

***Aquatic Pesticide Monitoring Program***

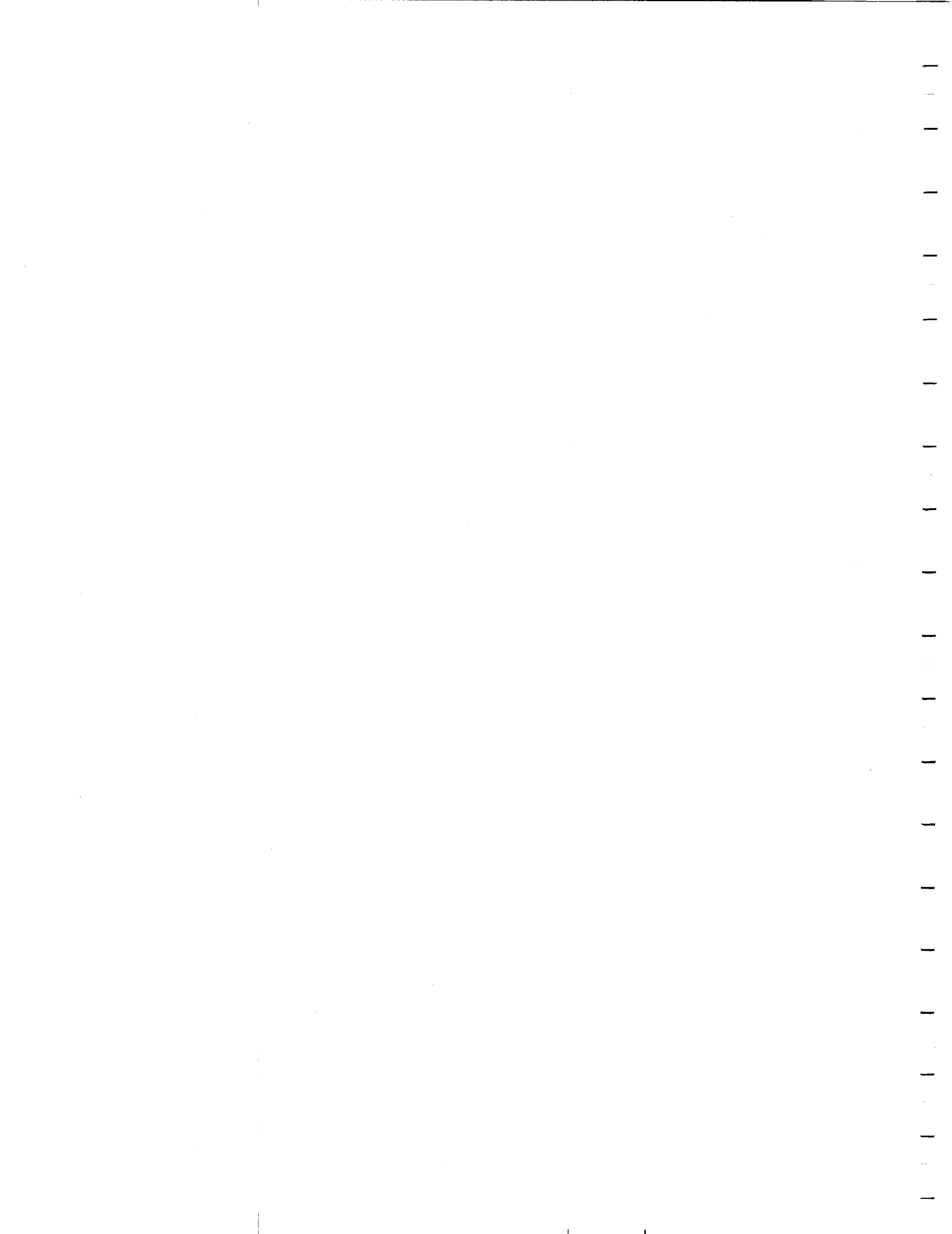
# **Quality Assurance Project Plan**

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San Francisco Estuary Institute





# Quality Assurance Project Plan Aquatic Pesticides Monitoring Program

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## **1. INTRODUCTION**

This document presents the Aquatic Pesticides Monitoring Program (APMP) quality assurance and quality control (QA/QC) protocols and requirements for contract laboratories. It includes:

1. A summary of the APMP and its organization.
2. An overview of quality assurance and control in the APMP.
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), U.S. EPA's Puget Sound Estuary Program, National Oceanic and Atmospheric Administration's (NOAA) National Status and Trends (NS&T) Program, and U.S. EPA, Office of Water. 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 that 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 samples requires specific guidance from policy makers and environmental managers identifying the desired uses of the data are. Conversely, the scientific defensibility of environmental management decisions depends in part 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 APMP 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 APMP quality assurance and control system was designed to accommodate evolving information needs by the data users within the 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 APMP DQCs expressed in terms of accuracy, precision, completeness, and method detection limit requirements. The DQCs for the APMP 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 storage and shipping containers
2. Sample equipment (tubing, pumps)
3. Ship/Boat (exhaust, metal surfaces, lubricants)
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 steps
4. Analytical instruments and equipment (tubing, corrosion, etc.)
5. Reagents
6. Containers
7. Transfer equipment (vials, syringes, etc.)

