APPENDIX E

COMMENCEMENT BAY DAMAGE ASSESSMENT

QUALITY ASSURANCE PLAN

December, 1995

Commencement Bay

Damage Assessment

Quality Assurance Plan

Analytical Chemistry

Prepared by

NOAA/NMFS/Environmental Conservation Division

December 1995

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Introduction

The National Oceanic and Atmospheric Administration (NOAA) is acting as lead Federal Trustee for assessing damage and injury in Commencement Bay. The legal and procedural framework for damage claims for injury or destruction of natural resources resulting from the release of hazardous substances is provided under Superfund legislation and its amendments (Superfund Amendments and Reauthorization Act of 1986 (P.L. 99-499).

This Quality Assurance (QA) Plan is in support of laboratory testing and characterization of contaminants in environmental samples (sediments and biota)—i.e., selected PCBs, DDTs, pesticides and other organochlorine compounds (sediments and biota), PAHs (sediments and biota), plithalates (sediments) selected phenols (sediments), selected metals (sediments), and butyltins (sediments)—collected from the selected stations in Hylebos, Waterway (located along the southeastern shore of Commencement Bay) and in Commencement Bay, Tacoma, Washington. This plan does not address the collection or generation of these samples. The requirements specified in this plan are designed to: (1) monitor the performance of the measurement systems to maintain statistical control and provide rapid feedback so that corrective measures can be taken before data quality is compromised and (2) verify that reported data are sufficiently complete, comparable, representative, unbiased and precise so as to be suitable for their intended use.

This QA Plan is consistent with the intent of NRDA regulations, as provided in 43 CFR Subtitle A, subpart C and satisfies the requirements listed in the National Contingency Plan and relevant EPA guidance for QA/QC plans. It has been prepared in general accordance with the “Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans” (Stanley and Verner, 1983). Some of the items specified in the above document, however, are extensively addressed in other QA or work plans prepared for this damage assessment and are only summarized or referenced herein.

Many of the requirements described in this document are based on protocols developed by NOAA’s National Status and Trends Program, EPA’s Puget Sound Estuary Program and EPA’s Environmental Monitoring and Assessment Program-Estuaries. All three of

these programs are designed to measure low-level (i.e. low parts per billion) concentrations of contaminants in marine and estuarine sediments and biota, and thus serve as a useful prototypes for this QA plan even though they are not subject to the stringent legal requirements of a damage assessment.

This QA plan will be revised as appropriate, as changes are made to the QA program and the damage assessment.

Section 1.0
Project Description

Samples, including sediments and fish tissues, will be analyzed for the presence and concentrations of a variety of contaminants (Tables 1.1 and 1.2). The QA and work plans under which these samples were generated or collected are independent documents and not included or considered herein. This QA plan describes the minimum requirements to be taken to provide for the chemical (and associated physical normalizing parameters) analyses of the previously generated or collected samples in a technically sound and legally defensible manner.

More detailed descriptions of the procedures and protocols under which the samples were collected, including sample custody procedures are given in the work plans for each individual project. A brief summary of the types of samples to be analyzed under this plan is given in Table 1.1. The list of analytes to be determined in the samples is presented in Table 1.2. The compounds selected for analysis are representative of the contaminants known to have been released into the area and capable of describing the exposure of the resources, as well as indicating the magnitude and extent of the injury to the resources.

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Table 1.1 Sample Summary

Sample	Analytes	Preservative
Sediment	organics[1]	Frozen (-20°C)
	metals	Frozen (-20°C)
	butyltins	Frozen (-20°C)
Tissue		
liver	PCBs, DDTs, pesticides, HCBD	Frozen (-20°C)
stomach contents	AHs, PCBs, DDTs, pesticides, HCBD	Frozen (-20°C)

[1]AHs, PCBs (including selected congeners) DDTs, pesticides, phthalates, phenols, other chlorinated hydrocarbons (see Table 1.2).

Table 1.2. List of Analytes

Organics (semivolatiles)

Low molecular weight AHs *(sediments, stomach contents)*

Naphthalene
Acenaphthylene
Fluorene
Anthracene
Acenaphthene
Phenanthrene
2-Methylnaphthalene
LAH [sum of low molecular weight AHs]

High molecular weight AHs *(sediments, stomach contents)*

Fluoranthene
Pyrene
Chrysene
Benzo(*a*)pyrene
Dibenz(*a*,*h*)anthracene
Benz(*a*)andu-acene
Benzofluoranthenes (sum of *b* + *k)*
Indeno(*1,2,3-cd*)pyrene
Benzo(*ghi*)perylene
HAH [sum of high molecular weight AHs]

Table 1.2. List of Analytes, continued.

