PCBs in Sediments from Selected Sites In Puget Sound

Quality Assurance Project Plan

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Background and Problem Statement

Background

The sediments of Puget Sound have become a chief repository for polychlorinated biphenyls (PCBs). The ability of PCBs to persist in the environment, combined with the redistribution of PCBs from point sources to the environment at large, has caused PCBs to be present in remote areas with no local PCB sources. These PCBs may then be absorbed by benthic invertebrates and other organisms associated with sediments. These absorbed PCBs may then be transferred to organisms that prey upon them (e.g. fish). This process can result in the bioaccumulation of PCBs to high and toxic levels in fish and fish predators. In particular, it has been documented that humans consuming PCB laden fish may exhibit toxic responses (Kissinger, 2001).

Decisions about the remediation of PCB contaminated sediments require knowledge of the relationship between PCB levels in sediment and PCB levels in the tissues of aquatic organisms. The Puget Sound Ambient Monitoring Program (PSAMP) has produced much of the PCB information for Puget Sound, particularly from Ecology's Marine Sediment Monitoring Program (MSMP) and the Washington Department of Fish and Wildlife's (DFW) sampling of various fish species (e.g. English sole, rockfish, salmon, and shellfish).

PCB levels in edible muscle tissue of English sole (*Pleuoronectes vetulus*) have been monitored through the PSAMP program since 1989 (O'Neill et. Al., 1995). Analysis of PCB data in English sole tissue and sediment samples has permitted correlation of PCB concentrations between these environmental media (PSWQAT, 1988). This correlation relationship is a quantitative description of PCB bioaccumulation from sediment to fish tissue. An important use of this relationship is risk analysis for humans consuming PCB contaminated fish and consequent sediment remediation decisions based on this analysis.

Limitations in analytical chemistry have made it difficult to precisely quantify low levels of PCBs in sediments. This results in uncertainty in the correlation between sediment and fish tissue PCB levels at low sediment PCB concentrations. Recently, lower detection limits for PCBs in sediments have been achieved. Uncertainty in the correlation between sediment and fish tissue PCB levels could be reduced by pairing old PCB fish tissue chemistry data with new sediment chemistry data obtained with more sensitive analytical techniques. The PSAMP program also has PCB English Sole data without corresponding sediment data. Collection of matching sediment PCB chemistry would further strengthen the correlation relationship.

Problem Statement

Characterization of PCB bioaccumulation from sediments is important for the management of PCB contaminated sediment. Adequate sediment PCB concentration data to support this characterization are lacking from particular sites in Puget Sound. The sites with inadequate sediment PCB data are those where English Sole PCB data exist and sediment PCB data are either lacking or had historical detection limits up to ten times the current capability of 2-5 ug/Kg (dry weight) for individual Aroclors.

Project Description

Project Goal

The goal of this project is to determine PCB levels in sediments from selected PSAMP sites. The PCB data will be used to better characterize the bioaccumulation of PCBs in English Sole from sediment. The PCB data from this study, and its use, will help support actions described in Ecology's *Proposed Strategy to Continually Reduce Persistent, Bioaccumulative Toxins (PBTs) in Washington State* (Gallagher, 2000). PCB sediment concentration data may also be useful in characterizing background concentrations of PCBs in Puget Sound.

Surface sediments (top 2cm) will be collected at 15 sites in Puget Sound to supplement and fill existing data gaps in historical data sets. Sediment samples will be analyzed for: PCBs, total organic carbon, percent solids, and grain size distribution. PCBs will be quantified as Aroclors®. A set of 19 PCB congeners may also be determined for sediments from these sites.

Site Selection

The candidate sites and their coordinates are listed in Appendix A. Sites are listed in priority order for data collection. Review of historic sediment and fish tissue PCB data resulted in the first 15 sites (priority 1, 2, and 3) being selected for sampling during this project. Further reviews will ensure that relevant PCB sediment chemistry data does not already exist for a particular fish tissue PCB concentration datum. The remaining sites (priority 4 and 5) will not be sampled and remain listed for reference purposes.

The target sampling location for each site will be more accurately determined after reviewing the coordinates and paths of past trawling efforts that collected fish for tissue analyses. A number of fish trawls were usually conducted in the vicinity of the coordinates given in Appendix A. Actual sampling location for PCBs will avoid the historic fish-trawl tracks and be located within 200-400 meters from the coordinates recorded for the individual fish-trawls. The accuracy of historical positioning systems will be considered in selecting an appropriate distance from trawl-tracks to sample.