## 2. OVERVIEW OF THE APMP

### APMP Organization

#### Project Information

The Aquatic Pesticides Monitoring Program (APMP) began in 2002 and is funded by the California State Water Resources Control Board. The APMP was formed as a result of the ruling by the Ninth Circuit Court of Appeals that registration and labeling of aquatic pesticides under the federal pesticide law (Federal Insecticide, Fungicide, and Rodenticide Act, or FIFRA) does not preclude the requirement to obtain coverage under a National Pollutant Discharge Elimination System (NPDES) permit prior to discharging such pesticides into waters of the United States. Following the ruling, the State Water Resources Control Board now issues a general permit for dischargers of aquatic pesticides. Entities that have applied for a general permit include irrigation districts, municipal water supply districts, and mosquito vector control districts. The current objectives of the APMP are to develop, implement, and manage a statewide aquatic pesticide monitoring project. The San Francisco Estuary Institute (SFEI), as the entity designated to implement the Aquatic Pesticides Monitoring Program, is administering the program under a contract with the State Water Resources Control Board.

Conventional parameters measured by the APMP in water, sediment, and biological samples are listed in Table 1a. Trace element and organic pesticides measured by the APMP are listed in Table 1b. Due to the specific chemistries of several of these pesticides, nonstandard sample bottles are used. The appropriate sample bottle type is listed in Table 1b. Additional parameters may be added to these lists for future monitoring.

**Table 1a. Conventional parameters measured in the APMP.**

<b>Physical Parameters</b>	<b>units</b>
<b>Meteorological Data:</b>	
Cloudiness	Approximate
Air Temperature	Degrees Celsius
Water depth	M
Sediment collection depth	cm
Geometric profiles of water body	Cross-sections/ diagrams
Flow Rate (lotic systems)	Cfs (ft <sup>3</sup> /s)
Inflow Volume (lotic systems)	cc
Outflow Volume (lotic systems)	cc
Flow Diversions	Describe
Current from wind action (lentic systems)	Qualitative – none, mild, moderate, strong
Anthropogenic activities/ alterations	Describe
Wildlife presence	Describe
<b>Conventional Water Quality Parameters</b>	
Conductivity	µmho
Dissolved Organic Carbon	µg/L
Dissolved Oxygen (DO)	mg/L
Hardness (when salinity is < 5 ‰)	mg/L (CaCO <sub>3</sub> )
Salinity	psu (‰)
pH	PH
Temperature	°C
Total Chlorophyll a	mg/m <sup>3</sup>
Total Phosphorous	mg/L - P
Total Nitrogen	mg/L - N
Total Suspended Solids	mg/L
Alkalinity	mg/L (CaCO <sub>3</sub> )
Dissolved Calcium	mg/L
Dissolved Magnesium	mg/L
Dissolved Sodium	mg/L
Turbidity	NTU
Flow Rate (lotic systems)	Cfs (ft <sup>3</sup> /s)
<b>Sediment Quality Parameters</b>	
% gravel (> 2 millimeters)	% dry weight
% sand (2 mm > 62 µm)	% dry weight
% fines (< 62 µm )	% dry weight
Nitrate-Nitrogen	mg/kg
% solids	% dry weight
Temperature	°C
Total Nitrogen	mg/kg
Total Organic Carbon	mg/kg
Pore Water Pesticide Concentration	mg/l or µg/L
SEM-AVS (for copper treatments only)	SEM-AVS Ratio
Eh	mV

Toxicity Tests—Water and Sediment, TIE Development	units
Amphipod ( <i>Hyallela azteca</i> )	% survival
Rainbow trout ( <i>Oncorhynchus mykiss</i> )	% survival
Fathead Minnow ( <i>Pimephales promelas</i> )	% survival
Zooplankton ( <i>Ceriodaphnia dubia</i> )	% survival
Phytoplankton ( <i>Selenastrum capricornutum</i> )	% survival
Midge larvae ( <i>Chironomus tentans or riparus</i> )	% survival
Cattail seed germination ( <i>Typha spp.</i> )	% survival

**Table 1b. Trace elements and organic chemicals measured in the APMP.**

Synthetic Biocides	Sample Bottle Type	units in water; sediment; tissue
Acrolein	glass	µg/L; mg/kg; µg/kg
Copper (copper sulfate and chelated copper)	polyethylene	µg/L; mg/kg; µg/kg
2,4-D	glass	µg/L; mg/kg; µg/kg
Diquat dibromide	glass	µg/L; mg/kg; µg/kg
Fluridone	polyethylene	µg/L; mg/kg; µg/kg
Glyphosate	polyethylene	µg/L; mg/kg; µg/kg
Endothall	glass	µg/L; mg/kg; µg/kg
Malathion	glass	µg/L; mg/kg; µg/kg
Methoprene	glass	µg/L; mg/kg; µg/kg
Triclopyr	glass	µg/L; mg/kg; µg/kg

#### Data Usage

Data from this program are made available for scientific research, regulatory purposes, and public awareness. Examples of uses for APMP data follow:

1. Tracking Distribution and Trends: Seasonal, annual, and long-term patterns in pesticides found in the water bodies monitored.
2. Regulatory Objectives and Guidelines: Data are used by the APMP to evaluate achievement of various water, sediment, and tissue quality criteria and guidelines.
3. Describing Ecosystem Processes: Conventional water and sediment parameters are evaluated to better understand contaminant transport and fate processes, and resulting effects.
4. Integrated Contaminant Measurements: Bioaccumulation data may be used to determine time-averaged trends in contaminant concentrations and for comparison with other trend data.

### 3. OVERVIEW OF QUALITY ASSURANCE AND CONTROL IN THE APMP

#### Sample Collection, Preservation and Holding

Field personnel will strictly adhere to the APMP protocols to ensure the collection of representative and uncontaminated samples. Briefly, the key aspects of quality control associated with 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 emissions, winch wires, deck surfaces, ice used for cooling).
3. Samplers and utensils which come in direct contact with the sample will be made of inert materials that do not contaminate for the particular analytes measured in that sample and will be thoroughly cleaned between sampling stations.
4. Sample containers will be pre-cleaned and of the recommended type for minimizing contamination for the analytes measured.

