					
benzo(b)fluoranthene	Clam soft parts	1 composite of 29 individuals		4j	0.93
Port Washington Narrows (Grid # 47122F6H2)					
benzo(b)fluoranthene	Clam soft parts	1 composite of 9 individuals		4j	0.93

nd = Not detected
j = The analyte was positively identified. The associated numerical value is an estimate.
a = Numbers are averages of detected values.
b = National Toxics Rule. U.S. Environmental Protection Agency.
c = Not detected, listed in error.

Table 2. Recommendations for De-listing or Verification Sampling from Ecology Review of 1998 303(d) Listings.

Parameter	Data Source Basis for Listing	Tissue	Recommendation[a]		Reason for Recommendation
			De-List	Verify	
Ostrich Bay					
antimony	EA (1995)[b] multiple excursions	Crab/ Clam		x	Newer Ecology clam data show standards being met Verify crab listing
BEHP	EA (1995) 2 crab excursions	Crab/ Clam		x	Newer Ecology clam data show standards being met Verify crab listing
benzo(a)anthracene	EA (1995) 1 excursion	Crab		x	Infrequently detected
chrysene	EA (1995) 1 excursion	Crab		x	Infrequently detected
benzo(b)fluoranthene	EA (1995) 2 excursions	Crab		x	Infrequently detected
PCP	EA (1995) 1 excursion	Crab	x		Listed in error, PCP not detected
DCB	EA (1995) 3 excursions	Clam	x		Newer Ecology clam data show standards being met
Oyster Bay					
benzo(b)fluoranthene	Cubbage[c] (1992) 1 excursion	Clam		x	Criterion only marginally exceeded
Port Washington Narrows					
benzo(b)fluoranthene	Cubbage (1992) 1 excursion	Clam		x	Criterion only marginally exceeded

a = Johnson, 2001a. Recommendation to De-List or Verify Certain 303(d) Tissue Listings for WRIA 15 - Kitsap Watershed.

b = EA Engineering, 1995. Draft Remedial Investigation/Feasibility Study: Jackson Park Housing Complex/Naval Hospital Operable Unit 2-Marine Areas.

c = Cubbage, 1992. Contaminants in Fish and Clams in Sinclair and Dyes Inlets.

Study Goals and Objectives

The goal of this sampling effort was to verify the validity of the Dyes Inlet and Port Washington Narrows antimony, BEHP, and PAH listings for crab and clam tissue.

Study objectives were as follows:

- Obtain accurate and representative data on the concentrations of antimony, BEHP, and PAH in edible crab and clam tissues from the locations of interest.
- Compare the results to the 303(d) listing criteria to verify current validity of 1998 listings.
- Provide recommendations to the Ecology Water Quality Program and the Ecology Northwest Regional Office for retaining or removing the Dyes Inlet and Port Washington Narrows tissue parameters from the 303(d) list.

Methods

Site Selection

Samples for the present study were collected within the same geographic grids as the tissue samples that produced the original 1998 303(d) listings. Figure 2 shows sampling site locations. Appendix A has the site specific GPS coordinates, dates, and site descriptions.

Sample Collection

Chain-of-custody was maintained throughout the sample collection and preparation procedures. All samples were transported to the Ecology Headquarters chain-of–custody room and frozen in a secure freezer within one day of collection.

Crabs

Five of the seven 303(d) listings under investigation by this study were based on crab tissue sampled by EA Engineering (1995) in Ostrich Bay (Figure 2). EA Engineering sampled the Graceful cancer crab (*Cancer gracilis*). Although small and not commonly eaten, Ecology also collected the Graceful cancer crab, because no Dungeness or Rock crab were encountered.

Crab sampling and tissue preparation procedures were based on PTI (1991) and Puget Sound Water Quality Action Team (PSQWAT) (1997a,b) procedures. Twenty-nine crabs were collected using pots baited with salmon carcasses and set for 1-2 hours at depths ranging from 16-38 ft. (MLLW). The largest male crabs were taken as samples. Care was taken to avoid contact between the crabs and engine fumes, fuel, oil, bilge water, or other contaminants.

