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

Quality Assurance Project Plan

Art Johnson
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Washington State Department of Ecology
Environmental Assessment Program
Olympia, Washington

303(d) listings addressed by this project: Segment WA-15-0050 antimony, bis(2-ethylhexyl)phthalate, polyaromatic hydrocarbons

Approvals:

Dave Roberts_____Date_____
HQ-WQP

Dave Garland_____Date_____
NWRO-TMDL Unit Supervisor

Will Kendra _____Date_____
Section Manager, EAP Watershed Ecology Section

Dale Norton _____Date_____
Supervisor, EAP Toxics Studies Unit

Cliff Kirchmer_____Date_____
Ecology Quality Assurance Officer

Stuart Magoon _____Date_____
Director, Manchester Environmental Laboratory

Art Johnson_____Date_____
Project Lead, Toxics Studies Unit

Background and Problem Statement

Dyes Inlet and Port Washington Narrows (WA-15-0050) are on the 1998 303(d) list based on excursions for various metal and organic contaminants in the edible tissues of crabs and clams. The contaminants include but are not limited to antimony, bis(2-ethylhexyl)phthalate (BEHP), 3,3'-dichlorobenzidine (DCB), pentachlorophenol (PCP), and the polyaromatic hydrocarbons (PAH) benzo(a)anthracene, benzo(b)fluoranthene, and chrysene.

The listings are based on data reported in a remedial investigation of the Jackson Park Housing Complex/Naval Hospital on Ostrich Bay, at the south end of Dyes Inlet (EA Engineering, 1995) and a study of chemical contaminants in Sinclair and Dyes inlet fish and clams (Cubbage, 1992). Cubbage's samples included Port Washington Narrows, which connects Sinclair and Dyes Inlets, and also Oyster Bay at the south end of Ostrich Bay. These studies reported one or more tissue samples with concentrations exceeding the EPA National Toxics Rule (NTR) criteria used for 303(d) listing.

EAP reviewed the 1998 303(d) list to determine the best approach for addressing the various toxics listings. The above-mentioned listings did not appear warranted because they were based on questionable data or because newer data showed standards were being met (Johnson, 2001). These waterbodies are also listed for arsenic and mercury (Ostrich and Oyster Bay only) in shellfish tissue. These listings appear reasonable.

The listings in question are summarized in Table 1. EAP recommended that PCP and DCB be taken off the 303(d) list for the reasons indicated. Antimony, BEHP, and PAH were recommended for verification sampling, the subject of this QAPP.

Project Description

The goal of this sampling effort will be to verify the validity of the Dyes Inlet/Port Washington Narrows antimony, BEHP, and PAH listings for crab and clam tissue. Study objectives will be 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.
- Analyze the data for exceedances of NTR human health criteria.
- Provide recommendations to the Ecology Water Quality Program and the Ecology Northwest Regional Office for retaining or removing these Dyes Inlet and Port Washington Narrows tissue parameters from the 303(d) list.

Table 1. WRIA 15 303(d) Listings for Antimony and Miscellaneous Organics in Crabs and Clams from Ostrich Bay and Port Washington Narrows (segment WA-15-0050)

Waterbody Parameter Tissue	Data Source Basis for Listing	Recommendation De-List	Recommendation Verify	Reason for Recommendation
Ostrich Bay antimony crab / clam	EA (1995) multiple excursions		x	Newer EAP data show standards being met for clams
Ostrich Bay BEHP crab / clam	EA (1995) 2 crab excursions		x	Newer EAP data show standards being met for clams
Ostrich Bay PCP crab	EA (1995) 1 excursion	x		Listed in error, PCP not detected
Ostrich Bay DCB clam	EA (1995) 3 excurions	x		Newer EAP data show standards being met for clams
Ostrich Bay benzo(a)anthracene crab	EA (1995) 1 excursion		x	Criterion marginally exceeded
Ostrich Bay chrysene crab	EA (1995) 1 excursion		x	Criterion marginally exceeded
Ostrich Bay benzo(b)fluoranthene crab	EA (1995) 2 excursions		x	Criterion marginally exceeded
Oyster Bay benzo(b)fluoranthene clam	Cubbage (1992) 1 excursion		x	Criterion marginally exceeded
Port Wash. Narrows benzo(b)fluoranthene clam	Cubbage (1992) 1 excursion		x	Criterion marginally exceeded

Following Ecology (2001) guidance, the decision to recommend retaining a parameter on the 303(d) list will be based on finding at least one exceedance of the listing criteria. The NTR criteria for antimony, BEHP, and the three PAH compounds are 4,300 ug/Kg, 767 ug/Kg, and 0.93 ug/Kg, respectively (wet weight basis).

