

Quality Assurance Project Plan for the PCBs in Caulk Project (Taking Action for Clean Water Bay Area TMDL Implementation)

Subcontract for SWRCB Agreement No. 09-305-550-1 with
Association of Bay Area Governments

**Prepared by
Susan Klosterhaus
San Francisco Estuary Institute**



July 2010

San Francisco Estuary Institute
7770 Pardee Lane, 2nd Floor
Oakland, CA 94621

Quality Assurance Project Plan for the PCBs in Caulk Project (Taking Action for Clean Water Bay Area TMDL Implementation)

Subcontract for SWRCB Agreement No. 09-305-550-1 with
Association of Bay Area Governments

Approvals*:

Bill Ray, QA Officer, State Water Resources Control Board

Signature: _____ Date: _____

San Francisco Estuary Partnership

Signature: _____ Date: _____

San Francisco Estuary Institute

Signature: _____ Date: _____

*Signature implies that the signatory has reviewed the document, has no exceptions to its content, and agrees with the description of their agency's role in the project

Table of Contents

1. PROJECT MANAGEMENT	5
1.1. PROJECT BACKGROUND	5
1.2. PROJECT DESCRIPTION.....	6
1.3. QUALITY ASSURANCE PROJECT PLAN DESCRIPTION (QAPP).....	6
1.4. PROJECT ORGANIZATION AND RESPONSIBILITIES	7
1.4.1 SWRCB Project Manager (<i>Kari Holmes, California State Water Resources Control Board</i>).....	7
1.4.2 Project Manager (<i>Athena Honore, ABAG/SFEP</i>).....	7
1.4.3 Contractor (<i>SFEI</i>).....	7
1.4.4 Contractor Project Manager (<i>Susan Klosterhaus, SFEI</i>).....	7
1.4.5 Data Manager (<i>Don Yee or Jay Davis, SFEI</i>).....	8
1.4.6 Project Chemist (<i>Francois Rodigari, East Bay Municipal Utility District</i>).....	8
1.4.7 Other Collaborators (<i>Bay Area Stormwater Management Agencies Association, SF Bay Regional Water Quality Control Board</i>).....	8
1.5 DOCUMENTATION AND RECORDS.....	8
1.5.1 Laboratory Data Reduction and Review.....	8
1.5.2 Procedures to Verify Data Integrity.....	9
1.5.3 Treatment of Outliers.....	9
1.5.4 Data Management.....	9
2. FIELD SAMPLING.....	9
2.1 SAMPLING DESIGN	9
2.2 SAMPLING PROCEDURES	10
2.2.1 Sealant Testing Using Portable X-Ray Fluorescence (XRF).....	10
2.2.2 Sealant Sampling for Laboratory Analysis	11
2.3 SAMPLE HANDLING AND CUSTODY PROCEDURES.....	11
2.4 FIELD PERFORMANCE MEASUREMENTS	11
2.4.1 Field Duplicates.....	11
2.4.2 Field Blanks	11
3. ANALYTICAL METHODS	12
3.1 LABORATORY ANALYTICAL METHODS	12
3.2 DATA QUALITY OBJECTIVES	12
3.3 ANALYTICAL AND STATISTICAL CONTROL PARAMETERS	13
3.3.1 Analytical Batches	13
3.3.2 Accuracy	13
3.3.3 Precision.....	13
3.3.4 Sensitivity of the Analytical Method.....	14
3.3.5 Completeness	14
3.3.6 Representativeness.....	14
3.3.7 Comparability	14
4. LABORATORY QUALITY ASSURANCE AND CONTROL	15
4.1 LABORATORY REQUIREMENTS.....	15
4.2 LABORATORY PERSONNEL, TRAINING, AND SAFETY.....	15
4.3 QUALITY ASSURANCE DOCUMENTATION.....	16
4.4 LABORATORY PERFORMANCE AUDITS/CORRECTIVE ACTION	16
4.5 LABORATORY PERFORMANCE MEASUREMENTS.....	16
4.5.1 Method Blanks	17
4.5.2 Internal Standards	17
4.5.3 Replicate Samples.....	17
4.5.4 Laboratory Replicate Samples.....	17

4.5.5 Matrix Spike Replicate Samples.....	17
4.5.6 Matrix Spike Samples.....	17
4.5.7 Certified Reference Materials (CRMs)	17
4.6 LABORATORY QUALITY CONTROL PROCEDURES	17
4.6.1 Instrument Calibration.....	18
4.6.2 Documentation of Method Detection Limits	18
4.6.3 Limits of Quantitation.....	19
4.6.4 Record of Certified Reference Material.....	20
4.6.5 Routine Analysis of Certified Reference Materials or Laboratory Control Materials.....	20
4.7 PRECISION CRITERIA	21
4.8 LABORATORY REPLICATES FOR PRECISION	21
4.9 ACCURACY CRITERIA.....	21
4.10 CONTINUING CALIBRATION CHECKS	22
4.11 LABORATORY REAGENT BLANKS.....	22
4.12 SURROGATES.....	22
4.13 INTERNAL STANDARDS	23
4.14 DUAL-COLUMN CONFIRMATION	23
4.15 MATRIX SPIKES AND MATRIX SPIKE DUPLICATES	23
4.16 FIELD REPLICATES	24
5. ASSESSMENTS AND PROJECT OVERSIGHT.....	24
5.1 CONTRACTOR QUALITY CONTROL	24
5.2 ASSESSMENTS AND RESPONSE ACTIONS	24
5.3 REPORTS TO MANAGEMENT	25
6. DATA VALIDATION AND USABILITY	25
6.1 DATA VERIFICATION	25
6.2 DATA VALIDATION	25
6.3 RECONCILIATION WITH USER REQUIREMENTS	25
7. REFERENCES.....	26
8. APPENDIX: ANALYTICAL METHOD FOR PCBS IN SEALANTS.....	27

1. Project Management

1.1. Project Background

Elevated polychlorinated biphenyl (PCB) levels threaten the health of people and wildlife consuming fish from San Francisco Bay (RWQCB, 2008). A Total Maximum Daily Load (TMDL) to address PCB impairment of all segments of San Francisco Bay was adopted by the San Francisco Bay Regional Water Quality Control Board in February 2008. The San Francisco Bay PCBs TMDL Project Report (RWQCB 2004) found that urban runoff was one of the major sources of PCB loads to the Bay and concluded that controlling sources of PCBs to urban runoff was one of two top priorities for TMDL implementation. Based on this recommendation, the Clean Estuary Partnership (CEP) evaluated available data on sources of PCBs in urban runoff and recommended approaches for addressing two potentially significant sources, past PCBs releases that have contaminated soil and sediments and PCB-containing historic building materials, specifically uncontained materials like sealants, caulking and paint (LWA et al. 2006). When the building materials fail or buildings are remodeled, residues can be transported away from the building during rainstorms, through landscape irrigation overflows, or by pavement washing (forecourts and footpaths surrounding the buildings) and find their way into the stormwater drainage system. In addition, when buildings are demolished, PCBs may be released onto the ground and can be washed off into stormwater drains by rainfall. While these are logical pathways, we lack data to determine which buildings have PCBs at levels that may be concerning, the magnitude of losses to stormwater, or how PCBs in buildings could be better managed.

A survey of 1,348 buildings in Switzerland constructed between 1950 and 1980 found that almost half of the buildings contained PCBs, almost 10% of the buildings contained sealants with PCB concentrations exceeding 10% by weight, and the total PCBs reservoir in Switzerland was an estimated 50-150 metric tons (Kohler et al. 2005). Less rigorous studies have been conducted in Boston (Herrick et al. 2004) and Toronto (Melymuk et al. 2008) with similar findings; however no such evaluation is known for California. A Swedish study also found that significant quantities of PCBs were released into soil and water runoff during building remodeling (Astebro et al. 2000). Both the Swiss and Swedish governments have developed active programs to manage PCB-containing building materials in response to public health concerns, which relate to both direct exposures and the adverse effect of PCBs on Europe's fisheries.

In 2007 the California State Water Resources Control Board awarded the Association of Bay Area Governments (ABAG) a grant that includes several tasks for implementation of Bay Area Total Maximum Daily Loads (TMDLs). The project was halted under the state bond freeze in December 2008 and restarted under the American Recovery and Reinvestment Act of 2009 (ARRA) through the State Revolving Fund in August of 2009. One of the tasks in the master grant is the PCBs in Caulk Project (referred to herein as the Project), which includes characterizing the use of PCBs in historic building materials in the San Francisco Bay Area. The San Francisco Estuary Institute (SFEI) is the subcontractor for Task 7.5.2.2 of SWRCB Agreement No. 09-305-550-01.