Each crab selected for analysis was killed with a blow to the ventral nerve cord. The crabs were individually wrapped in aluminum foil, put in double plastic bags, labeled with the date and location of collection, and placed in coolers containing blue ice. The crabs were kept dorsal side down so that body cavity liquids would drain away from muscle tissue.

Clams

Ecology's draft 303(d) listing policy for toxics in edible tissue requires a minimum sample size of one composite formed from at least five individual organisms or three individual samples (Ecology, 2001). The organisms sampled can be of varied species within the same waterbody.

Ecology collected Native littleneck clams (*Protothaca staminea*) and Japanese littlenecks (*Tapes japonica*) for this evaluation. The samples for the original 303(d) listing were a mix of Japanese littlenecks, Heart cockle (*Clinocardium nuttali*), Butter clams (*Saxidomus giganteus*), and Native littleneck (Cubbage, 1992). Ecology collected Native and Japanese littlenecks, because they were most abundant in the study area and are the most commonly harvested

species. Specimens ranged in size from 36-50 mm in diameter. Ninety clams were harvested from Oyster Bay. Sixty clams were taken from Port Washington Narrows at Evergreen Park. Clam specimens were harvested in the interdidal zone within an area approximately 50' x 50' at both sites.

The original listing was based on samples collected in January. Ecology collected samples in July and August of 2001 for better representation of contaminant levels during peak recreational harvest. Recreational harvesting is currently prohibited by the Washington State Department of Health at all three sampling sites (Meriwether, 2002).

Clam sampling and sample preparation procedures are based on unpublished guidelines prepared by Glen Patrick, Office of Toxic Substances, Washington State Department of Health (Johnson, 1997). These are modifications of procedures used for PSAMP shellfish monitoring.

Clam diggers used clean rakes and shovels, uncontaminated by grease or oil. Prior to collection stainless steel buckets were pre-cleaned by washing with detergent and rinsing with acetone and de-ionized water. Rakes, shovels, and buckets were washed with sea water between sampling sites.

The clams were rinsed thoroughly with on-site sea water to remove any adhering mud or sand, then placed in one-gallon glass jars with Teflon lid-liners, cleaned to EPA (1990) QA/QC specifications. The clams were not depurated. Each jar was labeled with date and location of collection, wrapped in bubble-wrap to avoid breaking, and placed on ice in coolers.

Sample Preparation

All tissues were removed using techniques intended to minimize potential for sample contamination. Only non-corrosive stainless steel instruments were used. Persons preparing the samples wore non-talc polyethylene gloves and worked on aluminum foil. The gloves and foil were changed between individual samples. All tissue composite samples were placed in 8-oz glass containers with Teflon lid-liners, cleaned to EPA (1990) QA/QC specifications.

Resecting instruments and blender parts were cleaned by washing in hot tap water with Liquinox detergent, followed by sequential rinses with tap water, 1% reagent-grade nitric acid, de-ionized water, and pesticide-grade acetone. All items were then air dried on aluminum foil in a fume hood before use.

All sample containers were labeled with sampling site, sampling date, species, tissue type, sample number, and analysis requested. The samples were frozen and taken by courier to Manchester Environmental Laboratory. The samples were stored frozen at Manchester Laboratory until analyzed.

Crabs

The 29 individual crabs were separated into three composite samples of 9-10 crabs each. The range of carapace widths for each composite was recorded to the nearest millimeter (85-100 mm)

(Appendix A). After rinsing the crabs with tap water followed by de-ionized water to remove any remaining debris, muscle tissue was removed from the claw, legs, and body and placed in 8-oz jars.

When removing body meat, care was taken not to include hepatopancreas tissue or other organs. Shell fragments were not included in the samples. The resected samples were homogenized to uniform color and consistency by hand with stainless steel implements.

Clams

The clams were separated into three composites per site. The composites included approximately equal numbers of small, medium, and large specimens (36-50 mm) (Appendix A). There were 30 clams in each of the Oyster Bay composites and 20 clams in each of the Port Washington composites.

After rinsing the clams with tap water followed by de-ionized water to remove any remaining debris, the entire soft parts were removed. The soft parts were homogenized to uniform color and consistency in a plastic and stainless steel Kitchen-Aid blender and placed in 8-oz jars. Shell fragments were not included.

