

Quality Assurance Project Plan
for the
**Regional Stormwater Monitoring and Urban BMP Evaluation: A
Stakeholder Driven Partnership to Reduce Contaminant Loadings**

SWRCB Agreement No. 04-139-552-0

Prepared for:

**San Francisco Regional Water Quality Control Board
Bay Area Stormwater Management Agencies Association**

**San Francisco Estuary Institute
GeoSyntec**

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July 27th, 2006

GROUP A: PROJECT MANAGEMENT

1. TITLE AND APPROVAL SHEETS

Quality Assurance Project Plan

For

PROJECT NAME: Regional Stormwater Monitoring and Urban BMP Evaluation: A Stakeholder Driven Partnership to Reduce Contaminant Loadings

PROPOSAL ID NUMBER: SWRCB Agreement No. 04-139-552-0

DATE: July 27, 2006

RESPONSIBLE ORGANIZATION: San Francisco Estuary Institute

REVISION NUMBER: 1

APPROVAL SIGNATURES

(Add or delete signature lines as needed)

GRANT ORGANIZATION:

APPROVAL SIGNATURES

GRANT ORGANIZATION:

GRANT ORGANIZATION:

Project Manager: _____

Signature: _____ Date: _____

QA Officer: _____

Signature: _____ Date: _____

The signatures of the above indicate both approval of the plan and commitment to follow the procedures noted.

REGIONAL BOARD (SWRCB):

Contract Manager: _____

Signature: _____ Date: _____

QA Officer: _____

Signature: _____ Date: _____

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LIST OF STANDARD OPERATING PROCEEDURES

<i>Equipment / Instrument</i>	<i>SOP reference</i>
DMA80	EPA 7473
GC/ECD	EPA 8082
GC/MS	EPA 1668
CHN analyzer	EPA 415.1, 440.0

Appendix A. Example field data and chain of custody forms

3. DISTRIBUTION LIST

(Numbers in parentheses indicate number of copies)

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If the QAPP is being prepared under the jurisdiction of the State Water Resources Control Board (SWRCB) rather than a Regional Board (RWQCB), substitute the SWRCB information for the RWQCB information.

Number each individual copy of the QAPP sent to the above persons. Then it will be easier to ensure that all older versions of the QAPP are retrieved when those named on the distribution list receive the updated QAPP.

4. PROJECT/TASK ORGANIZATION

4.1 Involved parties and roles.

Table 1 presents critical contact representatives for the Study. Figure 1 shows the project organization.

Table 1. (Element 4) Key Personnel responsibilities.

Name	Organizational Affiliation	Title	Contact Information (Telephone number, fax number, email address.)
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The Urban BMP 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.

Contract Manager (SWRCB / Water Board)

The Contract Manager at the State Water Resources Control Board (SWRCB) / San Francisco Bay Regional Water Quality Control Board (Water Board) will be responsible for ensuring that all work performed through the SFEI Prop 13 Grant Project is consistent with grant proposal and project objectives. The Contract Manager will review all workplans produced as a result of the project implementation prior to their implementation. The Contract Manager will be notified of any proposed deviations from project proposal or workplans, and will need to give approval of major deviations.

Project Manager (SFEI)

The Project Manager will be responsible for oversight of day-to-day efforts associated with the Urban BMP Grant Project. The Project Manager will be responsible for planning and implementation of the data collection and interpretation program. Additionally, the Project Manager will act as the liaison between Subcontractors (GeoSyntec, AXYS Analytical, and Moss Landing Marine Laboratories) and the Contract Manager. The Project Manager will also be responsible for ensuring that sampling personnel adhere to the provisions of the Monitoring Plan (MP) and the Quality Assurance Project Plan (QAPP) and for custody of samples until receipt by analytical laboratory. Oversight of all efforts performed by the Subcontractors,

including field sampling, laboratory analysis, data interpretation, and reporting are also the responsibility of the Project Manager.

Data Manager (SFEI)

The Data Manager will be responsible for receipt and review of all project related documentation and reporting associated with both field efforts and analysis.

Quality Assurance Officer (SFEI)

The project quality assurance (QA) officer and will be responsible for verifying compliance of all analytical data with the requirements established by the Urban BMP Grant Project QAPP before its use for interpretive purposes. Analytical data will be generated by AXYS Analytical and MPSL-DFG. Subcontract laboratories will perform analyses of the samples collected independent of SFEI. The Project QA Officer will be responsible for maintaining and making changes to the QAPP as needed. The SFEI QA officer will not work on any other part of the project. All data generation will be carried out completely independently from the QA process.

Quality Assurance Officer (Water Board)

The Water Board quality assurance (QA) officer and will be responsible for verifying that the SFEI project manager and team have followed all the QA procedures as specified by the Grant and interpreted in the Quality Assurance Project Plan.

Technical Support (GeoSyntec)

GeoSyntec will assist during the data collection and with the interpretation of the data collected.

Subcontractor Laboratories

The Laboratory Project Manager and Chemists at each selected analytical laboratory will be responsible for ensuring that the laboratory's quality assurance program and standard operating procedures are consistent with the Urban BMP Project QAPP, and that laboratory analyses meet all applicable requirements or explain any deviations. The Laboratory Project Manager will also be responsible for coordinating with the SFEI Project Manager and other staff (e.g. Data Manager, QA Officer) as required for the project. Analyses for trace organic compounds and organic carbon will be performed by AXYS Analytical Ltd., P.O. Box 2219, Mills Road West, Sidney, British Columbia, Canada (AXYS). Analyses for Hg and suspended sediment concentrations and grainsize will be conducted at the Moss Landing Marine Pollution Studies Laboratory – Department of Fish and Game, 7544 Sandholdt Road, Moss Landing CA 95039 (MPSL-DFG).

Other Collaborator (Bay Area Stormwater Management Agencies Association (BASMAA))

The Bay Area Stormwater Management Agencies Association (BASMAA) is an important and integral part of the oversight team on this project. Through attendance in meeting, phone conferences and phone calls, they provide substantial in-kind services and guidance on the project. BASMAA will continue to fill the oversight role and in addition assist with the selection of monitoring locations, field logistics, and permission to access field locations (encroachment permits etc). BASMAA will coordinate its involvement through the Project Manager, and will be encouraged to review and comment on all aspects of the Urban BMP Grant Project, including the project MP and QAPP.

Several Bay Area groups are interested in the methods being explored by the Urban BMP Grant Project as a potential tool for controlling sediment-associated TMDL pollutants in urban runoff, including the Sources Pathways and Loadings Work Group (SPLWG) of the Regional Monitoring Program (RMP), and the PCB and Hg Work Groups of the Clean Estuary Partnership (CEP), a coalition of BASMAA, the Bay Area Clean Water Agencies (BACWA), and the Regional Water Board. To help these groups disseminate relevant information among related projects and stakeholders, BASMAA will serve as liaison between these groups and the Project through the following activities:

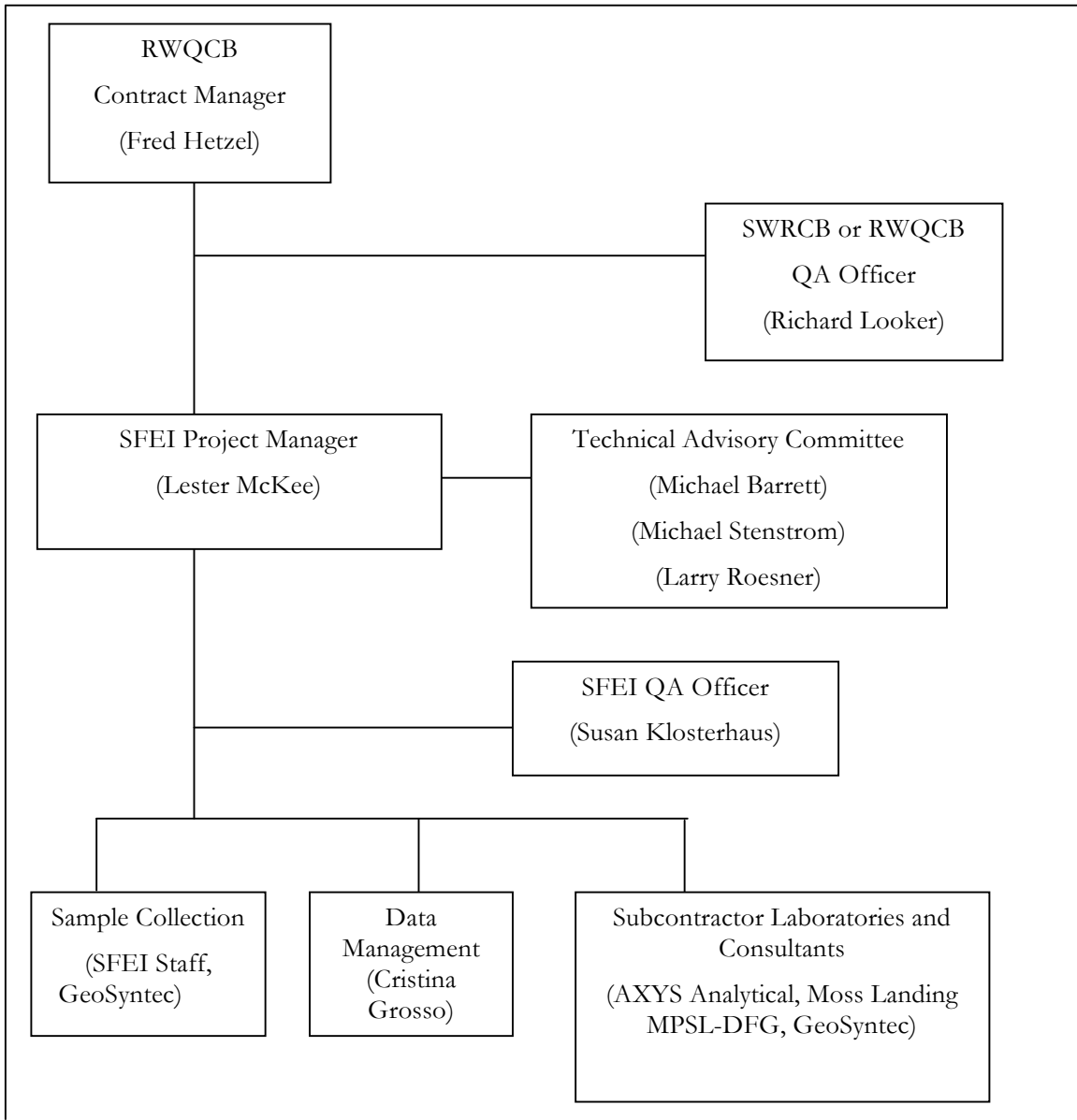
- Attending meetings

- Addressing information requests by these groups that are not addressed by the deliverables and schedule of the Urban BMP Grant Project.
- Providing selected documents upon request and soliciting review of draft products.

BASMAA will support the above communications where practicable within the timeline established for the Urban BMP Grant Project.

4.4 Organizational chart and responsibilities

Figure 1. Project Organization Chart



5. PROBLEM DEFINITION/BACKGROUND

5.1 Problem statement.

Introduction

High concentrations of PCBs and Hg in fish tissue were factors in the Office of Environmental Health Hazard Assessment (OEHHA) issuing an interim health advisory for people consuming fish from San Francisco Bay (OEHHA, 1997). This in turn led the San Francisco Bay Regional Water Quality Control Board (Water Board) to list the Bay as impaired by PCBs and Hg. The Water Board is currently developing a Total Maximum Daily Load (TMDL) for PCBs in San Francisco Bay (SFBRWQCB, 2003a) and has completed the TMDL report for Hg (SFBRWQCB, 2003b). Both TMDLs assert the significance of urban runoff and call for more, improved, and enhanced best management practices (BMPs) in urban areas to reduce nonpoint source loadings of these contaminants in urban runoff. However, there is presently no consensus on which BMPs to apply in urban areas to best address this call. This project aims to develop plans to implement the Hg and PCB TMDLs through the development of specific information on urban runoff BMPs and pollutant loadings and to address the Region 2 specific priority 204 ["...implementation strategies associated with Total Maximum Daily Loads (TMDLs)"].

