Aquatic Pesticide Monitoring Program

Quality Assurance Program Plan

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Aquatic Pesticides Monitoring Program Quality Assurance Program Plan

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For the
Aquatic Pesticide Monitoring Program

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February 2004

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TABLE OF CONTENTS

LIST OF TABLES

APMP	Aquatic Pesticides Monitoring Program
ASTM	American Society of Testing and Materials
BPTCP	Bay Protection and Toxic Cleanup Program
Chla	Chlorophyll a
COC	Chain of Custody
CRM	Certified Reference Material
DOC	Dissolved Organic Carbon
DO	Dissolved Oxygen
DQC	Data Quality Criteria
EC_{50}	Effect Concentration of Pesticide that produces a specific measurable effect in 50% of the test organisms within stated study time
EPA	Environmental Protection Agency
ELAP	Environmental Laboratory Accreditation Program
ELISA	Enzyme-Linked Immunosorbent Assay
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
GC	Gas Chromatography
GC-ECD	Gas Chromatography-Electron Capture Detection
GLP	Good Laboratory Practice
GPS	Global Positioning System
LC_{50}	Concentration at which a toxicant is lethal to 50% of test organisms
LCM	Laboratory Control Material
LOEC	Lowest Observable Effects Concentration
LOQ	Limit of Quantitation
MDL	Method Detection Limits
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NELAP	National Environmental Laboratory Accreditation Program
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
NOEC	No Observable Effect Concentration
NPDES	National Pollutant Discharge Elimination System
NRCC	National Research Council Canada
NS&T	National Status and Trends Program
OSHA	Occupational Safety and Health Administration
ORP	Oxidation Reduction Potential
PMSD	Percent Minimum Significant Difference
QA/QC	Quality Assurance/Quality Control
QAPP	Quality Assurance Program Plan
RSD	Relative Standard Deviation
SFEI	San Francisco Estuary Institute
SOP	Standard Operating Procedure
STDEV	Standard Deviation
SWRCB	State Water Resources Control Board
TOC	Total Organic Carbon
TSS	Total Suspended Solids

1. INTRODUCTION

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

- A summary of the APMP and its organization.
- An overview of quality assurance and control in the APMP.
- Quality assurance and control measures in the field.
- 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 the San Francisco Estuary Institute (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 criteria, 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 field and laboratory contamination sources that may need to be taken into account when evaluating sample data quality:

A. Field

- Sample storage and shipping containers
- Sample equipment (tubing, pumps)
- Ship/Boat (exhaust, metal surfaces, lubricants)
- Personnel (dirty hands, general carelessness)
- Atmospheric deposition
- Preservatives

B. Laboratory

- Atmospheric deposition
- Personnel
- Chemical contamination from extraction and/or preparation steps
- Analytical instruments and equipment (tubing, corrosion, etc.)
- Reagents
- Containers
- Transfer equipment (vials, syringes, etc.)

2. OVERVIEW OF THE APMP

Program Background

The APMP began in 2002 and is funded by the California State Water Resources Control Board (SWRCB). The APMP was formed as a result of the Talent decision by the U.S. 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 Unites States. Following the ruling, the SWRCB now requires a permit for the discharge of aquatic pesticides. Public entities that are covered by this permit include irrigation districts, municipal water supply districts, and mosquito vector control districts. The SFEI, as the entity designated to implement the APMP, is administering the program under contract to the SWRCB.

Program Criteria

The criteria of the Aquatic Pesticide Monitoring Program are to implement comprehensive monitoring and special studies to evaluate the environmental quality impacts associated with the application of aquatic pesticides and to explore less toxic (non-chemical) alternatives to the use of aquatic pesticides. This will include providing funds for demonstration projects to document promising non-chemical control methods. The primary focus shall be to provide information to the SWRCB and the Regional Water Quality Control Boards (RWQCBs) to enable SWRCB and RWQCBs to choose appropriate sampling methods and develop environmental quality criteria for effective regulation of discharges of aquatic pesticides to surface waters.

Data Usage

Data from this program are made available for scientific research, environmental management purposes, and public awareness. Specific management questions to be addressed by this monitoring program are listed below:

- Are the selected analytical and sample collection methods sufficient to measure aquatic pesticides in the environment:
    - at concentrations allowing differentiation between "background" levels and those typically encountered in the environment following use at common or recommended application rates?
    - at or below the minimum concentrations which might be expected to impact resident biota and other non-target species?
- What spatial and temporal distribution of sampling is needed to determine the extent and persistence of aquatic pesticides after their release into treated water bodies?
- What other water and sediment quality parameters should be measured to better understand and predict environmental distribution and persistence of aquatic pesticides and their effects on non-target species?
- Do aquatic pesticides bioaccumulate in organisms?
- Are there measurable effects (compared to untreated control sites) on resident organisms or populations that indicate an impact of aquatic pesticides?
- Are there sufficient data to support development of appropriate water, sediment, and tissue quality criteria and guidelines?
- How effectively do non-chemical methods control target aquatic pests?
- How do non-chemical control methods impact water quality and non-target species?
- How do non-chemical control impacts compare with those of chemical control methods?

Project Tasks

In order to answer the management questions posed, APMP will use a triad sampling approach as recommended by the EPA (Barbour 1999), that will entail the simultaneous collection of chemistry, toxicity, and biological assessment data. Areas to which aquatic pesticides are applied will be monitored pre- and post-treatment for the following:

- Pesticide concentrations and water quality characteristics in water samples.
- Pesticide concentrations and sediment quality parameters (for pesticides suspected to partition to sediments and persist in the environment).
- Pesticide concentrations in organisms (resident fish and bivalves sampled for pesticides suspected to bioaccumulate).
- Population level impacts of the pesticides measured through community surveys of non-target plants and animals.