Laboratory Procedures

The samples were analyzed at the Ecology Manchester Environmental Laboratory. Table 3 shows the analytical methods used and detection limits achieved. A full suite of priority pollutant PAHs was analyzed. Laboratory methods used are comparable to those used in EA Engineering and Ecology studies that designated the original 303(d) listings.

Table 3. Laboratory Procedures

Analyte	Detection Limits (wet weight)	Analytical Method
Antimony	50 ug/kg	EPA 200.8
BEHP	14-20 ug/kg	EPA SW 8270/1625 mod.*
PAH	0.73-3.6 ug/kg	EPA SW 8270 mod. *

*isotopic dilution

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Data Quality

Manchester Laboratory staff prepared written quality assurance (QA) reviews of the PAH, BEHP, and antimony data for this project. The review included an assessment of sample conditions on receipt at the laboratory, compliance with holding times, instrument calibration, procedural blanks, laboratory control samples, standard reference material, and matrix spike recoveries. All data quality objectives specified in the QA Project Plan for this study were met (Johnson, 2001b). No significant problems were encountered in the chemical analyses, and the data are usable as qualified. The QA reviews (case narratives) are located in Appendix B. Complete chemical data are available on request.

The precision of the chemical data reported here can be gauged from results of analyzing duplicate aliquots of selected tissue samples, summarized in Table 4. All duplicates agreed within 7% or better, based on detected compounds, showing the precision of analysis was good.

Table 4. Precision of Duplicate Analysis (ug/kg, wet weight).

Station ID	Tissue	Antimony	BEHP
Ostrich	crab	50u	26u
Ostrich Dup	crab	50u	14u
RPD	crab	nc	nc

Station ID	Tissue	Chrysene	Benzo(a)anthracene	Benzo(b)fluoranthene	Pyrene	Fluoranthene
Oyster	clam	1.7	0.73u	0.62j	3.1	5.3
Oyster Dup	clam	1.6	0.9uj	0.57j	3.1	5.2
RPD	clam	6%	nc	8%	0%	1.9%

uj =The analyte was not detected at or above the reported estimated result.
u = The analyte was not detected at or above the reported value.
nc = Not calculated because compounds were not detected.
j = The analyte was positively identified. The associated numerical value is an estimate.
RPD = Relative percent difference.

The 303(d) listing criteria for individual PAHs are extremely low (0.93 ug/kg). Because of this, a Standard Reference Material (SRM) was analyzed to determine the accuracy of the PAH clam data obtained. Similar SRMs are not available for the other contaminants.

The SRM used for PAH was National Institute of Standards (NIST)1974A: Organics in Mussel Tissue. The results of Manchester Laboratory's analysis of this material are compared to the NIST certified values in Table 5.

Table 5. Results on Standard Reference Material (ug/kg).

Compound	NIST Certified Values	Manchester Values	Recovery
Phenanthrene	2.53+/- 0.28	6.1	241%
Fluoranthene	18.6 +/- 1.0	16.2	87%
Pyrene	17.26+/-0.74	16.1	93%
Benzo(a)anthracene	3.71+/-0.54	2.1	57%
Chrysene	5.04+/-0.26	8.4	167%
Benzo(b)fluoranthene	5.28+/-0.42	3.9	74%
Benzo(k)fluoranthene	2.30+/-0.10	3.5	152%
Benzo(e)pyrene	9.56+/-0.21	5.8	61%
Indeno(1,2,3-cd)pyrene	1.62+/-0.32	1.0	62%
Benzo(ghi)perylene	2.5+/-0.25	2.2	88%

These data show that Manchester results are biased high for phenanthrene (241% recovery), chrysene (167% recovery), and benzo(k)fluoranthene (152% recovery). Manchester Laboratory has observed similar interferences for chrysene in previous analyses with this method (Huntamer, 2002). Therefore, marginal exceedances of 303(d) criteria for chrysene and benzo(k)fluoranthene, described later in this report, should be viewed with caution.

Results and Discussion

The results of this current verification study and Ecology's 303(d) listing criteria are summarized in Table 6.