PCBs *(sediments, stomach contents, tissues)*

PCBs, total	selected PCB congeners (Nos. 18, 28, 44, 52, 66, 101, 105, 118, 128, 138, 153, 170, 180, 187, 195, 206, 209)

DDTs *(sediments, stomach contents, tissues)*

p,p'-DDE	*p,p'*-DDD
p,p'-DDT	

Pesticides/0ther *(sediments, stomach contents, tissues)*

Aldrin	Dieldrin
Chlordane [sum of α and γ]	Lindane
Heptachlor	Hexachlorobutadiene (HCBD)
Hexachlorobenzene (HCB)	

Phthalates *(sediments)*

Dimethylphthalate	Diethylphthalate
Di-n-butylphthalate	Butylbenzylphthalate
Di-n-octylphthalate	bis(2-Ethylhexyl)phthalate

Phenols *(sediments)*

Phenol	2-Methylphenol
4-Methylphenol	2,4-Dimethylphenol
Pentachlorophenol	

Chlorobenzenes *(sediments)*

1,3-Dichlorobenzene	1,4-Dichlorobenzene
1,2-Dichlorobenzene	1,2,4-Trichlorobenzene

Toxic metals/organometals *(sediments)*

Antimony	Arsenic
Cadmium	Chromium
Copper	Lead
Mercury	Nickel
Silver	Zinc

Butyltins (Tetra-, tri-, di- and monobutyltins)

Section 2.0
Project Organization and Responsibilities

2.1 Project Leaders
The Project Leaders/Principal Investigators are:

Sediments/Fish Tissues
John Stein, Ph.D.
(206) 860-3338; FAX (206) 860-3335
Sin-Lam Chan, Ph.D.
(206) 860-3330; FAX (206) 860-3335
NOAA/NMFS
2725 Montlake Blvd. E.
Seattle, WA 98112

2.2 Quality Assurance
Carol-Ann Manen is the QA Coordinator reporting directly to the Case Management Team. Dr. Manen is responsible for the preparation and implementation of this Quality Assurance Plan. She may receive assistance in the coordination and performance of laboratory technical audits and independent data validation from the QA Contractor (EcoChem). The QA Coordinator has the authority and responsibility to cease or temporarily halt activities not in keeping with this QA Plan. The QA Coordinator will work closely with laboratory representatives and the project team to assure that project and data quality objectives are met. All instructions, requests and other communications between the laboratory representatives and the QA Contractor will go through the QA Coordinator. These people may be reached at:

Carol-Ann Manen, Ph.D. (QA Coordinator)
(301) 713-3038 FAX 301-713-4387
NOAA Damage Assessment Center
1305 East West Highway, Rm. 10218
Silver Spring, Maryland 20910

Ann Bailey (QA Contractor)
(206) 233-9332 FAX 206-233-0114
EcoChem, Inc.
801 Second Ave, Suite 1401
Seattle, Washington 98104-1504

2.3 Analytical Laboratories

Analytical work is provided to the Commencement Bay Damage Assessment through contracts with the Environmental Conservation Division, Northwest Fisheries Science Center (ECD/NWFSC). The designated Project Managers are responsible for assuring that all analyses performed by that group meet project and data quality objectives. These Project Managers are:

Sediments/Fish Tissues—Organic Chemistry

Margaret Krahn, Ph.D.
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Sediments-Toxic—Metals, Organotins

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3.0
Sample Handling and Chain of Custody Procedures

Chain of custody procedures will be used for all samples throughout the analytical process and for all data and data documentation, whether in hard copy or electronic format. Sampling procedures, including sample collection and documentation, are part of the work plans of the individual projects and as such, are not considered here. Sena Camarata, Peggy Krahn, and Doug Burrows will have the password to the electronic data fides.

3.1 Sample Preservation

A summary of the types of samples collected for analyses is given in Table 1.1. Sample preservation and field treatment of samples for analyses are described in relevant sampling SOPs. Briefly, sediment and tissue samples are frozen rapidly as soon after collec-

tion as possible. Once frozen, the samples are maintained frozen, at -20°C or colder until extracted or prepared for analysis. Because most analytes involved in this damage assessment are known to be extremely stable, sample holding times are not an issue.

3.2 Chain of Custody

Each container is considered to be an individual sample and will be assigned a unique ID and have a separate entry on the chain of custody record.

Chain of custody records will be completed in ink.

A sample is considered in "custody" if:

- it is in the custodian's actual possession or view,
- it is retained in a secured place (under lock) with restricted access, or
- it is placed in a container and secured with an official seal(s) such that the sample cannot be reached without breaking the seal(s).

Samples are kept in the custody of designated sampling and/or field personnel until shipment.

3.3 Sample Shipping

Any transfer or movement of samples will use chain of custody procedures. The original signed, and dated chain of custody record accompanies the sample(s); a copy is retained by the sample shipper. All shipments will comply with DOT regulations (49 CFR, Parts 172 and 173).

3.4 Sample Receipt

Immediately upon receipt of samples, the recipient win review the shipment for consistency with the accompanying chain of custody record and sample condition before signing and dating the chain of custody record. Sample condition(s) will be noted on the original chain of custody sheet at this time. If there are any discrepancies between the chain of custody record and the sample shipment, the, recipient will contact the sample shipper immediately.

3.5 Intra-Laboratory Sample Transfer

The laboratory sample custodian or designee will maintain a laboratory sample-tracking record, similar to the chain of custody record, that will follow each sample

through all stages of laboratory processing. The sample-tracking record will show the name or initials of responsible individuals, date of sample extraction or preparation, and sample analysis.

3.6 Inter-Laboratory Sample Transfer

Transfer of samples from one analytical laboratory to another, i.e. for grain size or TOC analysis, will follow chain of custody, sample shipping and receipt procedures described above.

3.7 Sample Archival

All unanalyzed samples and unutilized sample aliquots or extracts will be held by the laboratory in a manner to preserve sample integrity at a secure location with chain of custody procedures for one (1) year after the QA Contractor has validated the data package for that particular set of samples. All archived materials will be accessible for review upon request. These materials will become the responsibility of the QA Coordinator at the end of the archival period.