Organization and Schedule

Project Lead – Art Johnson (360/407-6766)
Field Sampling/Report Preparation – Morgan Roose (360/407-6458)
EAP Toxics Studies Unit Supervisor – Dale Norton (360/407-6765)
Manchester Environmental Laboratory Director – Stuart Magoon (360/871-8801)
Manchester Inorganics Unit Supervisor – Jim Ross (360/871-8808)
Manchester Organics Unit Supervisor – Bob Carrell (360/871-8804)
Ecology Quality Assurance Officer – Cliff Kirchmer (360/407-6455)

August 2001……..…Sample collection
September 2001…….Tissue samples submitted to laboratory
November 2001…….Laboratory analyses completed
December 2001……..Draft project report completed
January 2002……. Final project report completed and data entered into EIM database

Data Quality Objectives

Table 2 shows project targets for accuracy and reporting limits.

Table 2. Measurement Quality Objectives

Parameter	Accuracy (% deviation from true value)	Precision (RSD)	Bias (% of true value)	Required Reporting Limit (wet)
Antimony	30%	10%	10%	50 ug/Kg
BEHP	60%	20%	20%	50 ug/Kg
Chrysene	60%	20%	20%	0.90 ug/Kg
Benzo(a)anthracene	60%	20%	20%	0.90 ug/Kg
Benzo(b)fluoranthene	60%	20%	20%	0.90 ug/Kg

The reporting limits are based on past performance by Manchester Laboratory, using the analytical methods selected for this project (Johnson, 1998a,b; Johnson 2000). They are lower than the NTR antimony and BEHP criteria by an order of magnitude to minimize effects of measurement imprecision when comparing the data to the criteria. The reporting limits for the PAH compounds are at the 0.93 ug/Kg criterion, but are the best currently achievable through Manchester and are more than an order of magnitude lower than the analyses that resulted in the listings.

Sampling Design

Three composite samples of crab muscle tissue will be collected and analyzed from the EA Engineering (1995) study area off Jackson Park (Figure 1). Five to ten individual crabs will be used for each composite, depending on the species obtained. It was not possible to determine the number of individuals per composite in the EA Engineering study. EA Engineering analyzed the graceful cancer crab (*Cancer gracilis*), a small species not used for human consumption. EAP will analyze harvested crab species if possible (rock crab or Dungeness crab). The samples will be collected in August 2001; EA Engineering collected in August and November.

Sample size for Jackson Park was selected to balance representativeness against cost. Although the EA Engineering data on which these listings are based were for larger numbers of samples, it has already been established that these data are unreliable (Johnson 1998a,b; Johnson, 2001). Therefore a larger, more expensive sampling effort is not warranted.

Three composite clam tissue samples each will be analyzed from the Oyster Bay and Port Washington Narrows sites sampled by Cubbage (Figure 1). Thirty clams will be used for each composite. Cubbage analyzed two composites from Port Washington Narrows and one composite from Oyster Bay. Cubbage used anywhere from 9 to 29 clams per composite and mixed species, most of which were native or Japanese little necks, but including butter clams and cockles. EAP will target littlenecks. The clam samples will also be collected in August 2001. Although Cubbage collected in December and January, August samples will be more representative of contaminant levels during the peak recreational harvest. This area is currently closed to commercial harvest.

For 303(d) listings based on toxics in edible tissue, Ecology requires a minimum sample size of one composite formed from at least three individual organisms (Ecology, 2001).