### **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 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 APMP's performance-based protocols for all analytical laboratories consist of two basic elements:

*Initial demonstration of laboratory capability-* Prior to the initial analysis of samples, each laboratory must demonstrate proficiency in several ways:

1. Written protocols for the analytical methods to be employed for sample analysis will be submitted to the Program for review,
2. Method detection limits (MDLs) and the procedures for determining them will be provided for each analyte,
3. An initial calibration curve will be established for each analyte, the calibration curve shall include a low calibration point set at 3 to 5 times the MDL and include a minimum of 5 calibration points for trace organics,
4. Acceptable performance will be shown on known or blind reference material (see section Laboratory Quality Control Procedures, Initial Demonstration of Capability), and
5. Long-term standard reference material results on reference material with analyte concentrations comparable to those in APMP field samples will be submitted.

*Ongoing demonstration of capability-* Following a successful first phase, the laboratory will demonstrate its continued capabilities in several ways:

1. The laboratory will participate in an on-going series of inter-laboratory comparison exercises and provide results,
2. Calibration checks will be performed during analyses, and

3. Analysis of laboratory method blanks, fortified samples, and certified reference materials (see section Laboratory Quality Control Procedures, Ongoing Demonstration of Capability) will be made with field samples analyzed.

Immediately following the analysis of each sample batch, results for the various QA/QC samples will be reviewed by laboratory personnel. When these results indicate that DQCs are not met, specific corrective actions are required before the analyses of subsequent sample batches may proceed.

### **Information Management**

Various data and information generated from the APMP are stored at SFEI. The digital data generated from sample analyses arrive at SFEI in various formats that are then converted to standard APMP database format.

### **Sample Tracking**

Chain of custody (COC) forms are compiled each time control of samples is transferred from the field to a receiving laboratory or between laboratories. In addition to standard shipping information, the following information is required: sampling event number, site name and code, collection date, sample type, analysis required, preservatives added, and other remarks as needed.

### **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 any subsequent batch. In addition, each laboratory will establish a system for detecting and reducing transcription and calculation errors prior to reporting data.

Only data that have met DQCs or that have explained deviations appropriately will be accepted from the laboratory. When QA requirements have not been met, the samples will be reanalyzed when possible. Only the results of the reanalysis should be submitted, provided they are acceptable.

## **4. FIELD QUALITY ASSURANCE AND QUALITY CONTROL**

### **Field Performance Measurements: Terminology**

The following is a list of definitions of field performance measurements that are frequently included in sampling protocols. Some of these measurements only need to be taken when an established procedure is changed, whereas 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.
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 Blanks: These account for contamination introduced by the field sampling equipment in addition to the above sources.
5. Field Blanks: These account for all of the above sources of contamination that might be introduced to a sample as well as those due to 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.
6. Field Replicates: These account for variability in the field collection and laboratory analysis.

### **Field Performance Measurements Used by the APMP**

Routine preparation, collection, and analysis of all the field performance samples mentioned above would be redundant and inefficient. Since trace contaminants 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 or adaptable to the collection of trace organic samples.

Field replicates of all types of samples to be analyzed will be routinely collected so that evaluation of variability includes performance of the sampling system. Short-term environmental variability, most notably due to swift currents and non-homogeneous suspended sediment loads, can affect the sampling precision. The sampling site that has the least variability will usually be included as one field replicate. Since sediment contaminant concentrations can vary greatly within small distances, sediment field replicates taken cannot be used to separate natural variability from that introduced by the sampling and analysis systems, and any sediment field replicate samples collected will mainly be used to evaluate reproducibility of data by the analytical labs. For tissue samples, comparing two sub-samples of fewer animals each would primarily assess variability in the animals rather than variability in sample collection and analysis. Therefore, for assessing analytical variability, tissue samples from a location will be collected and later homogenized as a single composite sample, and differences among sub-samples will be evaluated.

Source solution blanks will be made with Milli-Q or Nanopure water (or equivalents, free of trace organic or element contaminants as appropriate for the analyses to be performed), and acids, solvents, and other reagents sufficiently clean to prevent measurable contamination will be used in all aspects of cleaning, storage, and analysis. The sample bottles will be cleaned and stored appropriate for the sample types that will be contained (e.g., rinsed with acid solution for trace metal water containers, empty and dry for trace organics). Contamination of these source solutions and containers will be routinely checked and corrective steps taken whenever contamination of source solutions is indicated.

In studies performed for other SFEI projects, bottle blanks that were generated showed that the “trace-metal clean” polyethylene to be used for APMP water samples are not a significant source

of trace element contamination. Certified trace-metal and organic free borosilicate glass containers will be used for water organics and sediment samples.

Travel blanks will not be 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 measures taken to keep the sample bottles in an enclosed micro-environment. Equipment blanks for water samples will not be collected due to the high improbability of contamination of equipment with target pesticides. Sediments will be collected with a van Veen grab sampler, but equipment blanks will not be taken for sediments. The sediment sampling protocol is discussed further in the section below on field blanks. If tissue samples are hand collected then equipment blanks are not needed.