1.2. Project Description

The objective of this element of the PCBs in Caulk Project is to obtain Bay Area-specific estimates on PCB loadings to urban runoff from historic building materials. While many structures were historically built with a variety of materials known to contain PCBs, including caulking/sealants, grouts, paints, and flame retardant coatings of acoustic ceiling tiles, the focus of this Project is caulking/sealants that were used between rigid components of buildings and other structures. The results from implementing this SAP will inform the development of BMPs for the handling of PCB-contaminated caulking. This SAP contains information on the data-collection phase of the Project, which will obtain Bay Area-specific information on the presence of PCBs in sealants used in historic buildings and other structures.

In collaboration with Bay Area Stormwater Management Agencies Association (BASMAA), the San Francisco Bay Regional Water Quality Control Board (Water Board), and local municipalities, the San Francisco Estuary Institute (SFEI) will test or sample structures that have the potential to contain PCBs in their exterior sealants or caulking (herein referred to as only 'sealants'). Other members of the Project team will identify buildings and secure permission to test a minimum of ten Bay Area structures. Structures to be tested or sampled will be identified based on structure type, year of construction, and whether or not the sealants have been replaced or renovated since the original date of construction. Based on the results of this identification process, and in cooperation with structure owners, this SAP will be implemented to obtain Bay Area-specific information on the PCB content of sealants. As appropriate, data generated from the sampling phase will be used to support BMP development and implementation. All testing and sampling conducted during the above-mentioned activities will be in compliance with this SAP.

It is likely that sealant testing in participating buildings or structures will occur through the use of a portable X-ray fluorescence (XRF) detector to estimate PCB concentrations. If permission is granted, physical sealant samples will be collected from structures and sent to a qualified analytical laboratory for confirmation of PCB content according to the this Quality Assurance Project Plan (QAPP).

1.3. Quality Assurance Project Plan Description (QAPP)

This QAPP outlines procedures to be followed by project personnel to insure usability and representativeness of data collected through the Project implementation. The QAPP will be submitted to the State Water Resources Control Board (SWRCB) as part of the work to complete Task 7.5.2.2 of the master agreement, and under Task 1 of SFEI's subcontract under that agreement, which has a term of January 27, 2010 through December 1, 2011.

This QAPP is based largely on the QAPP produced for the Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP; Lowe et al. 1999) and the State of California Surface Water Ambient Monitoring Program (SWAMP; Puckett 2002). Though samples collected and analyzed in the Project are very different from those collected by the RMP, the field sampling control and laboratory control procedures contained within this QAPP were

developed to be consistent with those of the RMP to ensure consistency with datasets of potential comparative value, mainly the RMP and other SFEI datasets and the datasets developed by other Bay Area programs collected in conformance with Water Board data requests.

Making environmental management decisions in a scientifically defensible way depends on the sensitivity of the measurement system and the levels of confidence and certainty in the data. The purpose of this document is to maximize the probability that environmental data collected through the Project will meet the expectations of the data users. The Data Quality Objectives (DQOs) presented in this QAPP are intended to maximize the probability that the data actually represent conditions in the environment while minimizing artifacts due to sample collection and processing.

1.4. Project Organization and Responsibilities

The project will make use of the cooperative efforts of several parties involved in the design and implementation of the various components of the project. The main roles and responsibilities are defined below.

1.4.1 SWRCB Project Manager (Kari Holmes, California State Water Resources Control Board)

The SWRCB Project Manager oversees performance of the project agreement and monitors progress of the project. Technical review will be delegated to Jan O'Hara at the San Francisco Bay Regional Water Quality Control Board.

1.4.2 Project Manager (Athena Honore, ABAG/SFEP)

The Project Manager will be responsible for ensuring that all work performed through the Project is consistent with the project proposal and objectives, and for oversight of all efforts associated with the project. Additionally, the Project Manager will act as the liaison between the Contractor and the SWRCB Project Manager.

1.4.3 Contractor (SFEI)

The Contractor will be responsible for all efforts associated with the data collection phase, including SAP and QAPP development, data and sample collection, data management and interpretation, and reporting. The Contractor is also responsible for oversight of the subcontractor performing the laboratory analysis.

1.4.4 Contractor Project Manager (Susan Klosterhaus, SFEI)

The Contractor Project Manager will be responsible for ensuring that testing and sampling personnel adhere to the provisions of the QAPP and SAP. The Contractor Project Manager is also responsible for custody of any samples collected until receipt by the analytical laboratory.

1.4.5 Data Manager (Don Yee or Jay Davis, SFEI)

The Data Manager will be responsible for receipt and review of all project related documentation and reporting associated with laboratory PCB analysis. The Data Manager will serve as the project quality assurance officer and will be responsible for verifying compliance of all analytical data with the requirements established by the Project QAPP before its use for interpretive purposes.

1.4.6 Project Chemist (Francois Rodigari, East Bay Municipal Utility District)

The Project Chemist at the selected analytical laboratory will be responsible for ensuring that the laboratory's quality assurance program and standard operating procedures are consistent with the Project QAPP, and that laboratory analyses meet all applicable requirements or explain any deviations. The Project Chemist will also be responsible for coordinating with the Data Manager and Project Manager as required for the project. All laboratory analyses will be performed by the East Bay Municipal Utility District, Oakland, CA.

1.4.7 Other Collaborators (Bay Area Stormwater Management Agencies Association, SF Bay Regional Water Quality Control Board)

Bay Area Stormwater Management Agencies Association (BASMAA) and Water Board staff will be involved in the design and implementation of the Project. BASMAA and the Water Board will coordinate their involvement through the Project Manager, and will be given the opportunity to review and comment on all relevant project documents, including, but not limited to, the project QAPP, SAP, and draft and final reports. BASMAA will serve as liaison between the municipalities and the Project Manager by providing summary information about the project and its objectives to the municipalities that may wish to participate in the project. BASMAA will also attempt to identify structures that meet the structure criteria within each municipality that may be available for testing and/or sampling and will attempt to secure permission from structure owners for testing or sampling.

1.5 Documentation and Records

All appropriate project-related materials (e.g., field notes, reports, photographs, laboratory reports, etc.) will be delivered to and maintained by the Contractor Project Manager or the Data Manager for the project duration. A discussion of some of the key parts of the documentation process is shown below.

1.5.1 Laboratory Data Reduction and Review

The laboratory analyst who performs the analysis is responsible for reviewing the initial dataset for accuracy and acceptability. Where calculations are not performed by a validated software system, a second reviewer should verify a minimum of 10% of the calculations. The Project Chemist should also check the data report for completeness and errors prior to submission to the Data Manager.

The analytical laboratory will report the analytical data via an analytical report consisting of, at a minimum:

- letter of transmittal
- analytical results in SWAMP format
- quality control results
- chain of custody information
- case narrative
- copies of all raw data

In addition to the printouts supplied by the analytical laboratory, test results should also be delivered to the Data Manager in MS Excel compatible electronic format.

1.5.2 Procedures to Verify Data Integrity

The integrity of the data generated in the laboratory is assessed through the evaluation of the results of the analysis of various quality control (QC) samples by the Data Manager. The numerical criteria for evaluation of these QC samples is specific to the analysis being performed and shall be consistent with laboratory Standard Operating Procedures (SOPs).

1.5.3 Treatment of Outliers

Only data that have met data quality criteria, or data that have acceptable deviations explained, will be submitted by the Project Chemist to the Data Manager. When QA requirements have not been met, the samples will be reanalyzed when possible. Only the results of the reanalysis will be submitted, provided they are acceptable.

1.5.4 Data Management

The Data Manager will review the data deliverables provided by the Project Chemist for completeness and errors. Data will be validated according to this QAPP to ensure that Data Quality Objectives (DQOs) are met. Data will be delivered to the Data Manager or Contractor Project Manager in SWAMP format.

2. Field Sampling

2.1 Sampling Design

Exterior sealants from a minimum of ten Bay Area structures will be tested for Cl using a portable XRF analyzer. The number of structures and sites selected is based on the requirement

in section C.12.b in the Municipal Regional Stormwater NPDES Permit, which this project seeks to implement. Other members of the Project team, in collaboration with SFEI, will identify structures for testing using the criteria outlined in the technical memo (Moran et al. 2007) and secure permission to test them. If permission is granted, physical sealant samples will also be obtained from structures and sent to a qualified laboratory for PCB analysis according to this QAPP. Project budget constraints and the number of structures for which permission to sample is received determine the number of structures to be sampled during the Project.

Testing and sampling will focus on structures constructed between 1957 and 1977, the era when structures are most likely to contain PCB in their sealants (Moran et al. 2007) and, to the extent feasible and supporting data are available, on sealants used on structure exteriors and those that have not been renovated or remodeled since construction. Structures may include, but are not limited to, transportation infrastructure (e.g. roads, bridges, sidewalks) and/or privately- or publicly-owned buildings. An estimate of the volume and surface area of the sealant on the exterior of each structure will also be determined to estimate the total mass of PCBs in the structure's sealants. This information, along with other site characteristics such as imperviousness, slope, and flow paths to the stormwater system, will be used to estimate potential PCB loadings from structural sealants to urban stormwater runoff. Additional information on the sampling design can be found in the 'Field Sampling and Analysis Plan' for the Project.