Study Purposes

The purpose of this project is to generate an improved understanding of the effectiveness of stormwater management in the Bay Area and prioritize the implementation of further efforts to improve Bay water quality. The final outcome will be two implementation plans, one for PCBs and one for Hg that describe (through stakeholder censuses based on sound scientific input) the application of BMPs (source control, treatment control and maintenance activities) and scenario's (combinations of these BMPs) to apply under each current or historic use category or land use situation. These need to be compatible with BMPs developed to control other pollutants of concern. The products and information from this project will be important tools for local runoff managers who need to effectively allocate resources to make load reductions for TMDL pollutants. Many of the outcomes of the project (in particular, the BMP review and evaluation tasks) will be applicable to similar efforts in other regions of California and overall the project will serve as a template for other areas of California.

Details of the Study are presented in the sampling and analysis work plan (see Appendix B. A summary of the study design is presented below (Section 6).

5.2 Decisions or outcomes.

The desired outcome is measurements of the distribution of PCBs and mercury in urban watersheds that will facilitate development of methods to effectively reduce their impact on local ecosystems.

5.3 Water quality or regulatory criteria

This information is not being collected to satisfy regulatory criteria, although the information generated will be used in developing strategies for implementing TMDLs in the region.

6. PROJECT/TASK DESCRIPTION

6.1 Work statement and produced products.

The overall project is organized in to major phases:

- 1) An existing information and data review and data gaps analysis;
- 2) Further data compilation and field data collection and sampling to fill data gaps;
- 3) The development of two implementation plans that will outline a recipe for addressing the load reduction objectives outlined in the TMDLs.

This Monitoring Plan (MP) addresses the second phase of the project. In order to achieve the project purpose (an improved understanding effectiveness of BMPs and prioritization for the implementation of BMPs for Hg and PCB management in urban areas) phase 2 of the project focuses on existing data analysis using a geographic information system (GIS) and field data collection. SFEI project staff with assistance from GeoSyntec project staff will compile existing spatial data including storm sewershed boundaries, sediment source estimates, BASMAA bed sediment mercury and PCB concentrations, car wrecking facilities, PG&E facilities, railway lines, stormwater pump stations, first flush volume estimates, annual flow volume estimates, and wastewater treatment facilities. These data will be used to help prioritize watersheds and storm sewersheds for collections of soil, sediment and water samples. We will then collect between 400-500 samples for analysis of PCB, Hg, and organic carbon concentrations. About 80 of these will be analyzed for grain size distribution, about 120 will be analyzed for suspended sediment concentration, and about 30 samples will be analyzed for concentrations of PCBs and Hg in three grain size fractions (<25, 25-75, >75 micron) to provide information for structural treatment options for stormwater. At the end of the sampling and analysis we should have information on concentrations of Hg found in soils, sediments, and water in key areas known to be contaminated, concentrations of Hg and PCBs in three grain sizes in road dust, street sweeping material, and street washing water and an evolving consensus through stakeholder (BASMAA and Water Board Staff) on BMP scenarios to achieve loads reductions.

6.2. Constituents to be monitored and measurement techniques.

The Study will focus on PCBs and mercury, with measurements of organic carbon and particle grain size distribution to develop a better understanding of pollutant partitioning and transport in these urban watersheds. In the reconnaissance sampling of watersheds covering a large number of sites, analyses of bulk (unfractionated) samples for total PCBs (as Aroclors) and total mercury will be conducted to identify potential sites for more detailed study. Follow up studies at selected sites will investigate mercury concentrations in specific size fractions of sediment and runoff as well as individual PCB congeners in those fractions.

6.3 Project schedule

An abbreviated timetable for sampling and analytical portions of the Project is presented below.

Table 2. (Element 6) Project schedule timetable.

Activity	Anticipated Date of Initiation	Anticipated Date of Completion	Deliverable	Deliverable Due Date
Field Sample Collection	January 1, 2007	July 30, 2007	Samples delivered to laboratory	Hours to days after collection depending on analytical hold times
Sample Analysis	May 10, 2007	September 31, 2007	Samples chemically analyzed & reported	Within 2 months of receipt
Data Management and Reporting	January 1, 2007	October 30, 2007	Sampling and analysis data reported	Within 1 month of lab reporting
Data analysis and Final Report	November 1, 2007	December 31, 2007	Draft and final reports	Before termination of project

6.4 Geographical setting

Although data synthesis components of the Project will include data from all nine counties discharging to the San Francisco Bay, field operations in this Project will be conducted in selected watersheds within the San Francisco Bay region, within the counties of San Francisco, San Mateo, Santa Clara, Alameda, and Contra Costa. Study areas will be in selected urbanized portions of watersheds within those counties as follows:

Richmond – Hensley St. area	San Jose – South 7 th . St. area
Richmond – Hensley St. near the intersection with Richmond Pkwy.	San Jose – South 7 th . St. area at the end of Needles Drive.
Richmond – Harbor area	Sunnyvale – HENDY Av. area
Richmond – Harbor area, West Ohio Ave near Garrard Blvd.**	San Carlos – Southern Pacific Strip (between SPR and Hwy 101)
Oakland – Ettie St.	San Carlos – Southern Pacific Strip – Harbor Blvd/Taylor Wy.
San Leandro – 880 corridor (east and west)	South San Francisco – San Mateo Av. area
Hayward – Zone 4	South San Francisco – San Mateo Av. area on South Linden Av.
Hayward – Zone 4 at Cabot Blvd.	Daly City – Bayshore Blvd. area
San Jose – Airport area	

6.5 Constraints

This portion of the project is constrained by its budget and the need to complete work within the granted time. Additional constraints may include restricted access to some sites further investigations following results of samples collected from publicly accessible areas.

7. QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

7.1 Data Quality Objectives

Table 3. Summary of primary measurements.

Measurement or Analyses Type	Applicable Data Quality Objective
PCBs, mercury	Sensitivity, Accuracy, Precision, Completeness
TOC, SSC, grain size	Sensitivity, Accuracy, Precision, Completeness
Site notes (GPS and narrative)	Accuracy, Precision, Completeness

The quantitative measurements that estimate the true value or concentration of a physical or chemical property always involve some level of uncertainty. The uncertainty associated with a measurement generally results from 1) natural variability of a sample; 2) sample handling conditions and operations; 3) spatial and temporal variation; and 4) variations in collection or analytical procedures. Stringent QA and QC procedures are essential for obtaining unbiased, precise, and representative measurements and for maintaining the integrity of the sample during collection, handling, and analysis, as well as for measuring elements of variability that cannot be controlled. Stringent procedures also must be applied to data management to assure that accuracy of the data is maintained.

Data Quality Objectives (DQOs) are established to ensure that data collected are sufficient and of adequate quality for the intended use. DQOs include both quantitative and qualitative assessment of the acceptability of data. The qualitative goals include representativeness and comparability, and the quantitative goals include completeness, sensitivity (detection and quantization limits), precision, accuracy, and contamination.

Field measurements for the project consist primarily of notes taken at the collection site and any known watershed activities that might influence data interpretation (such as construction activities), with geographic location (latitude and longitude) and narrative notes to pinpoint the precise location and details of the sample collection. DQOs for the field operations are to document collections precisely enough the same site can be

resampled at a later date to within approximately 1 meter. Prior to use in the field, any GPS equipment should be tested for accuracy from a known location. The goal for completeness is to have notes for all (>99%) sites where samples are collected sufficient to allow resampling of the sites.

DQOs for the laboratory analytical components of the Study are elaborated in sections below, and a summary of the DQOs is presented in Tables 4a and 4b.

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 are 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 are 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, butyrate tubing, and/or inert chemical coatings) and will be thoroughly cleaned between sampling stations.
- Separate samples will be collected for each analysis, thus avoiding the need for sub-sampling and sample splitting between labs— when this is not possible for logistical reasons such as insufficient material available, 1) some of the analyses (to be selected by the Project Manager, as appropriate for the collection method, sample containers, and preservation/storage) will not be conducted on those samples, or 2) SFEI staff, or the first laboratory to receive the sample, will process and split the sample in a manner as recommended by all other laboratories to receive subsamples and 3) the data will be flagged according to field notes.
- Sample containers will be pre-cleaned and of the recommended type.

Although the information review phase of the Project included data on possible sources from all counties surrounding San Francisco Bay, collected samples are not expected to be fully inclusive of the entire region given limited time and resources. Areas of focus include those for which sufficient supporting information about infrastructure for potential management practices will be readily available within the Project time frame.

Comparability

Comparability is the degree to which data can be compared directly to other relevant studies. For this investigation, sampling and analytical methods were adapted from those employed for the RMP (Lowe et al., 1999, Bell et al., 1999) and the previous investigations undertaken by the ACCWP (Gunther et al. 2001, Salop et al., 2002) in order to facilitate comparability among results of the various investigations. Although the first component of the Project (e.g. reconnaissance surveys) may employ PCB analytical methods less sensitive and specific (i.e. Aroclor rather than congener methods) than those in some of the previous cited studies, for the objectives of the survey component, the decrease in comparability is less critical than the increase in sample numbers possible through use of less expensive analytical methods. Followup sample collection and analyses for some of these sites can be used to assess the comparability of the survey methods to more sensitive and specific analyses (e.g. PCB congeners) used later in this Project and previously in other studies.

No data will be accepted as primary data within this project except those data collected under the guidelines of this QAPP. Any data derived from the review of the work of others will be referenced and discussed taking into account the level of knowledge about its data quality.

Completeness

Completeness is defined as the percentage of valid data collected and analyzed compared to the total expected to be obtained under normal operating conditions. Overall completeness accounts for both sampling (in the field) and analysis (in the laboratory) completeness. Valid samples include those for compounds in which the concentration is determined to be below detection limits.

Completeness is expressed as overall completeness for a given parameter for each component of the Project (e.g. for reconnaissance of PCBs in samples from ~100 sites). Under ideal circumstances, the objective is to collect 100 percent of all field samples desired, with successful laboratory analyses on 100% of measurements (including QC samples). However, circumstances surrounding sample collections and subsequent laboratory analysis are influenced by numerous factors, including weather, shipping damage or delays, sampling crew or lab analyst error, and QC samples failing DQOs. An overall completeness of greater than 90% is considered acceptable for the Project.

Sensitivity

Different indicators of the sensitivity of an analytical method to measure a target parameter are often used including instrument detection limits, method detection limits, and reporting limits. For the Project, MDL is the measurement of primary interest, as many environmental samples will have low concentrations of the target trace pollutants, with results often detected, not quantified (DNQ). The method detection limit (MDL) is 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 instrument detection limit (“IDL”) is the lowest concentration of analyte that an analytical instrument can detect that is statistically different from the response obtained from the background instrumental noise. The IDL indicates the absolute sensitivity of the analytical technique or instrument. It is established by adding the analyte to reagent blank water or solvent to give a concentration within a few times the estimated IDL and by calculating the standard deviation, S, for seven or more replicate measurements. The IDL should be determined at least on a quarterly basis for all analyses, or more frequently as specified by laboratory SOPs. For some analytical methods, IDL is dynamically determined through analysis of the background noise during each analytical run.

The method detection limit (“MDL”) is the lowest concentration of analyte in distilled water, solvent, or another appropriate clean matrix that a method can detect reliably and that is statistically different from a blank carried through the complete method, including extraction and pretreatment of the sample. The MDL is specified based on replicate analyses of seven or more measurements with a specified confidence level and defined as three times the standard deviation of replicate analyses of a sample that is 1 to 5 times the estimated detection limit for the analyte of concern. The MDL should be determined at a minimum on an annual basis. MDLs should be expressed in concentration units equivalent to those for field measurements, for a typical or target sample size (e.g. 1g dry sediment per analysis):

$$\text{Sample specific MDL } (\mu\text{g/g dry wt}) = \frac{\text{MDL } (\mu\text{g/analysis})}{\text{Sample size (g dry wt/analysis)}}$$

The method used for deriving sample MDLs (whether for individual samples or for a standardized typical sample size) should be declared in the narratives or comments in the data reports.

The reporting or practical quantification limit (RL or PQL) is the lowest level at which measurements become quantitatively meaningful and which are achievable on a routine day-to-day basis. The reporting detection limit is defined as approximately three to four times the MDL or ten times the IDL, or may be defined as the concentration for the minimum calibration point (expressed in concentration units equivalent to those for field samples). Analytical measurements above the MDL but below the RL should be reported as measured, but may be qualified by the laboratory as estimated or detected but not quantified (DNQ).

Target MDLs for this study are listed in Table 4. MDLs for PCBs and mercury are selected to yield quantitative results for samples with pollutant concentrations notably different from those in the Bay or in similar areas (within the same or other watersheds).