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. Because assessment of a monitoring vessel's aura of contamination at the time of sampling is not straightforward, true field blanks are difficult to obtain. Collection of a field blank by pumping a "solution blank" (Milli-Q water) through the system on board a monitoring vessel does not adequately address the issues of potential contamination of the water sample by the monitoring vessel since unlike the sample, it would have no contact with the boat below the waterline. Such a field blank (essentially an on-site equipment blank) can measure contamination of the sampling equipment and perhaps aerosol contamination, but it cannot differentiate vessel contamination from water contaminants already present without the vessel. Steps to mitigate 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 minimize contamination of the sample by the boat, a 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.

Because of the inability to collect a true field blank, the analyte concentrations of environmental water samples will be considered accurate if they are 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 (Berman et al. 1983; Bowers and Windom 1981; Boyle et al. 1981; Bruland et al. 1985; Flegal and Stukas 1987; Landing et al. 1995; Schaule and Patterson 1981; Yeats et al. 1995).

Trace metal sample bottles will be rinsed with a weak acid solution and then three times with deionized water prior to use. The bottles will always be handled with polyethylene-gloved clean hands.

Pre-cleaned bottles for sampling organic contaminants will be stored empty, dry, and tightly capped. For trace organic sampling, containers will be routinely checked for contamination. Eliminating leachable plastics (e.g., non-Teflon<sup>®</sup> materials) from all aspects of trace organic sample handling, storage, and transport is difficult due to the preponderance of plastics in containers and shipping material (e.g., coolers, bags, foam, bubble wrap), but exposure to sampled material will be minimized.

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 stainless steel and will be thoroughly cleaned prior to field use. Equipment will also be cleaned with laboratory grade detergent between stations and rinsed with hydrochloric acid 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 for trace element analyses, and into pre-cleaned certified glass jars with Teflon<sup>®</sup>-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.

Animals collected for tissue samples will be handled in the field according to established protocols that are designed to minimize sample contamination. Tissue destined for trace element analysis will be placed in polyethylene ziploc bags, placed on dry ice, and kept frozen until homogenization and analysis. Tissue samples used for trace organic analysis will be wrapped in Teflon<sup>®</sup> foil.

## **5. LABORATORY QUALITY ASSURANCE AND CONTROL**

### **APMP Laboratory Requirements**

The APMP requires all laboratories to demonstrate capability continuously through:

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

This is a “performance-based” approach for analyses of trace contaminants, involving continuous laboratory evaluation through the use of accuracy-based materials (e.g., CRMs), laboratory matrix spikes, laboratory method blanks, calibration standards, laboratory and field replicate samples, and others as appropriate. The definitions and uses 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 APMP 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 APMP’s data quality criteria (DQCs). The APMP DQCs were developed based on the kinds of general management questions that the environmental data need to help answer. The APMP has developed specific guidelines for measurement precision, accuracy, and levels of detection that are reflected in sampling, handling, and analysis requirements to satisfy a large spectrum of potential management questions. Each laboratory will 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.,

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<sup>1</sup> 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).



low parts per quadrillion and parts per billion) analysis of organic and inorganic contaminants in water or sediments. Recommended methods for the APMP are those developed in various academic research programs and those used in the NOAA NS&T Program (Lauenstein and Cantillo, 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 manner that includes:

1. A program of scheduled maintenance of analytical balances, microscopes, and other 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 differ < 2 percent from 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 resistance of the reagent water will exceed 10  $\mu$ mhos/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 QAPPs, 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 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 APMP 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 APMP 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 APMP 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 APMP 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 APMP analyses will be well versed in good laboratory practices (GLPs), 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 GLPs will be implemented accordingly.

#### Quality Assurance Documentation

All laboratories will have the latest revision of the APMP QAPP. In addition, the following documents and information will be current and available to all laboratory personnel participating in the processing of APMP 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 APMP.
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 APMP 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 APMP 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 continual basis through laboratory intercomparison studies (round robins) such as 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 APMP 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 extraction blanks or preparation blanks): These account for contaminants present in the preservative and analytical solutions and equipment used during the preparation and quantification of the parameter.
2. Internal Standards: These account for error introduced by the analysis.
3. 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.
4. Replicate Samples: These are replicates of extracted material that measure the instrumental precision.
  - a. Laboratory Replicate Samples: These are replicates of the raw material that are extracted and analyzed to measure laboratory precision.
  - b. Matrix Spike Replicate Samples: These are used to assess both laboratory precision and accuracy. They are 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).
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 evaluate and diagnose errors introduced during the analysis. The remainder of this document will provide APMP 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 APMP 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 2 and 3), 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, prepared in an independent manner, and ideally having certified concentrations of target analytes (e.g., 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. If the instrument response is demonstrated to be linear over the entire concentration range 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. Otherwise, only data which result from quantification within the demonstrated working calibration range should be reported by the laboratory (i.e., quantification by extrapolation is not acceptable). Samples outside the calibration range will be diluted or concentrated, as appropriate, and reanalyzed.

For immunoassays such as ELISA, QA/QC samples including blanks and calibration standards are read along with other samples using an automated plate reader (e.g., Hyperion Micro Reader 3). Once all the wells have been read, the software calculates and prints the results, including parameters for the standard calibration curve. An  $r^2$  for the curve of 0.97 or above is considered good. If it is less than 0.97, best professional judgment should be used in continuing the test and interpreting the test results for reporting.

### *Initial documentation of method detection limits*

Analytical chemists have coined a variety of terms to define "limits" of detection; definitions for some of the more commonly used terms are provided by Keith (Keith et al. 1983; Keith 1991). In the APMP, 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 APMP 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 analyte 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 APMP (see Table 4). These MDLs have been derived empirically from reported literature or other monitoring and research efforts. 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 or a reference material in the appropriate range. Recoveries for organic analyses shall be between 50 and 150% for at least 90% of the target analytes.