2.2 Sampling Procedures

Once a structure has been identified as meeting the selection criteria and permission is granted to perform the testing or collection of sealant samples, an on-site survey of the structure will be used to identify sealants and sealant locations on the structure to be tested or sampled. It is expected that sealants from a number of different locations on each structure may be tested; however, inconspicuous locations on the structure will be targeted for any physical sealant sampling.

2.2.1 Sealant Testing Using Portable X-Ray Fluorescence (XRF)

A portable XRF analyzer (Innov-X Systems, Woburn, MA) will be used as a screening tool to estimate the concentration of chlorine (Cl) and other elements in sealants in many locations on each structure. The analyzer will also be calibrated for Cl using plastic pellet European reference materials (EC680 and EC681) upon first use. The XRF analyzer will be 'standardized' using procedures recommended by the Innov-X representative each time the instrument is turned on and prior to any sealant monitoring. A 30 second measurement in soil/light element analytical program (LEAP) mode will be used. Field personnel will wipe the sealant surface to be sampled with a laboratory tissue to remove any debris that may potentially interfere with the XRF analysis. At least one XRF reading will be collected from each type of sealant present on the structure (e.g., window sealant, joint between concrete blocks, and joint between concrete at base of building and surrounding concrete surface). If Cl is detected, a minimum of two additional readings will be conducted at the same location on the structure to determine analytical variability and at other locations on the structure to determine variability in Cl concentration within sealant type on each structure. The XRF analyzer will record the estimated concentration

of a variety of elements in the sealant and the Cl concentration will be recorded on field datasheets. XRF analysis will also be conducted on any sealant samples following their collection from the structure.

2.2.2 Sealant Sampling for Laboratory Analysis

Where permission is granted to collect sealant samples, selection of the appropriate samples to collect will be made at the time of sampling by the Project Manager in consultation with the structure owner. Following XRF analysis on the intact material, a one inch strip (or ~10 g) of the sealant sample will be removed from the structure using a utility knife with a solvent-rinsed, stainless-steel blade. Field personnel will wear Nitrile gloves during sample collection to prevent sample contamination. The sample will be placed on a clean surface, where it will undergo a second XRF analysis. The sample will then be placed in a labeled, laboratory-cleaned glass jar. The samples will be kept in a chilled cooler until returned to SFEI, where the samples will be refrigerated pending delivery under chain-of-custody (COC) to the analytical laboratory. The procedure for replacement of the sealant will be coordinated with each municipality or structure owner.

2.3 Sample Handling and Custody Procedures

Sufficient sampling information must be recorded in the field that allows tracking sample shipments from field to laboratory and from laboratory through data processing and quality assurance. Custody for samples remains with the sampling personnel until time of receipt by the analytical laboratory. Samples will be kept under refrigeration (4 degrees Celsius) until delivery to the laboratory. Samples will be transported to the laboratory in a chilled cooler.

2.4 Field Performance Measurements

Following is a list of field performance measurements that are typically included in sampling protocols.

2.4.1 Field Duplicates

The analysis of field duplicate samples would evaluate within-structure variability of PCB concentrations in sealants, which has not been previously documented. Sealant PCB concentrations have the potential to vary spatially within each structure due to variability in the volume of Aroclor mixture(s) and the type of Aroclor mixture(s) added in each batch of sealant prepared on site during construction.

Assessment of within-structure variability of PCB concentrations in sealants is not a primary objective of the Project, therefore field duplicate samples will not be collected. Due to budget limitations, GC-MS analysis of only one sealant sample per sealant type on each structure will maximize the number of Bay Area structures and structure types that may be analyzed in the Project.

2.4.2 Field Blanks

Collection of sealant field blank samples has been deemed unnecessary due to the difficulty in collection and interpretation of representative blank samples and the use of precautions that minimize contamination of the samples. Additionally, PCBs have been reported to be present in percent concentrations when used in sealants; therefore any low level contamination (at ppb or even ppm level) due to sampling equipment and procedures is not expected to affect data quality because it would be many orders of magnitude lower than the concentrations deemed to be a positive PCB signal.

3. Analytical Methods

3.1 Laboratory Analytical Methods

The samples will be analyzed for PCBs using a modified EPA 8270 protocol (semi-volatile organic compounds by gas chromatography-mass spectrometry). The full analytical method is attached in the Appendix. Hold times will follow EPA method 1668 (i.e. one year to extract and one year for extracts if samples and extracts are stored at -10 °C). Sealant samples will be stored in refrigerators at 4°C in wide mouth glass jars (30, 60, or 125 ml) until analysis. The minimum sample size is 10 g dry weight. PCB analytical results will be reported as IUPAC congeners.

The congener list will include:

- the 40 congeners routinely monitored by the RMP (PCBs 8, 18, 28, 31, 33, 44, 49, 52, 56, 60, 66, 70, 74, 87, 95, 97, 99, 101, 105, 110, 118, 128, 132, 138, 141, 149, 151, 153, 156, 158, 170, 174, 177, 180, 183, 187, 194, 195, 201, and 203),
- PCB 11, a non-Aroclor congener commonly detected in wastewater effluent and environmental samples (Rodenburg et al. 2010),
- the coplanar PCBs 77, 126, and 169, ‘dioxin-like’ congeners which contribute substantially to the dioxin toxic equivalents observed in San Francisco Bay sport fish.

A summary of sampling and analysis specifics are shown in Table 1.

Table 1. Analytical Methods, Hold Times, and Miscellaneous Sampling Information

Matrix	Analyte	Extraction Method	Extraction Hold Time	Analytical Method	Hold Time (after extraction)	Container Type	Min. Sample Weight
Solid	PCBs	EPA 8270	365 days	Modified EPA 8270D	365 days	Glass jar	10 g dry weight

3.2 Data Quality Objectives

Data Quality Objectives (DQOs) and their associated data quality indicators (DQIs, e.g. method blank and matrix spike) for the Project are listed in Table 3 (‘Batch QC Requirements’) of the Appendix. Information on certified reference materials (CRMs) and the analysis of laboratory

replicate samples is not included in Table 3. A CRM for PCBs in sealants does not exist, therefore a CRM will not be analyzed. Regarding laboratory replicates, a minimum of one per batch of 20 or fewer samples will be analyzed in duplicate and the target performance criteria for these is a relative percent difference (RPD) of <35%. If duplicate samples have a RPD >35%, selected samples may be re-analyzed to investigate variability in PCB concentrations within a sample.

3.3 Analytical and Statistical Control Parameters

3.3.1 Analytical Batches

Samples will be processed in analytical batches, not to exceed twenty samples per any one batch. Laboratory personnel will review the results for the various QA/QC samples immediately following the analysis of each sample batch. These results will then be used to determine when data quality criteria have not been met, and corrective actions will be taken before processing a subsequent sample batch. When data quality criteria are not met, specific corrective actions are required before the analyses may proceed.

3.3.2 Accuracy

Accuracy describes how closely the reported analytical concentration relates to its true environmental value. The “absolute” accuracy of an analytical method can be assessed using Certified Reference Materials (CRMs)¹ only when certified values are available for the analytes of interest. Nevertheless, the concentrations of many analytes of interest may be provided only as non-certified values in some of the more commonly used CRMs. A laboratory fortified sample matrix (commonly called a matrix spike, or MS) and a laboratory fortified sample matrix duplicate (commonly called a matrix spike duplicate, or MSD) will be used both to evaluate the effect of the sample matrix on the recovery of the compound(s) of interest. Therefore, control limit criteria are based on “relative accuracy,” which is evaluated for each analysis of the CRM or Matrix Spike by comparison of a given laboratory’s values to the “true” or “accepted” and the expected values. In the case of CRMs, this includes both certified and noncertified values. The “true” values are defined as the 95% confidence intervals of the mean.

3.3.3 Precision

The precision of data is a measure of the reproducibility of an analytical measurement when an analysis is repeated. It is reported in Relative Percent Difference (RPD) or Relative Standard Deviation (RSD). Laboratory replicate samples and MS/MSD samples will be run according to the frequency outlined in Table 3 of the Appendix. The Relative Percent Difference (RPD) will be calculated as a measure of precision.

¹ Certified reference materials (CRMs) are samples in which chemical concentrations have been determined accurately using a variety of technically valid procedures; these samples are accompanied by a certificate or other documentation issued by a certifying body (e.g., agencies such as the National Research Council Canada (NRCC), US EPA, US Geological Survey, etc.). Standard Reference Materials (SRMs) are CRMs issued by the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards (NBS).