Precision

Precision is used to measure the degree of mutual agreement among individual measurements of the same property under prescribed similar conditions. Overall precision usually refers to the degree of agreement for the entire sampling, operational, and analysis system. It is derived from reanalysis of individual samples (laboratory replicates) or multiple collocated samples (field replicates) analyzed on equivalent instruments and expressed as the relative percent difference (RPD) or relative standard deviation (RSD). Analytical precision can be determined from duplicate analyses of field samples, laboratory matrix spikes, and/or reference material samples. The analytical precision of duplicate measurements of samples or spikes will serve as the overall precision for the Project.

Analytical precision is expressed as the RPD for duplicate measurements.

$$RPD = \frac{X_1 - X_2}{(X_1 + X_2)/2} \times 100\%$$

Where X_1 is the first sample result and X_2 is the duplicate sample result. In cases where more than one replicate is measured from a single sample or taken from a given site (on a scale presumed to be homogenous), rather than deriving RPDs for each pairwise combination, RSD can instead be calculated:

$$RSD = \frac{\text{stdev}(X_1, X_2, \dots, X_N)}{\text{average}(X_1, X_2, \dots, X_N)} \times 100\%$$

The target RPD (or RSD) is 35% or less for trace organics (PCBs) and mercury, and 20% for TOC. If the RPD (or RSD) exceeds the target for over 30% of the parameters in an analysis, the analysis is rerun. If after rerunning the analysis, RPD (or RSD) for a substantial number of analytes still exceed the target, the problem is further investigated, to identify whether potential problems originate in field sampling or laboratory handling and analysis. Additional corrective actions including flagging of data or reanalysis of samples are taken where possible and as needed.

In cases where there is insufficient field sample to analyze both lab duplicates and matrix spike duplicates, a duplicate of the unspiked sample is generally preferred, due to the possibility of spiking too high, resulting in precision measurement for a concentration range not found in typical samples. Analyzing a laboratory replicate for a field sample different from that used for matrix spikes can alleviate a problem of insufficient sample material. In extreme cases where there is sufficient material for only a single analysis of each sample from the project, other samples such as blank spikes, reference materials, or samples from another project may be used to evaluate analytical precision, again with caveats on the relevance of evaluations for samples with much higher concentrations. Similar to accuracy assessments, due to variability near the MDL, control limit criteria for precision only apply to analytes with average values that are at least three (3) times the MDL established by the laboratory.

Accuracy

Accuracy describes the degree of agreement between a measurement (or the average of measurements of the same quantity) and an acceptable reference or true value. The “true” values of the parameters measured in the Project are unknown and the overall accuracy (including representativeness) cannot be assessed. However, accuracy of certain portions of a measurement process can be evaluated. For the Study, analytical accuracy, characterized through the use of reference samples and laboratory matrix spikes in the laboratory operation, is considered acceptable for the overall accuracy of the Project. Accuracy is expressed as % recovery for reference materials:

$$\% \text{ Recovery} = \frac{MV}{EV} \times 100\%$$

Here MV is the measured value and EV is the true expected (reference) value.

For matrix spikes, recovery is calculated from the original sample (N = native unspiked) result, the expected value (EV = native + spike concentration), and the measured value with the spike (MV):

$$\% \text{ Recovery} = \frac{(MV-N)}{(EV-N)} \times 100\%$$

Here EV-N = (native + spike) – native, which is the same as the spike concentration alone.

Based on typical results attained by experienced analysts in the past for programs such as the RMP, accuracy control limits have been established both for individual compounds and combined groups of compounds (Tables 3, 4, and 5).

Surrogate standards are also spiked into samples for some analytical methods and used to correct for losses in the analytical process. Although recoveries on surrogates are to be reported, control limits for surrogates are method and laboratory specific, and no project specific recovery targets for surrogates are specified, so long as overall recovery targets for accuracy (with matrix spikes and reference materials) are achieved. In accordance with the methodology of the California Surface Water Ambient Monitoring Program (SWAMP) QA Management Plan (Puckett, 2002), “Each laboratory will set its own warning limit criteria based on the experience and best professional judgment of the analyst(s). It is the responsibility of the analyst(s) 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).” The warning limits used by the laboratory will be provided in the standard operating procedures submitted to the Project. Data will be reported as surrogate-corrected values.

A recovery target of 65-135% for both reference materials and matrix spikes is considered acceptable for trace organics (including PCBs) and mercury in sediment. Recovery targets for TOC in sediments are 80-120% of the reference or certified value. If the recovery falls outside of this range for over 30% of reported parameters in analysis of reference materials, the problems need to be identified, corrected, and the instrument re-calibrated, and samples in that batch rerun if possible. If the recovery for a matrix spike/duplicate falls outside of target range, possible causes must be investigated, identified, the analysis needs to be rerun where possible. If the spike continues to fall outside of the target range, the analysis rerun if sufficient material is available, and/or other corrective actions such as data flagging may be taken.

No individual analyte value shall exceed the target limits more than once in consecutive analyses without appropriate documentation and consultation with the Data Manager and/or QA Officer. Additional leeway may be granted for analytes with reference but not certified values, or for those with 95% confidence intervals already outside the recovery targets. 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 greater than three (3) times the MDL established by the laboratory.

In cases where project field samples have insufficient material, the laboratory may instead spike a similar blank matrix (e.g. sand for sediment) or samples from other projects with similar expected concentrations. Spikes should be at least double the native concentrations in samples to allow quantitative assessment, but less than 100 times higher. If spiking concentrations are found too high in the first analyzed batch, additions in later analysis batches must be reduced. If expected native concentrations are unknown, spikes should be made at approximately 100 times the MDL or 10 times the quantization limit, and adjusted upward in later batches as needed.

Contamination

Collected samples may inadvertently be contaminated with target analytes at many points in the sampling and analytical process, from the materials shipped for field sampling, to the air supply in the analytical laboratory. Blank samples evaluated at multiple points in the process chain help assure that pollutants measured in samples actually originated from the target matrix in the sampled environment and are not artifacts of the collection or analytical process.

Method blanks (also called laboratory reagent blanks, extraction blanks, procedural blanks, or preparation blanks) are used to assess laboratory contamination during all stages of sample preparation and analysis. For all analyses, one method blank will be run for every 20 samples, with at least one run in every sample batch. The method blank will be processed through the entire analytical procedure in a manner identical to the samples. Method blanks should be less than the MDL or not exceed a concentration of 10% of the lowest reported sample concentration. A method blank concentration $>2xMDL$ or $>10\%$ of the lowest reported sample concentration 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 likely contamination source(s) and the steps taken to eliminate/minimize the contaminants shall be included in narrative of the data report. If supporting data is presented demonstrating sufficient precision in blank measurement that the 99% confidence interval around the average blank value is $<MDL$ or $<10\%$ of the lowest measured sample concentration, then the average blank value may be subtracted.

Table 4a. (Element 7) Data quality objectives for field measurements.

Parameters	Method	Accuracy	Precision	Completeness
Latitude & longitude	GPS readings	$\pm 5m$	$\pm 5m$	$>99\%$
Site metadata	Narrative notes		$\pm 1m$ resolution	$>99\%$

Field crews collect only informational data (sampler malfunctions, etc.)

Table 4b. (Element 7) Data quality objectives for laboratory measurements.

Parameters	Accuracy	Analytical Precision ²	MDL	Completeness	Blank contamination
Mercury	75-125%	$\pm 25\%$	0.1 ug/g dry wt 0.1 ng/L water	$>90\%$	ND or $<30\%$ min field sample
PCB Aroclors	65-135%	$\pm 35\%$	0.1 ug/g dry wt 1 ug/L water	$>90\%$	ND or $<30\%$ min field sample
PCB Congeners	65-135%	$\pm 35\%$	1 pg/g dry wt 10 pg/L water	$>90\%$	ND or $<30\%$ min field sample
TOC	80-120%	$\pm 20\%$	0.5 mg/g dry wt 50 ug/L water	$>90\%$	ND or $<30\%$ min field sample
SSC	95-105%	$\pm 5\%$	0.6 mg/L	$>90\%$	N/A
Grainsize	95-105%	$\pm 5\%$	N/A	$>90\%$	N/A

8. SPECIAL TRAINING NEEDS/CERTIFICATION

8.1 Specialized training or certifications.

There are no specialized field certifications required for this study. Analytical laboratories are to be certified for the analyses conducted at each laboratory, by ELAP, NELAP, or an equivalent *accreditation program as approved by the Project Manager*.

8.2 Training and certification documentation.

There are no specialized field certifications required for this study. Certification documents for laboratories are to be maintained by the laboratories, and provided to the Project Manager or other project staff (e.g. Data Manager and/or QA Officer) as requested.

8.3 Training personnel.

No training required – SFEI staff working on this project are field trained for the types of data collection anticipated.

Table 5. (Element 8) Specialized personnel training or certification.

In narrative form above.

9. DOCUMENTS AND RECORDS

9.1 Field Documentation

All field data gathered for the Project are to be recorded in field notebooks, and scanned or transcribed to electronic documents to permit easy access by Project staff and other parties as needed. All appropriate project-related materials will be delivered to and maintained by the Data Manager. A discussion of some of the key parts of the documentation process is shown below.

- These data records are to be maintained for at least an eight year period by the Project.
- Field data are required to be reported to the Project Data Manager at least once per quarter, or more frequently as appropriate.
- Data are reported to the Project data manager electronically in a format as specified.
- All hard copies of data are kept on file by the Project staff conducting field work, or with the Data Manager.

Proper documentation of sampling locations and methods is important to interpretation of grant results. Overall documentation will include information recorded on sample labels, field logbooks, data collection forms, and photographic documentation.

Field Logbooks

Sampling personnel will record relevant information in bound logbooks. All information should be recorded in permanent ink. Any changes made to recorded information will be made using single strike-through and will be initialed and dated by the person making the change.

Forms

Field data sheets will be compiled for each site, and shall include at a minimum: date, names of crew members, narrative description of the sampling site (general location), other relevant catchment information such as constructions activities, weather conditions, sample matrix, whether sediment is submerged or exposed (if sediment), method used to collect sample, and sample IDs collected for analysis or archive. Additionally, a minimum of one set of latitude/longitude per sample site shall be obtained from an appropriate GPS unit and recorded at time of sampling.

Photographic Documentation

Photographic documentation is an important part of sampling procedures. An associated photo log will be maintained documenting sites and subjects associated with photos. The date function on the camera shall be turned on. A copy of all photographs should be provided to the Data Manager, preferably on CD-ROM, at the conclusion of sampling efforts and maintained for grant duration.

Sample Identification

Samples will be assigned unique sample identification codes to provide a method for tracking each sample, and codes will be recorded on sample labels. Each sample will be identified by a unique code that indicates the sampling date, type, and sample number. The following is an example of the sample identification code for the samples:

YYYYmmDD-S-XX-N-A

where: YYYYmmDD indicates year (4 digit), month, date, 24-hour, and minute; S indicates solid (L will be used for Liquid); XX indicates sampler's initials; N indicates the sample number, which will start at '01' and increase by one consecutively with each sample collected, and A designates any post-field processing such as sieving or settling experiments.

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 analytical laboratory.

9.2 Laboratory Analyses Documentation

Data Reporting/Submission Format

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

1. letter of transmittal
2. chain of custody information
3. analytical results for field and quality control samples
4. case narrative
5. copies of all raw data

The Data Manager will review the data deliverables provided by the laboratory for completeness and errors. Submissions approved by the Data Managers are then passed along to the QA Officer for review of QA/QC. In addition to the laboratory's standard reporting format, all results meeting data quality objectives and results having satisfactory explanations for deviations from objectives shall be reported in tabular format on electronic media, in a format compatible with or easily transformed to that outlined in the Interim SWAMP Information System Management Plan, currently used for the reporting of RMP data. The specific format and any needed templates for electronic data are to be agreed upon by the SFEI Data Manager and the Laboratory Project Manager.

As they become available, and *after* internal laboratory QA/QC review, *draft* data produced from laboratory analyses are sent in electronic format. These *draft* data are not for distribution or application in any manner, other than for the initial review by Project staff. Upon completion of their preliminary review of the *draft* data, the Project staff will provide any concerns/comments (if any) in writing to the respective laboratory, as well as to the Project Manager. The Project staff will notify the lab know if it approves of this *draft* data in its current format. If there are any concerns regarding the *draft* data, the concerns must be addressed in writing by the analytical lab. After the concerns are addressed and corrective actions taken (such as reviewing for transcription errors, reanalysis, and data flagging), data will be resubmitted for as *draft* data for re-review. After Project staff concerns have been addressed, they will notify the laboratory and approve the data as final.