Three composite crab samples from Ostrich Bay were analyzed for antimony, BEHP, and PAH. No detectable analytes were found in any of these samples. The detection limit for antimony was 50 ug/kg. Detection limits for BEHP ranged from 14-26 ug/kg (wet weight). Detection limits for the PAHs were 0.76-0.80 ug/kg.

Three composite clam samples from Oyster Bay were analyzed for PAH. The following compounds were detected: fluoranthene, pyrene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene . Except for chrysene, all PAH concentrations were below the 303(d) listing criterion.

The results for chrysene ranged from 1.6-1.8 ug/kg. However, as previously described, the chrysene data are biased high. When adjusted for recovery in the SRM analyzed in conjunction with these samples, the chrysene concentrations in the Oyster Bay clam samples are at the 303(d) criterion (1.0 vs 0.93 ug/kg, Table 7). Analysis of a laboratory duplicate (Table 4) and results from the Oyster Bay field replicates (Table 6) show that the precision of the chrysene data for clams is on the order of 0.1-0.2 ug/kg. Given this level of precision and the uncertainty associated with measuring concentrations near the detection limit, these results provide no conclusive evidence that the chrysene concentrations in Oyster Bay clams exceed the listing criterion.

Three composite clam samples from Port Washington Narrows were analyzed for PAHs. Results showed the concentrations were much higher than in Oyster Bay, typically by a factor of 2. Seven PAHs were detected in one or more of the composites: phenanthrene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene.

Four parameters were above 303(d) listing criterion in the Port Washington samples: benzo(a)anthracene, chrysene, benzo(b)fluoranthene, and benzo(k)fluoranthene. Ranging from 1.2-2.5 ug/kg, the samples exceed the 303(d) listing criterion of 0.93ug/kg. When adjusted for SRM recovery, concentrations of benzo(k)fluoranthene do not exceed the 303(d) listing criterion (Table 7).

Table 6. Results of Verification Sampling of Crab and Clam Tissue from Dyes Inlet and Port Washington Narrows* (ug/kg, wet weight)

Parameter	Ostrich Bay Crabs				Oyster Bay Clams				Port Wash Narrows Clams			303(d) Criteria
	428086	428086 (Dup)	428087	428088	428080	428080 (Dup)	428081	428082	428083	428084	428085	
antimony	50u	50u	50u	50u	na	na	na	na	na	na	na	4,300
bis(2-ethylhexyl)phthylate	26u	14u	20u	16u	na	na	na	na	na	na	na	767
phenanthrene	0.80u	na	0.80u	0.76u	0.73u	0.90u	0.83u	0.74u	0.80u	5.4	0.8u	none
fluoranthene	0.80u	na	0.80u	0.76u	5.3	5.2	5.1	4.8	8.2	8.6	8.4	425,500
pyrene	0.80u	na	0.80uj	0.76uj	3.1	3.1	3.0	2.7	5.9	6.0	6.0	330,000
benzo(a)anthracene	0.80u	na	0.80u	0.76uj	0.73u	0.90uj	0.83u	0.74u	**1.5**	**1.8**	**1.8**	0.93
chrysene	0.80u	na	0.80u	0.76u	**1.7**	**1.6**	**1.6**	**1.8**	**2.1**	**2.5**	**2.4**	0.93
benzo(b)fluoranthene	0.80u	na	0.80uj	0.76uj	0.62	0.57	0.48	0.50	**1.3**	**1.3**	**1.3**	0.93
benzo(k)fluoranthene	0.80u	na	0.80u	0.76uj	0.76	0.78	0.72	0.66	**1.2**	**1.2**	**1.4**	0.93

* = Results are from individual composites samples
na = Not analyzed
u = The analyte was not detected at or above the reported value
uj = The analyte was not detected at or above the reported estimated result
bold = Exceeds 303 (d) criteria

Table 7. Sample Concentrations Adjusted for Standard Reference Material Recovery (ug/kg).