Attempts will be made to locate stations as close as possible to the target locations, yet the final location for sites and sampling will be determined in the field by the project leader based on consideration of actual site conditions. Conditions that may affect site location include: inability to obtain an acceptable sample due to hard substrate or debris such as shell fragments; the target location is hazardous due to vessel traffic; and on site currents, wind, and sea conditions.

Project Organization and Schedule

Organization

Project Manager	Keith Seiders (360) 407-6689	Project management, direct field operations, QAPP and report preparation
Project Assistant	Morgan Roose (360) 407-6458	Assist in all phases of project
Client (TCP-HQ)	Lon Kissinger (360) 407-6237	Project review, site selection, coordination with WDFW staff regarding fish tissue sites
CSU Supervisor	Dale Norton (360) 407-6765	Project review
WES Section Manager	Will Kendra (360) 407-6698	Project review
Manchester Laboratory	Stuart Magoon (360) 871-8801	Coordinate laboratory analysis

Schedule

Field Sample Collection	May-June, 2001
Laboratory Analysis Complete	September, 2001
Data Transmittal to Client	October, 2001
Draft Report	November, 2001
Final Report	December, 2001
Data Entry into EIM and SEQUAL	December, 2001

Data Quality Objectives

Precision and Bias

Where applicable, Puget Sound Estuary Protocols (PSEP) for collection, preservation, transportation, storage, and analysis of samples will be followed in an effort to limit sources of bias (PSEP, 1996). The precision and bias routinely achieved with the methods selected will be adequate for the purposes of this project. For reference, selected PSEP control limits used by Ecology's Sediment Management Unit for QA1 review of sediment data are summarized in Appendix C.

Representativeness

Representativeness of the data will be attained through site selection and the use of composite sampling at each site. At each station, three individual grabs will be composited for an individual sample. Details of the compositing procedure are listed below in the sampling procedures section.

Completeness

The amount of useable data will be maximized by following accepted cleaning protocols, in conjunction with careful packaging and transport of samples to avoid breakage. Excess sample for PCB analysis will be collected and saved frozen in the event re-analysis is required. An additional sample for grain size analysis will also be collected and refrigerated in case re-analysis is needed. The target for usable data for this project will be 95%.

Comparability

The parameters and analytical methods selected for this project are expected to yield results that are comparable to the results from historical sampling efforts. The project will use the recommended protocols for the Puget Sound Estuary Program (PSEP, 1996) so that data are comparable to other monitoring efforts. The upper 2 cm of the sediment collected for analysis will be comparable to historic PSAMP sediment data which are used for developing BSAFs.

A practical quantitation limit (PQL) of 2-5 ug/kg dry weight for PCB compounds (reported as individual Aroclors) is the target for this project using EPA method 8082. A PQL of 0.02-0.10 ug/kg dry weight for PCB congeners may be achieved for samples analyzed using EPA method 1668a. This method quantifies 150 individual congeners with the remainder quantified as groups of congeners.

Field Procedures

Sampling will be conducted from either of two vessels: Ecology's 20' Boston Whaler or the *R.V. Kitiwake*, a 42' research vessel owned and operated by Mr. Charles Eaton of Seattle, Washington. Stations will be located and positions recorded using a state-of-the-art Global Positioning System (GPS). During sampling, the vessel's engine exhaust will be directed downwind of the work area to avoid contamination. Care will be taken while operating the vessel in shallow water so as not to disturb the sediments being sampled.

Sampling methods will follow PSEP protocols (PSEP, 1996) and requirements of the Sediment Management Standards (Ecology, 1995a,b). A field log which describes the material collected in each grab will be kept during the sampling effort. A sample for each site will consist of a composite of three individual grab samples from that site. The sites for the individual grabs for each composite will be located within 200-400 meters of historic trawl track coordinates.

Samples will be collected using a 0.1 m^2 stainless steel van Veen grab. A grab will be considered acceptable if: it is not over-filled with sediment, overlying water is present and not excessively turbid, the sediment surface is relatively flat, and the desired depth of penetration (>10cm) has been achieved. The overlying water will be siphoned off and a sub-sample from the top 2 cm of sediment will be removed with stainless steel scoops, placed in a stainless steel bowls, and homogenized by stirring. Material in contact with the side walls of the grab will not be retained for analysis.

