1999 Quality Assurance Project Plan Regional Monitoring Program for Trace Substances

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Much of the guidance provided in this document is based on protocols developed for the Bay and Toxic Cleanup Program, EPA's Puget Sound Estuary Program (US EPA, 1989), as well as those developed over many years for the National Oceanic and Atmospheric Administration's (NOAA) National Status and Trends (NS&T) Program and EPA's Environmental Monitoring and Assesment Program. The 1993 Quality Assurance Plan for the Virginian Province developed by R.M. Valente and C.J. Strobel was particularly helpful and has been extensively quoted throughout this document. Many other individual research and monitoring programs also provided quidance for this document. The authors and project managers of those guidance documents are all gratefully acknowledged.

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1. INTRODUCTION

This document presents the San Francisco Estuary Institute's (SFEI) quality assurance and quality control (QA/QC) protocols and requirements for contract laboratories associated with the Regional Monitoring Program for Trace Substances (RMP). It includes:

1. A summary of the RMP and its organization.
2. An overview of quality assurance and control in the RMP.
3. Quality assurance and control measures in the field.
4. Quality assurance and control measures in the laboratory.

Much of the guidance provided in this document is based on protocols developed for the Bay Protection and Toxic Cleanup Program (BPTCP), EPA's Puget Sound Estuary Program (US EPA, 1989), as well as those developed over many years for the National Oceanic and Atmospheric Administration's (NOAA) National Status and Trends (NS&T) Program. Many other individual research and monitoring programs also provided guidance for this document. Detailed descriptions of field and laboratory methods are available through SFEI.

Definition of Quality Assurance and Control

Ideally, a monitoring program is based on specific management questions which lead to the formulation of quantitative measurement endpoints. These measurement endpoints are used to develop data quality criteria (DQCs) and performance standards based on realistic confidence and certainty levels. The analysis of monitoring samples requires specific guidance from policy makers and environmental managers as to what the desired uses of the data are. Conversely, what kinds of environmental management decisions can be made in a scientifically defensible way depends on the sensitivity of the measurement system and the levels of confidence and certainty in the data. The purpose of this document is to maximize the probability that environmental data collected by the RMP will meet the expectations of the data users. The DQCs outlined in this document are intended to ensure, to the greatest extent possible, that the data truly represent conditions in the environment with negligible artifacts due to sample collection and processing.

The RMP quality assurance and control system was designed to accommodate evolving information needs by the data users within the inherent constraints of the best available sampling and analytical methodologies. The acceptable or unavoidable variability that is introduced through the sampling and measurement system, as well as the desired sensitivity levels that allow quantitative comparisons to receiving water quality objectives, are reflected in the RMP DQCs expressed in terms of accuracy, precision, completeness, and method detection limit requirements. The DQCs for the RMP were established based on instrument manufacturers' specifications, scientific experience, and historical data. Individual contract laboratories are given the greatest degree of flexibility in their analytical procedures, as long as they can demonstrate that DQCs are being met and that data comparability between laboratories and analytical matrices are documented.

Quality control can also be described as a system that accounts for and quantifies as many potential measurement errors as possible in order to evaluate the uncertainties associated with any given measurement. Errors that influence environmental measurements can be introduced in the field, during shipment, and in the laboratory. The following are some examples of sources of field and laboratory contamination that may need to be taken into account when evaluating sample data quality:

A. Field

1. Sample containers
2. Sample equipment (tubing, pumps)
3. Ship (exhaust, metal surfaces)
4. Personnel (dirty hands, general carelessness)
5. Atmospheric deposition
6. Preservatives

B. Laboratory

1. Atmospheric deposition
2. Personnel
3. Chemical contamination from extraction and/or preparation
4. Analytical instruments and equipment (tubing, corrosion, etc.)
5. Reagents
6. Containers

2. Overview of the RMP

RMP Organization

Project Information

The Regional Monitoring Program for Trace Substances (RMP) began in 1993 and evolved out of a pilot program funded under the State's Bay Protection and Toxic Cleanup Program, after the San Francisco Bay Regional Water Quality Control Board (Regional Board) had developed a funding and implementation structure.

At this time, 74 public and private entities that discharge treated wastewater and cooling water, that manage stormwater runoff, or that are involved in dredging activities contribute the financial resources necessary to conduct the RMP. Many of these program participants also contribute expertise or logistical support. The San Francisco Estuary Institute (SFEI), as the entity designated to implement the Regional Monitoring Strategy, is administering the program under a Memorandum of Understanding with the Regional Board.

Currently, about 170 individual chemical parameters are analyzed in water, sediment, and tissue two to three times per year. Bioassays on water and sediment samples are also conducted to determine possible toxicity to selected organisms. Originally, most of the station locations were chosen so they would be as far as possible from the influence of major contaminant sources and to be as representative as possible of "background" contaminant concentrations. In subsequent years, more stations have been added that are located close to tributaries. Two stations adjacent to the wastewater outfalls of the Cities of San Jose and Sunnyvale are monitored using RMP methodology under a special agreement with the two National Pollutant Discharge Elimination System permit holders and the Regional Board.

Objectives

The current objectives for the RMP are to:

1. Describe patterns and trends in contaminant concentration and distribution.
2. Describe general sources and loadings of contamination to the Estuary.
3. Measure contaminant effect on selected parts of the Estuary ecosystem.
4. Compare monitoring information to relevant water quality objectives and other guidelines.
5. Synthesize and distribute information from a range of sources to present a more complete picture of the sources, distribution, fates, and effects of contaminants in the Estuary ecosystem.

Table 1. Conventional parameters, trace elements, and organic chemicals measured in the RMP.

Conventional Water Quality Parameters	
Conductivity	µmho
Dissolved Organic Carbon	µg/L
Dissolved Oxygen (DO)	mg/L
Hardness (when salinity is < 5 $^{0}/_{00}$)	mg/L ($CaCO_3$)
pH	pH
Phaeophytin	mg/m^3
Salinity	psu
Temperature	°C
Total Chlorophyll *a*	mg/m^3
Total Suspended Solids	mg/L
Dissolved Phosphates	mg/L - P
Dissolved Silicates	mg/L - Si
Dissolved Nitrate	mg/L - N
Dissolved Nitrite	mg/L - N
Dissolved Ammonia	mg/L - N
Sediment Quality Parameters	
% gravel (> 2 millimeters)	% dry weight
% sand (2 mm > 62 µm)	% dry weight
% silt (4 µm–62 µm)	% dry weight
% clay (< 4 µm)	% dry weight
% solids	% dry weight
Temperature	°C
Total Nitrogen	mg/kg
Total Organic Carbon	mg/kg
Pore Water:	
pH	pH
Total Ammonia	µg/kg
Hydrogen Sulfide	µg/kg
Bivalve Parameters	
Bivalve Percent Survival	%
% moisture	%
% lipid	%
Bivalve Condition:	
Total Volume	ml
Shell Volume	ml
Dry Flesh Weight	grams
Physical Condition Index	g/ml
Fish Parameters	
% lipid	%
% moisture	%
length	cm
Toxicity Tests—Water and Sediment	
Eohaustorius estuarius	% survival
Mytilus edulis	% survival

Table 1 (continued). Conventional parameters, trace elements, and organic chemicals measured in the RMP. Blank units mean that the parameter is not sampled for that matrix (water, sediment, or tissue).

Trace elements analyzed in water, sediment, and tissues. (Dissolved and Total)
* indicates near-total rather than total concentrations (see Smith and Flegal, 1993).

	Water	**Sediment** (dry weight)	**Tissue** (dry weight)
Aluminum*		mg/kg	mg/kg
Arsenic	µg/L	mg/kg	mg/kg
Cadmium*	µg/L	mg/kg	mg/kg
Chromium	µg/L	mg/kg	mg/kg
Copper*	µg/L	mg/kg	mg/kg
Iron*		mg/kg	
Lead*	µg/L	mg/kg	mg/kg
Manganese*		mg/kg	
Mercury	µg/L	mg/kg	mg/kg
Nickel*	µg/L	mg/kg	mg/kg
Selenium	µg/L	mg/kg	mg/kg
Silver*	µg/L	mg/kg	mg/kg
Zinc*	µg/L	mg/kg	mg/kg
Tetrabutyltin (TTBT)			µg/kg
Monobutyltin (MBT)			µg/kg
Dibutyltin (DBT)			µg/kg
Tributyltin (TBT)			µg/kg

Table 1 (continued). Conventional parameters, trace elements, and organic chemicals measured in the RMP.