Parameter	SRM (%)	Oyster Bay (mean)	Adjusted for Recovery	Port Washington Narrows (mean)	Adjusted for Recovery	303(d) Listing Criteria
benzo(b)fluoranthene	74	0.52	0.70	1.3	1.8	0.93
benzo(a)anthracene	57	nd	nd	1.7	3.0	0.93
chrysene	167	1.7	1.0	2.3	1.4	0.93
benzo(k)fluoranthene	152	0.72	0.47	1.3	0.8	0.93

The historical data and the data from this current study are presented with the 303(d) listing criteria in Table 8. Due to advances in analytical technique, much lower detection limits were achieved in the analysis from this study.

Table 8. Comparison of Historical and Present Study Data (ug/kg, wet weight).

Parameter	Tissue	Detection Frequency	EA Engineering (1995)	Detection Frequency	Present Study	303(d) listing criterion
Ostrich Bay						
antimony	Crab muscle	7 of 24	13,500	0 of 3	50u	4,300
bis(2-ethylhexly)phthalate	Crab muscle	2of 24	4,800	0 of 3	26u	767
benzo(b)fluoranthene	Crab muscle	1 of 11	210	0 of 3	0.80u	0.93
benzo(a)anthracene	Crab muscle	1 of 11	180	0 of 3	0.80u	0.93
chrysene	Crab muscle	1 of 11	170	0 of 3	0.80u	0.93
Parameter	Tissue	Detection Frequency	Ecology (1992)	Detection Frequency	Present Study	303(d) listing criterion
Oyster Bay						
benzo(b)fluoranthene	Clam soft parts	1 of 1	4j	3 of 3	0.53	0.93
chrysene	Clam soft parts	0 of 1	96u	3 of 3	1.7*	0.93
Port Washington Narrows						
benzo(b)fluoranthene	Clam soft parts	1 of 1	4j	3 of 3	1.3	0.93
benzo(a)anthracene	Clam soft parts	0 of 1	95u	3 of 3	1.7	0.93
chrysene	Clam soft parts	0 of 1	95u	3 of 3	2.3	0.93
benzo(k)fluoranthene	Clam soft parts	0 of 1	95u	3 of 3	1.3*	0.93

u = The analyte was not detected at or above the reported value
j = The analyte was positively identified. The associated numerical value is an estimate
* These data biased high, see text.
Average values are shown for multiple samples.

The contaminant concentrations measured in Ostrich Bay crabs during this verification study are orders of magnitude lower than the data reported in EA Engineering (1995). The more recent findings are consistent with clam samples previously collected from this area by Ecology (Johnson, 1998a).

The reason for the discrepancy in the EA Engineering and Ecology data is not known. Sample contamination or errors in laboratory analyses are suspected, especially for antimony and bis(2-ethylhexyl)phthalate. There are no known sources of either chemical in the study area. The overwhelming majority of the EA Engineering samples failed to show detectable levels of the five listed chemicals.

The low-level PAH analysis employed for Oyster Bay and Port Washington Narrows clams revealed several compounds previously undetected by Cubbage (1992), who only reported benzo(b)fluoranthene. Benzo(b)fluoranthene concentrations in the verification samples were lower than those reported for Cubbage's samples by about a factor of 4.

Recommendations

Recommendations from this investigation are listed below and displayed in Table 9:

- Ostrich Bay should be de-listed for antimony, BEHP, benzo(a)anthracene, chrysene, and benzo(b)fluoranthene in crab tissue. These contaminants were not detected in the verification samples.

- Oyster Bay should be de-listed for benzo(b)fluoranthene in clam tissue. Concentrations in the verification samples ranged from 0.48 - 0.62 ug/kg, compared to the listing criterion of 0.93 ug/kg.

- Oyster Bay should not be added to the list for chrysene in clam tissue. Although the analysis conducted for the verification study gave results of 1.6 - 1.8 ug/kg, the chrysene data were found to be biased high.

- The Port Washington Narrows listing for benzo(b)fluoranthene in clam tissue should be retained.

- Port Washington Narrows should be added to the list for benzo(a)anthracene and chrysene in clam tissue. The new data showed concentrations of 1.5 - 1.8 ug/kg and 2.1 - 2.5 ug/kg, respectively, compared to the 0.93 ug/kg criterion.