3.8 Data and Data Documentation

All data and data documentation, whether in hard copy or electronic format, is the responsibility of the QA Coordinator acting on behalf of Counsel to the Case Management Team. These materials will all be clearly marked with “Attorney Work Product.”

The QA Coordinator will receive from ECD/NWFSC data tables and QA documentation suitable for QA assessment. If the QA Contractor needs more information (or information in a different format than that provided by ECD/NWFSQ the QA Coordinator will contract with (hire) a “QA Specialist” who will have the responsibility for formatting ECD/NWFSC’s data into a package suitable for validation by the QA Contractor. All original data and data documentation developed by the laboratory for a given data package will be kept by the laboratory in a secure location under chain of custody procedures for one (1) year after the QA Contractor has validated that data package. All archived materials will be accessible for review upon request. These materials will become the responsibility of the QA Coordinator upon termination of the archival period.

A copy of the data will be transferred from the QA Specialist to the QA Contractor by commercial courier. The QA Contractor will document receipt of packages and maintain a record of the method and date of data submittal with the complete data package. The QA Contractor will maintain the copy of the data packages and related validation documentation in a secure location for a period of one (1) year from the date of validation.

Section 4.0
Laboratory Operations

All laboratories providing analytical support for the Commencement Bay Damage Assessment must have the appropriate facilities to store and prepare samples, and appropriate instrumentation and staff to provide data of the required quality within the time period dictated. Laboratories are expected to conduct operations using good laboratory practices, including:

- A program of scheduled maintenance of analytical balances, laboratory equipment and instrumentation.

- Routine checking of analytical balances using a set of standard reference weights (ASTM class, NIST Class S-1, or equivalents).

- Recording all analytical data in logbooks; each entry signed and dated by the analyst.

Monitoring and documenting the temperatures of cold storage areas and freezer units.Laboratory operations will be evaluated by the QA Coordinator through technical systems audits, performance evaluation studies, and performance in the NIST-managed intercomparison program. Personnel in any laboratory performing analyses for this damage assessment should be well versed in good laboratory practices, including standard safety procedures. It is the responsibility of the laboratory manager and/or supervisor to ensure that safety training is mandatory for all laboratory personnel. The laboratory is responsible for maintaining a current safety manual in compliance with the Occupational Safety and Health Administration (OSHA) or equivalent state or local regulions. Proper procedures for safe storage, handling and disposal of chemicals should be followed at all times; each chemical should be treated as a potential health hazard and good laboratory practices should be implemented accordingly.

4.1 Quality Assurance Documentation

All laboratories must have the latest revision of the Commencement Bay Damage Assessment Quality Assurance Plan (this document). In addition, the following documents and information must be current and available to all laboratory personnel participating in the processing of CBDA samples:

- Laboratory Standard Operating Procedures (SOPs)—Detailed instructions for performing routine laboratory procedures.

- Instrument performance study information—Information on instrument baseline noise (instrument signal used for analyte quantification will be ≥5 times background noise), calibration standard response, analytical precision and bias data, detection limits, etc. This information usually is recorded in logbooks or laboratory notebooks, data tables, folders, and electronic data bases.

- Control charts or data tables-These must be developed and maintained throughout the project for all appropriate analyses and measurements.

4.2 Laboratory Performance Audits

Prior to sample analysis, a QA performance audit will be performed to determine if the laboratory has the capability to perform analyses in compliance with the objectives of this Project. Additionally, at least once during the project, a formal laboratory audit will be conducted by the QA Coordinator. The checklists used for the laboratory audits are based on requirements outlined in “Good Laboratory Practice Standards” (40 CFR Part 792) and audit procedures of the EPA National Enforcement Investigations Center, “NEIC Procedures Manual for the Contract Evidence Audit and Litigation Support for EPA Enforcement Case Development” (EPA 330/9-89-002). The laboratory and Program Manager will be informed of the findings and recommendations of the audit before the auditors leave the facility. A written report discussing the audit will be submitted to the Case Management Team.

4.3 Participation in Intercomparison Exercises

Each analytical laboratory is required to participate, whenever possible, in the intercomparison exercises managed by NIST for NOAA and the EPA. A variety of samples including accuracy-based solutions, sample extracts, and representative matrices (e.g., sediment or tissue samples) are utilized in these exercises, which typically take place once a year. Laboratories are required to analyze the sample(s) and must submit their results in a timely manner to NIST. Upon review by NIST, laboratories which fail to achieve acceptable performance will be required to provide an explanation to the QA Coordinator and/or undertake appropriate corrective actions.

Section 5
Assessment of Data Quality

The purpose of this QA Plan is to develop and document analytical data of known, acceptable, and defensible quality. The quality of the data is presented as a set of statements that describe in precise quantitative terms the level of uncertainty that can be associated with the data without compromising their intended use. These statements are referred to as Data Quality Objectives (DQOs) and are usually expressed in terms of precision, accuracy, completeness, and comparability. The DQOs for this damage assessment for completeness are presented in Table 5.1; those for accuracy and precision are presented in Table 6.2.

TABLE 5.1 Summary of Data Quality Objectives

Data Type	Completeness Goal
Organic analytes	90%
Toxic metals	90%
Butyltins	90%
Percent moisture	90%

Completeness goals are the percentage of expected results to be obtained successfully.

The Commencement Bay Damage Assessment will make extensive use of the replicate analysis of standard reference materials (SRM) or certified reference materials (CRM) to demonstrate the precision, accuracy and comparability of the chemical analytical data.