Trace organic chemical analyses in water (pg/L), sediment (µg/kg), and tissue (µg/kg):

PAHs	**Synthetic Biocides**	**Other Synthetic Compounds (IUPAC numbers)**
1-Methylnaphthalene	**Cyclopentadienes**	Hexachlorobenzene
2,3,5-Trimethylnaphthalene	Aldrin	
2,6-Dimethylnaphthalene	Dieldrin	**PCB congeners:**
2-Methylnaphthalene	Endrin	8, 18, 28, 31, 33, 44, 49, 52,
Biphenyl		56, 60, 66, 70, 74, *77**, 87,
Naphthalene	**Chlordanes**	95, 97, 99, 101, 105, 110,
1-Methylphenanthrene	alpha-Chlordane	118, *126**, 128, 132, 138,
Acenaphthene	cis-Nonachlor	141, 149, 151, 153, 156,
Acenaphthylene	gamma-Chlordane	158, *169**, 170, 174, 177,
Anthracene	Heptachlor	180, 183, 187, 194, 195,
Fluorene	Heptachlor Epoxide	201, 203
Phenanthrene	Oxychlordane	
Benz(a)anthracene	trans-Nonachlor	**Dioxins and dioxin like-compounds** (fish tissue only):
Chrysene		
Fluoranthene	**DDTs**	2,3,7,8-TCDD
Pyrene	o,p'-DDD	1,2,3,7,8-PCDD
Benzo(a)pyrene	o,p'-DDE	1,2,3,4,7,8-HCDD
Benzo(b)fluoranthene	o,p'-DDT	1,2,3,6,7,8-HCDD
Benzo(e)pyrene	p,p'-DDD	1,2,3,7,8,9-HCDD
Benzo(k)fluoranthene	p,p'-DDE	1,2,3,4,6,7,8-HCDD
Dibenz(a,h)anthracene	p,p'-DDT	1,2,3,4,6,7,8,9-OCDD
Perylene		2,3,7,8-TCDF
Benzo(ghi)perylene		1,2,3,7,8-PCDF
Indeno(1,2,3-cd)pyrene	**HCH**	2,3,4,7,8-PCDF
Dibenzothiophene	alpha-HCH	1,2,3,4,7,8-HCDF
C1-Chrysenes	beta-HCH	1,2,3,6,7,8-HCDF
C2-Chrysenes	delta-HCH	1,2,3,7,8,9-HCDF
C3-Chrysenes	gamma-HCH	2,3,4,6,7,8-HCDF
C4-Chrysenes		1,2,3,4,6,7,8-HCDF
C1-Dibenzothiophenes	**Other**	1,2,3,4,7,8,9-HCDF
C2-Dibenzothiophenes	Chlorpyrifos	1,2,3,4,6,7,8,9-OCDF
C3-Dibenzothiophenes	Dacthal	
C1-Fluoranthene/Pyrenes	Diazinon	
C1-Fluorenes	Endosulfan I	
C2-Fluorenes	Endosulfan II	
C3-Fluorenes	Endosulfan Sulfate	
C1-Naphthalenes	Mirex	
C2-Naphthalenes	Oxadiazon	
C3-Naphthalenes		
C4-Naphthalenes		
C1 Phenanthrene/Anthracenes		
C2-Phenanthrene/Anthracenes		* co-planar PCBs to be
C3-Phenanthrene/Anthracenes		analyzed in fish tissue only
C4-Phenanthrene/Anthracenes		

Note: Organochlorines analyzed by GC-ECD will be determined using two columns of differing polarity (e.g., DB-5 and DB-17) in order to separate coeluting congeners and reduce the influence of interferences.

Data Usage

Data from this program are made available for scientific research, regulatory purposes, and public awareness. The RMP currently produces an annual report that includes all the data, a summary of results, and some interpretation. Examples of how the data are used by the RMP follows:

Trends:
Seasonal, annual, and long-term patterns in contaminants found in the Estuary.

Objectives and Guidelines:
Data are used by the RMP to evaluate achievement of various water, sediment, and tissue quality guidelines.

Conventional Water and Sediment Parameters:
Conventional water and sediment parameters are evaluated to see how they affect contaminant levels. For example, how does sediment grain-size affect sediment PAH concentrations, or how does DOC in water affect water pesticide concentrations?

Integrated Contaminant Measurements:
Bioaccumulation data may be used to determine time-averaged trends in contaminant concentrations and for comparison with other trend data.

Principal Contacts

Table 2 below presents the principal contact representatives, their affiliation with the RMP, abbreviations used in this report, and current phone numbers:

Table 2. Principal contact representatives for the 1999 RMP.

Name, Title and Affiliation	Abbreviation used in this report	Contact Phone Number
Dr. Rainer Hoenicke, Project Manager & Quality Assurance Officer, San Francisco Estuary Institute	SFEI	(510) 231–5731
Dr. Bruce Thompson, Chief Scientist, San Francisco Estuary Institute	SFEI	(510) 231–5613
Dr. Andrew Gunther and Jordan Gold, Field Coordinators, Applied Marine Sciences	AMS	(510) 373–7142
Dr. Russell Flegal, Principal Investigator, Department of Environmental Toxicology, UCSC	UCSCDET	(408) 459–2093
Dr. Walter Jarman, Principal Investigator, University of Utah, Energy and Geoscience Institute	UUEGI	(801) 585–3082
Dr. Scott Ogle, Principal Investigator, Pacific Eco-Risk Laboratories	PER	(510) 313-8080
Mr. Richard Manson, Principal Investigator, Brooks-Rand, Ltd.	BRL	(206) 632–6206
Mr. John Hunt, Principal Investigator, Marine Pollution Laboratory, Granite Canyon, UCSC	UCSCGCL	(408) 624–0947
Mr. Michael Kellogg, Principal Investigator, City and County of San Francisco	CCSF	(415) 242–2218
Mr. William Ellgas, Principal Investigator, Bay Area Dischargers Association	BADA	(510) 465–5462
Mr. Russell Fairey, Principal Investigator, Moss Landing Marine Laboratory	MLML	(408) 633–6035
Dr. Ron Tjeerdema, Principal Investigator Department of Chemistry and Biochemistry, UCSC	UCSCDCB	(408) 459–2917
Dr. Myrto Petreas, Principal Investigator Hazardous Materials Laboratory, Cal EPA	EPAHML	(510) 540–3624

3. Overview of Quality Assurance and Control in the RMP

Sample Collection, Preservation and Holding

Field personnel will strictly adhere to the RMP protocols to ensure the collection of representative, uncontaminated water, sediment, and tissue chemistry samples. Briefly, the key aspects of quality control associated with chemistry sample collection are as follows:

1. Field personnel will be thoroughly trained in the proper use of sample collection gear and will be able to distinguish acceptable versus unacceptable samples in accordance with pre-established criteria.
2. Field personnel will be thoroughly trained to recognize and avoid potential sources of sample contamination (e.g., engine exhaust, winch wires, deck surfaces, ice used for cooling).
3. Samplers and utensils which come in direct contact with the sample will be made of non-contaminating materials (e.g., glass, high-quality stainless steel and/or Teflon®) and will be thoroughly cleaned between sampling stations.
4. Sample containers will be pre-cleaned and of the recommended type.

Laboratory Operations

The QA/QC requirements presented in the following sections are intended to provide a common foundation for each laboratory's protocols; the resultant QA/QC data will enable an assessment of the comparability of results generated by different laboratories and different analytical procedures. It should be noted that the QA/QC requirements specified in this plan represent the minimum requirements for any given analytical method.