- Port Washington Narrows should not be listed for benzo(k)fluoranthene. Although the analysis conducted for the verification study gave results of 1.2 - 1.4 ug/kg, the benzo(k)fluoranthene data were found to be biased high.

Table 9. Final Recommendations from 303(d) Verification Sampling.

			Final Recommendation			
Parameter	Data Source Basis for Listing	Tissue	De-List	Retain on List	Add to List	Reason for Recommendation
Ostrich Bay						
antimony	EA (1995) multiple excursions	crab/ clam	Yes			Results from this study show standards being met
BEHP	EA (1995) 2 crab excursions	crab/ clam	Yes			Results from this study show standards being met
benzo(a)anthracene	EA (1995) 1 excursion	crab	Yes			Results from this study show standards being met
chrysene	EA (1995) 1 excursion	crab	Yes			Results from this study show standards being met
benzo(b)fluoranthene	EA (1995) 2 excursions	crab	Yes			Results from this study show standards being met
Oyster Bay						
benzo(b)fluoranthene	Cubbage (1992) 1 excursion	clam	Yes			Results from this study show standards being met
chrysene	Current study	clam			No	No clear evidence that samples exceed standards
Port Washington Narrows						
chrysene	Current study	clam			Yes	Samples from this study exceeded the 303(d) listing criterion
benzo(a)anthracene	Current study	clam			Yes	Samples from this study exceeded the 303(d) listing criterion
benzo(b)fluoranthene	Cubbage (1992) 1 excursion	clam		Yes		Samples from this study exceeded 303(d) listing criterion
benzo(k)fluoranthene	Current study	clam			No	Samples from this study are below the 303(d) listing criterion when adjusted for bias

References

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Appendices

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Appendix A

Sampling Site and Biological Information

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Table A1. Station Location Details

Station	Date Collected	Tissue	GPS Coordinates	Number of Animals	Size of Shell (mm)	Description
Oyster Bay	7/19/2001	Clams	47° 34.185 N 122°40.393 W	90	36-50	In front of the Oyster Bay Inn
Port Washington Narrows	8/31/2001	Clams	47° 34.497 122° 37.572	60	36-50	At Evergreen Park (approx. 40 ft. north of dock)
Ostrich Bay	9/6/2001	Crabs	47° 35.30-47° 34.766 122° 41.10-122° 41.083	29	85-100	Along west shore of Ostrich Bay in vicinity of Jackson Park

Datum=NAD 83

Table A2. Sample Collection and Biological Information

Sample I.D.	Date Collected	Date Prepared	Species	Sample Location	Number of Animals	Size of Shell (mm)	Body Part
428080	7/19/2001	10/11/2001	Native and Japanese Littlenecks	Oyster Bay	30	36-50	Entire animal
428081	7/19/2001	10/11/2001	"	Oyster Bay	30	36-50	Entire animal
428082	7/19/2001	10/11/2001	"	Oyster Bay	30	36-48	Entire animal
428083	8/31/2001	10/11/2001	"	Port Washington Narrows	20	36-50	Entire animal
428084	8/31/2001	10/11/2001	"	Port Washington Narrows	20	36-50	Entire animal
428085	8/31/2001	10/11/2001	"	Port Washington Narrows	20	36-50	Entire animal
428086	9/6/2001	10/12/2001	Graceful Cancer Crab	Ostrich Bay	9	87-88	Muscle
428087	9/6/2001	10/12/2001	"	Ostrich Bay	9	89-97	Muscle
428088	9/6/2001	10/12/2001	"	Ostrich Bay	10	85-100	Muscle

Native Littlenecks=*Protothaca staminea*
Japanese Littlenecks=*Tapes japonica*
Graceful Cancer Crab=*Cancer gracilis*

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Appendix B

Case Narratives

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Manchester Environmental Laboratory

7411 Beach Drive E, Port Orchard Washington 98366

CASE NARRATIVE

November 14, 2001

Subject: Dyes Inlet / Port Washington Narrows

Samples: 01-428086 to -428088

Case No. 2043-01
Officer: Art Johnson

By: Dickey D. Huntamer
Organics Analysis Unit

Bis-2-EthylHexyl-Phthalate (BEHP)
Isotopic Dilution

Analytical Methods

The tissue samples were Soxhlet extracted with sodium sulfate using an hexane/methylene chloride solvent mixture following the Manchester modification of the EPA SW 846 8270 method and EPA Method 1625. An isotopically labeled analog of the target analyte (BEHP) was added to the samples prior to extraction. After extraction the samples were cleaned up Gel Permeation Chromatography and 20% Florisil. Samples were concentrated to a final volume of 0.5 milliliter for analysis. The samples were analyzed by capillary GC/MS. Normal QA/QC procedures followed.