Documentation for analytical data is kept on file at the laboratories, or may be submitted with analytical results. These may be reviewed during external audits of the Project, as needed. These records include the analyst's comments on the condition of the sample and progress of the analysis, raw data, instrument printouts, and results of calibration and QC checks. Paper or electronic copies of all analytical data, field data forms and field notebooks, raw and condensed data for analysis performed on-site, and field instrument calibration notebooks are kept as part of the Project archives for a minimum period of eight years.

Other Laboratory QA/QC Documentation

All laboratories will have the latest version of the Project QAPP in electronic format. In addition, the

following documents and information from the laboratories will be current, and they will be available to all laboratory personnel participating in the processing of Study samples as well as to SFEI project officials:

1. Laboratory QA plan: Clearly defines 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.
2. Laboratory SOPs: Contain instructions for performing routine laboratory procedures, describing exactly how a method is implemented in the laboratory for a particular analytical procedure. Where published standard methods (e.g. EPA methods) allow alternatives at various steps in the process, those approaches chosen by the laboratory in their implementation (either in general or in specific analytical batches) are to be noted in the data report, and any deviations from the standard method are to be noted and described.
3. Instrument performance information: Contains information on instrument baseline noise, calibration standard response, analytical precision and bias data, detection limits, scheduled maintenance, etc.
4. Control charts: Control charts are developed and maintained throughout the project for all appropriate analyses and measurements for purposes of determining sources of an analytical problem or in monitoring an unstable process subject to drift. Control charts serve as internal evaluations of laboratory procedures and methodology and are helpful in identifying and correcting systematic error sources. Control limits for the laboratory quality control samples are ± 3 standard deviations from the certified or theoretical concentration for any given analyte.

Records of all quality control data, maintained in a bound notebook at each workstation, are signed and dated by the analyst. Quality control data include documentation of standard calibrations, instrument maintenance and tests, and analyses of CRMs. Control charts of the data are generated by the analysts monthly or for analyses done infrequently, with each analysis batch. The laboratory quality assurance specialist will review all QA/QC records with each data submission. The laboratories will provide QA/QC reports to SFEI with each batch of submitted field sample data.

Upon return from the field, all written field note will be photocopied and stored in a paper file in the Project Managers office. All paper forms of data or correspondence from the labs will be photocopied and one copy kept in the Data Manager's files and the other stored in a paper file in the project managers office. Digital forms of data derived from either field or laboratory sources will be backed up weekly as part of SFEI's normal backup procedures.

At anytime when there are changes to the QAPP either requested by the State or by any member of the project team, it will be the Project Managers responsibility to distribute copies of the revised QAPP to parties described in section A3 Distribution List.

Table 6. (Element 9) Document and record retention, archival, and disposition information.

	Document Type	Retention	Archival	Disposition
Field Records	Field Data Sheets	SFEI	SFEI	Hardcopy
Analytical Records	Analytical reports	Laboratory	Laboratory	Electronic files or hardcopy printout
Data Records	Electronic tables/database	SFEI	SFEI weekly backup	electronic files
Laboratory QA/QC	Lab QAPP, SOPs, maintenance & control records	Laboratory	Laboratory	Notebooks, electronic files, and/or hardcopy

GROUP B: DATA GENERATION AND ACQUISITION

10. SAMPLING PROCESS DESIGN

10.1 Sampling site selection

The number of sites to be sampled and samples to be collected are largely restricted by the budget set aside for laboratory analyses in the SFEI Prop 13 Grant Project contract language. Overall we have budget for sampling 300-450 locations for either soil or sediment material or water. The sampling design includes two components: 1) Hotspot / Orange Zone Reconnaissance Characterization and 2) Hot spot / Orange Zone detailed evaluation.

Orange Zone Reconnaissance Characterization

In this component we will sample sediments and soils to test the effectiveness of the Orange Zone methodology in identifying contaminant source areas to which management could be focused to help achieve TMDL goals. The Project team will sample bed sediments in stormwater conveyances that drain known or suspected Hg and/or PCB Orange zones / hotspots. Information from previous work products (SFEI and GeoSyntec, 2006; GeoSyntec and SFEI, 2006), along with information gained from non-measurement data sources will be put together and the criteria listed in the monitoring plan and used to make final decisions on sampling locations. Within confirmed Orange Zones we will carry out one more step to identify historic businesses or activity areas where PCBs and Hg were used. Sediment in stormwater conveyances will be sampled and analyzed using methods aiming to achieve no worse than 0.1 part per million (ppm) detection limits for both Hg (method 7473) and PCBs (method 8082) in small (typically ~2 g) samples. We anticipate concentrations of Hg in >1 ppm and PCBs concentrations >5 ppm in stormwater conveyance sediments downstream from orange zones and Hotspots based on our screening level study (SFEI and GeoSyntec 2006).

In areas with elevated contaminant concentrations, we will sample soils and sediments in public right-of-ways, side walks / street sidings, and street surfaces adjacent to premises where use of Hg and/or PCBs is/was known to occur. Samples will be analyzed for PCBs using spectrometry (HRGC/HRMS) following EPA Method 1668a and for Hg using cold vapor atomic fluorescence following U.S. EPA method 1631e. Low detection limit methods will be used in this instance because we intend to complete grainsize specific analyses and use congener patterns to better understand differences between locations based on our understanding of use characteristics. Our objectives are to better determine the number of Hotspots / Orange Zones in the Bay area, apply the bed sediment methodology as a prospecting method for PCBs in other areas, and for Hg in particular, fully develop a “Hg prospecting methodology”. Interim products from this component will also be used to prioritize locations for detailed follow-up field sample capture and analysis to be completed in Component 2.

Table 7. Criteria for selecting sampling sites from among identified Hotspots and Orange Zones for reconnaissance study.

Priority	Indicator
High	<ul style="list-style-type: none"> • Previously identified Hg or PCB spill site • Historic land use associated with Hg or PCB-containing materials • Historic or current areas where Hg or PCB containing equipment is being recycled (dismantlers, recyclers, auto wreckers) • Sites with outdoor storage yards and storage tanks
Medium	<ul style="list-style-type: none"> • Storm sewersheds with large areas associated with historic railway spur lines • Storm sewersheds with many PG&E yards

	<ul style="list-style-type: none"> • Present / former industrial sites exhibiting poor housekeeping • Storm sewersheds with high (>70%) industrial land use • Present / former industrial sites with poor sediment retention • Sites with known recent large-scale window replacements (potential for PCB-containing caulks to be disturbed)
Low	<ul style="list-style-type: none"> • Non-industrial land uses • Sites with history of Hg or PCB-related activities with no current potential for sediment loading to stormwater system

Orange Zones Detailed Evaluation

In confirmed Orange Zones where we have evidence of contaminants in conveyances as well as on street surfaces or properties, we will examine characteristics of sediments and waters that transport or are likely to transport pollutants during the wet season. The size distribution of particles carrying pollutants and the concentrations of pollutants on each size fraction will help to determine the potential efficacy of various control measures. In this Component (2) we will carry out detailed evaluation of concentrations of Hg and PCBs in runoff from Orange Zones / hotspots, street dust, street sweeping materials, street wash water.

Locations for stormwater sampling will be selected based on the criteria above (Table 7) and any available preliminary information from concentrations in Orange Zone Reconnaissance Characterization samples described above. Use of the latter is contingent on receiving the first component data from the labs before the first rains of the wet season. Collection of water samples will occur during early season storm events to try to capture “first flush”, when we expect concentrations of both suspended sediments and contaminants will be greater (McKee et al., 2003). All samples in stormwater will be analyzed for total concentrations of Hg (method EPA 1631e), PCBs (method EPA 1668 revision A) and suspended sediment (method ASTM D 3977) in water (mass / unit volume). All samples analyzed for PCBs will also be analyzed for organic carbon (DOC and POC) (method EPA 415.1 or 440.0). About 1:3 samples in stormwater will be analyzed for concentrations of Hg and PCBs (mass / unit mass) in three grain size fractions: <0.025, 0.025 - 0.075 mm, and >0.075 mm. The same 1:3 proportion of water samples will be analyzed (standard sieves) for grain size distribution (% finer than).

Locations for analysis of street sediments, sweeping materials, and street washing will also be focused on industrial areas. Given the City of San Francisco has a combined sewer system, preference will be given to selecting areas for study there because effluent associated with any street washing exercise can be allowed to drain to the sewer systems, avoiding the need for alternate disposal methods. Samples will be analyzed following the methods for water soil and sediment listed above. All samples will be analyzed for concentrations on each size fraction (<0.025, 0.025 - 0.075 mm, and >0.075 mm).

The objectives of Component 2 are to provide data (in many cases first-of-its-kind) with interpretations to provide stakeholders information on options for offsite treatment of runoff from Hotspots in *Orange Zones*, street sweeping and washing effectiveness as management measures, development and testing of a “prospecting methodology” for finding Hg Hotspots, and prioritizing areas for applying management measures (to be described in the implementation plans – the end product of this Grant Project).

10.2 Sample types collected

Soil and sediment samples will make up the majority of environmental samples to be collected for the SFEI Prop 13 Grant Project. However, a small number of sampling personnel should be prepared to collect samples from a variety of sampling environments. The following types of samples may be encountered.

Soil and Sediment Samples, Dry

Dry soil and sediment samples may be present on-site in surface areas such as unpaved lots and storage yards, or may have accumulated at stormwater conduits, public right-of-ways, etc.

Soil and Sediment Samples, Wet

Wet soil and sediment samples may be collected from within on-site stormwater facilities such as road gutters, drop inlets, open channels, and underground pipes.

Street sweeping materials

Sediments will be sampled from the hoppers contents of street sweeper machines. These might include standard brush sweepers or later technology models (so called high intensity sweepers) that incorporate water spray and vacuum in addition to brushes.

Street washing water

Representative water samples will be taken from street wash water. A power washing exercise will be carried out in selected industrial areas. Water will be captured below the rim of the drop inlet to determine the mass of contaminant removed during the washing exercise.

Flowing Stormwater

Samples will be collected from flowing stormwater during early season rain events from potentially any type of stormwater conveyance system including road gutters, drop inlets, open channels, and underground pipes.

Field Blanks

True sediment field blanks (e.g., ultra-pure sand processed through sampling) are not collected, although bottle/equipment blanks (e.g. extractions with sampling containers) will be used to assess contamination not originating from sampled sediments. Aqueous field blanks using pre-cleaned sampling equipment to collect reagent grade water will be collected and forwarded for analysis.

Field Duplicates

Adjacent samples will be collected as field duplicates for bedded conveyance and surface street sediments as mass allows, to compare impacts from small-scale variation and collection procedures against larger watershed scale variation. For aqueous samples, field duplicates will be collected successively from the same media using identical techniques. For both sediment and aqueous samples, field duplicates will be collected at a minimum rate of one duplicate for every twenty (20) sites sampled.

Unprocessed Splits

Some samples undergoing post-collection processing (e.g. drying and sieving) will have unprocessed split samples taken where sufficient material remains, to evaluate potential losses or contamination introduced by the sample processing. Unprocessed splits will be collected at the frequency of one for every 20 samples processed, as total sample size allows.

Number of Samples

Number of samples is largely dependant on budget. One of the key issues underlying the need to collect samples is that there is no similar data available in the literature on Hg and PCB concentrations in different grain size fractions in the urban stormwater conveyance system. This is probably the case for at least two reasons, 1. The substances have not been historically regulated to the same extent as nutrients, pathogens and other trace metals, and 2. The laboratory analysis methods have only just been developed to the point where urban managers can get good data and the laboratory methods for these substances on grainsize are still not full developed. As such, we have put together a sampling plan, but since this is first of its kind data, the scientist must have discretion to modify sampling as information is learned. The table below provides an estimate of sample numbers.

Maximum number of samples planned for each component of the study. Note samples numbers may vary depending on site conditions and rational scientific arguments.

	PCBs	Hg	SSC	Organic Carbon	Grain size
Soils and sediments	312	312		312	52
Water samples	114	114	114	114	18
Street dust, street sweepings, and street washing water	54	54	6	54	18

11. SAMPLING METHODS

The following section describes multiple field sampling techniques that could potentially be used, depending on site-specific conditions encountered during inspections and sampling operations. Where appropriate, procedures for sediment sampling mobilization and implementation will follow those implemented during the previous ACCWP investigations (Salop et al., 2002). These sampling procedures were developed based in large part on those in use by the RMP (Bell et al., 1999) and the USGS National Water Quality Assessment Program (NAWQA) [Shelton and Capel, 1994]. Selection of appropriate sampling procedures will be made at time of sampling by Field Project Manager and recorded in the field logbook.