3.3.4 Sensitivity of the Analytical Method

The method detection limit (MDL) is the ability of a method to distinguish between the analytical noise and the measurement signal and can be used to define the analytical limit of detectability. The MDL represents a quantitative estimate of low-level response detected at the maximum sensitivity of a method.

3.3.5 Completeness

Completeness is defined as “a measure of the amount of data collected from a measurement process compared to the amount that was expected to be obtained under the conditions of measurement” (Stanley and Verner, 1985). Ideally, 100% of the data would be available for interpretation. However, the possibility of data becoming unavailable, for example, due to laboratory error, insufficient sample volume, or samples broken in shipping must be expected. For this project, the target for completeness is 95%.

3.3.6 Representativeness

The representativeness of data is the ability of the sampling locations and the sampling procedures to adequately represent the true condition of the sample sites. Field personnel will strictly adhere to the field sampling protocols to ensure the collection of representative, uncontaminated samples. The most important aspects of quality control associated with chemistry sample collection are as follows:

- Field personnel will be thoroughly trained in the proper use of sample collection equipment and will be able to distinguish acceptable versus unacceptable samples in accordance with pre-established criteria.
- Field personnel will be thoroughly trained to recognize and avoid potential sources of sample contamination (e.g., dirty hands, insufficient field cleaning).
- Samplers and utensils that come in direct contact with the sample will be made of non-contaminating materials (e.g., glass, stainless steel, and/or inert chemical coatings) and will be thoroughly cleaned between sampling stations.
- Sample containers will be pre-cleaned and of the recommended type.

3.3.7 Comparability

Comparability is the degree to which data can be compared directly to other relevant studies. For this investigation, sampling and analytical methods were designed to be comparable to those employed in other studies of PCBs in sealants (references listed in section 1.1 of the ‘Field Sampling and Chemical Analysis Plan’ for this Project).

4. Laboratory Quality Assurance and Control

4.1 Laboratory Requirements

The analytical laboratory for the Project has the appropriate facilities to store, prepare, and process samples. Moreover, appropriate instrumentation and staff to provide data of the required quality within the project schedule are also required. Laboratory operations must include the following procedures:

- A program of scheduled maintenance of analytical balances, laboratory equipment, and instrumentation.
- Routine checking of analytical balances using a set of standard reference weights (American Society of Testing and Materials (ASTM) Class 3, NIST Class S-1, or equivalents).
- Checking and recording the composition of fresh calibration standards against the previous lot, wherever possible. Acceptable comparisons are $< 2\%$ of the previous value.
- Recording all analytical data in bound (where possible) logbooks, with all entries in ink, or electronic format.
- Monitoring and documenting the temperatures of cold storage areas and freezer units once per week.
- Verifying the efficiency of fume hoods.
- Having a source of reagent water meeting ASTM Type I specifications available in sufficient quantity to support analytical operations. The conductivity of the reagent water will not exceed 18 megaohms at 25°C. Alternately, the resistivity of the reagent water will exceed 10 mmhos/cm.
- Labeling all containers used in the laboratory with date prepared, contents, initials of the individual who prepared the contents, and other information, as appropriate.
- Dating and safely storing all chemicals upon receipt. Proper disposal of chemicals when the expiration date has passed.
- Having QAPP, SOPs, analytical methods manuals, and safety plans readily available to staff.
- Having raw analytical data, such as chromatograms, accessible so that they are available upon request. Laboratories will be able to provide information documenting their ability to conduct the analyses with the required level of data quality. Such information might include results from interlaboratory comparison studies, control charts and summary data of internal QA/QC checks, and results from certified reference material analyses. That laboratory should maintain all project related data for a minimum of five years.

4.2 Laboratory Personnel, Training, and Safety

Each laboratory providing analytical support for this project must have a designated on-site QC Officer for the particular analytical component(s) performed at that laboratory. This individual will serve as the point of contact for project staff in identifying and resolving issues related to data quality.

Personnel in any laboratory performing analyses for the project will be well versed in good laboratory practices, including standard safety procedures. It is the responsibility of the particular analytical component project officer, laboratory manager, and/or supervisor to ensure that safety training is mandatory for all laboratory personnel. Each laboratory is responsible for maintaining a current safety manual in compliance with the Occupational Safety and Health Administration (OSHA), or equivalent state or local regulations. The safety manual will be readily available to laboratory personnel. Proper procedures for safe storage, handling, and disposal of chemicals will be followed at all times; each chemical will be treated as a potential health hazard and good laboratory practices will be implemented accordingly.

4.3 Quality Assurance Documentation

The chemical laboratory will be provided with the Project QAPP. In addition, the following documents and information will be current, and will be available to all laboratory personnel participating in the processing of samples:

- Laboratory QA Plan: Clearly defined policies and protocols specific to a particular laboratory, including personnel responsibilities, laboratory acceptance criteria and corrective actions to be applied to the affected analytical batches, qualification of data, and procedures for determining the acceptability of results.
- Laboratory Standard Operating Procedures (SOPs): Containing instructions for performing routine laboratory procedures.
- Laboratory Analytical Methods Manual: Step-by-step instructions describing exactly how a method is implemented in the laboratory for a particular analytical procedure.
- Instrument Performance Information: Information on instrument baseline noise, calibration standard response, analytical precision and bias data, detection limits, etc. This information may be recorded in logbooks or laboratory notebooks or stored electronically.
- Control Charts: Control charts are useful in evaluating internal laboratory procedures and are helpful in identifying and correcting systematic error sources. Contract laboratories are encouraged to develop and maintain control charts whenever they may serve in determining sources of analytical problems.

4.4 Laboratory Performance Audits/Corrective Action

No additional performance audits will be required as part of this Project. However, participation in performance audits or other intercomparison studies are encouraged.

4.5 Laboratory Performance Measurements

Laboratory performance measurements (also known as Data Quality Indicators) are designed to determine whether data quality criteria are met, as defined below.

4.5.1 Method Blanks

Also called laboratory reagent blanks or preparation blanks, method blanks account for contaminants present in the solvents, preservatives, analytical solutions, or other laboratory equipment used during the quantification of the parameter.

4.5.2 Internal Standards

Internal standards account for error introduced by the analytical instrument.

4.5.3 Replicate Samples

Replicate samples of the raw material can be extracted and analyzed to measure laboratory precision or variability of a chemical in the material.

4.5.4 Laboratory Replicate Samples

Laboratory replicate samples are replicates of extracted material that assess the measurement precision.

4.5.5 Matrix Spike Replicate Samples

Matrix spike replicate samples are used to assess both measurement precision and accuracy. They are especially useful when field samples may not contain many of the target compounds because measuring non-detects in replicates does not allow the data reviewer to measure the precision or the accuracy of the data in an analytical batch.

4.5.6 Matrix Spike Samples

Matrix spike samples are field samples to which a known amount of contaminant is added and measured to determine potential analytical interference present in the field sample.

4.5.7 Certified Reference Materials (CRMs)

Analysis of CRMs is another way of determining measurement accuracy, especially if a CRM contains a certified value at concentrations similar to those expected in the samples to be analyzed. These types of samples serve to check if errors are introduced during the analysis process and at what step(s) and at what magnitude(s).

4.6 Laboratory Quality Control Procedures

The performance-based protocols for analytical chemistry laboratories consist of several elements, as follow:

4.6.1 Instrument Calibration

Upon initiation of an analytical run, after each major equipment disruption, and whenever on-going calibration checks do not meet recommended DQIs (Table 3, Appendix), the system will be calibrated with a full range of analytical standards. Immediately after this calibration procedure, the initial calibration must be verified through the analysis of a standard obtained from a source different from the standards used to initially calibrate the instrumentation. This second standard must be prepared independently and should ideally have certified concentrations of target analytes. Frequently, calibration standards are included as part of a run, interspersed with actual samples. However, this practice does not document the stability of the calibration and is incapable of detecting degradation of individual components, particularly pesticides, in standard solutions used to calibrate the instrument. The calibration curve is acceptable if it has a r^2 of 0.990 or greater for all analytes present in the calibration mixtures. If not, the calibration standards, as well as all the samples in the batch must be re-analyzed. All calibration standards will be traceable to a recognized organization for the preparation and certification of QA/QC materials (e.g., National Institute of Standards and Technology (NIST), National Research Council Canada (NRCC), US EPA, etc.).

Calibration curves will be established for each type of analyte and batch analysis from a calibration blank and a minimum of three analytical standards of increasing concentration, covering the range of expected sample concentrations. Only data from quantification within the demonstrated working calibration range may be reported by the laboratory (i.e., quantification based on extrapolation is not acceptable). Alternatively, if the instrument response is linear over the concentration ranges to be measured in the samples, the use of a calibration blank and one single standard that is higher in concentration than the samples may be appropriate. Samples outside the calibration range will be diluted or concentrated, as appropriate, and reanalyzed.