The RMP's performance-based protocols for all analytical laboratories consist of two basic elements:

1. Initial demonstration of laboratory capability. Prior to the initial analysis of samples, each laboratory will demonstrate proficiency in several ways: written protocols for the analytical methods to be employed for sample analysis will be submitted to the Program for review; method detection limits (MDLs) for each analyte will be provided, including the method used for determining MDLs; an initial calibration curve will be established for all analytes, the calibration curve shall include a calibration point set at 3 to 5 times the MDL and should include a minimum of 5 calibration points for trace organics; acceptable performance will be shown on known or blind reference material (see Laboratory Quality Control Procedures, Initial Demonstration of Capability, p. 20.); and long-term standard reference material results on reference material with comparable analyte concentrations as those in RMP field samples will be submitted.
2. Ongoing demonstration of capability. Following a successful first phase, the laboratory will demonstrate its continued capabilities in several ways: participation in an on-going series of interlaboratory comparison exercises, routine analysis of certified reference materials, calibration checks, and analysis of laboratory reagent blanks and fortified samples. (See Laboratory Quality Control Procedures, Ongoing Demonstration of Capability, p. 22.)

The results for the various QA/QC samples will be reviewed by laboratory personnel immediately following the analysis of each sample batch. These results will then be used to determine when data quality criteria have not been met, and corrective actions will be taken before processing a subsequent sample batch. When data quality criteria are not met, specific corrective actions are required before the analyses may proceed.

Information Management

Various data and information generated from the RMP are stored at SFEI. The digital data generated from the sampling cruises arrive at SFEI in various formats and are converted to standard RMP database format. After final QA checks, the data are uploaded to the RMP database in Oracle®. Data tables are generated from this database. The same database is also accessible through SFEI's website (http://www.sfei.org).

Sample Tracking

RMP sample collection personnel have developed a comprehensive system for recording sampling information in the field and tracking sample shipments. This component is included in the *RMP Field Operations Manual* (http://www.sfei.org/rmp/docs/fom_1.html).

Data Reporting Requirements

As previously indicated, laboratory personnel will verify that the measurement process was "in control" (i.e., all specified data quality criteria were met or acceptable deviations explained) for each batch of samples before proceeding with the analysis of a subsequent batch. In addition, each laboratory will establish a system for detecting and reducing transcription and/or calculation errors prior to reporting data.

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

4. Field Quality Assurance and Quality Control

Field Performance Measurements: Terminology

Following is a list of definitions of field performance measurements that are frequently included in the sampling protocol. Some of these measurements only need to be taken when an established procedure is changed, while others need to be taken at various intervals throughout the sampling process.

1. Source Solution Blanks: These account for any pre-existing contamination in the water or preservatives used to prepare the sample containers as well as the field or travel blanks.
2. Bottle Blanks: These account for contamination in sampling containers, in addition to any contamination due to the source solution.
3. Travel Blanks: These account for contaminants introduced during the transport process between the laboratory and field site, in addition to any contamination from the source solution and container.
4. Equipment Blank: These account for contamination introduced by the field sampling equipment.

5. Field Duplicates: These account for variability in the field and laboratory.
6. Field Blanks: These account for all of the above sources of contamination that might be introduced to a sample as well as that which would be due to the sampling equipment and the immediate field environment. Field 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. Field blanks for sediment analyses generally consist of ultra pure sand. True field blanks for biological tissue samples do not exist.

Field Performance Measurements Used by the RMP

Routine preparation, collection, and analysis of all the field samples mentioned above would be redundant and inefficient. Since trace metals in environmental water samples are orders of magnitude lower than in sediments or tissues, the field QA/QC measures are much more rigorous for water samples. Most QA/QC steps taken to minimize trace element sampling artifacts are also applicable for the collection of trace organic samples.

Source solution blanks will be made with Milli-Q or Nanopure water (free of trace organic and element contaminants), and trace-metal grade acids will be used in all aspects of cleaning, storage, and analysis. The sample bottles will be cleaned and stored filled (water containers only) with acid solution. Contamination of these source solutions will be routinely checked, and corrective steps taken whenever contamination of source solutions are indicated.

Bottle blanks that were generated early on in the monitoring program showed that the "trace-metal clean" polyethlene and Teflon® bottles used for all three of the RMP samples are not a source of trace element contamination. Certified trace-metal-free borosilicate glass containers will be used for sediment samples, and measurements of bottle blanks will be conducted for each lot.

Travel blanks are not routinely used for water, sediment, or tissue samples. The possibility of contamination during the transport between the laboratory and field site will be mitigated by the measures taken to keep the sample bottles in an enclosed micro-environment. All water sample bottles will be quadruple-bagged and kept inside a tightly closed plastic bucket. They will be filled with a weak acid solution, so any metals leached from the container will be kept in solution. This storage solution will be discarded immediately prior to sampling, followed by five rinses with the sample. The sample bottles will be removed from the plastic bags only in a class 100 clean laboratory, except during active sample. The bottles will always be handled with polyethylene-gloved clean hands.

Equipment blanks for water samples will be collected periodically in the laboratory by pumping Milli-Q water through the sample tubing connected to a filter cartridge. The sampling equipment will consist of a dual-head peristaltic pump which pumps water up through the inlet length of Teflon® tubing connecting to C-flex tubing, and finally to the outlet length of Teflon® tubing. The Teflon® and C-flex tubing will be connected via polypropylene Y connector fittings. Filtered samples will additionally pass through a 0.45 micrometer polycabonate filter cartridge attached to the outlet end. The sample will be exposed to the interior of the Teflon® and C-flex tubing, the Y fittings, and the filter cartridge, all of which will have been rigorously cleaned with ultra-pure reagents. Sediments will be collected with a van Veen grab sampler. However, equipment blanks will not be taken. The sediment sampling protocol is discussed further in the field blanks section. Since bivalves will be hand collected, equipment blanks are not relevant for tissue samples.

Field duplicates will only be routinely collected for water samples. Water will be filtered in duplicate so that evaluation of the sampling system precision includes the filter cartridge. Short-

term environmental variability, most notably due to swift currents and non-homogeneous suspended sediment loads will affect the sampling precision. Golden Gate station (BC20) probably has the least variability, and will, therefore, usually be included as a field duplicate. Two or three additional stations at different locations of the Bay will also be collected in duplicate.

Since sediment concentrations in the Estuary vary spatially, a field duplicate would be unable to separate natural variability from that introduced by the sampling and analysis system. In 1994, triplicate samples were taken at three RMP stations to assess within-station variability. Variability was shown to be parameter-specific for trace elements with certain metals exhibiting less than 3% variability between triplicates and others up to 40% variability between triplicates.

Field duplicates in bivalve tissue samples will not be collected *per se.* Between 40 and 100 bivalves are deployed at each site. They will be hand-collected and later homogenized as a single sample. Two sub-samples of fewer animals each, would assess variability in the animals rather than assess precision in technique or environmental variability.

Field blanks for water will be generated under actual field conditions and will be treated in the exact same manner as the environmental field samples in both the field and laboratory. True field blanks are, however, difficult to obtain because assessment of the monitoring vessel's aura of contamination at the time of sampling is not straight-forward. True field blanks are not routinely collected by any worker in this field and are not routinely reported in the literature. Collection of a field blank by pumping the "source solution" (Milli-Q water) through the system on deck does not adequately address the issues of potential contamination of the water sample by the monitoring vessel since metals are ubiquitous on boats. Therefore, a field blank merely measures contamination of the sampling equipment, which is already accounted for, and perhaps aerosol contamination, but it cannot sort out vessel contamination from water contamination present without the vessel sitting in the source water. Mitigation steps for this potential problem will be taken. To avoid aerosol contamination the sample tubing inlet and outlet will be kept covered until the engines are turned off, and the engine will remain off until sampling is completed and the tubing inlet and outlet are once again covered. To avoid possible contamination of the sample by the boat, the 15–20 foot sampling pole will be extended over the windward side, oriented up-current from the vessel and upwind from the equipment and personnel.

To get around the inability to collect a true field blank, the metal concentrations of environmental water samples will be considered accurate if they are oceanographically consistent (Boyle *et al.,* 1981), and comparable values are obtained by intercalibration studies (Patterson and Settle, 1976). These mitigation methods have been adopted by many workers in the field following extensive experience (Bewers and Windom, 1981; Boyle *et al.,* 1981; Schaule and Patterson, 1981; Berman *et al.,* 1983; Bruland *et al.,* 1985; Flegal and Stukas, 1987; Landing *et al.,* 1995; Yeats *et al.,* 1995).