Holding Times

The samples were stored frozen until analysis. All analysis-holding times were within the recommended limits.

Blanks

Low levels of some target compounds were detected in the laboratory blanks. Compounds that were found in the sample and in the blank were considered real and not the result of contamination if the levels in the sample are greater than or equal to 10 times the area counts of the compounds in the associated method blank.

Surrogates

The isotopically labeled target compound recoveries were generally within acceptable limits. The first pair of laboratory blanks, OBT1289A1 and A2 had lower recoveries but were still above the 18-364% limits allowed by EPA Method 1625. Since isotopic dilution methodology corrects for low or high isotope recoveries no additional qualifiers were added to the results.

Matrix Spike And Matrix Spike Duplicate

Matrix spikes were analyzed with the samples. Matrix spike levels were 50 ug/Kg. Matrix spike recoveries were 50% and 70% with a 33% Relative Percent Difference (RPD). Matrix spike recoveries were within acceptable limits.

An Initial Demonstration of Capability (IDC) consisting of four Lab Fortified Blanks (LFB) spiked at 100 ug/Kg were also analyzed with the samples. Recoveries were acceptable and ranged from 95% to 130%.

Analytical Comments

No bis-2-ethylhexylphthalate (BEHP) was detected in any of the samples. No significant problems were encountered in the analysis other than the apparent contamination of one of the two extracts of sample –428086. It was greater than 10 times the amount in the corresponding duplicate sample but was still less than ten times the laboratory blanks. The sample was re-extracted and analyzed as indicated by the different extraction and analysis dates from the duplicate sample –428086 (LDP1). The second analysis results were consistent with the results from the duplicate. The data is acceptable as qualified.

Data Qualifier Codes

U - The analyte was not detected at or above the reported value.

J - The analyte was positively identified. The associated numerical value is an estimate.

UJ - The analyte was not detected at or above the reported estimated result.

REJ - The data are unusable for all purposes.

NAF - Not analyzed for.

N - For organic analytes there is evidence the analyte is present in this sample.

NJ - There is evidence that the analyte is present. The associated numerical result is an estimate.

E - This qualifier is used when the concentration of the associated value exceeds the known calibration range.

Bold - The analyte was present in the sample. (Visual Aid to locate detected compound on report sheet.)

Manchester Environmental Laboratory

7411 Beach Drive E, Port Orchard Washington 98366

CASE NARRATIVE

November 15, 2001

Subject: Dyes Inlet/ Port Washington Narrows

Samples: 01-428080 to -428088

Case No. 2043-01

Officer: Art Johnson

By: Dickey D. Huntamer
Organics Analysis Unit

Polynuclear Aromatic Hydrocarbons
SIM Isotopic Dilution

Analytical Methods

The tissue samples were Soxhlet extracted with sodium sulfate using a hexane/methylene chloride solvent mixture following the Manchester modification of the EPA SW 846 8270 method. Isotopically labeled analogs of most of the target analytes were added to the samples prior to extraction. After extraction the samples were cleaned up using Gel Permeation Chromatography (GPC) and silica gel. The sample extracts were concentrated to a volume of 0.5 milliliter and analyzed by capillary GC/MS in the SIM mode. Normal QA/QC procedures followed.

Holding Times

The samples were stored frozen until analysis. All analysis-holding times were within the recommended limits.

Blanks

Low levels of some target compounds were detected in the laboratory blanks. Compounds that were found in the sample and in the blank were considered real and not the result of contamination if the levels in the sample are greater than or equal to three times the area counts of the compounds in the associated method blank.

Surrogates

The isotopically labeled target compound recoveries were generally within acceptable limits. Since isotopic dilution methodology corrects for low or high isotope recoveries no additional qualifiers were necessary.