4.6.2 Documentation of Method Detection Limits

The method detection limit (MDL) is the ability of a method to distinguish between the analytical noise and the measurement signal and can be used to define the analytical limit of detectability. The MDL represents a quantitative estimate of low-level response detected at the maximum sensitivity of a method. The Code of Federal Regulations (40 CFR Part 136) gives the following definition: “The MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.” MDLs will initially be determined according to 40 CFR 136.2 (f) and Appendix B of 40 CFR 136. Determining the MDL with this procedure is elaborate and need not be determined annually provided that:

- No process or method changes have been made.
- Check samples containing an analyte spike at about 2x MDL indicate that the sample is detected. The required frequency of check samples is quarterly. The matrix and the amount of sample (i.e., dry weight of sediment) used in calculating the MDL will match as closely as possible the matrix of the actual field samples and the amount of sample typically used. In order to ensure comparability of results among different laboratories,

target MDL values for the initial chemical analytes have been established for the project. Most are considerably lower than water quality objectives or sediment quality guidelines and provide the foundation for having a high level of certainty in the data.

Laboratories will confirm the ability to analyze low-level samples with each batch. This will be accomplished by analyzing a method blank spiked at 3 to 5 times the method detection limit. Recoveries for organic analyses shall be between 50 and 150% for at least 90% of the target analytes.

4.6.3 Limits of Quantitation

Taylor (1987) states that “a measured value becomes believable when it is larger than the uncertainty associated with it.” The uncertainty associated with a measurement is calculated from the standard deviation of replicate measurements of a low concentration standard or a blank. Normally, the MDL is set at three times the standard deviation of replicate measurements, as it is at this point that the uncertainty of a measurement is approximately $\pm 100\%$ at the 95% level of confidence. Values at the MDL may not reflect a signal much above zero and, therefore, are quantitatively not very meaningful. The limit of quantitation (LOQ), as established by the American Chemical Society, is normally ten times the standard deviation of replicate measurements, which corresponds to a measurement uncertainty of $\pm 30\%$ (see Taylor, 1987). By these standard definitions, measurements below the MDL are not believable, measurements between the MDL and LOQ are only semi-quantitative, and confidence in measurements above the LOQ is high. Target MDLs for PCBs in sealant samples are shown in Table 2.

Table 2. Target Method Detection Limits (MDLs) for PCBs in Sealant Samples

Synonym	Analyte	Target MDL ($\mu\text{g}/\text{kg}$ dry weight)
IUPAC#8	2,4'-DICB	3.6
IUPAC#18	2,2',5'-TRCB	6.7
IUPAC#28	2,4,4'-TRCB	1.8
IUPAC#31	2,4',5'-TRCB	1.6
IUPAC#33	2',3,4-TRCB	2
IUPAC#44	2,2',3,5'-TECB	2
IUPAC#49	2,2',4,5'-TECB	0.64
IUPAC#52	2,2',5,5'-TECB	1.6
IUPAC#56	2,3,3',4'-TECB	0.78
IUPAC#56/60	2,3,3',4'/2,3,4,4'-TECB	2
IUPAC#60	2,3,4,4'-TECB	1.2
IUPAC#66	2,3',4,4'-TECB	0.92
IUPAC#70	2,3',4',5'-TECB	1.1
IUPAC#74	2,4,4',5'-TECB	1.1
IUPAC#70/74	2,3',4',5'/2,4,4',5'-TECB	2.2
IUPAC#77	3,3',4,4'-TECB	2
IUPAC#87	2,2',3,4,5'-PECB	2
IUPAC#87/97	2,2',3,4,5'/2,2',3',4,5'-PECB	4.8

IUPAC#95	2,2',3,5',6-PECB	0.99
IUPAC#97	2,2',3',4,5-PECB	2.8
IUPAC#99	2,2',4,4',5-PECB	1.5
IUPAC#101	2,2',4,5,5'-PECB	0.68
IUPAC#105	2,3,3',4,4'-PECB	3.5
IUPAC#110	2,3,3',4',6-PECB	2.9
IUPAC#118	2,3',4,4',5-PECB	3.4
IUPAC#126	3,3',4,4',5-PECB	5
IUPAC#128	2,2',3,3',4,4'-HXCB	1.5
IUPAC#132	2,2',3,3',4,6'-HXCB	2.3
IUPAC#138	2,2',3,4,4',5'-HXCB	2.1
IUPAC#141	2,2',3,4,5,5'-HXCB	2.1
IUPAC#149	2,2',3,4',5',6-HXCB	2
IUPAC#151	2,2',3,5,5',6-HXCB	1.9
IUPAC#153	2,2',4,4',5,5'-HXCB	1.9
IUPAC#156	2,3,3',4,4',5-HXCB	1.2
IUPAC#158	2,3,3',4,4',6-HXCB	2.3
IUPAC#169	3,3',4,4',5,5'-HXCB	2
IUPAC#170	2,2',3,3',4,4',5-HPCB	1
IUPAC#174	2,2',3,3',4,5,6'-HPCB	0.86
IUPAC#177	2,2',3,3',4',5,6-HPCB	1.4
IUPAC#180	2,2',3,4,4',5,5'-HPCB	0.93
IUPAC#183	2,2',3,4,4',5',6-HPCB	0.99
IUPAC#187	2,2',3,4',5,5',6-HPCB	0.78
IUPAC#194	2,2',3,3',4,4',5,5'-OCCB	0.98
IUPAC#195	2,2',3,3',4,4',5,6-OCCB	1.2
IUPAC#201	2,2',3,3',4,5',6,6'-OCCB	0.76
IUPAC#203	2,2',3,4,4',5,5',6-OCCB	1.2
IUPAC#209	DECB	5

4.6.4 Record of Certified Reference Material

As CRMs are routinely included in analysis of batches of reputable laboratories, the historical record of results may also serve as a suitable performance indicator.

4.6.5 Routine Analysis of Certified Reference Materials or Laboratory Control Materials

A laboratory control material (LCM) is similar to a certified reference material in that it is a homogeneous matrix that closely matches the samples being analyzed. A “true” LCM is one that is prepared (i.e., collected, homogenized, and stored in a stable condition) strictly for use in-house by a single laboratory. Alternately, the material may be prepared by a central laboratory and distributed to others (so-called regional or program control materials). Unlike CRMs, concentrations of the analytes of interest in LCMs are not certified but are based upon a statistically valid number of replicate analyses by one or several laboratories. In practice, this

material can be used to assess the precision (i.e., consistency) of a single laboratory, as well as to determine the degree of comparability among different laboratories. If available, LCMs may be preferred for routine (i.e., day to day) analysis because CRMs are relatively expensive. As noted in section 3.2, CRMs can not be analyzed in this Project.

4.7 Precision Criteria

Each laboratory is expected to maintain control charts for use by analysts in monitoring the overall precision of the CRM or LCM. Upper and lower control chart limits (e.g., warning limits and control limits) will be continually updated; control limits based on 99% confidence intervals around the mean are recommended. The relative standard deviation (RSD) will be calculated for each analyte of interest in the CRM based on the last 7 CRM analyses. However, as noted in section 3.2, CRMs can not be analyzed in this Project. Precision will be monitored by the analysis of replicate samples and continuing calibration check solutions (Table 3, Appendix).

4.8 Laboratory Replicates for Precision

A minimum of one sealant sample per batch of 20 samples or fewer will be processed and analyzed in duplicate for precision. The relative percent difference between two replicate samples or the relative standard deviation between more than two replicate samples (RPD or RSD respectively) will be less than the DQIs listed in Table 3 of Appendix B for each analyte of interest. Following are the calculations:

$$\text{RPD} = \frac{\text{ABS (rep 1 - rep 2)} \times 100}{\text{Average (rep 1, rep 2)}}$$

$$\text{RSD} = \frac{\text{STDEV (all replicate samples)} \times 100}{\text{Average (all replicate samples)}}$$

ABS — absolute value

STDEV — standard deviation

If results for any analytes do not meet the DQI for the RPD or RSD, calculations and instruments will be checked. A repeat analysis may be required to confirm the results. Results that repeatedly fail to meet the objectives indicate sample non-homogeneity, unusually high concentrations of analytes, or poor laboratory precision. In this case, the laboratory is obligated to halt the analysis of samples and investigate the source of the imprecision before proceeding. Due to the nature of the samples, sample homogeneity is likely to be the source of such imprecision.