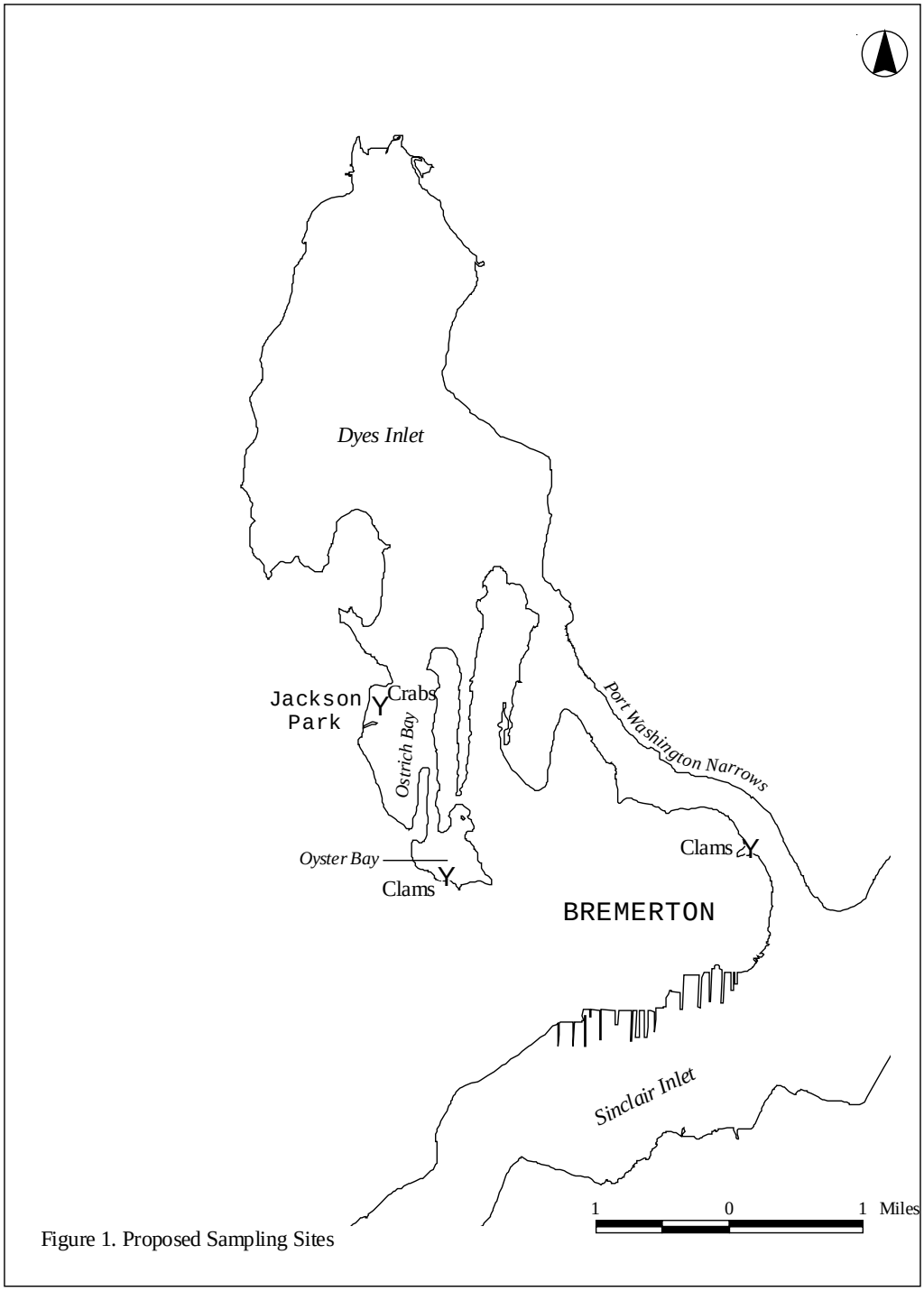

Figure 1. Proposed Sampling Sites

Table 3 shows the number of samples to be analyzed and an estimate of the laboratory cost.

Table 3. Number of Samples and Lab Cost Estimate

Analysis	Field Samples	Matrix Spikes	Duplicate Analyses	SRM Analyses	Total Analyses	Cost per Analysis	Cost Subtotals
Antimony	3	2	1		6	68	408
BEHP	3	2	1		6	600	3600
PAH	9	2	1	1	13	600	7800
Percent Lipids	9		1		10	34	340
Percent Solids	9		1		10	10	100
						TOTAL LAB COST =	12248

Field Procedures and Tissue Preparation

Crabs

Crab sampling and tissue preparation procedures are based on PTI (1991) and Puget Sound protocols (Puget Sound Water Quality Action Team, 1997a,b).