Sub-samples of the homogenized sediment will be placed in glass jars with teflon lid liners. Sample containers will meet EPA specifications for cleanliness (EPA, 1990). Separate 4-oz jars will be used for PCB and PCB archive sample; 2-oz jars will be used for TOC and grain size samples will be placed in 8-oz glass jars. Percent solids data will be reported with the PCB results. Sample containers will be placed in polyethylene bags to reduce the possibility of contamination. All samples will be placed on ice immediately after collection, refrigerated, and transported to the Ecology Manchester Environmental Laboratory (MEL) within five days. Storage temperatures and holding time requirements are listed in Table 1. Chain-of-custody will be maintained throughout the study.

Pre-cleaned sampling equipment and sample containers will be used to collect, manipulate, and store the sediment samples. Sampling equipment will be pre-cleaned by washing with Liquinox detergent, followed by sequential rinses with hot tap water, deionized water, pesticide-grade acetone, allowed to air dry, and wrapped in aluminum foil until used in the field. The same cleaning procedure will be used to pre-clean the grab-sampling device prior to field outings. Between stations, cleaning of the grab will consist of thoroughly brushing with on-site water. If oil or visible contamination is encountered, the grab will be cleaned between samples with a detergent wash followed by a rinse with on-site water. Back-up sampling equipment, sample containers, and spare parts will be carried during field sampling as preventative maintenance.

Table 1: Recommended Containers, Preservatives, and Holding times for Sediment samples (PSEP, 1996).

Analyte	Container	Preservation Technique	Holding Time
Percent Solids	Glass or Polyethylene	Freeze, -18°C	6 months
		Refrigerate, 4°C	14 days
TOC	Glass or Polyethylene	Freeze, -18°C	6 months
		Refrigerate, 4°C	14 days
Grain Size	Glass or Polyethylene	Refrigerate, 4°C	6 months
PCBs	Glass	Freeze, -18°C	1 year
		Refrigerate, 4°C	14 days

Laboratory Procedures

Analytical methods and target reporting limits for analysis of samples from this project are shown in Table 2. All analyses will be conducted at the Manchester Environmental Laboratory (MEL), with the exception of grain size and PCBs using Method 1668a, which may be analyzed at a laboratory selected by MEL.

Table 2: Analytical Methods and Expected Reporting Limits for this Puget Sound Sediment PCB Study.

Analyte	Method	Reference	Expected Reporting Limit	Laboratory
Percent Solids	Gravimetric (160.3)	PSEP, 1996	0.1%	MEL
Total Organic Carbon	Combustion/CO2 Measurement @ 70°C (9060)	EPA, 1996	0.1%	MEL
Grain Size	Sieve and Pipet	PSEP, 1996	0.1%	Contractor
PCBs (as Aroclors)	(EPA 8082) GC-ECD	EPA, 1996	2-5ug/kg, dry weight	MEL
PCB Congeners (150 individual plus groups)	(EPA 1668a) Hi Res MS	EPA, 1996	0.02-0.10 ug/kg, dry weight	Contractor

The estimated number of samples and analytical costs for the Puget Sound Sediment PCB Study are shown in Appendix B.

Quality Control and Data Quality Assessment

The standard QA/QC procedures used by MEL will be satisfactory for this project. Specific recommendations for QC samples, control limits, and corrective actions are documented in MEL's Quality Assurance Manual (Kirchmer et al, 1989). At a minimum laboratory quality control samples for PCBs will include analysis of surrogate spikes, method blanks, and duplicate matrix spikes. Surrogate recoveries will provide an estimate of accuracy for the entire analytical procedure. Method blanks can indicate contamination from the sampling and analytical procedures. Matrix spikes may provide an indication of bias due to interference from the sample matrix.

Precision will be estimated from the results of blind field and laboratory duplicates, and duplicate matrix spikes. Field QC samples will include two blind duplicates for all parameters. The blind duplicate will be second three-grab composite collected from different locations within the 200-400 meter zone of the trawl tracks. This sample will be submitted to the laboratory as a separate station. Routine QA/QC samples for chemical analysis to be run for this project are summarized in Table 3.

Table 3: Summary of QC Samples to be Reported for This Sediment PCB Study.

Analyte	Method Blanks	Lab Duplicate	Blind Field Duplicate	Matrix Spike	Matrix Spike Duplicate	Surrogates
Percent Solids	NA	2	2	NA	NA	NA
TOC	NA	2	2	NA	NA	NA
Grain Size	NA	2	2	NA	NA	NA
PCBs	2	2	2	2	2	All Samples

NA= Not applicable

The quality of all laboratory and field data will be determined by review of: laboratory case narratives for analyses, sampling and laboratory methods, results from QA procedures, and any other information pertaining to the quality of the data for this project. Quality control limits described in Appendix C will also be used in assessing data quality.