It is expected that samples may be collected from a number of different types of facilities within an individual site. Examples may include surface soils or sediments, within manholes, drop inlets, sump basins, etc, for sample types described in the previous section.

In certain instances, sampling techniques may need to be adjusted in response to sampling conditions present (see Nonconformance / Corrective Action section). Additional safety considerations may need to be made in such cases where, for example, traffic control or confined space entry is required to conduct sampling.

11.1 Sampling Procedures

Soil and Sediment Samples, Dry

Field personnel will collect the surface soil or sediment samples using a Kynar-coated (or similar) trowel or scoop. Any sampling location covered with vegetation will be cleared of vegetation or large gravel prior to collecting the sample. The soil or sediment will be scooped from the sample location with the trowel and placed into the compositing bucket or in the sample container if no compositing will take place. In cases where samples are taken from street surfaces or other impervious (or hard packed) areas, a small nylon pre-cleaned brush will be used in conjunction with the trowel (e.g. Chutke et al., 1995). In the event that soil samples will be collected from below the ground surface, a Kynar-coated (or similar) hand auger will be used to reach the desired depth. The hand auger will then be decontaminated and used to collect the soil from the specified depth. The soil will then be placed from the hand auger directly into the compositing bucket or in the sample container if no compositing will take place.

When all of the soil samples from a given site have been collected in the compositing bucket, the soil will be composited in the field by mixing thoroughly by hand with a poly glove on for 2 minutes (timed). From there, the sample will be passed through a 2 mm mesh to remove larger sediments and debris and retain the part of the sample that carried the majority of the contaminant concentration. The composite sample will then be scooped with the trowel into a laboratory-provided glass container, sealed, labeled, and placed in a chilled cooler pending delivery under chain-of-custody (COC) to the laboratory.

Soil and Sediment Samples, Wet

Procedures for collection of wet soil and sediment samples are similar to those for dry samples. Additional steps may include removal of overlying water using peristaltic pump or similar. Where access to the sediment surface is limited, a stainless steel Ekman (or similar) dredge will be used. In this case, the dredge will be dropped onto the sediment surface aiming at a penetration of 5 cm and then triggered by hand or with a messenger. The top 2-3 cm of the sample will then be scooped out of the dredge or if appropriate, the whole sample tipped into the compositing bucket. The need for additional required field equipment is likely to be

identified through process of site inspections to be conducted prior to field sampling operations. The composite sample will then be scooped with the trowel into a laboratory-provided glass container, sealed, labeled, and placed in a chilled cooler pending delivery under chain-of-custody (COC) to the laboratory. There it will be dried (60 degrees Celsius). The sample will then be passed through a 2 mm mesh to remove larger sediments and debris and retain the part of the sample that carried the majority of the contaminant concentration.

Street sweeping materials

Sediments will be sampled from the hoppers contents of street sweeper machines. This will be achieved but dumping the contents of the sweeper hopper (typically 2 m^3) onto clean polythene plastic and mounding the contents into a cone shape. This will then be spread out into 8 approximately equal segments. A Kynar-coated (or similar) trowel or scoop will be used to take an inorganic sample from each of the 8 segments. Large vegetative mater will be removed before each sub sample is placed in a compositing bucket. The composite sample will then be field sieved (2 mm) and put into a laboratory-provided glass container, sealed, labeled, and placed in a chilled cooler pending delivery under chain-of-custody (COC) to the laboratory. There it will be dried (60 degrees Celsius). The sample will then be passed through a 2 mm mesh to remove larger sediments and retain the part of the sample that carried the majority of the contaminant concentration.

Street washing water

Water will be captured below the rim of the drop inlet to determine the mass of contaminant removed during the washing exercise. A composite sample will be attained by clean hand techniques (e.g. Bloom, 1995) by placing (for 3 seconds) a laboratory prepared 1 liter Teflon sampling bottle with a 2 inch opening directly under the center of the flow as it passes into the drop inlet. In addition, a sampling for PCB analysis will be taken in the same manner except a laboratory pre-cleaned amber bottle will be used. This exercise will be repeated until each bottle is completely fill. This will be repeated 3 times during the washing exercise and three discrete samples retained for analysis. The samples will be sealed, redouble-bagged, labeled, and placed in a chilled cooler pending delivery under chain-of-custody (COC) to the laboratory.

Rain-induced flowing Stormwater

Samples from drop inlets will be taken in the same manner as street washing water. Samples will be collected from flowing stormwater in open channels or underground pipes using a DH81 sampler and extension handles to attain a length of up to 5 meters (length depends on diameter and storm sewer depth below ground). The sampler will be fitted with Teflon components, an exchangeable laboratory cleaned series of Teflon 1 L sampling bottles and caps/nozzles. If water depth is not sufficient (100 mm), no sample shall be taken. After sample rinsing three (3) times, a depth integrated iso-kinetic center channel single vertical sample from a flowing stormwater conveyance will be taken by passing the sample bottle into and out of the water column at an even rate until the sample bottle hold approximately 800 mL. In no more than one in 10 samples (1:10), a 16-30L sample will be taken for analysis of Hg on grainsize (<math><25, 25-75, >75\text{ micron}</math>). The sample will then be decanted immediately into a 1L amber bottle for PCB analysis. Lastly, the exercise will be repeated until the Teflon bottle is completely filled (necessary for Hg). The sample bottle will be loaded into and removed from the DH81 sampler following clean hands protocols (e.g. Bloom, 1995). The samples for Hg will be sealed, redouble-bagged, labeled, and placed in a chilled cooler pending delivery under chain-of-custody (COC) to the laboratory.

Nonconformance / Corrective Actions

Site inspections or conditions present at time of sampling may identify other sampling media of interest beyond what has been proposed through the SFEI Prop 13 Grant Project MP. In this eventuality, the Project Manager will discuss any requested changes to the sampling procedures with the Project Manager and Contract Manager and, if time allows, submit a written proposal to the Water Board for authorization to proceed with proposed sampling or analysis of collected samples. Field personnel may collect samples without prior approval of the Project Manager and Contract Manager, but in no event will analysis be conducted on these samples without approval of both parties.

Collection of Archives

As sampling media allows, an archive will be collected for each sampling site for potential future additional analyses. The archive will be processed and handled identically to the sample designated for analysis while in the field, and will be transferred to cold storage facilities at our laboratories after completion of field activities or at appropriate intervals. Archives will be kept for a minimum of 1 year. At the end of 1 year or before at the laboratories request, the local stakeholder group will be informed so that if desired the samples can be transferred to another cold storage facility at a cost incurred outside of this present grant.

11.2 Decontamination Procedures

Cleaning methods will follow protocols adapted from the NOAA National Status and Trends Program for use by the Regional Monitoring Program (Bell et al., 1999) and clean hand protocols will be those of Bloom (1995).

Initial Equipment Cleaning

Appropriate sampling equipment is prepared in the laboratory a minimum of four days prior to sampling. Equipment that is pre-cleaned includes:

- Kynar (or similar) coated sample scoops, trowels, etc.
- Kynar (or similar) coated compositing bucket
- Wash bottles for deionized water, hydrochloric acid, and methanol
- Hand auger (if identified by inspections)

Prior to sampling, all equipment will be thoroughly cleaned. Equipment is soaked (fully immersed) for three days in a solution of Alconox, Liquinox, or similar detergent and deionized water. Equipment is then rinsed three times with deionized water. Equipment is next rinsed with a dilute solution (1-2%) of hydrochloric acid, followed by a rinse with petroleum ether, followed by another set of three rinses with deionized water. All equipment is then allowed to dry in a clean place. The cleaned equipment is then wrapped in aluminum foil or stored in clean Ziploc bags until used in the field.

Field Cleaning Protocol

All sampling equipment used will be rinsed with deionized water between uses at different locations within a site. All sampling equipment used at a particular sampling site will be field-cleaned prior to use at a different sampling site. The field-cleaning protocol calls for 1) removal of sediments using deionized water and a scrub brush; 2) scrubbing of the sampling gear and compositing equipment with an Alconox, Liquinox, or similar solution; 3) rinse with deionized water; 4) rinse with dilute HCL (1-2%); 5) rinse with methanol; and 6) rinse with deionized water.

Table 8. (Element 11) Sampling locations and sampling methods (*In narrative*).

Narrative provided instead above and in section 6.

12. SAMPLE HANDLING AND CUSTODY

When all required field measurements have been made and all necessary field observations have been recorded, collected samples will be sent to the analytical labs. Each group of samples is documented with a chain-of-custody (COC) form, with sufficient sample identification information to link to the specific time and location of sampling. Table 9 summarizes containers, preservation, and holding-time requirements for samples that are shipped to laboratories for analyses.

Sample Containers

At each sediment sampling site the goal will be to collect 10 or more grams of sediment, although in many instances this may not be feasible. Water samples will range between 10-50 liters per site, with the aim of obtaining sufficient material to analyze the particulate phase. At the conclusion of sampling for a specific site, and following any processing by the field crew (e.g. sample compositing or sieving), collected material will be transferred into appropriate pre-cleaned containers provided by the analytical laboratory for analysis, and where sufficient material allows, one or more archives.

Sample Homogenization

Samples may be collected as individual grabs from sites, or may be collected as subsamples of material composited from multiple locations within an individual site. Where samples are composited, sampling personnel will transfer collected material to a pre-cleaned Kynar (or similar) coated container for homogenization. Sampling personnel shall cover the container with clean aluminum foil when not actively adding or mixing material. At the conclusion of sampling within a site, sampling personnel will use pre-cleaned Kynar (or similar) coated stirring implements to homogenize the sample material to a uniform appearance. Depending on viscosity of matrix, the sample material will either be poured directly from the homogenizing container to the sample container or will be transferred using stirring implements. Sample material touching the threads or outside of the sample container will be discarded.

Table 9. (Element 12). Sample handling and custody.

Parameters	Container	Preservation/Storage	Holding Time
<i>Water Samples</i>			
Mercury	Teflon bottles with Teflon-lined lid	Acidified, 0-4°C Frozen -20°C	90 days analysis ^a 28 days ^b
PCB (Aroclors)	Glass amber bottles with Teflon-lined lid	Dark, 0-4°C	7 days to extract 40 days analysis
PCB (congeners)	Glass amber bottles with Teflon-lined lid	pH 2-3 (sulfuric acid), dark, 0-4°C	1 year
DOC/POC	Glass bottles with Teflon-lined lid	Dark, 0-4°C Acidified 48hrs, 0-4°C	7 days 28 days ^a
SSC	Glass bottles with Teflon-lined lid	Dark, 0-4°C	7 days
Grain size	Glass bottles with Teflon-lined lid	Dark, 0-4°C	6 months
<i>Soil/Sediment samples</i>			
Mercury	Glass bottles with Teflon-lined lid	Acidified 48hrs, 0-4°C Frozen -20°C	90 days ^a 28 days ^b
PCB (Aroclors)	Glass bottles with Teflon-lined lid	Dark, <4°C	14 days to extract 40 days analysis
PCB (congeners)	Glass bottles with Teflon-lined lid	Dark <4°C, until Frozen <-10°C in lab	1 year
TOC	Glass bottles with Teflon-lined lid	Frozen -20°C	100 days
Grain size	Glass bottles with Teflon-lined lid	Dark, 0-4°C	6 months

^a Acidified to pH <2.0 (within 48 hours of sample collection).

^b when using Method 7473

Sample Sieving

Grab or composite samples may be sieved as wet or dry samples, depending upon the state of the sample at collection and the analysis to be performed. Unprocessed split samples will also be analyzed to ensure that sample handling does not result in contaminant loss or gain in processing. Samples dry-sieved will be oven dried at 60°C to constant weight (<1% change in weight) before sieving. Samples will be wet-sieved with ultra-pure water, with negligible concentrations of target analytes. The volume of water used in processing will be recorded to allow estimates of the maximum possible contributions of the wash water to contaminating measured samples.

Sample Preservation and Storage

At the conclusion of sample processing at each site, all samples will be wrapped in protective material and stored on wet or blue ice in the field. At the conclusion of sampling days, samples will be processed by the field crew or will be stored chilled until processed. Following any needed processing, all samples will be stored chilled or frozen as appropriate, or shipped directly to the analytical laboratory.

Sample Custody and Shipment

Samples will be distributed via express delivery, with itemized chain-of-custody forms. Sufficient sampling information must be recorded in the field and that allows tracking sample shipments from field to laboratory and from laboratory through data processing. All samples should be shipped in accordance with laboratory procedures. If requested, laboratories will often send detailed shipping and handling instructions. The following instructions are the most stringent requirements associated with analytical laboratories used for the RMP.