Up to ten crabs will be collected at each sampling site, using baited pots set overnight. If rock or Dungeness crab are encountered only male crabs with carapace widths greater than the legal limit will be taken. If only the graceful crab is caught, then the largest individuals will be taken. Care will be taken to avoid having the crabs coming in contact with engine fumes, fuel, oil, bilge water, or other contaminants. Sampling site coordinates will be recorded from a GPS.

Each crab selected for analysis will be killed with a blow to the ventral nerve cord The crabs will be individually wrapped in aluminum foil, put in double plastic bags, labeled with date and location of collection, and placed in coolers containing blue ice. The crabs will be kept shell side down so that body cavity liquids drain away from muscle tissue. The samples will be transported to the Ecology Headquarters chain-of–custody room within one day of collection and frozen in a secure freezer.

Muscle tissue will be resected from the crabs using techniques to minimize potential for sample contamination. Only non-corrosive stainless steel instruments will be used.

Persons preparing the samples will wear non-talc polyethylene gloves and work on aluminum foil. The gloves and foil will be changed between samples.

The carapace width of each crab will be recorded to the nearest millimeter. After rinsing the shell with tap water and deionized water to remove any remaining debris, muscle tissue will be removed from the legs and body and placed in 8 oz. glass containers with Teflon lid-liners, cleaned to EPA (1990) QA/QC specifications. When removing body meat, care will be taken not to include hepatopancreas tissue. Shell fragments will not be included in the samples.

Tissues from five to ten individual crabs will be composited for each sampling site. The resected samples will be homogenized to uniform color and consistency with stainless steel implements.

Cleaning of resecting instruments and blender parts will be done by washing in tap water with Liquinox detergent, followed by sequential rinses with tap water, 1% reagent-grade nitric acid, de-ionized water, and pesticide-grade acetone. The items will then be air dried on aluminum foil in a fume hood before use.

Each sample container will be labeled with sampling site, sampling date, species, tissue type, sample number, and analysis requested. The samples will be refrozen and taken by courier to Manchester Laboratory. The samples will be stored frozen at Manchester until analyzed.

Field activities will be recorded in ink in a bound notebook of waterproof paper. Chain-of-custody will be maintained throughout the above procedure.

Clams

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

Approximately 30 individual clams will be collected at each site. The clams should taken from individual digs within a 100 ft. stretch of beach. Sampling site coordinates will be recorded from a GPS.

Native or Japanese littlenecks will be collected whenever possible. All specimens taken for analysis will be legal size (> 1 ½ inch for clams) and unbroken.

Clam diggers will use clean rakes or shovels, uncontaminated with grease or oil. The shellfish will be placed in stainless steel buckets, pre-cleaned by washing with detergent and rinsing with acetone and deionized water. If gloves are used, these must be new. Rakes, shovels, buckets, and gloves will be washed with sea water between sampling sites.

The shellfish will be rinsed thoroughly with 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 will not be depurated. Each jar will be labeled with date and location of collection, wrapped in bubble-wrap to avoid breaking, and placed in coolers with ice. The samples will be transported to the Ecology Headquarters chain-of–custody room within one day of collection and frozen in a secure freezer.

Tissues will be removed using techniques to minimize potential for sample contamination. Only non-corrosive stainless steel instruments will be used. Persons preparing the samples will wear non-talc polyethylene gloves and work on aluminum foil. The gloves and foil will be changed between samples.

The range (minimum and maximum) of shell widths for the shellfish being included in each composite will be recorded to the nearest millimeter. The composite will include approximately equal numbers of small, medium, and large individuals. Shell fragments will not be included in the samples.

After rinsing the shellfish with tap water and deionized water to remove any remaining debris, the entire soft parts will be removed and placed in 8-oz. glass containers with Teflon lid-liners, cleaned to EPA specifications. The tissues from 30 individual clams and mussels will be composited for each sampling site. The soft parts will be homogenized to uniform color and consistency with stainless steel implements.

Cleaning of resecting instruments and blender parts will be done by washing in tap water with Liquinox detergent, followed by sequential rinses with tap water, 1% reagent-grade nitric acid, de-ionized water, and pesticide-grade acetone. The items will then be air dried on aluminum foil in a fume hood before use.

Each container will be labeled with sampling site, sampling date, species, tissue type, sample number, and analysis requested. The samples will be refrozen and taken by courier to Manchester Laboratory. The samples will be stored frozen at Manchester until analyzed.