Corrective Actions

The analyst is responsible for monitoring the analysis and troubleshooting problems as they occur. It is important to identify analytical problems as soon as possible so that corrective actions can be taken prior to the expiration of holding times. It is the responsibility of the laboratory to communicate analytical problems to the project manager during the analysis so that the project manager may have input into the course of corrective action. This communication is critical when the laboratory is experiencing difficulty in meeting any project specified requirements, including expected reporting limits. It is important for the project manager and laboratory to agree on what constitutes a reasonable corrective action.

Performance and System Audits

MEL participates in performance and system audits of their routine procedures. Results of these audits are available on request. The Environmental Assessment Program Lab Accreditation Unit must accredit all contract laboratories performing work for Ecology. The accreditation process includes performance and system audits.

Data Reduction, Review, and Reporting

MEL's Standard Operating Procedures for data reduction, review, and reporting will meet the needs of this project. Within 45 days from the receipt of the samples a case narrative and data package will be provided to Ecology's project lead with all sample results. At a minimum, this data package will include the following; a description of analyses performed, any problems encountered, all sample results, an evaluation of quality assurance data, and a description of data qualifiers. All data will have 100% verification and errors corrected by the laboratory.

A draft report of the survey results will be provided to the client within 90 days of receipt of the complete data package from MEL. At a minimum this report will contain the following:

- A map of the study area showing sampling sites.
- Latitude/longitude coordinate of each sampling site.
- Descriptions of field and laboratory methods.
- Discussion of data quality and the significance of any problems encountered in the analyses.
- Summary tables of the physical/chemical data collected and comparison to applicable Sediment Quality Standards.
- Data transmittal in electronic format to the client and DFW staff.
- Recommendations for follow-up work if warranted.

After completion of the project, the data generated will be entered into Ecology's Environmental Information Management System (EIM). Project data will be provided to the client in an appropriate format for their entry into the latest version of SEDQUAL which is maintained by the Sediment Management Unit of the Toxic Cleanup Program.

References

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Appendix A. Candidate Site Locations and Characteristics.

Priority	Site	Lat N	Long W	Est. Depth (ft)	Proposed Sampling Platform	Avg Muscle Aroclor 1260 (µg/kg, ww)	Year Fish Sampled	Muscle Sample Type	Count
1	Carr Inlet #1	47 12.755	122 37.595	516	Kittiwake	8.7	1996	composites	1
1	Outer Commencement Bay	47 17.134	122 25.645	190	Kittiwake	29.0	1995	composites	2
1	Pickering Passage	47 17.650	122 52.650	60	whaler	6.1	1996	composites	3
1	Blake Island	47 33.239	122 29.076	60-106	whaler	31.8	1995	composites	4
1	Shilshole	47 42.310	122 23.790	60-138	Kittiwake	16.9	1995	composites	5
1	Strait of Juan de Fuca	48 09.675	123 23.240	168	Kittiwake	3.9	1994	composites	6
2	Hood Canal - Middle	47 32.225	123 01.825	84-125	whaler	2.0	1996	composites	7
2	Hood Canal - South	47 22.480	123 00.095	112	whaler	2.5	1996	composites	8
2	Point Roberts	48 58.625	123 05.495	30-360	Kittiwake	2.5	1994	composites	9
2	Vendovi Island	48 38.385	122 38.475	192	Kittiwake	2.0	1994-97	indiv & composites	10
3	Apple Cove Point	47 51.320	122 30.240	21	Kittiwake	11.2	1995	composites	11
3	Dash Point	47 20.200	122 22.595	48-168	Kittiwake	17.6	1995	composites	12
3	Port Townsend	48 05.074	122 45.825	66-96	Kittiwake	10.4	1994	composites	13
3	Possession Point	47 52.090	122 23.430	498	Kittiwake	8.5	1995	composites	14
3	Strait of Georgia	48 51.919	122 57.980	450	Kittiwake	3.3	1995	composites	15
	sites not selected for sampling								
4	Birch Point	48 58.145	122 49.960	38	whaler	3.8	1994	composites	16
4	Case Inlet #1	47 11.419	122 47.874	120	Kittiwake	10.6	1996	composites	17
4	Hood Canal - North	47 50.130	122 38.245	60-130	Kittiwake	4.8	1995	composites	18
4	Liberty Bay	47 41.805	122 36.485	48	whaler	19.5	1995	composites	19
4	Nisqually Reach	47 09.684	122 40.158	190	Kittiwake	14.7	1996-97	composites	20
4	Saratoga Passage	48 09.229	122 32.540	234	Kittiwake	16.7	1994	composites	21
4	Wollochet	47 16.054	122 36.510	60-112	Kittiwake	14.4	1996	composites	22
5	Commencement Bay-Thea Foss	47 15.515	122 26.082	60	whaler	32.8	all years	indiv & composites	23
5	Duwamish River	47 33.611	122 20.682	48	whaler	99.1	1995	composites	24
5	Dyes Inlet	47 36.975	122 41.185	83-100	Kittiwake	12.9	1995	composites	25
5	Eagle Harbor	47 37.170	122 30.665	54	whaler	24.4	1995	composites	26
5	Elliott Bay	47 36.381	122 20.710	150	Kittiwake	35.8	all years	indiv & composites	27
5	Port Gardner	47 59.125	122 14.620	60-180	Kittiwake	9.4	1995	composites	28
5	Sinclair Inlet	47 32.844	122 39.029	48	whaler	76.6	all years	indiv & composites	29