#### *Limits of quantitation*

Taylor (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, where the uncertainty of a measurement is approximately  $\pm 100\%$  at the 95% level of confidence. Values at the MDL may not reflect a signal much above zero and, therefore, are quantitatively not very robust. The limit of quantitation (LOQ), as established by the American Chemical Society, is normally ten times the standard deviation of replicate measurements, which corresponds to a measurement uncertainty of  $\pm 30\%$  (Taylor 1987). By these standard definitions, measurements below the MDL are not believable, measurements between the MDL and the LOQ 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 may be used to evaluate performance of analytical laboratories new to the APMP 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) in interlaboratory comparison exercises. A new laboratory's performance generally will be considered acceptable if its submitted values are within DQCs (Tables 2 and 3) 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 APMP target MDL (~LOQ). If the results for the initial analysis fail to meet these criteria, the laboratory may be required to repeat the analysis until the performance criteria are met, prior to the analysis of APMP field samples.

#### *Record of certified reference materials*

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*

APMP laboratories analyzing applicable contaminants are required to participate in intercomparison exercises similar to those conducted jointly by NIST and NRCC or similar parties. 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 APMP 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.

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

Routine analysis of CRMs (when available) or LCMs represents a particularly vital aspect of the “performance-based” APMP 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 2 and 3); 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 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 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 2 and 3.

#### *Laboratory replicates for precision*

A minimum of one field sample per batch of APMP samples submitted to the laboratory will be processed and analyzed in replicate for precision. The relative standard deviation among replicate samples (RSD expressed as percent) will be less than the DQC listed in Tables 2 and 3 for each analyte of interest. Following are the calculations:

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

STDEV — standard deviation

If results for any analytes do not meet the DQC for RSD, calculations and instruments will be checked. A repeat analysis may be required to confirm the results. Results that repeatedly fail to

meet the objectives indicate sample heterogeneity, 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.

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 some analytes of interest to the APMP 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 2 and 3). For each class of organic analytes, 70% of the individual analytes will be within the certified 65% confidence interval ( $\pm 1$  STDEV of the consensus value); no individual analyte value shall exceed the 99% confidence interval ( $\pm 3$  STDEV) more than once in consecutive analyses without appropriate documentation and consultation with the APMP QA officer. For inorganic analyses, the laboratory’s value will be within the 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 target MDL.

#### *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 laboratory) are not met, the initial calibration will have to be repeated. The calibration check for organic analytes shall not deviate more than  $\pm 25\%$  from the known value. If possible, any 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 RSD between the results of this reanalysis and the original analysis exceeds precision DQCs (Tables 2 and 3), 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 RSDs between initial and reanalysis results are within DQCs (Tables 2 and 3). Only results from the reanalysis will be reported by the laboratory. If it is not possible 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 flag the data and prepare a narrative explanation to accompany the submitted data.

#### *Laboratory method blank*



Laboratory method blanks (also called 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 method blank will be 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 contain analyte concentration less than the MDL or 30% of the lowest reported sample concentration. A method blank concentration  $> 2x$  the MDL or  $> 30\%$  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 sources and the steps taken to identify and eliminate/minimize them shall be included in the transmittal letter. Subtracting method blank results from sample results is not permitted, except where  $3xSTDEV$  of the mean blank measurement can be demonstrated to be less than the MDL.

#### *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 APMP completeness goals of 95–98% for all analyses.

#### *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 the APMP.

#### *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 needed. 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 samples 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 gas chromatography- electron capture detection (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 MS/MSDs for matrices without appropriate CRMs. 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 analytes from the APMP list as is feasible and appropriate for that analysis. The final spiked concentration of each analyte in the sample will be at least 5-10 times the MDL for that analyte and preferably also within the range of expected concentrations in field samples. 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 low recovery value is not discovered, the instrument response should be checked with calibration standards. 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 can also be useful for assessing laboratory precision. The RSD between MS/MSD results should be less than the target criterion listed in Tables 2 and 3 for each analyte of interest.

#### *Field replicates and field split samples*

As part of the regular quality assurance program of the APMP, 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, may 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 variability in the sample matrix and collection and homogenization methods.

### **QA Procedures for Ancillary Parameters**

#### Water Ancillary Measurements

##### *DOC*

Field samples will be obtained and analyzed from every station, with one duplicate sample collected during each sampling day. 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 precision and accuracy are  $\pm 5\%$ .

##### *TSS*

The analytical balance used in the gravimetric measurement of TSS has will be calibrated for each analysis batch and will be periodically checked by a service representative. A minimum of three blanks will be 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. The precision criterion is  $\pm 5\%$ .

##### *Field probes*

Calibration of any field meters (e.g. hand-held pH, temperature, conductivity, DO, turbidity or other measurements) should be checked in the field at least once daily and recalibrated using certified standards where possible. Checks of instrument calibration will be made prior to sampling at each location.

#### Sediment Ancillary Measurements

##### *TOC*

Blanks and a reference material approved by the instrument manufacturer will be analyzed a minimum of three times daily during sample analysis. The precision criterion is 3% RSD and accuracy criterion is  $\pm 3\%$ .

##### *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 replicate to determine precision. The precision criterion is  $\pm 20\%$ .

Fish Tissue

### *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 replicates. For repeated analysis of SRMs, lipids should be within 30% of the consensus value. For laboratory replicates, RSD should also be  $<30\%$ .