5.1 Precision

Precision is the degree of mutual agreement among individual measurements of the same property under prescribed similar conditions, such as replicate measurements of the same sample. Precision is concerned with the "closeness" of the results. Where suitable reference materials are available, precision will be expressed as the relative standard deviation (RSD) for the repeated measurements. This use of reference materials allows for the long-term measurement of precision but does not include homogenization as a source of analytical variability. Where suitable reference materials are not available, precision will be expressed as the relative standard deviation (RSD) between a pair of replicate data from duplicate samples. It is recognized that precision erodes as the limit of detection is approached.

5.2 Accuracy

Accuracy is the degree of agreement of a measurement with an accepted reference value and may be expressed as the difference between the two measured values or as a percentage of the reference value. Reference materials will be used for AHs, chlorinated pesticides, PCBs, phenols, chlorinated benzenes, plithalates, and elements. See Table 6.2 for criteria.

5.3 Comparability

Comparability expresses the confidence with which one data set can be evaluated in relationship to another data set. For the Commencement Bay Damage Assessment, comparability of the chemical analytical data is established through the use of:

(1) program-defined general analytical methodology, detection limits, accuracy and precision requirements and reporting formats;

(2) common NIST-traceable (or other) calibration and reference materials;

(3) participation in interlaboratory comparison exercises.

5.4 Completeness

Completeness is a measure of the proportion of data specified in the sampling plan which is determined to be valid. For the analytical chemistry component of this damage assessment, the data quality objective for completeness is 90%, i.e. no more than 10% of the analytical data will be qualified as unreliable (see Table 7.2).

6.0
Quality Control Procedures

No official procedure has been approved by regulatory agencies for low-level (i.e., parts per billion) analysis of contaminants in marine sediments and biological tissue. No particular analytical method, therefore, is specified for this project but the QA/QC requirements will provide a common foundation for each laboratory's protocols. This "common foundation" includes: (1) the specification of the analytes, to be identified and quantified and the minimum sensitivity of the analytical methods and (2) the use of NIST or other calibration materials, whenever possible (no NIST calibration solutions are available for phenol, plithalate, chlorinated benzene, or butyltin compounds).

In addition, prior to the analysis of samples, each laboratory must provide written protocols for the analytical methods to be used; calculate detection limits for each analyte in each matrix of interest and establish an initial calibration curve in the appropriate concentration range for each analyte. The laboratory must demonstrate its continued proficiency by participation in refereed intercomparison exercises and repeated analyses of reference materials, calibration checks, laboratory method blanks.

Lastly, the laboratory may be audited once before samples are analyzed and once during the project in order to determine and document if the laboratory has the capability to analyze the samples and is performing in compliance with the QA plan.

6.1 Specification of Analytes

The analytes to be determined are listed in Table 1.2.

6.2 General Analytical Methodology

Considerable retention time data, which can be used for comparison, exist for PCBs and DDTs and certain other organic analytes as determined on fused silica capillary columns with a 95% dimethyl, 5% diphenyl polysiloxane coating (DB-5). For this reason, a DB-5 column 30-meters or more in length will be the primary column used in quantitating the organic analytes and butyltins listed in Table 1.2.

Approximately 10% of all samples analyzed by GC/ECD for organic analytes will also be analyzed by Mass Spectroscopy/Selected Ion Monitoring (MS/SIM) for independent confirmation of compound identification. Samples for GUMS confirmation will be those previously analyzed with the DB-5 column and will be selected for GC/MS confirmation on the basis of the concentration of analyte present and the representativeness of the sample. These data will not be used for quantitation.

6.3 Initial Demonstration of Proficiency

Accuracy-based, sediment and tissue samples provided by NIST/NRCC (or others) are to be analyzed (or have recently been analyzed) by the laboratory proposing to perform analytical work for this damage assessment. Results from the analysis of these samples are used to evaluate laboratory performance prior to selection of laboratories for field sample analyses. The laboratory's performance is considered acceptable if a majority of reported values (that are > 10 x detection limit) are within ±50% of the reference value, and the relative standard deviation of replicate results does not exceed 30% for the majority of results. No accuracy based materials are available for phenols, plithalates, chlorinated benzenes and butyltins in sediments. However, the SRM 1941 contains most of the phenol, chlorobenzene, and phthalate analytes at concentrations; ≥ 10 ng/g. Our recent analyses of this material gave precise results (n=5) and the results for matrix spike samples analyzed with the series of SRMs showed acceptable recoveries; therefore, the SRM may be used for QA for phenols, plithalates, and chlorobenzenes in sediment in place of matrix spikes.

6.4 Standard Operating Procedures for Analytical Methods

Prior to the analysis of field samples, each laboratory is required to submit written Standard Operating Procedures (SOPs) detailing the procedures used in sample preparation and analysis and data reduction and reporting. Copies of the SOPs from each analytical laboratory are archived with this plan as part of the QA documentation.

6.5 Determination of Method Detection Limit (MDL)

The analytical laboratory will establish and report a method detection limit for each analyte of interest in each matrix. The target MDLs for this project are specified in Table 6.1. The target MDLs will be validated by following the method in 40CFR, part 136 (based on precision) and by analyzing an SRM that has values in the range of the MDLs. Application of the 40CFR method to a highly precise determination such as tissue analysis can result in artificially low MDLs; therefore, we have revised the QA evaluation criteria for method blanks (tissue sets) so that 5 analytes can exceed 3x the MDL (Table 6.2 of the QAP).