Samples approaching field blanks have been obtained for the RMP by collecting relatively pristine oceanic water well beyond coastal influences, using the same research vessel and sampling equipment as during a normal sampling cruise. The field blank will not be collected during the cruise, because of the extra time required to motor the boat beyond coastal influences. Routine collection of these oceanic blanks will not be conducted due to cost constraints.

For trace organic sampling, containers will be routinely checked for contamination, and plastic material for storage, transport, and protection of samples will be avoided. Only ultra-pure solvents will be used in the preparation of the XAD resin and filters that capture the particulate and dissolved fraction of the water samples. The XAD resin and filters through which about 100 liters of water are pumped will remain enclosed and inaccessible to aerial contamination. Tests on travel blanks of XAD columns and of a solvent-extracted glass fiber filter have shown either no

measurable levels of analytes or levels one to two orders of magnitude lower than field concentrations (Jarman, in prep).

Collection of true sediment field blanks is logistically difficult and has been deemed unnecessary due to precautions taken that minimize contamination of the samples. Sediment samples will be collected with a van Veen grab sampler based on modified NOAA Status and Trends, Benthic Surveillance Project methods (Lauenstein and Young, 1986; SFEI, 1997) All surfaces of sediment sampling and processing instruments coming into contact with the sample will be made of inert materials, such as Teflon® or stainless steel coated with Dykon®, and will be thoroughly cleaned prior to field use. Equipment will also be cleaned with Alkonox detergent between stations and rinsed with hydrochloric acid, followed by methanol, to avoid any carryover contamination from one station to another. Sampling, compositing, and homogenization will be conducted on board ship with gloved hands, and the homogenate will be placed into pre-cleaned polyethylene or Teflon® containers for trace element analyses, and into pre-cleaned certified glass jars with Teflon®-lined lids for trace organic analyses. The homogenization bucket will always be covered with aluminum foil during the collection of the sediment samples to avoid sample contamination via aerial deposition.

Bivalves will be handled in the field according to established protocols of the California State Mussel Watch Program designed to minimize sample contamination. Bivalves destined for trace element analysis will be placed in polyethylene ziploc bags, placed on dry ice, and kept frozen until homogenization and analysis. Bivalves used for trace organic analysis will be wrapped in aluminum foil.

5. Laboratory Quality Assurance and Control

RMP Laboratory Requirements

The San Francisco Estuary Institute requires all Regional Monitoring Program laboratories to demonstrate capability continuously through:

1. Strict adherence to common QA/QC procedures.
2. Routine analysis of certified reference materials (CRMs)[1].
3. Regular participation in an on-going series of interlaboratory comparison exercises.

This is a “performance-based” approach for measurements of low-level contaminant analyses, involving continuous laboratory evaluation through the use of accuracy-based materials (e.g., CRMs), laboratory matrix spikes, laboratory reagent blanks, calibration standards, laboratory- and field-duplicated blind samples, and others as appropriate. The definition and use of each of these types of quality control samples are explained in later sections.

Quality control operates to make sure that data produced are satisfactory, consistent, and dependable. Under the RMP performance-based chemistry QA program, laboratories are not required to use a single, standard analytical method for each type of analysis, but rather are free to choose the best or most feasible method within the constraints of cost and equipment that is suitable for meeting the RMP’s data quality criteria (DQCs). The RMP DQCs were developed based on the kinds of general management questions that the environmental data are supposed to

[1] Certified reference materials (CRMs) are samples in which chemical concentrations have been determined accurately using a variety of technically valid procedures; these samples are accompanied by a certificate or other documentation issued by a certifying body (e.g., agencies such as the National Research Council Canada (NRCC), US EPA, US Geological Survey, etc.). Standard Reference Materials (SRMs) are CRMs issued by the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards (NBS). A useful catalogue of marine science reference materials has been compiled by Cantillo and Calder (1992).

help answer. The RMP has developed specific guidelines for measurement precision, accuracy, and levels of detection that are reflected in sampling, handling, and analysis requirements that can satisfy a large spectrum of potential management questions. Each laboratory will, however, continuously demonstrate proficiency and data comparability through routine analysis of accuracy-based performance evaluation samples, split samples, and reference materials representing actual sample matrices. No single analytical method has been officially approved for low-level (i.e., low parts per quadrillion and parts per billion) analysis of organic and inorganic contaminants in water or estuarine sediments. Recommended methods for the RMP are those developed in various academic research programs and those used in the NOAA NS&T Program (Lauenstein *et al.,* 1993).

All laboratories providing analytical support for chemical or biological analyses will have the appropriate facilities to store, prepare, and process samples, and appropriate instrumentation and staff to provide data of the required quality within the time period dictated by the project. Laboratories are expected to conduct operations in a way that includes:

1. A program of scheduled maintenance of analytical balances, microscopes, laboratory equipment, and instrumentation.
2. Routine checking of analytical balances using a set of standard reference weights (American Society of Testing and Materials (ASTM) Class 3, NIST Class S-1, or equivalents).
3. Checking and recording the composition of fresh calibration standards against the previous lot. Acceptable comparisons are < 2 percent of the previous value.
4. Recording all analytical data in bound (where possible) logbooks, with all entries in ink, or electronic format.
5. Monitoring and documenting the temperatures of cold storage areas and freezer units once per week.
6. Verifying the efficiency of fume hoods.
7. Having a source of reagent water meeting ASTM Type I specifications (ASTM, 1984) available in sufficient quantity to support analytical operations. The conductivity of the reagent water will not exceed 18 megaohm at 25°C. Alternately, the resistivity of the reagent water will exceed 10 μmhos/cm.
8. Labeling all containers used in the laboratory with date prepared, contents, initials of the individual who prepared the contents, and other information as appropriate.
9. Dating and safely storing all chemicals upon receipt. Proper disposal of chemicals when the expiration date has passed.
10. Having QAPP, SOPs, analytical methods manuals, and safety plans readily available to staff.
11. Having raw analytical data, such as chromatograms, accessible so that they are available upon request.

Laboratories will be able to provide information documenting their ability to conduct the analyses with the required level of data quality. Such information might include results from interlaboratory comparison studies, control charts and summary data of internal QA/QC checks, and results from certified reference material analyses.

Data Formatting and Transfer

Laboratories will also be able to provide analytical data and associated QA/QC information in a format and time frame agreed upon with the RMP Project Manager or designee. Each year data formatting and reporting expectations will be clearly identified and distributed to participating laboratories.

Laboratory Personnel, Training, and Safety

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

To ensure that the samples are analyzed in a consistent manner throughout the duration of the project, key laboratory personnel will participate in an orientation session conducted during an initial site visit or via communications with RMP staff. The purpose of the orientation session is to familiarize key laboratory personnel with the QAPP and the QA/QC program. Participating laboratories may be required to demonstrate acceptable performance before analysis of samples can proceed, as described in subsequent sections. Laboratory operations will be evaluated on a continuous basis through technical systems audits, and by participation in interlaboratory, round-robin programs. Meetings shall be held with all participating laboratories at regular intervals to continually review QA/QC procedures, and to revise/update the QAPP.

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

Quality Assurance Documentation

All laboratories will have the latest revision of the RMP QAPP. In addition, the following documents and information will be current, and they will be available to all laboratory personnel participating in the processing of RMP samples, as well as to SFEI project officials:

1. Laboratory QA Plan: Clearly defined policies and protocols specific to a particular laboratory, including personnel responsibilities, laboratory acceptance criteria and corrective actions to be applied to the affected analytical batches, qualification of data, and procedures for determining the acceptability of results.
2. Laboratory Standard Operating Procedures (SOPs): Containing instructions for performing routine laboratory procedures.
3. Laboratory Analytical Methods Manual: Step-by-step instructions describing exactly how a method is implemented in the laboratory for a particular analytical procedure. Contains all analytical methods utilized in the particular laboratory for the RMP.

4. Instrument Performance Information: Information on instrument baseline noise, calibration standard response, analytical precision and bias data, detection limits, etc. This information is usually recorded in logbooks or laboratory notebooks.

5. Control Charts: Control charts are useful in evaluating internal laboratory procedures and are helpful in identifying and correcting systematic error sources. Contract laboratories are encouraged to develop and maintain control charts whenever they may serve in determining sources of analytical problems.