Personnel shipping samples should ensure COCs (Appendix A) are filled out completely and legibly and that:

1. All samples in shipment are represented on COC
2. All samples on COC are included in shipment
3. Information on COC and sample container label (e.g., sample ID, collection date, collection time, analysis) are in agreement
4. COC lists appropriate grant ID and Data Manager
5. COCs are signed by responsible party

Sediment samples can be shipped on wet ice, blue ice, or a combination. Check with the individual laboratory to determine their preference for shipping. If wet ice is used, ensure that ice is double wrapped in Ziploc type bags to minimize potential for leakage and that shipping container is leakproof.

Glass containers will need to be cushioned more than plastic containers. General packaging guidelines are to:

1. Select an appropriate size cooler for shipment
2. Place a layer of packing material on the bottom of cooler
3. Insert samples separated by sufficient packing material
4. Place temperature blank in with samples
5. Cover with appropriate ice
6. Place additional packing material on top to fill up airspace
7. Insert completed COC in sealed Ziploc bag at top of cooler
8. Wrap duct tape or shipping tape (1) around circumference of cooler at joint between cooler and lid and (2) over top of cooler to encircle completely to keep from opening if dropped
9. Fill out and adhere custody tape to the outside of the cooler at the joint between cooler and lid.

Samples should typically not be shipped on a Thursday or Friday to prevent temporarily lost samples from sitting unrefrigerated over weekends. Thursday shipping is sometimes acceptable if the contract laboratory accepts Friday deliveries. Due to seven day sample hold time associated with chilled samples for analysis of PCBs (by EPA 8082), water sampling should be limited to Monday, Tuesday, or Wednesdays to meet with requirements for shipping and laboratory extraction unless prior arrangement is made with the analytical laboratory. Water samples analyzed by EPA 1668 or sediment samples by 8082 have more lenient holding time requirements (1 year once preserved to pH 2-3, or 14 days to extract, respectively) and may be collected on other days as needed.

The shipping personnel should notify the laboratory in advance when a shipment is made. Contact can be made via email, phone, or fax and the method of delivery and airbill number should be communicated. Shipping personnel should then follow up with the laboratory or shipping company the day shipment is to be completed to verify the shipment was received.

Laboratory Chain of Custody Procedures

Sample custody transfers to the analytical laboratory at the time of receipt. Upon receipt of samples, laboratory sample custodian should first verify sample integrity. Verification should include:

1. Presence of custody seal
2. Samples at appropriate temperature
3. Chain of custody forms in agreement with samples
4. Sample containers intact
5. Samples labeled appropriately

Any questions on shipments should be brought to the attention of the Project Manager for resolution. Custody procedures followed by the laboratory should then follow laboratory standard operating procedures.

13. ANALYTICAL METHODS

Upon receipt at the laboratories, samples are logged in with all the information on the field data sheet entered into the computer, together with the sample identification number. In addition, a second copy of the field sheet is retained in a site file. Additional information pertaining to the condition of the sample as it arrives at the laboratory is recorded and used in subsequent quality control checks. This information includes an assessment of leakage and gross contamination, compliance with sample bagging requirements, and the assignment of an analytical processing code that is based upon the amount of sample.

13.1 Laboratory Sample Processing

Field samples sent to the laboratories will be processed within their recommended hold time. Each sample may be assigned unique laboratory sample identification (ID) numbers for tracking processing and analyses of samples within the laboratory. This laboratory sample ID (if differing from the field team sample ID) must be included in the data submission, within a lookup table linking the field sample ID to that assigned by the lab.

Samples arriving at the laboratory are to be stored under conditions appropriate for the planned analytical procedure(s), unless they are processed for analysis immediately upon receipt. Samples to be analyzed should only be removed from storage when laboratory staff are ready to proceed.

13.2 Analytical Method Requirements

Table 10 lists the required parameters to be measured, methods to be used, and the reporting units. Detailed procedures of sample preparation, analytical methods and practices are described in the following documents:

1. EPA Method 3540c: Soxhlet Extraction. <http://www.epa.gov/sw-846/pdfs/3540c.pdf>
2. EPA Method 8082: Polychlorinated Biphenyls (PCBs) by Gas Chromatography <http://www.epa.gov/sw-846/pdfs/8082.pdf>
3. EPA Method 1668 Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS. <http://www.epa.gov/Region3/1668a.pdf>
4. EPA Method 7473: Mercury In Solids And Solutions By Thermal Decomposition, Amalgamation, And Atomic Absorption Spectrophotometry <http://www.epa.gov/sw-846/pdfs/7473.pdf>
5. EPA Method 415.1 Total Organic Carbon In Water (Combustion or Oxidation) method: http://web1.er.usgs.gov/nemi/method_pdf/5403.pdf holding times: http://www.epa.gov/Region9/qa/pdfs/415_1dqi.pdf
6. EPA Method 440.0: Determination of Carbon and Nitrogen in Sediments and Particulates of Estuarine/Coastal Waters Using Elemental Analysis http://www.epa.gov/nerlcwww/m440_0.pdf
7. EPA Method 1631e: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry <http://www.epa.gov/waterscience/methods/1631e.pdf>
8. ASTM D422: Standard Test Method for Particle-Size Analysis of Soils <http://www.astm.org>

Minor changes of sample preparation procedures to accommodate differences in sample size may be

acceptable. Before changes or modifications of the procedures are implemented, a report containing supporting data is required to be submitted and approved by SFEI and the Science Advisory Team.

Table 10. (Element 13) Field analytical methods. (Not applicable)

Not applicable

Table 11. (Element 13) Laboratory analytical methods.

<i>Media/Parameter</i>	<i>Sampling Method</i>	<i>Analytical Method</i>	<i>Reporting Units</i>
<i>Water Sample Particulates</i>			
Mercury	Depth integrated vertical	EPA 1631	µg/kg
PCBs	Depth integrated vertical	EPA 1668	µg/kg
DOC, POC	Depth integrated vertical	EPA 415.1 or 440.0	%
SSC	Depth integrated vertical	ASTM D3977-97 (Method C)	mg/L
Grainsize	Depth integrated vertical	Seive-pipette (Guy, 1969)	Weight%
<i>Sediment Samples</i>			
Mercury	Grab	EPA 7473	µg/kg
PCBs	Grab	EPA 1668 or 8082	µg/kg
TOC	Grab	EPA 415.1 or 440.0	%
Grain size	Grab	ASTM D422M/PSEP	%

14. QUALITY CONTROL

14.1 Field Quality Control Operations

Field equipment is to be routinely checked and calibrated according to manufacturers' instruction manuals.

Field quality control is described in detail in SOPs for sampling operations. Following is a description of terminology that is frequently used in the measurement of quality assurance in field operations. Some of these measurements (source solution blanks, bottle blanks) only need to be taken when an established procedure is changed, while others (field blanks and field duplicates) need to be taken at various intervals throughout the sampling process.

Source solution blank

Source solution blanks account for any pre-existing contamination in the water, solution, or preservatives used to prepare the sample containers. Source solution blanks will be made with Milli-Q or Nanopure water (free of target contaminants), and trace-metal grade acids will be used in all aspects of cleaning, storage, and analysis. Contamination of these source solutions will be routinely checked, and corrective steps taken whenever contamination of source solutions is indicated. If the problem persists, of the following options may be used:

- High blank values are corrected by altering the leaching and washing procedure until the analyte concentrations are reduced. The manufacturer is contacted to see if the manufacturing process can be altered to lessen the problem.
- In the event of elevated deionized water blanks, treatment equipment is inspected and repaired if necessary so that the resulting water quality is within specifications.

Bottle blank

Bottle blanks account for contamination in sampling containers, in addition to any contamination due to the source solution. Bottle blanks will be generated early on in the monitoring program. Certified trace-metal-free borosilicate glass containers and trace-metal free high density polyethylene plastic containers will be used for sample collections. Measurement of bottle blanks will be conducted for each batch of containers.

Field/System blank

Field and system blanks account for sources of contamination that might be introduced to a sample from source solutions, sampling bottle, sampling equipment, during transport between the laboratory and field site, as well as contamination from the immediate field environment. Field/system blanks are generated under actual field conditions and are subjected to the same aspects of sample collection, field processing, preservation, transport, and laboratory handling as the environmental samples.

True sediment field blanks (e.g., ultra-pure sand processed through sampling) are not collected, although bottle/equipment blanks (e.g. extractions with sampling containers) will be used to assess contamination not originating from sampled sediments. Aqueous field blanks using pre-cleaned sampling equipment to collect reagent grade water will be collected and forwarded for analysis. Field blanks will be collected with the first collection of each sample matrix and then at the frequency of a minimum of one blank per twenty (20) sites sampled.

Field duplicate

Proximate samples will be collected as field duplicates for bedded conveyance and surface street sediments as mass allows, to compare impacts from small-scale variation and collection procedures against larger watershed scale variation. For aqueous samples, field duplicates will be collected successively at a site from the same media using identical techniques. For both sediment and aqueous samples, field duplicates will be collected at a minimum rate of one duplicate for every twenty (20) sites sampled.

14.2 Laboratory Quality Control Operations

Concentrations of pollutants in environmental samples are often low. Therefore, a quality-assurance program for the chemical analysis of samples requires stringent laboratory conditions and careful control over all aspects of the analyses. Each step in the analytical process is a potential source of contamination and must be consistently monitored to ensure that the final measurement is not adversely affected by any processing steps.

To ensure that laboratory procedures are not contributing contaminants to a sample, several checks are made at various stages during sample processing and analysis. The sampling equipment to be used at the field sites are cleaned and wrapped in the laboratory. To ensure that the cleaning procedures remove all soluble impurities, randomly selected sampling equipment is tested approximately 1 in 20 samples.

Laboratories providing analytical support for the Project will have the appropriate facilities to store, prepare, and process samples in an ultra-clean environment (e.g. Class 100 Clean Room); and will have appropriate instrumentation and staff to perform analyses and provide data of the required quality within the time period dictated by the project. The laboratories are expected to satisfy the followings:

1. Demonstrate capability through pertinent certification and satisfactory performance in inter-laboratory comparison exercises.
2. Provide qualification statements regarding their facility and personnel.
3. Maintain a program of scheduled maintenance of analytical balances, laboratory equipment, and instrumentation.
4. Conduct routine checking of analytical balances using a set of standard reference weights (American Society of Testing and Materials Class 3, NIST Class S-1, or equivalents). Analytical balances are serviced at six-month intervals or when test weight values are not within the manufacturer's instrument specifications, whichever occurs first.
5. Conduct routine checking and recording the composition of fresh calibration standards against the previous lot. Acceptable comparisons are within 2% of the precious value.
6. Record all analytical data in bound (where possible) logbooks, with all entries in ink, or electronically.
7. Monitor and document the temperatures of cold storage areas and freezer units on a continuous basis.
8. Verify the efficiency of fume/exhaust hoods.

9. Have a source of reagent water meeting specifications described in Section 8.0 available in sufficient quantity to support analytical operations.
10. Label all containers used in the laboratory with date prepared, contents, initials of the individual who prepared the contents, and other information as appropriate.
11. Date and safely store all chemicals upon receipt. Proper disposal of chemicals when the expiration date has passed.
12. Have QAPP, SOPs, analytical methods manuals, and safety plans readily available to staff.
13. Have raw analytical data readily accessible so that they are available upon request.

In addition, laboratories involved in the Project are required to demonstrate capability continuously through the following protocols:

1. Strict adherence to routine QA/QC procedures.
2. Routine analysis of CRMs, if available.
3. Regular participation in annual certification programs.
4. Satisfactory performance at least annually in the analysis of blind Performance Evaluation Samples and/or participation in inter-laboratory comparison exercises.

Recommended Typical Laboratory Performance Measurements

The laboratory QA/QC will use a performance-based approach to ensure that data produced are consistent, dependable, and satisfactory. The performance-based approach involves continuous laboratory evaluation through the use of accuracy-based materials (e.g., CRMs), laboratory matrix spikes, laboratory reagent blanks, calibration standards, laboratory- and field-duplicates, and others as appropriate. Measurements of accuracy, precision, and detection limits are required to meet the data quality objectives as described in Section 3.0.