Data for organic analyte concentrations will be reported based on instrument responses that are within the range of the calibration standards. A quantitation limit for each analyte in a sample will be based on the smallest analyte peak measured in the lowest concentration multilevel standard, the sample weight, and appropriate response factors using the formula below or the multilevel calibration curve for CHs.

$$\textbf{conc (ng/g)} = \frac{\dfrac{\textbf{ng surrogate std}}{\textbf{area surrogate std}} \times \textbf{smallest analyte area} \times R_{rf}}{\textbf{sample weight (g, dry)}}$$

$$R_{rf} = \frac{\textbf{ng/µL of analyte in cal std}}{\textbf{area analyte in cal std}} \times \frac{\textbf{area surrogate in cal std}}{\textbf{ng/µL surrogate in cal std}}$$

If the analyte is not detected in a sample, the quantitation limit (as calculated above) will be reported, preceeded by a “less than” sign (<). Reported analyte concentrations in certain samples may be lower than the target MDL.

Table 6.1 Target Method Detection Limits

Semivolatile Organics	
Sediment (ng/g, dry weight)	
AHs, phenols, phthalates, chlorinated benzenes	4
Pesticides, PCB congeners	4
Tissue (ng/g, wet weight)	
AHs	4
Pesticides, PCB congeners	4
Toxic Metals (µg/g, dry weight)(Graphite furnace AA, GFAA; Inductively coupled plasma optical emission spectroscopy, ICP, Cold vapor AA, CVAA; Flame AA spectroscopy, FAAS)	
Antimony (GFAA)	1.2
Arsenic (GFAA, ICP)	0.14,13
Cadmium (GFAA)	0.005
Chromium (GFAA, FAAS)	1.0,1.8
Copper (GFAA, FAAS)	2.3,0.6
Lead (GFAA)	0.5
Mercury (CVAA)	0.02
Nickel (GFAA)	0.2
Silver (GFAA)	0.02
Zinc (1CP, FAAS)	1.9, 16
Buty1tins (ng/g, dry weight, as tin)	
Sediment, mono-, di-, tri-, tetrabutyltin	10

6.6 Quality Control Criteria for the Analytical Measurements

The results for the various QC samples will be reviewed by laboratory personnel immediately following the analysis of each sample batch. These results will then be used to determine when control limits (numerical data criteria) have been exceeded and corrective actions are required before the analyses may proceed. Control limits and required minimum frequency of analysis for each QC element or sample type are summarized in Table 6.2.

6.6.1 Initial Calibration

Acceptable calibration (initial and continuing) must be established and documented before sample analyses may begin. NIST/NRCC-provided (or other) calibration materials must be used, whenever possible, in establishing calibration. Initial calibration will be established with a multipoint standard calibration curve (for certain analyses, as indicated in Table 6.2). The correlation coefficient (r) for the curve will be greater than 0.9900. Failure to generate acceptable standard curves weekly (at a minimum) for > 90% of the analytes will require recalibration. Data corresponding to a calibration that does not meet the criteria will be qualified or not reported. A specific requirement for this project was to use methodology (and tune instrumentation) for low detection limits, therefore, samples with analytes above the calibration range will be diluted and reanalyzed or qualified based on agreement with the QA Coordinator (e.g., where only a few analytes exceed the calibraton range, it may not be necessary to reanalyze the sample). The lower limit of the calibration range will be the lower limit of quantitation. HCBD will be quantitated in tissue samples and stomach content samples based on an adjusted response factor for HCB (because HCBD was added to the list of analytes to be determined after the multilevel standards had been prepared and thus is not in our calibration solution). At the beginning of the project, the response curves for HCBD and HCB will be determined from a calibration solution containing these analytes and the GC standard. For sample analysis, a corrected response curve for HCB will be used for calculating the concentration of HCBD.

6.6.2 Continuing Calibration Verification (CCV). Continuing calibration verification (CCV) standards will bracket every 10 field sample analyses at a standard curve midpoint concentration. If CCV results do not meet specified criteria (Table 6.2), then all samples analyzed since the last acceptable CCV must be reanalyzed after recalibration.

6.6.3 Reference Materials

Reference materials (either certified or uncertified) of an appropriate matrix will be analyzed with every 10 field samples throughout the analytical program. The data resulting from the analysis of these samples will be reported in the same manner as that for field samples. These data will be the prime materials used to determine and document the accuracy and precision of the associated field sample data.

Table 6.3 Standard Reference Materials (SRMs) Used in the CBDA

NIST SRM 1941, 1941a Organics in Marine Sediment (certified)
NIST SRM 1974a Organics in Mussel Tissue (*Mytilus edulis*, being certified)
NRCC MESS-1, Metals in Marine/Estuarine Sediment (certified)
NRCC BCSS-1, Metals in Marine/Estuarine Sediment (certified)
NRCC PACS-1, Metals in Marine/Estuarine Sediment (certified)
Duwamish III, Butyltins in Estuarine Sediment (noncertified)
SQI, Butyltins in Marine Sediment (noncertified)

Only selected analytes may be certified in “certified” materials.

It is recognized that accuracy is usually best assessed using certified values (or advisory values for those analytes that are not certified), hence the term relative accuracy. Relative accuracy is computed by comparing the laboratory’s value for each analyte against either end of the range of values (i.e., 95% confidence limits) reported by the certifying agency. The laboratory’s value must be within 35% of either the upper or lower 95% confidence interval value for ≥70% of the analytes. Non-certified results can be compared but with less rigorous criteria. Accuracy control limit criteria (Table 6.2) will apply only for those analytes having concentrations in the SRMs greater than 10 times the laboratory’s target MDL.