Laboratory Performance Audits/Corrective Action

Initially, a QA performance audit will be performed by RMP QA staff to determine if each laboratory effort is in compliance with the procedures outlined in the QAPP and to assist the laboratory where needed. Additionally, technical systems audits will be conducted by a team composed of the RMP QA Officer or designee, and his/her technical assistants. Reviews may be conducted at any time during the scope of the study. Results will be reviewed with participating laboratory staff and corrective action recommended and implemented, where necessary. Furthermore, laboratory performance will be assessed on a continuous basis through the use of laboratory intercomparison studies (round robins). Laboratories performing organic and metal chemistry analyses will be required to participate in the annual National Status and Trends Intercalibration, and to report the findings in a timely fashion to the designated contact at NOAA and to the RMP QA Officer.

Laboratory Performance Measurements

Laboratory performance measurements included in the analysis stream and are designed to check if data quality criteria are met are briefly defined below.

1. Method Blanks (also called laboratory reagent blanks or preparation blanks): These account for contaminants present in the preservative and analytical solutions used during the quantification of the parameter.

2. Injection Internal Standards: This accounts for error introduced by the analytical instrument.

3a. Replicate Samples: These are replicates of extracted material that measure the instrumental precision.

3b. Laboratory Replicate Samples: These are replicates of the raw material that are extracted and analyzed to measure laboratory precision.

3c. Matrix Spike Replicate Samples: This is used to assess both laboratory precision and accuracy. This is particularly useful when the field samples analyzed do not contain many of the target compounds (measuring non-detects in replicate does not allow the data reviewer to measure the precision or the accuracy of the data in an analytical batch).

4. Matrix Spike Samples: These are field samples to which a known amount of contaminant is added and used to measure potential analytical interferences present in the field sample.

5. Certified Reference Materials (CRM): 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.

These types of samples serve to check if errors were introduced during the analysis process and if so, at what step(s) and at what magnitude. The remainder of this document will provide RMP guidance for general laboratory requirements, and protocols for checking and tracking possible sources of errors (outlined above) in the analytical process.

Laboratory Quality Control Procedures

The performance-based protocols utilized in the RMP for analytical chemistry laboratories consist of two basic elements: initial demonstration of laboratory capability (e.g., documentation that the analyses of samples are within the data quality criteria) and ongoing demonstration of capability. Prior to the initial analysis of samples, each laboratory will demonstrate capability and proficiency.

Initial Demonstration of Capability

Instrument Calibration

Upon initiation of an analytical run, after each major equipment disruption, and whenever on-going calibration checks do not meet recommended DQCs (see Tables 3 and 4), the system 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. However, this practice does not document the stability of the calibration and is incapable of detecting degradation of individual components, particularly pesticides, in standard solutions used to calibrate the instrument. The calibration curve is acceptable if it has a r^2 of 0.990 or greater for all analytes present in the calibration mixtures. If not, the calibration standards, as well as all the samples in the batch must be re-analyzed. All calibration standards will be traceable to a recognized organization for the preparation and certification of QA/QC materials (e.g., NIST, National Research Council Canada (NRCC), US EPA, etc.).

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 data which result from quantification within the demonstrated working calibration range may be reported by the laboratory (i.e., quantification based on extrapolation is not acceptable). Alternatively, if the 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.

Initial Documentation of Method Detection Limits

Analytical chemists have coined a variety of terms to define “limits” of detectability; definitions for some of the more commonly used terms are provided in Keith *et al*. (1983) and in Keith (1991). In the RMP, 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 Code of Federal Regulations (40 CFR Part 136) gives the following rigorous definition:

> The MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

The American Society of Testing and Materials (ASTM) defines the limit of detection as:

> A concentration of twice the criterion of detection...when it has been decided that the risk of making a Type II error is to be equal to a Type I error.

In order to compare MDLs in quantitative terms by different laboratories participating in RMP analysis, MDLs will initially be determined according to 40 CFR 136.2 (f) and Appendix B of 40 CFR 136. Determining the MDL with this procedure is elaborate and need not be determined annually provided that:

1. No process or method changes have been made.
2. Check samples containing an analyte spike at about 2x MDL indicate that the sample is detected. The required frequency of check samples is quarterly.

The matrix and the amount of sample (i.e., dry weight of sediment or tissue) used in calculating the MDL will match as closely as possible the matrix of the actual field samples and the amount of sample typically used. In order to ensure comparability of results among different laboratories, MDL target values have been established for the RMP (see Table 5). These MDLs have been derived empirically. Most are considerably lower than water quality objectives or sediment and tissue quality guidelines and provide the foundation for having a high level of certainty in the data.

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

Limits of Quantitation

Taylor (1987) states that “a measured value becomes believable when it is larger than the uncertainty associated with it”. The uncertainty associated with a measurement is calculated from the standard deviation of replicate measurements (s_0) of a low concentration standard or a blank. Normally, the MDL is set at three times the standard deviation of replicate measurements, as it is at this point that the uncertainty of a measurement is approximately ±100% at the 95% level of confidence. Values at the MDL may not reflect a signal much above zero and, therefore, are quantitatively not very meaningful. The limit of quantitation (LOQ), as established by the American Chemical Society, is normally ten times the standard deviation of replicate measurements, which corresponds to a measurement uncertainty of ±30% (see Taylor, 1987). By these standard definitions, measurements below the MDL are not believable, measurements between the LOQ and the MDL are only semi-quantitative, and confidence in measurements above the LOQ is high.

Initial Blind Analysis of Representative Samples

As appropriate, representative sample matrices which are uncompromised, homogeneous, and contain the analytes of interest at concentrations of interest will be used to evaluate performance of analytical laboratories new to the RMP prior to the analysis of field samples. The samples used for this initial demonstration of laboratory capability typically will be distributed blind (i.e., the laboratory will not know the concentrations of the analytes of interest) as part of the interlaboratory comparison exercises. Based on results that have typically been attained by

experienced RMP laboratories, a new laboratory's performance generally will be considered acceptable if its submitted values are within DQCs (Tables 3 and 4) of the known concentration, or the consensus value, of each analyte of interest in the samples. These criteria apply only for analyte concentrations equal to or greater than three times the RMP target MDL. If the results for the initial analysis fail to meet these criteria, the laboratory will be required to repeat the analysis until the performance criteria are met, prior to the analysis of RMP field samples.

Record of Certified Reference Material

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

Ongoing Demonstration of Capability

Participation in Interlaboratory Comparison Exercises

Through an interagency agreement, NOAA's NS&T Program and EPA's EMAP program jointly sponsor an on-going series of interlaboratory comparison exercises (round-robins). All the RMP analytical laboratories are required to participate in these intercomparison exercises, which are conducted jointly by NIST and NRCC. These exercises provide a tool for continuous improvement of laboratory measurements by helping analysts identify and resolve problems in methodology and/or QA/QC. The results of these exercises are also used to evaluate both the individual and collective performance of the participating analytical laboratories on a continuing basis and to insure that ongoing measurements are meeting DQCs. The RMP laboratories are required to initiate corrective actions if their performance in these comparison exercises falls below certain pre-determined minimal standards, described in later sections.

One exercise is usually conducted over the course of a year. In a typical exercise, NIST or NRCC will distribute performance evaluation samples of an "unknown" and a certified reference material (CRM) to each laboratory, along with detailed instructions for analysis. A variety of performance evaluation samples have been utilized in the past, including accuracy-based solutions, sample extracts, and representative matrices (e.g., sediment or tissue samples). Laboratories are required to analyze the sample(s) "blind" and will submit their results in a timely manner both to the RMP Coordinator and to NIST or NRCC (as instructed). Laboratories which fail to maintain acceptable performance may be required to provide an explanation and/or undertake appropriate corrective actions. At the end of each calendar year, coordinating personnel at NIST and NRCC hold a QA workshop to present and discuss the comparison exercise results. Representatives from participating laboratories are strongly encouraged to participate in the annual QA workshops, which provide a forum for discussion of analytical problems brought to light in the comparison exercises.