Matrix Spike And Matrix Spike Duplicate

Matrix spikes were analyzed with the samples. Not all analytes were in the matrix spikes. Matrix spike recoveries were within acceptable limits except for 2-methylphenanthrene. All Relative Percent Differences (RPD) were below 35%. Two lab-fortified blanks (LBF) were also analyzed with the samples. OCT1290A1 and OCT1290A2. All recoveries were within acceptable limits except for 2 methylphenanthrene, which tended to be high at 170% and 210%.

Analytical Comments

Samples –428080 to –428086 had benzo(a)anthracene, chrysene and benzo(b)fluoranthene detected at 3 ug/kg or less. Two other compounds, fluoranthene and pyrene also were detected in the samples at higher levels. Phenanthrene was detected in sample –428084 at 5.4 ug/Kg.

A NIST reference material 1974a, mussel tissue, was analyzed with the samples, OCT1290B1. The table below compares the results from this analysis to the certified values. Many of the analytes in this reference material are at or below the quantitation limits of the method. Due to the moisture content a maximum of about 8 grams can be extracted. The regular samples had 11 to 13 grams extracted. Despite the cleanup interferences also play a role in the analysis and can result in higher recoveries or non-detects.

Compound	Found	Value	Recovery
Phenanthrene	6.1	2,53 +- .28	241%
Fluoranthene	16.2	18.6 +/- 1.0	87%
Pyrene	16.1	17.26 +/- .74	93%
Benzo(a)anthracene	2.1	3.71 +/- .54	57%
Chrysene	8.4	5.04 +/- .26	167%
Benzo(b)fluoranthene	3.9	5.28 +/-.42	74%
Benzo(k)fluoranthene	3.5	2.30 +/- .10	152%
Benzo(e)pyrene	5.8	9.56 +/- .21	61%
Indeno(1,2,3-cd)pyrene	1.0	1.62 +/- .32	62%
Benzo(ghi)perylene	2.2	2.5 +/- .25	88%

No significant problems were encountered in the analysis. The data is acceptable as qualified.

Data Qualifier Codes

U - The analyte was not detected at or above the reported value.

J - The analyte was positively identified. The associated numerical value is an estimate.

UJ - The analyte was not detected at or above the reported estimated result.

REJ - The data are unusable for all purposes.

NAF - Not analyzed for.

N - For organic analytes there is evidence the analyte is present in this sample.

NJ - There is evidence that the analyte is present. The associated numerical result is an estimate.

E - This qualifier is used when the concentration of the associated value exceeds the known calibration range.

Bold - The analyte was present in the sample. (Visual Aid to locate detected compound on report sheet.)

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Manchester Environmental Laboratory

7411 Beach Drive E, Port Orchard Washington 98366

December 4, 2001

TO: Art Johnson

FROM: Jim Ross, Manchester Lab

SUBJECT: Metals Quality Assurance memo for Dyes Inlet/Port Washington Narrows

SUMMARY

All data for this project can be used without qualification.

Sample Receipt

The samples were received by the Manchester Laboratory on 10/15/01 in good condition.

Holding Times

All analyses were performed within the specified holding time (28 days Hg, 180 days all other metals).

Instrument Calibration

Instrument calibration was performed before each analytical run and checked by initial calibration verification standards and blanks. Continuing calibration standards and blanks were analyzed at a frequency of 10% during the run and again at the end of the analytical run. All initial and continuing calibration verification standards and blanks were within the relevant control limits.

Procedural Blanks

No detectable quantities of requested analytes were found in the procedural blanks.

Spiked Sample Analyses

All spikes were recovered within acceptable limits (75-125%).

Precision Data

Precision based on duplicate spike recoveries were acceptable for all analytes.

Laboratory Control Sample (LCS) Analyses

NIST 1974a was analyzed for the LCS. One aliquot of the sample was analyzed as received, but the result was below our limits of detection. The other was spiked at 20 ug/L, which is comparable to 1000 ug/Kg in the tissue. Recovery on the spiked sample was 111%.

Please call Jim Ross at (360) 871-8808 to further discuss this project.