Each laboratory will record the results for analytes in the SRM on control charts or tables. If the values exceed the control limits, then the entire batch of samples is to be considered suspect. The source of the error must be identified and corrected and the samples reanalyzed (depending on agreement with the QA Coordinator). In the case of analytes for which no concentration information is available, the laboratory will establish upper and lower control limits, based on three standard deviations of the mean. These control limits will be evaluated on a monthly basis.

6.6.4 Surrogate (Internal Standard) Recovery

All samples, where applicable in the analytical scheme, will be spiked with extraction surrogates (internal standards) as described in the laboratory SOPs. No surrogates will be used for metals.

6.6.5 Method (Reagent) Blanks

Method blanks are laboratory derived samples which have been subjected to the same preparation or extraction procedures and analytical protocols as project samples. A method blank will be analyzed at least with every 20 field samples analyzed. Acceptance criteria are provided in Table 6.2. Failure to meet acceptance criteria requires definitive corrective action to identify and eliminate the source(s) of contamination before the subsequent re-extraction and reanalysis of the blank and affected samples. Sample results will not be blank corrected.

6.6.6 Sample Duplicates

A sample duplicate will be analyzed at least with every 20 field samples. Acceptance criteria are provided in Table 6.2.

6.7 Quality Control Criteria Percent Moisture

Duplicates must be analyzed at least with every 20 field samples. The relative standard deviation will be less than or equal to 25%, or the batch must be reanalyzed.

6.8 Laboratory Qualification of Data

Sample results which presented analytical difficulties are qualified by the laboratory so that the data user is aware of the potential limitations of the data. Laboratory qualifiers are:

G	Result is an estimate in concentration because analytical interference caused difficulty with quantitation.
K	Analyte was detected and quantified but actual concentration is greater than the value shown because the analyte area exceeded that for the corresponding highest level standard, i.e., it was out of the calibration range. Because the methods are optimized for low detection limits, there will be some occasions when an analyte exceeds the calibration range and it is not reasonable to reanalyze the sample.
U	Analyte was not detected. The reported value is the method detection limit (MDL).
&	Surrogate recovery is outside acceptable limits (50%-125%).

TS Result was not corrected for recovery because surrogate recovery was outside acceptable limits (50%-125%). Result was quantitated based on the relative response of the injection internal standard (GC standard).

SC Surrogate was diluted out of range. Result was corrected for the surrogate recovery in the undiluted analysis of the same sample extract.

NR Result not reported for that analyte for some reason, the most common of which may be that in a reanalysis of a diluted extract, the analyte concentration was reported from a previous analysis.

NCA Analyte identified could not be confirmed because of coelution or analytical interference.

Section 7.0
Data Reduction, Validation and Reporting

7.1 Data Reduction

Data reduction is the process whereby raw data (analytical measurements) are converted or reduced into meaningful results (analyte concentrations). This process may be either manual or electronic. Primary data reduction requires accounting for specific sample preparations, sample volume (or weight) analyzed and any concentrations or dilutions required. In addition, the concentrations of the analytes will be calculated based on the recovery obtained for the surrogate compounds spiked into the sample prior to extraction (for those analyses in which surrogate standards are used) in order to best reflect the concentration of the compound in the original sample.

Primary data reduction is the responsibility of the analyst conducting the analytical measurement and is subject to further review by laboratory staff, the Project Manager and finally, independent reviewers. All data reduction procedures will be described in the laboratory's SOPs.

Concentrations greater than 10 will be reported as if 3 figures were significant and those less than 10 will be reported as if 2 figures were significant. In addition:

Organic analytes in sediments will be reported in ng/g, dry weight, corrected for surrogate recovery. Metals will be reported in μg/g, dry weight.

Organic analytes in tissues will be reported in ng/g, wet weight, corrected for surrogate recovery.

Results for analytes in method blanks will be reported as concentrations on the same basis as for the samples being analyzed, i.e., the average of the weights of the samples in the corresponding set are used in the calculations for the method blank.

Data generated from the analysis of blank samples will not be utilized for correction of analyte data.

For sernivolatile organic compounds and butyltins, surrogate compounds will be evaluated as percent recovery (%R). Recovery rates will be utilized to correct for method efficiency by calculating all analyte concentrations using the appropriate surrogate response factor.

Reference materials will be reported in units indicated on the certificate of analysis.

Continuing calibration factors will be presented as mean and relative standard deviation (RSD).

Duplicate sample results will be expressed as the mean and standard deviation (SD).

Total PCBs are calculated by summing the concentrations of PCB congeners 18, 28, 44, 52, 66, 101, 105, 118, 128, 138, 153, 170, 180, 187, 195, 206 and 209 and multiplying by 2 (NOAA 1989). If a result is reported as non-detected, then zero will be used in the summation.

7.2 Data Review and Validation

Data review is an internal review process where data are reviewed and evaluated by personnel within the laboratory. Data validation is an independent review process conducted by personnel not associated with data collection and generation activities.

Data review is initiated at the bench level by the analyst, who is responsible for ensuring that the analytical data are correct and complete, the appropriate SOPs have been followed and the QC results are within the acceptable limits. The Project Manager has final review authority. It is the Project Manager’s responsibility to ensure that all analy-

ses performed by that laboratory are correct, complete and meet project data quality objectives.