Routine Analysis of Certified Reference Materials or Laboratory Control Materials

Certified reference materials generally are considered the most useful QC samples for assessing the accuracy of a given analysis (i.e., the closeness of a measurement to the "true" value). CRMs can be used to assess accuracy because they have "certified" concentrations of the analytes of interest, as determined through replicate analyses by a reputable certifying agency using two independent measurement techniques for verification. In addition, the certifying agency may provide "non-certified" or "informational" values for other analytes of interest. Such values are determined using a single measurement technique, which may introduce unrecognized bias. Therefore, non-certified values must be used with caution in evaluating the performance of a laboratory using a method which differs from the one used by the certifying agency.

A laboratory control material (LCM) is similar to a certified reference material in that it is a homogeneous matrix which closely matches the samples being analyzed. A "true" LCM is one which is prepared (i.e., collected, homogenized, and stored in a stable condition) strictly for use in-house by a single laboratory. Alternately, the material may be prepared by a central laboratory and distributed to others (so-called regional or program control materials). Unlike CRMs, concentrations of the analytes of interest in LCMs are not certified but are based upon a statistically valid number of replicate analyses by one or several laboratories. In practice, this material can be used to assess the precision (i.e., consistency) of a single laboratory, as well as to determine the degree of comparability among different laboratories. If available, LCMs may be preferred for routine (i.e., day to day) analysis because CRMs are relatively expensive.

Routine analysis of CRMs or, when available, LCMs represents a particularly vital aspect of the "performance-based" RMP QA philosophy. At least one CRM or LCM must be analyzed along with each batch of 20 or fewer samples (i.e., QA samples should comprise a minimum of 5% of each set of field samples). For CRMs, both the certified and non-certified concentrations of the target analytes will be known to the analyst(s) and will be used to provide an immediate check on performance before proceeding with a subsequent sample batch. Performance criteria for both precision and accuracy have been established for analysis of CRMs or LCMs (Tables 3 and 4); these criteria are discussed in detail in the following paragraphs. If the laboratory fails to meet either the precision or accuracy control limit criteria for a given analysis of the CRM or LCM, the data for the entire batch of samples is suspect. Calculations and instruments will be checked; the CRM or LCM may have to be reanalyzed (i.e., reinjected) to confirm the results. If the values are still outside the control limits in the repeat analysis, the laboratory is required to find and eliminate the source(s) of the problem and repeat the analysis of that batch of samples until control limits are met, before final data are reported. The results of the CRM or LCM analysis will never be used by the laboratory to "correct" the data for a given sample batch.

Precision criteria: Precision is the reproducibility of an analytical method. Each laboratory is expected to maintain control charts for use by analysts in monitoring the overall precision of the CRM or LCM. Upper and lower control chart limits (e.g., warning limits and control limits) will be continually updated; control limits based on 99% confidence intervals around the mean are recommended. The relative standard deviation (RSD) will be calculated for each analyte of interest in the CRM based on the last 7 CRM analyses. Acceptable precision targets for various analyses are listed in Tables 3 and 4.

Laboratory Replicates for Precision

A minimum of one field sample per batch of RMP samples submitted to the laboratory will be processed and analyzed in duplicate or more for precision. The relative percent difference between two replicate samples or the relative standard deviation between more than two replicate samples (RPD or RSD respectively) will be less than the DQC listed in Tables 3 and 4 for each analyte of interest. Following are the calculations:

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

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

ABS — absolute value

STDEV — standard deviation

If results for any analytes do not meet the DQC for the RPD or RSD, calculations and instruments will be checked. A repeat analysis may be required to confirm the results. Results which repeatedly fail to meet the objectives indicate sample inhomogeneity, unusually high concentrations of analytes or poor laboratory precision. In this case, the laboratory is obligated to halt the analysis of samples and eliminate the source of the imprecision before proceeding.

Accuracy criteria: The "absolute" accuracy of an analytical method can be assessed using CRMs only when certified values are provided for the analytes of interest. However, the concentrations of many analytes of interest to the RMP are provided only as non-certified values in some of the more commonly used CRMs. Therefore, control limit criteria are based on "relative accuracy", which is evaluated for each analysis of the CRM or LCM by comparison of a given laboratory's values relative to the "true" or "accepted" values in the LCM or CRM. In the case of CRMs, this includes both certified and noncertified values. The "true" values are defined as the 95% confidence intervals of the mean.

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

There are three combined groups of compounds for the purpose of evaluating relative accuracy for organic analyses: PAHs, PCBs, and pesticides. For each group of analytes, 70% of the individual analytes will be within 35% of the certified 95% confidence interval; no individual analyte value shall exceed ±30% of the 95% confidence interval more than once in consecutive analyses without appropriate documentation and consultation with the RMP QA officer. For inorganic analyses, the laboratory's value will be within 20–25% of the certified 95% confidence interval for each analyte of interest in the CRM. 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 which are >3 times the MDL established by the laboratory.

Continuing Calibration Checks

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

If the control limits for analysis of the calibration check solution (set by the laboratories) are not met, the initial calibration will have to be repeated. The calibration check for 90% of the analyte shall not deviate more than ±25% from the known value for PAHs and ±20% for PCBs and pesticides. If possible, the samples analyzed before the calibration check solution that failed the DQCs will be reanalyzed following recalibration. The laboratory will begin by reanalyzing the last sample analyzed before the calibration check solution which failed. If the RPD between the results of this reanalysis and the original analysis exceeds precision DQCs (Tables 3 and 4), the instrument is assumed to have been out of control during the original analysis. If possible, reanalysis of samples will progress in reverse order until it is determined that the RPD between initial and reanalysis results are within DQCs (Tables 3 and 4). Only the re-analysis results will be reported by the laboratory. If it is not possible or feasible to perform reanalysis of samples, all earlier data (i.e., since the last successful calibration control check) are suspect. In this case, the laboratory will prepare a narrative explanation to accompany the submitted data.

Laboratory Reagent Blank

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

Completeness

Completeness is defined as “a measure of the amount of data collected from a measurement process compared to the amount that was expected to be obtained under the conditions of measurement” (Stanley and Verner, 1985). Field personnel will always strive to achieve or exceed the RMP completeness goals of 95–98% for water, sediment, or tissue samples.

Surrogates

The usage of the terms “surrogate”, “injection internal standard”, and “internal standard” varies considerably among laboratories and is clarified here.

Surrogates are compounds chosen to simulate the analytes of interest in organic analyses. Surrogates are used to estimate analyte losses during the extraction and clean-up process and must be added to each sample, including QA/QC samples, prior to extraction. The reported concentration of each analyte is adjusted to correct for the recovery of the surrogate compound, as done in the NOAA NS&T Program. The surrogate recovery data will be carefully monitored; each laboratory must report the percent recovery of the surrogate(s) along with the target analyte data for each sample. If possible, isotopically-labeled analogs of the analytes will be used as surrogates.

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 limit criteria used by the laboratory will be provided in the standard operating procedures submitted to SFEI.

Internal Standards

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

Dual-Column Confirmation

Dual-column chromatography is required for analyses using GC-ECD due to the high probability of false positives arising from single-column analyses.

Matrix Spike and Matrix Spike Duplicate

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

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

Recovery data for the fortified compounds ultimately will provide a basis for determining the prevalence of matrix effects in the samples analyzed during the project. If the percent recovery for any analyte in the MS or MSD is less than the recommended warning limit of 50 percent, the chromatograms (in the case of trace organic analyses) and raw data quantitation reports will be reviewed. If an explanation for a low percent recovery value is not discovered, the instrument

response may be checked using a calibration standard. Low matrix spike recoveries may be a result of matrix interferences and further instrument response checks may not be warranted, especially if the low recovery occurs in both the MS and MSD, and the other QC samples in the batch indicate that the analysis was “in control”. An explanation for low percent recovery values for MS/MSD results will be discussed in a cover letter accompanying the data package. Corrective actions taken and verification of acceptable instrument response will be included. Analysis of the MS/MSD is also useful for assessing laboratory precision. The RPD between the MS and MSD results should be less than the target criterion listed in Tables 3 and 4 for each analyte of interest.