1. Method blank- Method blanks account for contaminants present in the preservatives and analytical solutions used during the quantification of the measured parameter. They are used to assess laboratory contamination during all stages of sample preparation and analysis. Every set/batch of samples processed will contain a method blank. If contamination is found, its source will be investigated and minimized.
2. Matrix spike sample - Matrix spikes and matrix spike duplicate are used both to evaluate the effect of the sample matrix on the recovery of the analyte and to provide an estimate of analytical precision. A known amount of contaminant is added to the blank matrix or samples to assess potential analytical interference present in the field sample. A minimum of 5% of the total number of samples or one per sample batch will be analyzed for matrices with no reference materials. If adequate samples are not available, analysis of blank matrix spikes and blank matrix duplicates will be performed in lieu of the sample spikes and sample spike duplicates.
3. Certified reference materials - Analysis of CRMs is another way of determining accuracy of the analysis by comparing a certified value of material with similar concentrations as those expected in the samples to be analyzed. 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 agency such as the National Research Council Canada, US EPA, US Geological Survey, etc. Standard Reference Materials are CRMs issued by the National Institute of Standards and Technology ("NIST"), formerly the National Bureau of Standards.
4. Matrix spike samples - where CRMs are not available in a matrix at appropriate concentrations, laboratory precision and accuracy must be verified by low-level spike recoveries and by inter-comparison with other established laboratories using a technique with similar performance characteristics. The matrix spike and matrix spike duplicates at a rate of one per ten samples will serve as the check of ongoing precision and accuracy.
5. Replicate samples - In addition to method blanks, matrix spike samples, and field blanks (see Section 10.2), analyses may be performed for analytical and laboratory duplicates. Analytical duplicate samples are extract aliquots that measure the instrumental precision. Laboratory duplicate samples

are used to measure laboratory precision by evaluating analytical differences between splits of the same sample. At a frequency of not less than one sample in twelve, the analyst inserts a reference material, duplicate, or single-point standard whose concentration is in the working range of the procedure to verify correct operation.

All laboratory glass- and plastic-ware are evaluated prior to use to ensure that chemicals of interest are neither adsorbed to nor leached from the surfaces in contact with the sample.

Table 12. (Element 14) Sampling (Field) QC.

Matrix: Water, sediment		
Sampling SOP: Urban BMP SAP		
Analytical Parameter(s): PCBs, Hg		
# Sample locations: 300-400		
Field QC	Frequency/Number	Acceptance Limits
Field/Equipment Blanks	1 per 20 samples	<MDL, or <30% of lowest field sample
Field Replicates	1 per 20 samples	N/A

Table 13. (Element 14) Analytical QC.

Matrix: Water, Sediment, soil		
Analytical Parameter(s): PCBs		
Analytical Method/SOP Reference: EPA Methods 8082, 1668		
# Sample locations: 300-400		
Laboratory QC	Frequency/Number	Acceptance Limits
Method blank	1 per analytical batch	<mdl, or <30% of lowest field sample
Instrument blank	As specified by laboratory	<mdl
Lab duplicate	1 per 20 samples	RPD or RSD<35%
Lab control sample	1 per analytical batch	Within $\pm 35\%$ of target value
Matrix spike sample MSD	1 per analytical batch	Within $\pm 35\%$ of target value
Certified reference material	1 per 20 samples	Within $\pm 35\%$ of target value

Matrix: Water, Sediment, soil		
Analytical Parameter(s): Hg		
Analytical Method/SOP Reference: EPA Methods, 1631, 7473		
# Sample locations: 300-400		
Laboratory QC	Frequency/Number	Acceptance Limits
Method blank	1 per analytical batch	<mdl, or <30% of lowest field sample
Instrument blank	As specified by laboratory	<mdl
Lab duplicate	1 per 20 samples	RPD or RSD<25%
Lab control sample	1 per analytical batch	Within $\pm 25\%$ of target value
Matrix spike sample	1 per analytical batch	Within $\pm 25\%$ of target value
Certified reference material	1 per 20 samples	Within $\pm 25\%$ of target value

Matrix: Water, Sediment soil		
Analytical Parameter(s): POC/DOC/TOC		
Analytical Method/SOP Reference: EPA Methods 415.1, 440.0		
# Sample locations: 300-400		
Laboratory QC	Frequency/Number	Acceptance Limits
Method blank	1 per analytical batch	<mdl, or <30% of lowest field sample

Instrument blank	As specified by laboratory	<mdl
Lab duplicate	1 per 20 samples	RPD or RSD<20%
Lab control sample	1 per analytical batch	Within $\pm 20\%$ of target value
Matrix spike sample	1 per analytical batch	Within $\pm 20\%$ of target value
Certified reference material	1 per 20 samples	Within $\pm 20\%$ of target value

15. INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

Technical support for troubleshooting of all aspects of field operations is available through SFEI and for laboratory operations through the respective analytical laboratories.

15.1 Field equipment

The field sampling equipment does not require any calibration, but should be visually inspected prior to loading to identify problems that would result in sample loss (e.g. leaks, broken connectors). Routine maintenance on all equipment will be carried out according to the manufacturer's instructions and sampling SOPs. The field crew will ensure that maintenance schedules for each piece of equipment are followed and that adequate supplies of commonly used spare parts are on hand to minimize downtime. The following maintenance procedures are conducted regularly.

15.2 Laboratory Operations

Routine maintenance on all equipment will be carried out according to the manufacturer's instructions. A maintenance schedule is established for each instrument and included in the instrument's logbook. A record of all scheduled and unscheduled maintenance is kept. The record includes, at a minimum, the date, time, servicing person, and nature of the service. The log is reviewed periodically by the laboratory manager to determine that adequate spare-parts inventories and service agreements are in place. Instrument calibration will be performed as described in the SOPs and at intervals described in Table 14.

Table 14. (Element 15) Testing, inspection, maintenance of equipment

<i>Equipment / Instrument</i>	<i>Maintenance, Testing, or Inspection Activity</i>	<i>Responsible Person</i>	<i>Frequency</i>
DH81 sampler	Operation testing	SFEI staff	Prior to field sampling
Ekman dredge	Operation testing	SFEI staff	Prior to field sampling
GC/ECD	Routine maintenance	Laboratory staff	As specified by manufacturer
GC/MS	Routine maintenance	Laboratory staff	As specified by manufacturer
DMA80	Routine maintenance	Laboratory staff	As specified by manufacturer
CHN analyzer	Routine maintenance	Laboratory staff	As specified by manufacturer

16. INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

The procedures for and frequency of calibration will vary depending on the chemical and physical parameters being determined. Equipment is maintained and checked according to the standard procedures specified in the instrument operation instruction manual.

Upon initiation of an analytical run, after each major equipment disruption, and whenever on-going calibration checks do not meet recommended DQOs (see Tables 4a & 4b), analytical systems will be calibrated with a full range of analytical standards. Immediately after this procedure, the initial calibration

must be verified through the analysis of a standard obtained from a different source than the standards used to calibrate the instrumentation and prepared in an independent manner and ideally having certified concentrations of target analytes of a Certified Reference Material (“CRM”) or certified solution. Frequently, calibration standards are included as part of an analytical run, interspersed with actual samples.

Calibration curves will be established for each 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 those data resulting from quantification within the demonstrated working calibration range may be reported by the laboratory. Alternatively, if the instrumentation 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.

The calibration standards will be prepared from reference materials (neat or solutions) available from the EPA repository, or from available commercial sources. The source, lot number, identification, and purity of each reference material will be recorded. Neat compounds will be prepared weight/volume using a calibrated analytical balance and Class A volumetric flasks. Reference solutions will be diluted using Class A volumetric glassware. Individual stock standards for each analyte will be prepared. Combination working standards will be prepared by volumetric dilution of the stock standards. The calibration standards will be stored at -20 °C. Newly prepared standards will be compared with existing standards prior to their use. All solvents used will be commercially available, distilled in glass and judged suitable for analysis of selected chemicals. Stock standards and intermediate standards are prepared on an annual basis and working standards are prepared every three months.

Sampling and analytical logbooks will be kept to record inspections, calibrations, standard identification numbers, the results of calibrations, and corrective action taken. Equipment logs will document instrument usage, maintenance, repair and performance checks. Daily calibration data will be stored with the raw sample data.

Table 15. (Element 16) Analytical instrument testing, inspection, maintenance

<i>Equipment / Instrument</i>	<i>SOP reference</i>	<i>Calibration Description and Criteria</i>	<i>Frequency of Calibration</i>	<i>Responsible Person</i>
DMA80	EPA 7473	Standard curves $r > 0.995$	Each set-up	Laboratory staff
GC/ECD	EPA 8082	Standard curves $r > 0.995$	Each set-up	Laboratory staff
GC/MS	EPA 1668	Standard curves $r > 0.995$	Each set-up	Laboratory staff
CHN analyzer	EPA 415.1, 440.0	Standard curves $r > 0.995$	Each set-up	Laboratory staff

17. INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

Each monitoring site uses the same equipment and materials. Materials re-supplied to the sites by the laboratories must be of identical quality to those being replaced. Supplies will be inspected by field crews prior to loading of equipment.

All laboratory glass- and Teflon-ware are evaluated prior to use to ensure that chemicals of interest are neither adsorbed to nor leached from the surfaces in contact with the sample. Borosilicate glass or high-density polyethylene containers are used for standard solution preparation and storage. All volumetric glassware is Class A under American Society for Testing and Materials (ASTM) Standards E-287 for Burets, E-288 for Volumetric Flasks and E-969 for Volumetric (transfer) Pipets (Annual Book of ASTM Standards, Vol. 14.02). Dilutions and standards are prepared using both fixed and variable volumetric pipets. The bias and precision of the pipets are monitored by dispensing distilled water aliquots onto a semi-micro analytical balance accurate to 1×10^{-5} gram. Disposable plastic pipet tips, if used, are thoroughly rinsed with DI water before use to remove surface impurities.

Laboratory deionized water used for cleaning and solution preparation purposes has a specific conductance <1.0 μ S/cm. Deionized water samples are collected weekly and analyzed to verify water purity.

Table 16. (Element 17) Inspection/acceptance testing requirements for consumables and supplies.

Project-Related Supplies / Consumables	Inspection / Testing Specifications	Acceptance Criteria	Frequency	Responsible Individual
Sampling supplies	visual	no evident contamination or damage	each event	SFEI field staff

18. NON-DIRECT MEASUREMENTS (EXISTING DATA)

During the development of the initial deliverables of the Grant we were able determine a range of possible locations for field data acquisition. However, in order to make final sampling location selection, we will carry out further non-measurement data acquisition (“Orange Zone” mapping). “Orange zone” in this Project refers to areas within watersheds or in some cases whole sewersheds with concentrated use of either Hg or PCBs. An Orange Zone may include a number of “Hotspots” and associated lesser contaminated zones of influence (or halos). Using a geographic information system (GIS), the objectives of this component are to:

1. Create the base watershed layer and determine the number of discrete watersheds from Richmond south along the East Bay to San Jose and then back up the peninsula to San Francisco.
2. Qualify(quantify?) the sediment / water dilution potential, predict the watersheds with elevated soil concentrations and potentially the largest loads of Hg and PCBs,
3. Determine which contaminated watersheds have stormwater pumping facilities that might allow a watershed scale BMP such as diversion of the first flush winter storm to wastewater treatment,
4. Determine the distance (km) between pump stations in the most contaminated watersheds and treatment facilities,
5. Make a first cut on which treatment facilities might have available wet weather capacity,
6. Determine what part of the first flush volume might physically be treated, and
7. Determine which orange zones to focus characterization efforts on.

In addition we will estimate runoff volume during storms using the simple model (Davis et al., 2000) and use first storm of the season storm rainfall records for the last decade.

19. DATA MANAGEMENT

Data Verification And Validation

The objective of the data transformation and verification goals is to ensure that original data is not unknowingly systematically changed as it is transferred from field observations and instrument measurements to final reports. The specific goals are as follows:

1. Better than 99 percent accuracy in data entry from standard forms to computerized files.
2. Better than 99 percent accuracy in transferring data via computerized media.
3. No loss or gain in significant digits or detection limits when data are transformed by or transferred between responsible organizations.
4. No changes in field or laboratory data other than unit conversions without permanent documentation.

The SFEI QA Officer or designee will be responsible for data verification and validation. Field and laboratory data will be checked for completeness and conformance to procedures and DQOs contained in this QAPP.

Representative field sheets from each set of field collection staff and analytical reports at the start of the project from each reporting laboratory will be reviewed. Problems found will be reported to the appropriate staff or laboratory. Later reports will be periodically reviewed, especially if changes in field or laboratory staff or procedures are made.