External and independent data validation will be performed for all samples by the QA Contractor using a data package (Table 7.1) containing sufficient information to allow the independent validation of the sample identity and integrity, the laboratory measurement system, and resulting quantitative and qualitative data.

The original data packages will be archived by the laboratories for a maximum of one year after generation and then returned to project management. A copy of each package will be sent to the QA Contractor as soon as possible after development, for data validation. The QA Contractor will archive these copies for one (1) year after validation and then return these to project management.

Two levels of data validation will be performed: full or cursory validation. Full validation will consist of a review of the entire data package for compliance with documentation and quality control criteria for all the following items and cursory validation for the starred (*) items:

- Package completeness*
- Holding times from extraction to analysis*
- Instrument calibration, initial and continuing
- Blank results*
- Instrument performance
- Surrogate recovery (semivolatile organics and butyltins only)*
- Standard reference material results*
- Laboratory duplicate results
- Reported detection limits*
- Compound quantitation

Table 7.1 Laboratory Data Deliverables Per Sample Batch

Chain-of-Custody/Sample Receipt Checklist

Sample Data: Result summaries: including surrogate recoveries, % total solids, dilutions, etc.

Standards Data:
Target MDL data based on the method in 40 CFR, 136, or data from analyses

of SRM which has analytes at low concentrations (submitted once each year for each laboratory/matrix).

Calibration summaries: initial calibration data, standard curve equation, correlation coefficient, continuing calibration as RSD.

Quality Control Data (Method Blanks, SRMs):
Results summaries including surrogate recoveries, plus % recovery and %RSD, as applicable.

Case Narrative:
Special handling or analysis conditions.

Any circumstance that requires special explanation such as an exception to QA/QC conditions or control criteria, dilutions, reanalysis, etc.

Corrective actions/procedure alterations

As the project proceeds and the quality of the data is verified and documented, the level of validation will decrease such that 50% of the data packages will receive full review. Cursory validation will be performed on the remaining packages, i.e. only the starred items will be reviewed.

Qualifiers (Table 7.2) may be assigned to individual data points by the QA Contractor. These validation qualifiers will not replace qualifiers or footnotes provided by the laboratory, but will be added to the data summary tables to inform the data user whether or not the data met all project quality objectives. Both sets of qualifiers will be maintained in the database.

Table 7.2 Data Validation Qualifier Codes

U Analyte concentration is not significantly above the associated blank result. The result is judged to be the detection limit.

R Unreliable result. Data should not be used.

J Reported concentration may not be accurate or precise, as judged by associated calibration and/or reference material results.

UJ Not detected. Detection limit may be inaccurate or imprecise, as judged by the associated quality control results.

All discrepancies and requests for additional corrected data will be discussed with the laboratory prior to issuing the formal data validation report. Review procedures and findings during data validation will be documented on worksheets. A validation report will be. prepared for each data group/data package summarizing OC results, qualifiers, and possible data limitations. Only validated data with appropriate qualifiers will be released for general use.

Data are not considered final until QA Coordinator has performed assessment. Data will be subjected to validation at a later date.

Section 8.0
Corrective Action/Procedure Alteration

The analytical laboratories are required to adhere to the SOPs submitted by them to the QA Coordinator for this project. When the data from the analyses of any quality control sample exceeds the project specified control limits (Table 6.2) or indicates that the analytical method is drifting out of control, it is the immediate responsibility of the analyst to identify and correct the situation before continuing with sample analysis.

A narrative describing the problem noted, the steps taken to identify and correct the problem and the treatment of the relevant sample batches must be prepared and submitted with the relevant data package. If the action is a change from the accepted SOP, the SOP must be revised and re-submitted within 30 working days after problem was noted.

Section 9.0
Quality Assurance Reports to Management

Quality Assurance/Quality Control (QA/QC) reports will be submitted periodically to the Case Management Team by the QA Coordinator. These reports may be either formal or informal in response to the Case Management Team’s request. Upon termination

of the analytical work for this damage assessment, a formal QA report will be submitted. This report will include:

- General compliance with QA objectives
- Summary of technical and performance evaluation audits
- Summary of data validation reports
- Summary of laboratory control charts

Section 10.0
References

Stanley, T. W. and S. S. Verner. 1983. Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans. EPA/600/4-83/004. U. S. Environmental Protection Agency, Washington, D.C.

Table 6.2 Minimum Analytical Quality Control Criteria

Sample Type	Minimum Frequency	Acceptance Criteria
Semivolatile organics		
Performance Evaluation	Initial	Majority of values for SRM within ± 50% of reference value (except when < 10 x MDL). RSD not to exceed ± 30%
Calibration	Initial/weekly	At least a four point curve. Standard curve correlation (r) > 0.9900 for all analytes.
Continuing calibration	Must start and end analytical sequence and every 10 field samples	For AHs, pesticides, and PCBs, the relative standard deviation (RSD) of the analyte responses relative to the internal standard will be ≤ 25%. For phenols, phthalates and chlorobenzenes, the RSD will be ≤35% for ≥90% of the analytes.
Reference material	Every 10 field samples	Concentrations of ≥70% of individual analytes (AHs, PCBs, chlorinated pesticides) within 35% of either end of the 95% confidence interval range of the reference values. Does not apply to analytes with concentrations < 10 x MDL.
Method blank	Every 10 field samples	No more than 2 analytes (except naphthalene, certain phthalates and phenol) in sediments or 5 analytes in tissues are to exceed 3 x MDL, unless analyte not detected in associated sample(s) or analyte concentration > 10X blank value.
Sample duplicate	Every 20 field samples	RSD ≤ 50% or within 5 x MDL if less than 10 x MDL.
Internal standards/surrogates	Every sample	50-125 % recovery
Mass spectral confirmation	about 10% of field samples	Confirmation based on acceptable match of 2 ions (PCBs and pesticides).
Interlab comparisons	Once per year	As defined by NIST

Table 6.2 Minimum Analytical Quality Control Criteria, continued.