4.9 Accuracy Criteria

Based on typical results attained by experienced analysts in the past, accuracy control limits have been established both for individual compounds and combined groups of compounds (see matrix spike and continuing calibration check solutions, Table 3 in the Appendix). Due to the inherent

variability in analyses near the method detection limit, control limit criteria for relative accuracy only apply to analytes with true values that are >3 times the MDL established by the laboratory.

4.10 Continuing Calibration Checks

Calibration check solutions traceable to a recognized organization must be inserted as part of the sample stream. The source of the calibration check solution shall be independent from the standards used for the calibration. Calibration check solutions used for the continuing calibration checks will contain all the analytes of interest. The frequency of these checks is dependent on the type of instrumentation used and, therefore, requires considerable professional judgment. All organic analyses shall be bracketed by an acceptable calibration check. A calibration check standard shall be run every 12 hours at a minimum.

If the control limits for analysis of the calibration check solution (set by the laboratories) are not met, the initial calibration must be repeated. The calibration check for 90% of the analytes shall not deviate more than $\pm 20\%$ for PCBs. If possible, the samples analyzed before the calibration check solution that failed the DQIs will be reanalyzed following recalibration. The laboratory will begin by reanalyzing the last sample analyzed before the calibration check solution that failed. If the RPD between the results of this reanalysis and the original analysis exceeds precision DQIs (Table 3, Appendix), the instrument is assumed to have been out of control during the original analysis. If possible, reanalysis of samples will progress in reverse order until it is determined that the RPD between initial and reanalysis results are within DQIs. The laboratory will report only the re-analysis results. If it is not possible or feasible to perform reanalysis of samples, all earlier data (i.e., since the last successful calibration control check) are suspect. In this case, the laboratory will prepare a narrative explanation to accompany the submitted data.

4.11 Laboratory Reagent Blanks

Laboratory reagent blanks (also called method blanks, extraction blanks, procedural blanks, or preparation blanks) are used to assess laboratory contamination during all stages of sample preparation and analysis. For PCB analyses, one laboratory reagent blank will be run in every sample batch. The reagent blank will be processed through the entire analytical procedure in a manner identical to the samples. Reagent blanks should be less than the MDL. A reagent blank concentration > 2x the MDL or > 10% of the lowest reported sample concentration for one or more of the analytes of interest will require corrective action to identify and eliminate the source(s) of contamination before proceeding with sample analysis. If eliminating the blank contamination is not possible, all impacted analytes in the analytical batch shall be flagged. In addition, a detailed description of the contamination source and the steps taken to eliminate or minimize the contamination shall be included in the narrative. Subtracting method blank results from sample results is not permitted.

4.12 Surrogates

The usage of the terms “surrogate,” “injection internal standard,” and “internal standard” varies considerably among laboratories. Surrogates are compounds chosen to simulate the analytes of

interest in organics analyses. Surrogates are used to estimate analyte losses during the extraction and clean-up process and must be added to each sample, including QA/QC samples, prior to extraction. Each laboratory must report the percent recovery of the surrogate(s) along with the target analyte data for each sample.

Each laboratory will set its own warning limit criteria based on the experience and best professional judgment of the analyst. It is the responsibility of the analyst to demonstrate that the analytical process is always “in control” (i.e., highly variable surrogate recoveries are not acceptable for repeat analyses of the same certified reference material and for the matrix spike/matrix spike duplicate).

4.13 Internal Standards

For gas chromatography (GC) analysis, internal standards (also referred to as “injection internal standards” by some analysts) are added to each sample extract just prior to injection to enable optimal quantification, particularly of complex extracts subject to retention time shifts relative to the analysis of standards. Internal standards are essential if the actual recovery of the surrogates added prior to extraction is to be calculated. The internal standards can also be used to detect and correct for problems in the GC injection port or other parts of the instrument. The compounds used as internal standards will be different from those used as surrogates. The analyst will monitor internal standard retention times and recoveries to determine if instrument maintenance, repair, or changes in analytical procedures are indicated. Corrective action will be initiated based on the judgment of the analyst. Instrument problems that may have affected the data or resulted in the reanalysis of the sample will be documented properly in logbooks and internal data reports and used by the laboratory personnel to take appropriate corrective action.

4.14 Dual-Column Confirmation

Dual-column chromatography is required for analyses using GC-ECD due to the high probability of false positives arising from single-column analyses. GC-ECD will not be used in this Project, however.

4.15 Matrix Spikes and Matrix Spike Duplicates

A laboratory-fortified sample matrix (a matrix spike, or MS) and a laboratory fortified sample matrix duplicate (a matrix spike duplicate, or MSD) will be used both to evaluate the effect of the sample matrix on the recovery of the compounds of interest and to provide an estimate of analytical precision. A minimum of 5% of the total number of samples submitted to the laboratory will be selected at random for analysis as matrix spikes and matrix spike duplicates. A field sample is first homogenized and then split into three subsamples. Two of these subsamples are fortified with the matrix spike solution and the third subsample is analyzed to provide a background concentration for each analyte of interest. The final spiked concentration of each analyte in the sample will be at least 10 times the MDL for that analyte, as previously calculated by the laboratory. Additionally, the total number of spikes should cover the range of expected concentrations. Recovery is the accuracy of an analytical test measured against a known analyte addition to a sample. Recovery is calculated as follows:

$$\text{Recovery} = \frac{(\text{Matrix plus spike result} - \text{Matrix result}) \times 100}{\text{Expected matrix plus spike result}}$$

Recovery data for the fortified compounds ultimately will provide a basis for determining the prevalence of matrix effects in the samples analyzed during the project. If the percent recovery for any analyte in the MS or MSD is less than the recommended warning limit of 50 percent, the chromatograms and raw data quantitation reports will be reviewed. If an explanation for a low percent-recovery value is not discovered, the instrument response may be checked using a calibration standard. Low recoveries of matrix spikes may result from matrix interferences and further instrument response checks may not be warranted. This is especially true if the low recovery occurs in both the MS and MSD, and the other QC samples in the batch indicate that the analysis was “in control.” An explanation for low percent-recovery values for MS/MSD results will be discussed in the narrative accompanying the data package. Corrective actions taken and verification of acceptable instrument response will be included. Analysis of the MS/MSD is also useful for assessing laboratory precision. The RPD between the MS and MSD results should be less than the target criterion listed in Table 3 of the Appendix for each analyte of interest.

4.16 Field Replicates

The analysis of field replicates and field splits can provide an assessment of both inter-and intra-laboratory precision and variance in the sample matrix at the field site. Field replicates will not be analyzed in this Project (see ‘Field Sampling and Chemical Analysis Plan’ for more information).

5. Assessments and Project Oversight

5.1 Contractor Quality Control

The Project Manager will ensure that qualified personnel are employed in all phases of project implementation and that all personnel receive appropriate training to complete assigned tasks consistent with project workplans.

5.2 Assessments and Response Actions

No audits of sampling personnel will be required as part of this project. However, before any field sampling is conducted, the Contractor Project Manager will verify that proper equipment is available for all field personnel. This includes sampling equipment, safety equipment, and field measurement equipment (if appropriate). It will also be verified that all personnel involved in field activities have received sufficient training and are able to properly use the equipment and follow procedures. The Project Manager may also verify the application of procedures and equipment periodically. If the Project Manager or Field Program Manager finds any deficiencies, corrective actions will be put in place and reported, and follow-on inspections will be performed to ensure the deficiencies have been addressed.

No audits of analytical laboratories will be performed as part of this project. However, it is

expected that regularly performed audits of the analytical laboratory are conducted through other quality assurance programs (e.g., RMP). The analytical laboratory is responsible for making any corrections needed to address data quality issues relevant to the project and to report these corrective actions to the Data Manager.

5.3 Reports to Management

In addition to the QAPP, the Field Sampling and Chemical Analysis Plan, and reports produced through the implementation of the project, quarterly progress reports will be developed and submitted to the Project Manager by the contractor. These progress reports will document project status, any significant field or laboratory issues, timeliness of scheduled field and analytical activities, any significant QA problems, or other issues, and provide recommended solutions, if applicable.

6. Data Validation and Usability

Data verification and data validation are key steps in the completion of the Project. The Project incorporates the following definitions:

6.1 Data Verification

Data verification is confirmation by examination and provision of objective evidence that specified requirements have been fulfilled. Data verification is the process of evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual requirements.

6.2 Data Validation

Data validation is confirmation by examination and provision of objective evidence that the particular requirements for a specific intended use are fulfilled. Data validation is an analyte- and sample-specific process that extends the evaluation of data beyond method, procedural, or contractual compliance (i.e., data verification) to determine the analytical quality of a specific data set.

6.3 Reconciliation with User Requirements

For laboratory data, when the data are reported to the Data Manager, if there is an outlier, data fails to meet DQIs, or other question arises with the data, the Data Manager is responsible for determining the acceptability of the data in question. Usually, the Project Chemist is contacted directly to resolve any questions. When the Data Manager is satisfied with the accuracy of the laboratory data in question, the data is considered acceptable and may be used as part of the overall dataset.