## **QA Procedures for Toxicity Tests**

Water Bioassays

Replicate samples will be collected at each site for toxicity and water quality testing. Holding times will be minimized to prevent sample degradation, however, it should be recognized that followup toxicity tests and chemical analysis may not accurately reflect the composition of the fresh sample. Subsequent analyses will likely underestimate the initial concentration.

All tests should be initiated within 48 hours of sample collection. Where USEPA standard test species are used (*Pimephales promelas*, *Ceriodaphnia dubia*, *Selenastrum capricornutum*) toxicity tests should follow the USEPA protocols (USEPA 1994). Where larval rainbow trout *Onchorhynchus mykiss* are used, tests should follow California Department of Fish and Game protocols which are based on USEPA fathead minnow protocols. Tests with other organisms (e.g. *Hyalella azteca*) should follow the appropriate latest revisions of methods from USEPA (USEPA 2000a) or the Annual Book of ASTM Standards. Toxicity test acceptability criteria are listed in Table 5. Requirements for considering toxicity tests complete are summarized in Table 6. Criteria in tables are listed only as highlight examples; detailed criteria should be obtained directly from the appropriate methods description.

Best professional judgment should be used in the interpretation of results obtained when deviations in the test conditions have occurred, and all deviations and associated interpretations must be reported. Unacceptable tests will be reported to the Program QA Officer so corrective action can be taken and will be reported in the quarterly quality assurance reports. The APMP Manager and the laboratory manager will determine the course of corrective action. The Program can request a retest of the original sample or select a sample collected at a later date to substitute for the sample/test that failed acceptability criteria.

Precision criteria have not been established for toxicity tests. However, USEPA has developed percent minimum significant difference (PMSD) upper and lower bounds to be used to determine within-test sensitivity (USEPA 2000b). If they are performed according to the recommended guidelines and meet the test acceptability criteria contained therein, it is assumed that they provide the level of precision intended by the EPA (USEPA 1994).

During the months when toxicity tests are being conducted, the laboratory shall perform monthly *Ceriodaphnia dubia* reproduction and survival, fathead minnow survival and growth, and

*Selenastrum capricornutum* growth tests with the reference toxicant, NaCl. Trends in reference toxicant results will be considered when comparing sample test results. Toxicity test results will be reviewed if concurrent reference toxicant test results fall outside two standard deviations of the cumulative mean LC<sub>50</sub>.

#### Sediment Bioassays

Samples from reference sites are tested to characterize inherent site variability, and to establish a benchmark against which to compare contaminated sites. In addition to reference samples, control samples are also tested. Tests conducted on control sediments serve to verify the health of the test organisms and assure the proper maintenance of test conditions such as lighting, temperature, organism handling, and cleanliness of test equipment. When amphipods are used as test organisms, control sediments (often called "home sediments") are collected at the same time and place as the test organisms. With other infaunal test organisms, control sediments are well-sorted, fine-grain sand collected from remote sites with a well-documented history of low toxicity.

There should be a minimum five laboratory 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, for marine species acceptable salinities range from 17‰ to 23‰, acceptable dissolved oxygen concentrations range from 5.09 to 8.49 mg/L.

**Table 2a. WATER: Quality control criteria for analysis of organic compounds.**

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	DATA QUALITY CRITERIA	CORRECTIVE ACTION
<b>Method Blank</b>	<b>Contamination</b> by reagents, laboratory ware, etc.	One per batch	< MDL or < 30% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.
<b>Instrument Blank</b>	<b>Cross contamination</b>	NA	Set by laboratory	NA
<b>Certified Reference Material (CRM)</b>	<b>Accuracy</b>	NA	NA	NA
<b>Replicates:</b> (analytical and/or laboratory)  Applies to replicates of field samples, CRMs, matrix spike samples, etc.	<b>Precision</b> Instrument and/or overall reproducibility of a result.	One per batch	RSD < 35%	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, identify and eliminate source of imprecision and reanalyze.
<b>Matrix Spike</b>	<b>Accuracy</b>	1 per 20 field samples	Recovery within $\pm 50\%$ (50-150%)	Check CRM or LCM 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.
<b>Surrogate Spike</b>	<b>% Recovery</b> used to adjust sample results	One per sample	Set by analyzing laboratory (Report surrogate recovery and acceptance criteria in final report)	Check CRM or LCM recovery. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed
<b>Continuing Calibration Check solutions</b>	<b>Accuracy &amp; Precision</b>	At least every 12 hours	Known values for 90% of analytes shall not deviate more than $\pm 25\%$ for PAHs, and $\pm 20\%$ for PCBs and Pesticides.	Beginning with last sample before failure, recalibrate and reanalyze. Compare RSD and reanalyze.

MDL = method detection limit; RSD = relative standard deviation

**Table 2b. WATER: Quality control criteria for analysis of trace elements.**

<b>QA SAMPLE</b>	<b>QA MEASURE</b>	<b>MINIMUM FREQUENCY</b>	<b>CRITERIA</b>	<b>CORRECTIVE ACTION</b>
<b>Method Blank</b>	<b>Contamination</b> by reagents, laboratory ware, etc.	One per batch	< MDL or < 30% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.
<b>Certified Reference Material (CRM)</b>	<b>Accuracy</b>	1 per 20 field samples	Within 20–25% of the certified 95% confidence interval	Review raw data quantitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.
<b>Replicates:</b> (analytical and/or laboratory)  Applies to replicates of field samples, CRMs, matrix spike samples, etc.	<b>Precision</b>	One per batch	RSD < 15%; Hg, MeHg, 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.
<b>Matrix Spike</b>	<b>Accuracy</b>	1 per 20 field samples	Recovery > 50%	Check CRM or LCM recovery. Review raw data quantitation reports. Check instrument response using calibration standard. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed.
<b>Laboratory Control Material (LCM; optional)</b>	<b>Accuracy, Laboratory precision</b>	1 per 20 field samples	Within 20–25% of consensus value	Review raw data quantitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze LCM and samples. Repeat analysis until control limits are met.