Sample Type	Minimum Frequency	Acceptance Criteria
Metals		
Performance Evaluation	Initial	Majority of values within ± 50% of reference value. RSD not to exceed ± 30%
Calibration[1]	Initial/weekly	Four-eight point curve. Standard curve correlation (r) > 0.9900 for all analytes.
Continuing calibration	Must start and end analytical sequence and every 10 field samples	RSD ≤ 25% for any one analyte; RSD (average) ≤ 15% for 90% of the analytes
Reference material	Every 10 field samples	Concentrations of > 70% of individual analytes within 35% of either end of the 95% confidence interval range of the reference values. Does not apply to analytes with concentrations < 10 x MDL or to samples digested by the strong acid (EPA method 3051) procedure.
Method blank	Every 10 field samples	No more than 2 analytes to exceed 3 x MDL, unless analyte not detected in associated sample(s) or analyte concentration > 10X blank value.
Sample duplicate	Every 20 field samples	RSD ≤ 50% or within 5 x MDL if less than 10 x MDL.
Interlab comparisons	Once per year	As defined by NRCC

Table 6.2 Minimum Analytical Quality Control Criteria, continued.

Sample Type	Minimum Frequency	Acceptance Criteria
Butyltins		
Performance Evaluation	Initial	Majority of values within ± 50% of reference value in control material. RSD not to exceed ± 35%
Calibration[1]	Initial/weekly	Four point curve. Standard curve correlation (r) > 0.9900 for all analytes.
Continuing calibration	Must start and end analytical sequence and every 10 field samples	RSD ≤ 25% for any one analyte; RSD (average) ≤ 15% for all analytes
Reference (control) material	Every 10 field samples	Concentrations of > 70% of individual analytes within plus or minus 3 standard deviations of historical mean concentrations determined in the control materials. Does not apply to analytes with concentrations < 10 x MDL.
Method blank	Every 10 field samples	No more than 2 analytes to exceed 3 x MDL, unless analyte not detected in associated sample(s) or analyte concentration > 10X blank value.
Sample duplicate	Every 20 field samples	RSD ≤ 50% or within 5 x MDL if less than 10 x MDL.
Internal standards/surrogates	Every sample	50-125% recovery

List of Abbreviations

ACs	aromatic compounds
MM	aryl hydrocarbon hydroxylase
ANCOVA	analysis of covaniance
ANOVA	analysis of variance
BaP	benzo[*a*]pyrene
BDL	below detection limits
CB	chlorinated biphenyl
CHs	chlorinated hydrocarbons
CYPIA	cytochrome P4501A
DAC	Damage Assessment Center
DDTs	dichlorodiphenyltrichloroethanes
DNA	deoxyribonucleic acid
ECD	Environmental Conservation Division
FACs	fluorescent aromatic compounds
$FACs_{BAP}$	biliary FACs measured at benzo[*a*]pyrene wavelengths
$FACs_{NPH}$	biliary FACs measured at naphthalene wavelengths
$FACs_{PHN}$	biliary FACs, measured at phenanthrene wavelengths
FCA	foci of cellular alteration
GSI	gonadosomatic index
GS/ECD	gas chromatography/electron capture detection

GC/MS	gas chromatography/mass spectometry
HACs	high molecular weight aromatic compounds
HCB	hexachlorobenzene
HCBD	hexachlorobutadiene
HPLC/PDA	high-performance liquid chromatography with photodiode array detection
HSI	hepatosomatic index
HydVac	hydropic vacuolation of biliary epithelial cells
LACs	low molecular weight aromatic compounds
NMFS	National Marine Fisheries Service
NOAA	National Oceanic and Atmospheric Administration
NWFSC	Northwest Fisheries Science Center
NPH	naphthalene
PCBs	polychlorinated biphenyls
PAHs	polycyclic aromatic hydrocarbons
PHN	phenanthrene
pmol. mg-1min-1	picomoles/milligram/minute
ppb	parts per billion
Prolif	proliferation (in liver of fish)
PSAMP	Puget Sound Ambient Monitoring Program
QA	Commencment Bay Quality Assurance Plan (Appendix E)
QAP	Commencment Bay Quality Assurance Plan (Appendix E)

QA Plan	Commencment Bay Quality Assurance Plan (Appendix E)
RR_e	estimated relative risk
SAP	Sampling and Analysis Plan (Appendix A)
SDN	specific degeneration/necrosis (in liver of fish)
SE	standard
SRM	Standard Reference Materials. These materials are available from the U.S. National Institute of Standards and Technology, Gaithersburg, MD 20899
TCDD	2,3,7,8 - tetrachlorodibenzo-*p*-dioxin
TEQs	toxic equivalents
TEFS	toxic equivalent factors
Tox	toxicopathic