Priority categories:

1: No sediment PCB data; Aroclors routinely detected in fish tissue.

2: No sediment PCB data; Aroclors not routinely detected in fish tissue.

3: Sediment PCB data exist, yet had non-detect values at high detection limits; Aroclors found in fish tissue.

4: Sediment PCB data are available from 1997-1999 PSAMP/NOAA marine sediment monitoring efforts.

5: Sediment PCB data are available from 1989-1996 PSAMP marine sediment monitoring efforts.

Station locations are those from which PSAMP Fish Component sampled English sole muscle tissue, 1994 to 1996. Average Aroclor 1260 value presented as an estimate of PCB exposure (sum of Aroclors concentration will be roughly double that of Aroclor 1260) . Aroclor averages computed only for years 1994-1996. Some stations (baseline stations) had Aroclors sampled earlier (1991-93) and later (1997) as well. Latitude and longitude for these locations represent averages of midpoints of trawl-tracks for all years.

Appendix B
Estimate of Laboratory Analytical Costs

Analysis	Cost per Sample	Number of Samples	Duplicate Samples	MS+MSD & Blanks	Total Analyses	Cost Subtotals
TOC	$33	15	2	0	17	$561
Grain Size	$85	15	2	0	17	$1,445
PCB Aroclors only Method 8082	$130	15	2	4	21	$2,730
PCB Congeners Method 1668a	$1,100	2	1	2	5	$5,500
TOTAL	**$1,348**	47	7	6	60	**$10,236**

Appendix C
PSEP Control Limits Summary for Ecology's Sediment Quality Standards

Selected PSEP Quality Control Limits Used by Ecology's Sediment Management Unit for Conducting QA1 Reviews of Sediment Data Packages

Sample Type	Conventionals	Metals	Semivolatiles
Holding Times	Grain Size- 6 months @ 4°C S, NH3- 7 days @ 4°C TS,TVS,TOC- 14 days @ 4°C; 6 months @ -18°C	Metals except Hg- 6 months @ 4°C; 2 years @ -18°C Mercury- 28 days @ 4°C or –18°C	14 days @4°C[1] 1 year @-18°C[1]
Method Blanks Metals- (1 per 20 or 1 for <20) Organics- (1 per extraction batch)	≤ Detection Limit	≤ Detection Limit If ≥ DL, lowest conc. Must be 10x MB value	≤ Detection Limit
CRM Metals- (1 per 20 or 1 for <20) Organics- (1 per 50 or 1 for <50)	When analyzed for conventional such as TOC, organics control limits may be applied	Supplier specified limits for CRMs (usually 95% CI, but may include lab estab. Limits for RMs used as internal controls	Blind CRM unavailable Supplier specified limits for CRMs (usually 95% CI, but may include lab estab. Limits for RMs used as internal controls
Analytical Replicates Conventionals- (1 triplicate per 20 or for <20) Metals, Organics- (1 duplicate per 20 or for <20)	≤ 35% RPD for duplicates ≤ 35% for COV for triplicates	≤ 20% RPD	≤ 50% RPD
Matrix Spikes Metals- (1 per 20 or 1 for <20) Organics- (≤20, 2 per set and >20, add MS/MSD for 10% spikes)	NH3, TOC- 75-125% recovery Sulfides- 65-135% recovery	75-125% recovery	50-150% recovery
Surrogate Spikes Organics- (add to each sample)	NA	NA	50% recovery

1= Until extraction; extracts must be processed within 40 days
MS/MSD= Matrix Spike/Matrix Spike Duplicate
COV= Coefficient of Variation
RPD= Relative Percent Difference
CRM= Certified Reference Material
DL= Detection Limit
MB= Method Blank
CI= Confidence Interval