7. References

Astebro, A. et al. 2000. Emissions during replacement of PCB containing sealants – a case study. *Organohalogen Compounds* 46: 248-251.

Herrick, R.F. et al. 2004. An unrecognized source of PCB contamination in schools and other buildings. *Environmental Health Perspectives* 112:1051-1053.

Kohler, M. et al. 2005. *Environmental Science & Technology* 39: 1967-1973

Larry Walker Associates et al. 2006. PCB TMDL Implementation Plan Development. Prepared for CEP. Final Draft.

Lowe, S., R. Hoenicke, J. Davis, and G. Scelfo. 1999. *1999 Quality Assurance Project Plan, Regional Monitoring Program for Trace Substances*. San Francisco Estuary Institute, 1325 S. 46th Street, Richmond, CA 94804.

Melymuk, L. et al. 2008. Continuing sources of PCBs: the significance of building sealants. International Symposium on Halogenated Persistent Organic Pollutants, Birmingham, UK.

Moran, K. et al. 2007. Memorandum regarding ‘First Phase Support Information for PCB Portion of Taking Action for Clean Water Grant’. July 16 2007.

Puckett, M. 2002. *Quality Assurance Management Plan for the State of California's Surface Water Ambient Monitoring Program ("SWAMP")*. California Department of Fish and Game, Monterey, CA. Prepared for the State Water Resources Control Board, Sacramento, CA. 145 pages plus Appendices.

San Francisco Bay Water Board. 2004. PCBs in San Francisco Bay, TMDL Project Report, January 8.

San Francisco Bay Regional Quality Control Board (RWQCB). 2008. Total Maximum Daily Load for PCBs in San Francisco Bay: Final Staff Report for Proposed Basin Plan Amendment. http://www.waterboards.ca.gov/sanfranciscobay/water_issues/programs/TMDLs/sfbaypcbs/Staff_Report.pdf

Stanley, T.W. and S.S. Verner 1985. “The U.S. Environmental Protection Agency’s Quality Assurance Program.” In: *Quality Assurance for Environmental Measurements, ASTM STP 867*, J.K. Taylor and T.W. Stanley, Eds. American Society for Testing and Materials, Philadelphia, PA, pp.12–19.

Taylor J.K., 1987. *Quality Assurance of Chemical Measurements*. CRC Press Inc.

8. Appendix: Analytical Method for PCBs in Sealants



PCB CONGENERS BY GC/MS

1.0 SCOPE, APPLICATION, AND METHOD CAPABILITIES

- 1.1 This method is used for the determination of chlorinated biphenyl congeners (PCBs) in sediments, soils, and miscellaneous samples by gas chromatography/mass spectrometry.
- 1.2 The target analytes and current method detection limit (MDL) values can be reviewed on the Laboratory Service Division web site.

2.0 SUMMARY OF METHOD

- 2.1 Samples are homogenized and a sub-sample removed for moisture determination.
- 2.2 Samples (10 g wet weight) are spiked with a surrogate spiking solution and are extracted with 1:1 acetone/dichloromethane using a Dionex ASE extractor (SOP 325).
- 2.3 The extract is then dried through a sodium sulfate column and concentrated using a J2 Scientific AccuVap. An internal standard is then added to each extract and cleaned up with a one-step GPC.
- 2.4 An aliquot of the final extract is injected into the gas chromatograph (GC). The analytes are separated by the GC and detected by a mass spectrometer.

3.0 SAMPLE COLLECTION, PRESERVATION AND HOLDING TIMES

- 3.1 All samples must be iced or refrigerated at $<4^{\circ}\text{C}$ from time of collection until delivery to the laboratory. Store samples in the dark at $<-10^{\circ}\text{C}$.
- 3.2 There are no demonstrated maximum holding times associated with the PCBs in solid or other sample matrices. If stored in the dark at $<-10^{\circ}\text{C}$, solid samples may be stored for up to one year.

4.0 COMMENTS

- 4.1 Raw data from all blanks, samples, and spikes must be evaluated for interference. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.
- 4.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, thoroughly wash and rinse glassware, vessels, and syringes between samples. Whenever an unusually concentrated sample is encountered, it



should be followed by the analysis of solvent to check for cross contamination.

5.0 SAFETY

- 5.1 General laboratory practices for handling organic solvents apply to working with dilute PCB standards. In accordance with [Safety SOP 214](#), use approved eye protection and wear nitrile gloves. Prepare dilutions and spiked samples in a fume hood.
- 5.2 Chemical and other safety relation information is contained in the Material Safety Data Sheets (MSDS) that are maintained in the Laboratory Library and are available on-line at <http://hazard.com/msds/> and <http://msds.ehs.cornell.edu/msdssrch.asp>.

6.0 INSTRUMENTATION/EQUIPMENT

- 6.1 Dionex Accelerated solvent extraction (ASE) system- pre-extracted
- 6.2 Whatman 19.8 mm glass fiber filter (Dionex P/N 047017), or equivalent muffled.
- 6.3 Aluminum weighing dishes (VWR 25433-008 or equivalent)
- 6.4 Chromatography columns w/o reservoir, solvent rinsed stopcocks
- 6.5 Disposable Pasteur pipettes
- 6.6 Gel-permeation chromatography system - an HPLC pump, an auto sampler, and a fraction collector.
 - 6.6.1 GPC- Chromatographic column- Envirogel GPC Cleanup Column 19mm ID x 300mm Methylene Chloride (WAT036554, or equivalent)
- 6.7 GC columns- suggested 30 m x 0.25 mm ID 0.25 μ m film SPB-octyl capillary column (Supelco 2-4218, or equivalent). Retention time specified in Table 2 must be met prior to performing analyses.
- 6.8 Automated concentration system – AccuVap Inline & FLX Concentration System or AccuVap EVS
- 6.9 Perkin Elmer Clarus 500 GCMS, or equivalent, capable of scanning from 50 to 600 amu.

7.0 REAGENTS AND STANDARDS

- 7.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water produced by a Millipore Milli-Q system.



- 7.2 Native congener mix stock solutions for separation of individual congeners on the SPB-octyl column. Purchase Accustandard M1668A-1, M1668A-2, M1668A-3, M1668A-4, M1668A-5, or equivalent. The five solutions, measured individually, allow resolution of all 209 congeners to establish retention times for each congener.
- 7.3 Individual stock solutions of congeners of interest (Accustandard and Ultra Scientific).
- 7.4 Internal Standard: Tetrachloro-m-xylene Accustandard S-279-5x
- 7.5 Surrogate Solution: IUPAC #103 & #198 100ug/mL in isooctane. Accustandard C-103S-TP and C-198S-TP.
- 7.6 Acetone, methylene chloride and other appropriate solvents - Pesticide quality or equivalent.
- 7.7 Pelletized diatomaceous earth. Varian 0019-8003 or equivalent. Muffled.
- 7.8 Sodium sulfate. Muffled.
- 7.9 Ottawa sand. Muffled.
- 7.10 Glass Wool. Muffled.

8.0 PROCEDURE

8.1 Instrument Operating Conditions

Initial temperature:	75 °C, hold for 2 minutes
Temperature program:	15 °C/min to 150 °C, 2.5 °C/min to 290 °C, hold 1 min.
Sample volume:	2.5 µL
Injector temperature:	260 °C
Interface temperature:	250 °C
Flow:	1.0 ml/min
Scan Range:	10-62 min at 181-508 amu
Scan Time:	0.35 second

The GC conditions may be optimized for compound separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, blanks, and QC samples.

8.2 Preparation of Calibration and Check Standards

- 8.2.1 Combine and dilute the solutions in section 7.2 to produce at least 5 calibration solutions of the individual PCBs between 50 and 3770 ng/mL or higher if necessary.



8.2.2 A check standard (CCC), containing all congeners of interest is prepared at a concentration of 1000 ng/mL for native compounds and 500 ng/mL for the internal standard and surrogates (IUPAC 103&198).

8.3 Preparation of QC Samples

8.3.1 Spike/LCS standards - Prepare a standard solution containing all the PCBs of interest at concentrations of 1.0 µg/mL. Use 1.0 mL of the 1.0 µg/mL solution for spike blank and matrix spike samples. Use 150 µL for the LCS samples.

8.3.2 Surrogate solution - This solution is added to every sample (client and QC) before extraction. The solution contains congeners 103 and 198 at 0.50 µg/ml. Spike each sample with 1.0 mL.