Field Replicates and Field Split Samples

As part of the regular quality assurance program of the RMP, replicate sediment and tissue samples may be collected, homogenized, and placed in separate sample containers at a minimum of one pre-selected station for subsequent chemical analysis whenever funds allow. One of the sample containers for each trace organic and metals analysis will be submitted as a blind field replicate to the primary analytical laboratory. Another set of containers, called field splits, will be sent blind to additional laboratories selected to participate in the split sample analysis of trace elements and trace organics. The analysis of field replicates and field splits will provide an assessment of both inter-and intra-laboratory precision and variance in the sample matrix at the field site.

Table 3a. WATER: Quality control criteria for analysis of organic compounds.

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	CRITERIA	CORRECTIVE ACTION
Method Blank	**Contamination** by reagents, laboratory ware, etc.	One per batch	< MDL or < 10% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.
Instrument Blank	**Cross contamination**	NA	Set by laboratory	NA
Certified Reference Material (CRM)	**Accuracy**	NA	NA	NA
Replicates: (analytical and/or laboratory) Applies to replicates of field samples, CRMs, matrix spike samples, etc.	**Precision** Instrument and/or overall reproducibility of a result.	One per batch	RPD or RSD < 35%	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, identify and eliminate source of imprecision and reanalyze.
Matrix Spike	**Accuracy**	1 per 20 field samples	Recovery > 50%	Check CRM or LCS recovery. Review chromatograms and raw data quantitation reports. Check instrument response using calibration standard. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed.
Surrogate Spike	**% Recovery** used to adjust sample results	One per sample	Set by analyzing laboratory (Report surrogate recovery and acceptance criteria in final report)	Check CRM or LCS recovery. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed
Continuing Calibration Check solutions	**Accuracy & Precision**	At least every 12 hours	Known values for 90% of analytes shall not deviate more than ± 25% for PAHs, and ± 20% for PCBs and Pesticides.	Beginning with last sample before failure, recalibrate and reanalyze. Compare RPD and reanalyze.

MDL = method detection limit; RPD = relative percent difference; RSD = relative standard deviation (see page24 for equations)

Table 3b. WATER: Quality control criteria for analysis of trace elements.

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	CRITERIA	CORRECTIVE ACTION
Method Blank	**Contamination** by reagents, laboratory ware, etc.	One per batch	< MDL or < 10% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.
Certified Reference Material (CRM)	**Accuracy**	1 per 20 field samples	Within 20–25% of the certified 95% confidence interval	Review raw data quanitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.
Replicates: (analytical and/or laboratory) Applies to replicates of field samples, CRMs, matrix spike samples, etc.	**Precision**	One per batch	RPD or RSD < 15%; Hg, As, Se < 25% RSD of last 7 CRMs < 35%	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, then identify and eliminate source of imprecision and reanalyze.
Matrix Spike	**Accuracy**	1 per 20 field samples	Recovery > 50%	Check CRM or LCS recovery. Review raw data quantitation reports. Check instrument response using calibration standard. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed.
Laboratory Control Material (LCM; optional)	**Accuracy, Laboratory precision**	1 per 20 field samples	Within 20–25% of consensus value	Review raw data quanitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze LCM and samples. Repeat analysis until control limits are met.

MDL = method detection limit; RPD = relative percent difference; RSD = relative standard deviation

Table 3c. WATER: Quality control criteria for analysis of cognates.

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	CRITERIA	CORRECTIVE ACTION
Toxicity				
Ammonia, nitrate, nitrite, phosphate, silicate, chlorophyll *a*, TSS				
Method Blank	**Contamination** by reagents, laboratory ware, etc.	One per batch	< MDL or < 10% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.
Certified Reference Material (CRM)	**Accuracy**	Once per sample set. NA for chlorophyll *a* or TSS	NA	NA
Replicates: (analytical and /or laboratory) Applies to replicates, CRMs, matrix spike samples, etc.	**Precision**	One per batch. NA for TSS	RPD or RSD < 5%	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, then identify and eliminate source of imprecision and reanalyze.
Matrix Spike	**Accuracy**	1 per 20 field samples	Recovery > 50%	Review data reports and chromatographs. Check instruments.
DOC (Dissolved Organic Carbon)				
Method Blank	**Contamination**	One per batch	< MDL or < 10% of lowest sample	Reanalyze samples
Certified Reference Material (CRM)	**Accuracy**	Once per sample set	RPD < 5%	Recalibrate and reanalyze
Replicates	**Precision**	One per batch	RPD or RSD < 5%	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, then identify and eliminate source of imprecision and reanalyze.

MDL = method detection limit; RPD = relative percent difference; RSD = relative standard deviation

Table 4a. SEDIMENT AND TISSUE: Quality control criteria for analysis of organic compounds.

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	CRITERIA	CORRECTIVE ACTION
Method Blank	**Contamination** by reagents, laboratory ware, etc.	One per batch	< MDL or < 10% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.
Certified Reference Material (CRM)	**Accuracy** **Precision**	1 per 20 field samples	As a group: 70% of the analytes within 35% of the 95% confidence interval. Individually: No analyte outside 30% of 95% confidence interval for 2 consecutive analyses. RPD (if n=2) < 35% RSD (if n>2) < 35% RSD of last 7 CRMs < 35%	Review chromatograms and raw data quanitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.
Replicates	**Precision**	1 per 20 field samples	RPD < 35%	Recalibrate and reanalyze. If problem persists eliminate source of imprecision and reanalyze.
Matrix Spike	**Accuracy**	1 per 20 field samples	> 50% recovery if no CRM limits apply, otherwise use CRM limits.	Check CRM or LCS recovery. Review chromatograms and raw data quantitation reports. Check instrument response using calibration standard. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed.
Surrogate Spike or Internal Standard	**% Recovery** used to adjust sample results	One per sample	Set by analyzing laboratory (reported in QA report). (Report surrogate recovery and acceptance criteria in final report)	Check CRM or LCS recovery. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed.

MDL = method detection limit; RPD = relative percent difference; RSD = relative standard deviation

Table 4b. SEDIMENT AND TISSUE: Quality control criteria for analysis of trace elements.

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	CRITERIA	CORRECTIVE ACTION
Method Blank	**Contamination** by reagents, laboratory ware, etc.	One per batch	< MDL or < 10% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.
Certified Reference Material (CRM)	**Accuracy** **Precision**	1 per 20 field samples	Within 20-25% of the certified 95% confidence interval RPD (if n=2) < 10 or 35% RSD (if n>2) < 10 or 35% RSD of last 7 CRMs < 10 or 35% (35% applies to Hg, As, Se)	Review raw data quanitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.
Replicates	**Precision**	One per batch	RPD < 10% or 35% (35% applies to Hg, As, Se)	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, then identify and eliminate source of imprecision and reanalyze.
Matrix Spike	**Accuracy**	1 per 20 field samples	Recovery > 50%	Check CRM or LCS recovery. Review raw data quantitation reports. Check instrument response using calibration standard. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed.
Laboratory Control Material (LCM; optional)	**Accuracy & Precision**	One per batch	Within 20–25% of the consensus value	Review raw data quanitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze LCM and samples. Repeat analysis until control limits are met.

MDL = method detection limit; RPD = relative percent difference; RSD = relative standard deviation

Table 4c. SEDIMENT: Quality control criteria for analysis of cognates (total organic carbon, total nitrogen, and grain size).

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	CRITERIA	CORRECTIVE ACTION
Method Blank	**Contamination** by reagents, laboratory ware, etc.	One per batch	< MDL or < 10% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.
Certified Reference Material	**Accuracy**	TOC: every 15 samples. Grain Size: NA.	Within 95% confidence interval of the certified value	Review raw data quanitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.
Replicates	**Precision**	One per batch	RPD or RSD < 20% precision (grain size) 3% (TOC)	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, then identify and eliminate source of imprecision and reanalyze.
Laboratory control material (LCM)	**Accuracy & Precision**	One per batch of 20 or fewer samples.	Within 20–25% consensus value	Review raw data quanitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.

MDL = method detection limit; RPD = relative percent difference; RSD = relative standard deviation

Table 5. Target method detection limits for parameters or compound groups.