MDL = method detection limit; RSD = relative standard deviation

**Table 2c. WATER: Quality control criteria for analysis of cognates.**

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	CRITERIA	CORRECTIVE ACTION
<b>Toxicity</b>				
<b>Ammonia, nitrate, nitrite, phosphate, silicate, chlorophyll <i>a</i>, TSS</b>				
<b>Method Blank</b>	<b>Contamination</b> by reagents, laboratory ware, etc.	One per batch	< MDL or < 30% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.
<b>Certified Reference Material (CRM) or Standard</b>	<b>Accuracy</b>	Once per sample set. NA for chlorophyll <i>a</i> or TSS	Error < 10% (ammonia, nitrate, phosphate)	Check calculations and instruments. Recalibrate and reanalyze.
<b>Replicates:</b> (analytical and /or laboratory)  Applies to replicates, CRMs, matrix spike samples, etc.	<b>Precision</b>	One per batch. NA for TSS	RSD < 5%	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, then identify and eliminate source of imprecision and reanalyze.
<b>Matrix Spike</b>	<b>Accuracy</b>	1 per 20 field samples	Recovery within $\pm 50\%$	Review data reports and chromatographs. Check instruments.
<b>DOC (Dissolved Organic Carbon)</b>				
<b>Method Blank</b>	<b>Contamination</b>	One per batch	< MDL or < 30% of lowest sample	Reanalyze samples
<b>Certified Reference Material (CRM)</b>	<b>Accuracy</b>	Once per sample set	Recovery within $\pm 5\%$	Recalibrate and reanalyze
<b>Replicates</b>	<b>Precision</b>	One per batch	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; RSD = relative standard deviation



**Table 3a. 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 < 30% 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	As a group: 70% of the analytes within the 65% confidence interval ( $\pm 1$ SD). Individually: No analyte outside 99% confidence interval for 2 consecutive analyses.	Review chromatograms and raw data quantitation 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	Sed: RSD < 35% Tiss: RSD < 50% for conc. < 10ppb; RSD < 20% for conc. > 10ppb; RSD of last 7 CRMs < 35%	Recalibrate and reanalyze. If problem persists eliminate source of imprecision and reanalyze.
Matrix Spike	Accuracy	1 per 20 field samples	Recovery within $\pm 50\%$ if no CRM limits apply, otherwise use CRM limits.	Check CRM or LCM 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 LCM recovery. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed.

MDL = method detection limit; RSD = relative standard deviation

**Table 3b. SEDIMENT AND TISSUE: Quality control criteria for analysis of trace elements.**

<b>QA SAMPLE</b>	<b>QA MEASURE</b>	<b>MINIMUM FREQUENCY</b>	<b>CRITERIA</b>	<b>CORRECTIVE ACTION</b>
<b>Method Blank</b>	<b>Contamination</b> by reagents, laboratory ware, etc.	One per batch	< MDL or < 30% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.
<b>Certified Reference Material (CRM)</b>	<b>Accuracy</b>	1 per 20 field samples	Within the certified 95% confidence interval ( $\pm 2$ SD)	Review raw data quantitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.
<b>Replicates</b>	<b>Precision</b>	One per batch	RSD < 10%; Hg, MeHg, As, Se < 35%  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.
<b>Matrix Spike</b>	<b>Accuracy</b>	1 per 20 field samples	Recovery within $\pm 50\%$	Check CRM or LCM recovery. Review raw data quantitation reports. Check instrument response using calibration standard. Attempt to correct matrix problem and reanalyze sample. Qualify data as needed.
<b>Laboratory Control Material (LCM; optional)</b>	<b>Accuracy &amp; Precision</b>	One per batch	Within 20–25% of the consensus value	Review raw data quantitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze LCM and samples. Repeat analysis until control limits are met.

MDL = method detection limit; RSD = relative standard deviation

**Table 3c. SEDIMENT AND TISSUE: Quality control criteria for analysis of cognates (total organic carbon, total nitrogen, and grain size) and ancillary measures (lipids).**

<b>QA SAMPLE</b>	<b>QA MEASURE</b>	<b>MINIMUM FREQUENCY</b>	<b>CRITERIA</b>	<b>CORRECTIVE ACTION</b>
<b>Method Blank</b>	<b>Contamination</b> by reagents, laboratory ware, etc.	One per batch	< MDL or < 30% of lowest sample	Identify and eliminate contamination source. Reanalyze all samples in batch. Qualify data as needed.
<b>Certified Reference Material</b>	<b>Accuracy</b>	Grain Size: NA. TOC: every 15 samples. Lipid: One per batch	Within 95% confidence interval of the certified value, RSD < 30% (lipids)	Review raw data quantitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.
<b>Replicates</b>	<b>Precision</b>	One per batch	RSD < 20% (grain size) < 3% (TOC) < 30% (lipids)	Check calculations and instruments. Recalibrate and reanalyze. If problem persists, then identify and eliminate source of imprecision and reanalyze.
<b>Laboratory control material (LCM)</b>	<b>Accuracy &amp; Precision</b>	One per batch of 20 or fewer samples.	Within 20–25% consensus value	Review raw data quantitation reports. Check instrument response using calibration standard. Recalibrate and reanalyze CRM and samples. Repeat analysis until control limits are met.