Data Reduction

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 Laboratory Project Manager should also check the data report for completeness and errors prior to submission to the Data Manager.

Field Operations

Results of the site/field QA/QC activities are compiled in several types of reports. The reports, persons responsible for their preparation, were described in section 9.1 (field documentation). Data that are summarized in these various reports are also maintained as a permanent part of the database.

Laboratory Operations

The laboratory QA specialist will submit formal reports to the laboratory manager on a monthly basis. These reports include the results and evaluation of internal quality assurance program analyses and documentation of problems and associated corrective actions during that period. The reports also include documentation of method changes. These reports are summarized by the laboratory manager and submitted to SFEI on a monthly basis. SFEI will publish a quality assurance report at the conclusion of the Project.

Documents required to support the quality control/quality assurance activities of the analytical laboratory consist of logbooks, operations manuals, and a laboratory quality assurance plan. Each logbook entry is initialed and dated and the books are reviewed at least quarterly by the laboratory QA specialist or manager. These documents are:

1. Analyst's Log Book -- maintained by each analyst and contains a record of working standards preparation, reference sample results and daily notes.
2. Instrument Log Book -- maintained for each instrument at the work station and contains the maintenance schedule, record of performance of scheduled and unscheduled maintenance, daily instrument settings and calibration data, and observations.
3. Standard Solution Log -- contains all information pertinent to preparation of stock standard solutions, including all weights and volumes, confirmatory analyses, and a shelf life table.
4. Sample Handling SOP -- gives the procedures for receiving and preparing samples for analysis and permanent storage, cleaning of sample containers and lids, and packaging and shipping procedures.
5. Laboratory Quality Assurance Plan -- provides the laboratory-specific details for each topic contained in the Laboratory Operations section of this Quality Assurance Plan.

QA data will be tabulated, summarized, and submitted by the laboratories to SFEI on with each batch of reported data.

Data Reporting

The laboratories will send SFEI reports containing analytical data for submitted field samples and associated QC results. A list of messages concerning error or potential problems at the site is also sent with a cover letter.

Data generated for the Project, including all field data sheets, results of laboratory analyses and copies of the site log entries, will be under the custody of SFEI. If sample integrity is questionable, the quality assurance officer at the laboratories will consult with SFEI before deciding, on a case-by-case basis, whether to discard the sample or to analyze it and include it in the database with an appropriate "flag" or notation. At a minimum, all samples will be stored for the duration of the project.

Each data report package from the laboratories will consist of at least the following:

- A. A cover letter (both hard and electronic copy) transmitting the data report.
 1. Identify samples and ancillary information, such as rainfall, sample volume, etc., and reported units. The information should be submitted in the standard format required by SFEI.
 2. Explain how field and laboratory QA samples are associated with the Field Samples in the data submittal (e.g., all QA samples and field samples are associated by batch number. A batch number represents a set of samples (field and QA), prepared and analyzed together as a set under one calibration.).
 3. A summary of the procedures and instrumentation used, including:
 - a. Type and frequency of QA samples run and
 - i) Concentration range used for spiked samples or equivalent.
 - ii) Concentration range of calibration curves.
 - b. Sample volume extracted, if applicable.
 - c. Completeness of the analysis.
 - d. A list of definitions used for qualifying the results.
 4. Explain the QA/QC analyses: How do the results meet the data quality objectives outlined in the Project QAPP? Provide a summary table of sensitivity, precision, and accuracy achieved and explain any analytical problems and/or corrective actions taken. Examples of items to include are:
 - a. An explanation of any accuracy and recovery calculations that were outside DQOs as outlined in the QAPP.
 - b. Any contamination of the blanks.
 - c. Any analyte concentrations that were outside calibrated range.
 - d. Lost/broken samples.
- B. Tabulated results (actual chemical and ancillary data) in hard copy and electronic form. Reporting should follow the standard MDN or SFEI RMP reporting procedures and include:
 1. Method detection limit (MDL) with units
 2. Concentrations of the analytes of interest (same units as MDL)
 3. Quality assurance information for each analytical batch where applicable:
 - a. SRM results (absolute concentrations measured, certified value, and % relative to certified value)
 - b. % Recovery of the matrix spikes, matrix spike duplicate, or similar samples.
 - c. Field and lab replicate results as measured concentrations, and calculated %RSD or %RPD.
 - d. Method blank results in units equivalent to field sample concentrations so that the impact of contamination on sample values is readily apparent.

GROUP C: ASSESSMENT AND OVERSIGHT**20. ASSESSMENTS & RESPONSE ACTIONS**

Initially, the SFEI QA officer will perform a QA performance audit to determine if each laboratory is in compliance with the procedures outlined in the QAPP. Laboratory performance may be assessed on a continuous basis through the use of performance evaluation, laboratory inter-comparison exercises, and participation in annual certification programs. Additionally, technical systems audits may be conducted by a team composed of SFEI QA Officer or designee, and his/her technical assistants.

Performance Evaluation

Performance evaluation (“PE”) is a type of audit in which the quantitative data generated by the measurement system are obtained independently and compared with routinely obtained data to evaluate the proficiency of an analyst or laboratory. “Blind” PE samples are those whose identity is unknown to those operating the measurement system. The participating laboratories will forward copies of the results from the performance evaluation and/or the inter-laboratory comparison exercises to SFEI within two weeks after receiving the results.

Technical Systems Audit

The SFEI QA Officer may conduct technical systems audits at any time during the scope of the Project. A technical System Audit is a thorough and systematic onsite qualitative audit, where facilities, equipment, personnel, training, procedures, and record keeping are examined for conformance to the QAPP. Results will be reviewed with participating laboratory staff. Corrective actions will be implemented to address weaknesses found regarding the management structure, policy, practices, or procedures.

Corrective Action

In the course of analyses, if the results from the analysis of quality control or quality assurance samples exceed the established control limits, corrective action is taken. Once a requirement for corrective action has been identified, the laboratory manager and/or QA manager must be notified immediately. The QA manager is responsible for evaluating the situation and determining the appropriate corrective action. Corrective action steps include, but are not limited to:

1. Identify problem;
2. Assign investigation responsibility;
3. Determine the cause of the condition;
4. Take action to eliminate the problem;
5. Increase monitoring of the effectiveness of the corrective action; and
6. Verify that the problem has been eliminated.

The QA manager is responsible for verifying that initial action has taken place and appears effective; and after an appropriate duration, for checking to see if the problem has been fully resolved. Examples of corrective action include, but are not limited to:

1. Amend reporting forms.
2. Reanalyze samples if feasible.
3. Check instrumentation to make sure that it is operating properly.
4. Purchase and/or make new standards.
5. Recalibrate with fresh standards.
6. Replace suspect reagents.
7. Examine calculations.
8. Provide additional training in sample preparation and analysis.
9. Evaluate and amend procedures.

10. Accept the data and acknowledge the level of uncertainty or inaccuracy by flagging the data and provide an explanation of the qualification.

Further action would entail the preparation of new standards and confirmation of the correct standard concentrations by an independent analytical method. If these do not result in a finding of a specific problem, the manufacturer of the instrument is contacted about other checks that may be necessary in determining what the problem is followed by repair by the manufacturer. The laboratory's quality assurance specialist is responsible for ensuring the timely solution of identified problems within the analytical laboratory. Problems identified by the external quality assurance program are reported to the quality assurance manager who initiates, tracks, and documents the remedial actions.

21. REPORTS TO MANAGEMENT

At the conclusion of field sampling, laboratory analysis, and project quality assurance review, the contractor will develop and submit a data report to the Contract Manager. Interim reports may be prepared as needed to describe progress status including analytical results, if any. The data report will include a discussion of sampling results, summary tables, graphical representation of sampling sites and analytical concentrations, analytical reports, and an assessment of data quality.

A final report will be prepared at the conclusion of the Project. The final report will present a summary of the methodology, analytical data, an analysis and evaluation of the results, and recommendations for future direction. Reconciliation of results with project DQOs will be included in the evaluation.

Table 17. (Element 21) QA management reports.

Type of Report	Frequency	Projected Delivery Dates(s)	Responsible Party	Report Recipients
Interim	Quarterly	Dec 2006-Dec 2007	SFEI staff	SWRCB
Final		Dec 2007	SFEI staff	SWRCB

GROUP D: DATA VALIDATION AND USABILITY

22. DATA REVIEW, VERIFICATION, AND VALIDATION REQUIREMENTS

The analytical laboratory performing analysis should qualify or reject data from analytical batches if QA sample results are outside of DQOs. A subset of data from field samples should be spot checked for transcription or calculation errors in quantitation. Reporting through a laboratory information management system (LIMS), though not required, is encouraged to minimize human error in data handling. Procedures are described in the next section.

23. VERIFICATION AND VALIDATION METHODS

23.1 Data Verification

All data are checked for errors during the process of data entries. In addition to the quality control measures implemented during sample handling and processing, all sample data are subjected to computer verification. Chemical results not captured directly by data acquisition software are entered into the data management system directly from laboratory data forms. Keyboard data entry is stroke-verified and 5 percent of the entries will be spot checked by a second individual. Manually entered and computer-captured data are merged into a single file where control checks (defined in the computer programs) will ensure that the data are in the proper form and that all necessary information is provided. Aggregate statistics (mean, range, counts) for data will be used to find potential gross data handling errors.

23.2 Data Validation

The objective of data validation is to qualify project data in a manner that will facilitate the understanding and use of the data. Specific goals are as follows:

- a. Data and summaries of data made available through the project contain information that identifies instances where the Project's sampling or analysis protocols have been violated.
- b. All changes in data quality requirements, including data screening and flagging protocols, are applied retroactively to all data to the extent possible.
- c. The validity of project data is unaffected by changes in computer systems and software and data management procedures used in the Project.

Analytical data will be reviewed and validated by the chemists directly responsible for the individual assays and by their respective laboratory supervisor. Notations concerning laboratory related information that may impact sample results will be provided to SFEI. When QC samples do not meet the QC acceptance criteria, the entire sample set will be flagged. A sample flagging system will be used to record problems with sampling, analysis and other areas of concern. Codes and descriptions of data flags will be based on the RMP protocol.

The Principal Investigator of the Project at SFEI and/or designated staff will investigate data flagged by the laboratories. The overall database will also be reviewed and validated by the SFEI staff. The informal data validation performed by laboratory personnel and SFEI staff will meet the project requirements.

The Principal Investigator at SFEI in conjunction with staff from the laboratory will make decisions for any data removal. Such decisions will be based upon the nature and severity of the error. Only data generated during instrument malfunctions will be wholly excluded from the report, and these incidences will be thoroughly documented. All other suspect data will be qualified as appropriate.

24. RECONCILIATION WITH USER REQUIREMENTS

The purpose of this project is to generate an improved understanding of the effectiveness of stormwater management in the Bay Area and prioritize the implementation of further efforts to improve water quality for the management benefit of the State Water Resources Control Board. The final outcome will be two

implementation plans, one for PCBs and one for Hg that describe (through stakeholder censuses based on sound scientific input) the application of BMPs (source control, treatment control and maintenance activities) and scenario's (combinations of these BMPs) to apply under each current or historic use category or land use situation.

The data obtained will improve spatial characterization of the extent and severity of contaminant distribution in urban environments as well as provide information on the physical characteristics of contaminated particles that will help identify BMPs that have the greatest potential for reducing pollutant loadings to San Francisco Bay. The products and information from this project will be important tools for local runoff managers who need to effectively allocate resources to make load reductions for TMDL pollutants. Many of the outcomes of the project (in particular, the BMP review and evaluation tasks) will be applicable to similar efforts in other regions of California and overall the project will serve as a template for other areas of California.

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FIELD DATA SHEET

1. Collection Operator(s) _____

2. Station Name _____

2a. City San Francisco _____

3. Station Latitude _____ Longitude _____
 Cross streets or lot number _____

4. Sampling Start Time _____ Sampling End Time _____

5. Sample Type (sweepings, washwater, street dirt, drop inlet sediments, soils, other (please explain))

6. Sample IDs

Year	Month	Date	Solid / Liquid?	Sampler Initials	Sample Number
2007	09	21	S	LM	

(where:YYYYmmDD indicates year (4 digit), month, date; S indicates solid (L will be used for Liquid); XX indicates sampler's initials; N indicates the sample number, which will start at '01' and increase by one consecutively with each sample collected.

7. Sample weight or volume (state estimate or measured) 8oz

8. Comments on sample condition or site operation:

9. Photo documentation: (Y/N), photo number

10. Post field processing (Y/N), what? (drying, sieving, splitting, settling, sub-sampling)