Field activities will be recorded in ink in a bound notebook of waterproof paper. Chain-of-custody will be maintained throughout the above procedure.

Chemical Analysis

Table 4 shows the number of field samples to be analyzed, expected range of results, and the laboratory procedures to be used. All sample will be analyzed at Manchester Laboratory. Recommended holding times for tissue are two years for metals and one year for semivolatile organic compounds. Extracts for organics analysis should be analyzed within 40 days. (PSWQAT, 1997a,b).

Table 4. Laboratory Procedures

Analyte	Sample Matrix	Number of Samples	Expected Range of Results	Technique	Analytical Method
Antimony	tissue	3	<50 mg/Kg	ICP/MS	EPA 200.8
BEHP	tissue	3	<100 ug/Kg	GC/MS-SIM	EPA 1625/1653 mod.*
PAH	tissue	9	<10 ug/Kg	GC/MS-SIM	EPA 8270 mod.*
% lipid	tissue	9	0.1 - 1.0 %	gravimetric	EPA 608.5
% solids	tissue	9	10 - 20 %	gravimetric	EPA 160.3

*isotopic dilution, Manchester SOP

The samples for antimony analysis will be digested by microwave. Manchester will experiment with adding HCl to see if it stabilizes antimony.

BEHP and PAH will be analyzed by isotopic dilution.

The laboratory will save excess sample for 60 days from the time the data is sent to the project lead to give time for its review.

Quality Control

Table 5 shows the laboratory quality control (QC) samples to be analyzed for this project. No field QC samples will be analyzed.

Laboratory QC

Laboratory QC samples for metals will include a method blank, matrix spikes & matrix spike duplicates, and an analytical duplicate. The QC samples will be analyzed at the frequency indicated in Table 5.

Manchester will attempt to locate an appropriate lab control sample for antimony. If none can be found, a check standard will be prepared by spiking a tissue sample at approximately 4,300 ug/Kg, the criterion of interest. The tissue sample will be from a reference area known to have low levels of chemical contamination, to be provided by the project lead. A duplicate analysis (laboratory split) will provide an estimate of analytical variability for antimony.

Table 5. Laboratory Quality Control Procedures

Parameter	Method Blanks	Analytical Duplicates	Lab Control Sample	Stand. Ref. Material	Matrix Spike & Duplicate
Antimony	1	1	1	NA	1
BEHP	2	1	NA	NA	1
PAH	2	1	1	1	1
% lipid	1	1	1	NA	NA
% solids	NA	1	1	NA	NA

Laboratory QC samples for organics will include method blanks, a standard reference material, matrix spikes & matrix spike duplicates, and an analytical duplicate. The QC samples will be analyzed at the frequency indicated in Table 5. Because BEHP is a common laboratory contaminant and because PAH are being analyzed at an extremely low level, two method blanks will be analyzed for each analysis. This will provide an indication of blank variability, an important consideration in deciding if contamination is significant in comparison with sample responses.

The standard reference material will be NIST SRM 1974-A, Organics in Mussel Tissue. The certified values for benzo(a)anthracene, benzo(b)fluoranthene, and chrysene are 3.70, 5.28, and 5.04 ug/Kg (wet), respectively. No SRM is available for bis(2-ethylhexyl)phthalate. The matrix spikes for these compounds will be at 0.1 ug/10 grams (10 ug/Kg). A duplicate analysis (laboratory split) will provide estimates of analytical variability for the organics.

Results from analyzing the lab control samples will be used to judge if the MQOs have been met. Method blanks, duplicates, lab control samples, and matrix spikes will provide a way of judging if the precision and bias targets have been met. The SRMs will indicate directly if accuracy targets have been met.

Data Review, Verification, and Validation

The project lead will review Manchester's data and case narratives for errors or omissions and to ensure that the narratives accurately describe compliance of QC results with acceptance criteria. Data validation will be done by the project lead using professional judgement as to whether Manchester followed the procedures in the QAPP.

Data Quality Assessment

Once the data have been verified and validated, a determination will be made if DQOs (Table 2) have been met, in coordination with appropriate personnel at Manchester.

Once it has been determined that the data are satisfactory, the results will be compared to the NTR human health criteria. Following Ecology (2001) guidance, finding a single exceedance will result in a recommendation that the waterbody or waterbody parameter be retained on the 303(d) list.

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