MDL = method detection limit; RSD = relative standard deviation

**Table 4. Target method detection limits for parameters or compound groups.**

Medium	Compound	Target MDL
Water	Acrolein	0.2 µg/L
	Copper	1.0 µg/L
	2,4-D	0.005 µg/L
	Diquat dibromide	0.72 µg/L
	Fluridone (ELISA)	0.5 µg/L SePRO ELISA method
	Fluridone (HPLC-MS)	0.001 µg/L HPLC-MS
	Fluridone (HPLC)	0.05 µg/L HPLC-Flourescence
	Glyphosate	5.00 µg/L
	Endothall	TBD
	Methoprene	TBD
Sediment	Copper (Electrothermal)	1.0 mg/kg w/ Electrothermal AAS
	Copper (Flame AAS)	40 mg/kg w/ Flame AAS
	2,4-D	0.1 µg/kg
	Fluridone (HPLC-MS)	2.00 µg/kg HPLC-MS
	Fluridone (HPLC)	25.00 µg/kg HPLC- Flourescence
	Methoprene	TBD
Tissue	Copper	1.0 µg/kg
	2,4-D	0.1 µg/kg
	Fluridone	2.00 µg/kg
	Methoprene	TBD

**Table 5. Chronic and acute toxicity test acceptability criteria**

Chronic	Acute
<i>Ceriodaphnia dubia</i>	
(7 day test)	(24, or 24-96 hr tests)
Neonates < 24 hours old at test onset, selected from those born within an 16 hour window Control survival ≥ 80%, ≥ 60 % of surviving adults with ≥ 3 broods, and average ≥ 15 young per surviving female.	Neonates < 24 hours old at test onset, selected from those born within an 16 hour window Control survival ≥ 90%.
<i>Pimephales promelas</i>	
(7 day test)	(acute, TIE test)
Larvae < 48 hours old at test onset. Control survival ≥ 80% with average dry weight of 0.25 mg per surviving fish.	Larvae < 48 hours old at test onset. Control survival ≥ 90%.
<i>Selenastrum capricornutum</i>	
No chronic test	(acute, TIE test)
	Cells 4 - 7 days old at test onset. Control cell density ≥ 2x10 <sup>5</sup> cells/ml with < 20% coefficient of variation among replicates
<i>Amphipod (e.g., Hyallela Azteca)</i>	
(28 day test)	(10 day static test)
Organisms 7-14 day old at test onset, 1-2 day age range All controls mean survival ≥80%. Hardness, alkalinity and ammonia vary <50%, DO > 2.5 mg/L	Organisms 7-14 day old at test onset, 1-2 day age range All controls mean survival ≥80%. Hardness, alkalinity and ammonia vary <50%, DO > 2.5 mg/L

<i>Larval bivalve (e.g., Mytilus edulis)</i>	<i>(48 hr acute test)</i>
	Larvae < 4 hours old at test onset. Control survival $\geq 70\%$ oysters, 60% clams
<i>Larval insect (e.g., Chironomus tentans)</i>	<i>(10 day test)</i>
	Organisms 10 day old at test onset, >50% 3 <sup>rd</sup> instar Controls mean survival $\geq 70\%$ , controls mean size 0.48 mg ash free dry wt at end. Hardness, alkalinity and ammonia vary <50%, DO > 2.5 mg/L throughout test

**Table 6. Chronic and acute toxicity test completeness criteria**

<i>For all samples</i>	
pH, conductivity, total hardness, alkalinity determined	
<i>For each toxicity test species:</i>	
Dissolved oxygen, temperature, conductivity, and pH monitored at the initiation of each test and on the 24-hr-old solution at the time of renewal.	
If mortality $\geq 30\%$ , then dissolved oxygen, pH, conductivity, and ammonia must be measured on that sample at the time of renewal.	
Chronic	Acute
<i>Ceriodaphnia dubia</i>	
(7 day test)	(24, or 24-96 hr tests)
Mortality and reproduction measured daily Minimum 10 replicates of 1 organism each Acceptability criteria must be met	Mortality measured daily. Minimum of 2 replicates of 5 organisms each Controls minimum 4 replicates of 5 organisms each Controls included for all manipulations
<i>Pimephales promelas</i>	
(7 day test)	(acute, TIE test)
Mortality measured daily Growth measured at the end of the test Minimum 3-4 replicates of 10 organisms each Acceptability criteria met	Mortality measured daily. Minimum of 2 replicates of 5 organisms each Controls minimum 4 replicates of 5 organisms each Controls included for all manipulations
<i>Selenastrum capricornutum</i>	
No chronic test	(acute, TIE test)
	Growth measured at the end of the test 4 replicates with initial cell densities of $10^4$ cells/ml Controls minimum of 4 replicates with initial cell densities of $10^4$ cells/ml Controls included for all manipulations
<i>Amphipod (e.g., Hyalella azteca)</i>	
(28 day test)	(10 day test)
Growth and mortality measured at end of test. Minimum 5 replicates (8 preferred) of 10 organisms each	Growth and mortality measured at end of test. Minimum 5 replicates (8 preferred) of 10 organisms each
<i>Larval bivalve (e.g., Mytilus edulis)</i>	
	(48 hr acute test)
	Samples and controls 5 replicates with 200-250 larvae Percent normally developed measured at termination
<i>Larval insect (e.g., Chironomus tentans)</i>	
	(10 day test)
	Growth and mortality measured at end of the test. Minimum 5 replicates (8 preferred) of 10 organisms each

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