Test Material	Parameter	Target MDL	Units
Water	PAH	50	pg/L
Water	PCB	5	pg/L
Water	PESTICIDE	50	pg/L
Water	Ag	0.0001	µg/L
Water	As	0.1	µg/L
Water	Cd	0.001	µg/L
Water	Cr	0.001	µg/L
Water	Cu	0.01	µg/L
Water	Hg	0.1	ng/L
Water	Ni	0.01	µg/L
Water	Pb	0.001	µg/L
Water	Se	0.02	µg/L
Water	Zn	0.005	µg/L
Sediment	PAH	5	µg/kg
Sediment	PAH ALKYLATED	5	µg/kg
Sediment	PCB	1	µg/kg
Sediment	PESTICIDE	1	µg/kg
Sediment	Ag	0.001	mg/kg
Sediment	Al	200	mg/kg
Sediment	As	0.2	mg/kg
Sediment	Cd	0.001	mg/kg
Sediment	Cr	5	mg/kg
Sediment	Cu	2	mg/kg
Sediment	Fe	200	mg/kg
Sediment	Hg	0.00001	mg/kg
Sediment	Mn	20	mg/kg
Sediment	Ni	5	mg/kg
Sediment	Pb	0.5	mg/kg
Sediment	Se	0.01	mg/kg
Sediment	Zn	5	mg/kg
Tissue	PAH	5	µg/kg
Tissue	PAH ALKYLATED	5	µg/kg
Tissue	PCB	1	µg/kg
Tissue	PESTICIDE	1	µg/kg
Tissue	Ag	0.001	mg/kg
Tissue	Al	1	mg/kg
Tissue	As	0.1	mg/kg
Tissue	Cd	0.01	mg/kg
Tissue	Cr	0.5	mg/kg
Tissue	Cu	0.2	mg/kg
Tissue	Hg	0.00001	mg/kg
Tissue	Ni	0.2	mg/kg
Tissue	Pb	0.01	mg/kg
Tissue	Se	0.01	mg/kg
Tissue	Zn	10	mg/kg
Tissue	Butyltins	0.1	µg/kg

QA Procedures for Ancillary Parameters in Water, Sediment Toxicity, Bivalve Condition, and Fish Tissue

Several ancillary parameters are measured in water and sediment.

Water

Toxicity

There will be five replicates per sample, plus three for water quality. Test containers will be glass scintillation vials with 10 ml test solution. Organisms and samples will be maintained at appropriate temperatures. All instruments will be properly calibrated. Toxicity test procedures are considered unacceptable if the percentage of normal live larvae is below 70% of test controls. Acceptable temperatures range from 14° to 16°C; acceptable salinities range from 26‰ to 30‰; acceptable dissolved oxygen concentrations range from 5.09 to 8.49 mg/L.

DOC

Blanks will be analyzed a minimum of three times each day during sample analysis. The instrument will be calibrated with a standard curve at least once every 15 samples. Duplicate field samples will be obtained and analyzed from every station, with a minimum of three measurements being made on each field duplicate. The reported values are the averages of the six measurements made on the two duplicates from each stations. Although no standard for DOC in water is commercially available, an internal laboratory reference material will be analyzed a minimum of three times during sample analysis. The criteria for both precision and accuracy is ±5%.

TSS

The analytical balance used in the gravimetric measurement of TSS has an internal checking device and will be periodically checked by a service representative. A minimum of three blanks are analyzed during sample analysis. As sample volume permits, samples from approximately three stations will be analyzed in duplicate or triplicate. No standard is available for TSS. Precision is ±5%.

Chlorophyll

The fluorometer used to measure chlorophyll and phaeophytin will be calibrated twice annually using a chlorophyll standard that has been analyzed by UV-VIS spectrometry. A blank will be analyzed with the samples. Duplicate filtrates will be obtained in the field for each station and each filter will be analyzed at least once. The reported values are the averages of the measurements for the duplicate filtrates. The precision criterion is ±10%.

Nutrients

The spectrometer used to analyze nutrients (i.e., ammonia, nitrate, nitrite, phosphates, and silicates) will be calibrated with a standard curve based on dilutions of stock standards that are mixed fresh for the analysis of each cruise. Three blanks will be analyzed with each nutrient. Duplicate aliquots will be analyzed from the field sample for each station. As sample volume permits, at least one station will be analyzed in triplicate. The SPEC QCS reference material of nutrients in wastewater will be analyzed once during analyses for each cruise, although it contains reported concentrations of only ammonia, nitrate, and phosphate. There are no commercially-available reference materials for silicate and nitrite. The precision criterion is ±5% and accuracy criterion is ±10%.

Salinity

The salinometer used to analyze salinity will be calibrated annually with IAPSO Standard Seawater reference material. A minimum of two blanks will be analyzed during sample analysis. All stations will be analyzed twice and the reported values are the average of the measurements for each station. The precision criterion is ±1%.

CTD

The CTD will be returned to the manufacturer annually for recalibration of all probes. The resulting revised calibration constants will then be entered in a configuration file in SeaSoft (v. 4.035b) that is named corresponding to its date of implementation so that the appropriate configuration file can always be applied to any data set.

Sediment

Bioassays

There will be five replicates per sample, plus a sixth for water quality. Test containers will be glass for sediments and plastic for the reference toxicant. Organisms and samples will be maintained at appropriate temperatures. All instruments will be calibrated properly. Toxicity test procedures are considered unacceptable if amphipod survival in home sediment controls is less than 90%, or if survival in any control replicate is less than 80%. Acceptable temperature range is from 14° to 16°C, acceptable salinities range from 17‰ to 23‰, acceptable dissolved oxygen concentrations range from 5.09 to 8.49 mg/L.

TOC

Blanks and a reference material supplied by the instrument manufacturer, Coulometrics, Inc. will be analyzed a minimum of three times daily during sample analysis. The precision criterion is ±3% and accuracy criterion is ±1%.

Grain Size

Standard reference materials will be analyzed with every batch of samples. These include NIST SRM 1003b glass spheres and a narrow-sized garnet standard supplied by the instrument manufacturer. In addition, at least one sample in twelve will be analyzed in duplicate to determine precision. The precision criterion is ±20%.

Porewater Ammonia

The calibration of the ammonia probe on the pH/ORP meter will be checked before analysis of each station. The calibration curve will also be used for quantification of ammonia from millivolt potential readings made in the samples with the ammonia probe. The calibration curve will be made with reference standards of 10.0, 5.0, 1.0, and 0.1 ppm total ammonia using dilutions of a NIST-traceable 1,000-ppm standard (Corning #951007). New reference standards will be prepared and the probe will be recalibrated if the millivolt reading for a particular standard drifts by more than 10% from the original reading. During sample analysis the probe is allowed to remain in the sample until stable readings are achieved and recorded.

Porewater pH

Calibration of the pH probe on the pH/ORP meter will be performed before sampling each station using reference standards of 4.0, 7.0, and 10.0 pH acidity. The standards will be made before each cruise from NIST-traceable materials.

Bivalves and Fish Tissue

Bivalve Condition Index

The precision of displacement volume measurements will be estimated by making 10 separate measurements on a single organism.

Butyltins

Assessment of the distribution and environmental impact of butyltins require measurements in marine sediment and tissue samples at trace levels. Quality control of these measurements consists of checks on laboratory precision and accuracy. One laboratory reagent blank must be run with each batch of 25 or fewer samples. A reagent blank concentration between the MDL and 3 times the MDL will serve as a warning limit requiring further investigation based on the best judgment of the analyst(s). A reagent blank concentration equal to or greater than 3 times the MDL requires corrective action to identify and eliminate the source(s) of contamination, followed by re-extraction and reanalysis of the samples in the associated batch.

One laboratory fortified sample matrix (commonly called a matrix spike) or laboratory fortified blank (i.e., spiked blank) will be analyzed along with each batch of 25 or fewer samples to evaluate the recovery of the butyltin species of interest, if authorized and funded. The butyltins will be added at 5 to 10 times the MDLs as previously calculated by the laboratory. If the percent recovery for any of the butyltins in the matrix spike or spiked blank is outside the range 70 to 130 percent, analysis of subsequent sample batches will stop until the source of the discrepancy is determined and the system corrected.

Lipids

Lipid measurements are essential to interpretation of temporal or spatial trends in concentrations of organic contaminants in tissues. Data quality criteria for precision will apply to analysis of SRMs and laboratory duplicates. For repeated analysis of SRMS, RPD should be <35% or RSD should be <30%. For laboratory duplicates, RPD should be <35%.

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