8.4 Sample Preparation

8.4.1 Samples, duplicates, and matrix spikes are homogenized and a 10 gram subsample is weighed for extraction. Use a smaller sample size if the sample matrix is expected to be dirty or contains very high concentrations of PCBs. An additional subsample of each sediment samples is weighed for % solid determination. The sample for extraction, after weighing, is mixed with pelletized diatomaceous earth until a dry, free-flowing mixture is obtained. This mixture is then placed into an ASE extraction cell. Add the surrogate solution (1.0 mL of 8.3.2) and, if needed, the appropriate amount of spiking standard (8.3.1) to the ASE vessels. Extract the sample with 1:1 acetone/dichloromethane at elevated temperature and pressure. Total extraction time is ~ 30 min. See [SOP 325](#) for operational details.

8.4.2 The method blank, LCS, and spike blank samples are prepared with 10 grams of muffled Ottawa sand.

8.4.3 The extracts are dried with muffled granular Na₂SO₄.

8.4.4 If an aqueous layer is visible in the extract, slowly add about 16.5 gm of muffled Na₂SO₄ to extract and mix well prior to pouring extract into drying column.

8.4.5 Dried extracts are to be evaporated to dryness and diluted to 2.5 mL of MeCl₂ for GPC using an AccuVap.

8.4.6 Prior to GPC, filter the 2.5 mL extract through a 0.45µ PVDF Captiva 3mL columns if necessary.

8.4.7 Add 10 µL of internal standard into every extract. Bring volume to 2.5 mL.

8.4.8 Set up GPC clean-up with inline evaporation per [SOP 356](#).

8.4.9 Remove final extracts promptly upon completion of GPC clean-up and concentration. Replace slit septa caps with crimp caps.

9.0 CALIBRATION

9.1 Mass spectrometer calibration

- 9.1.1 Supelco SPB-Octyl fused silica capillary column (C/N 24218-U 30m x 0.25mm x 0.25µm film thickness) or comparable should be used.
- 9.1.2 The GC/MS system must be hardware-tuned to meet the criteria in Table 1 for a 50 ng injection of DFTPP. Analyses should not begin until all these criteria are met. Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions.

Table 1
DFTPP Key Ions and Ion Abundance Criteria
(EPA 625 Criteria)

Mass	Ion Abundance Criteria
51	30-60% of base peak of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40-60% of base peak
197	< 1% of mass 198
198	Base peak, defined as 100%
199	5-9% of mass 198
275	10-30% of mass 198
365	> 1% of base peak
441	Present but less than mass 443
442	> 40% of mass 198
443	17-23% of mass 442

9.2 Quantitative analysis

- 9.2.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary ions (Table 2).
- 9.2.2 If the %RSD of a compound's relative response factor (initial calibration) is 15% or less, then the concentration in the extract may be determined using the average response factor from the initial calibration data. Alternatively, a linear or quadratic regression with a coefficient of variance >0.998 may be used.
- 9.2.3 Use the data system to compute the concentration of the analyte in the sample, using an internal standard calibration. Calculate the concentration of the analyte in the initial sample.



Table 2 – Target Analytes, Retention Times, Selected Ions, and References

Compound	Retention Time	m/z	Reference
Tetrachloro-m-xylene	15.90	242+244	Internal Standard
IUPAC 103 (Surrogate)	28.37	324+326	Tetrachloro-m-xylene
IUPAC 198 (Surrogate)	47.89	428+430	Tetrachloro-m-xylene
IUPAC 8	16.96	222+224	IUPAC 103
IUPAC 18	19.18	256+258	IUPAC 103
IUPAC 28	23.24	256+258	IUPAC 103
IUPAC 31	22.93	256+258	IUPAC 103
IUPAC 33	23.46	256+258	IUPAC 103
IUPAC 44	26.10	290+292	IUPAC 103
IUPAC 49	25.58	290+292	IUPAC 103
IUPAC 52	25.08	290+292	IUPAC 103
IUPAC 56	31.03	290+292	IUPAC 103
IUPAC 60	31.25	290+292	IUPAC 103
IUPAC 66	30.34	290+292	IUPAC 103
IUPAC 70/74	30.01	290+292	IUPAC 103
IUPAC 87/97	33.30	326+328	IUPAC 103
IUPAC 95	29.08	326+328	IUPAC 103
IUPAC 99	32.67	326+328	IUPAC 103
IUPAC 101	32.08	326+328	IUPAC 103
IUPAC 105	38.42	326+328	IUPAC 103
IUPAC 110	34.12	326+328	IUPAC 103
IUPAC 118	37.18	326+328	IUPAC 103
IUPAC 126	41.64	326+328	IUPAC 198
IUPAC 128	41.65	358+360+362	IUPAC 198
IUPAC 132	39.05	358+360+362	IUPAC 198
IUPAC 138	40.34	358+360+362	IUPAC 198
IUPAC 141	39.26	358+360+362	IUPAC 198
IUPAC 149	35.96	358+360+362	IUPAC 198
IUPAC 151	35.00	358+360+362	IUPAC 198
IUPAC 153	37.26	358+360+362	IUPAC 198
IUPAC 156	44.59	358+360+362	IUPAC 198
IUPAC 158	40.73	358+360+362	IUPAC 198
IUPAC 170	47.28	394+396+322+324+326	IUPAC 198
IUPAC 174	42.30	394+396+322+324+326	IUPAC 198
IUPAC 177	43.01	394+396+322+324+326	IUPAC 198
IUPAC 180	45.98	394+396+322+324+326	IUPAC 198
IUPAC 183	42.30	394+396+322+324+326	IUPAC 198
IUPAC 187	41.67	394+396+322+324+326	IUPAC 198
IUPAC 194	52.56	428+430+432+356+358+360	IUPAC 198
IUPAC 195	50.17	428+430+432+356+358+360	IUPAC 198



Compound	Retention Time	m/z	Reference
IUPAC 201	44.00	428+430+432+356+358+360	IUPAC 198
IUPAC 203	48.81	428+430+432+356+358+360	IUPAC 198
IUPAC 209	56.33	494+504+424+432+214	IUPAC 198

10.0 QA/QC REQUIREMENTS

- 10.1 The batch QC Requirements are outlined in Table 3.
- 10.2 No more than 20 client samples can be included in an analytical batch.
- 10.3 Compute the percent recovery of the surrogate standard spiking solution using an internal standard calibration method.
- 10.4 Analyze the method blank immediately after the LCS to analyze freedom from contamination and carryover from the LCS.

Table 3 – Batch QC Requirements

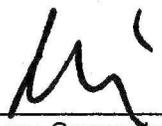
QC Type	Batch Requirement	Acceptance Criteria	Corrective Action
MS tuning check	Prior to analyzing samples	See Table 1 and section 8.5	Retune and adjust the MS
Calibration	Acceptable calibration	RF <20% RSD, or if using 1 st or 2 nd order regression, =/> 0.998	Correct instrument or standard problem. Recalibrate.
Spike Blank	Fortify at same concentration as MS samples	+/- 30 % recovery	Requires reextraction and reanalysis if more than 10% of the analytes fail to meet acceptance criterion.
Continuing Calibration Check	1 at the beginning of each analytical run, every 12 hrs and at the end of the run. Concentration at cal mid-range.	+/- 20% recovery.	Recalibrate. Rerun with fresh standard if CCC continues to fail. If recoveries are outside of the control limits flag sample with "N".
Low Level Spike Blank (LCS)	1 per batch. Concentration at lowest calibration level.	+/- 50% recovery.	If recoveries are outside of the control limits flag sample with "N".
Method Blank	1 per batch.	Target analytes below MDL.	Reanalyze method blank to confirm. May require re-extraction and reanalysis. Flag detected compounds in samples that are also present in the blank with a "B".



QC Type	Batch Requirement	Acceptance Criteria	Corrective Action
Matrix Spike	1 per batch or 10% of samples. Spike concentration set at the calibration mid-level.	±35% recovery	Flag spiked sample and base with "N", if recoveries are outside control limits.
Matrix Duplicate	1 per batch or 10% of samples.	Acceptance Criteria < 50 % RPD for concentrations > 10 MDL for 90% of analytes	Flag outliers with "**", samples < 10 MDL flagged with a V. Requires re-extraction and re-analysis if more than 10% of the analytes fail to meet the acceptance criterion.

11.0 REFERENCES

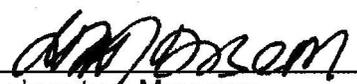
- 11.1 EPA Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment and tissue by HRGC/HRMS, Revision A (1999). U.S. EPA, Office of Science and Technology, 401 M Street, SW, Washington, DC, 20460.
- 11.2 EPA Method 625. Base/Neutral and Acids. 40 CFR Part 136 Appendix A. Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater. Revised as of July 1st, 1995.
- 11.3 EPA Method 8270D, Revision 4, February 2007. Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS). SW846 On-line.
<http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/8270d.pdf>



Laboratory Supervisor



Quality Control Assurance Officer



Laboratory Manager