Non-chemical control methods will be similarly examined for:

- Impacts on water quality parameters.

Potential impacts of aquatic pesticides on beneficial uses will be examined in the laboratory via:

- Biochemical and/or physiological testing on a range of organisms for sublethal effects including reduced reproduction and growth.

It is anticipated that it will require multiple years of effort to obtain adequate data to inform regulatory development and other environmental management actions.

Sampling plan

Sampling sites will be selected from throughout the state with the intention of covering sufficient geographical areas and different end uses to provide a distribution of the range of aquatic environments and different types of pesticides that are applied. Sites will generally be visited prior to and multiple times following pesticide applications. Some sites will be revisited on subsequent reapplications of pesticide to evaluate potential cumulative effects. The scope of the program currently is not sufficient to cover all aquatic pesticide use categories in all regions of the state, but the primary objective of the program is to serve as a demonstration for the development and evaluation of more comprehensive statewide monitoring schemes and establishment of appropriate water quality criteria for aquatic pesticides. Sites will be monitored during the period from July 2002 to October 2004.

Sampling site selection procedures

1. Sites will be selected according to the Site Priority Matrix (Appendix A).
2. Within sites, representative sampling stations will be selected based on field site reconnaissance within the area targeted for pesticide application. Where possible, an analogous untreated reference site will be located at the site as well. The number of stations and frequency of collection for each metric will be performed according to the Sample Matrix (Appendix B). Field reconnaissance will be conducted by the APMP Field Manager and pesticide applicator personnel prior to pesticide application. Representative stations will be selected by the following factors:
    a. In areas where normal pesticide application could and/or does occur
    b. In areas where sampling is logistically possible and practical (boat access, property access, appropriate water and/or sediment depth)
    c. In areas where anthropogenic inputs or natural disruptions are minimized

Sample collection operating procedures

For Freshwater Sampling Locations:

1. Each station will be predetermined from field reconnaissance and generally located on a map. Once in the field, locate general area of stations, assign GPS coordinates to each station using a hand-held global positioning system (GPS), and then confirm station location on a map.
2. At each station: complete the Physical Habitat Quality Field Form for either lentic or lotic systems (located in the field binder) to document site characteristics and land use. Review the information with all field technicians after sampling for accuracy and completeness.
3. Complete the top portion of the Field Data Sheet (located in the field binder) with station ID, date, time, station depth, weather conditions, water color/clarity, latitude, longitude, EPE, and tidal cycle (if applicable). Note flow rate, flow diversions, flow volumes, anthropogenic impacts, wildlife presence, and anything else worth noting. Draw profiles of the water body from both aerial and cross-section views.
4. Sample Containers: Samples containers will either be provided by contract laboratories or by project staff according to contract specifications. Bottles will be labeled prior to

transport to the field according to each site-specific sampling plan. Spare bottles and labels will also be taken to the field.

5. Water Quality Measurements: Water quality measurements will be collected at every station during every sampling event using field meters. Personnel using the meters must be trained on their use and care prior to field use.
    a. A multifunctional water quality meter (e.g. WTW Multi 340:/SET or equivalent) is used with several probes, submerged into the water column to collect the following readings:
        i. dissolved oxygen
        ii. pH and temperature
        iii. specific conductance and salinity.
        iv. redox potential (Eh) of both water and soil.

        For each measurement, record the water depth. Although temperature can be measured by several probe types, the temperature value measured by the pH probe should be the value recorded on the field data sheet. At a minimum, surface readings should be taken at one-meter depth or mid water column for sites shallower than two meters. If possible, data (particularly DO) from the bottom, middle and top portions of the water column should also be taken. The probes will be rinsed with deionized water after each use and blotted dry prior to recapping and storage.
    b. Turbidity will be measured either in the field on site or samples can be placed in pre-cleaned containers, stored on ice in a cooler, and in a refrigerator at 4ºC on return to the laboratory. Samples measured in the laboratory will be processed within two weeks of collection. For laboratory turbidity measurements, the containers will be removed from the refrigerator and stored in the dark until they reach ambient temperature (approximately one hour). Turbidity measurements are then completed using the same procedures as in the field.
    c. Chlorophyll a (Chla) will be collected using a hand-held filter pump apparatus with a 0.8 micron, 47 mm diameter mixed cellulose ester filter. Between 500 mL and 1 L of site water should be filtered for each Chla sample. Filters are then wrapped in aluminum foil, placed in Ziploc bags, labeled with sample ID and volume of site water filtered, and stored on ice in coolers. Samples are subsequently shipped to an analytical laboratory for analysis.
6. Water Chemistry and Water Toxicity Sampling: Water chemistry and toxicity samples will be collected prior to and following pesticide applications. The appropriate volume and bottle type for samples are denoted on the Field Reference Sheet (Appendix C). A portable peristaltic pump will be used to transfer water from the water body being sampled to the appropriate sample container. Approximate sampling location will be denoted by a symbol on the aerial view sketch drawn on the back of the Field Data Sheet.
7. Sediment Chemistry and Toxicity Sampling: Sediment chemistry and sediment toxicity will be collected prior to and after (usually two weeks) pesticide application. Sediments are never collected immediately after pesticide application. Sediment will be collected with either a Van Veen, Ponar, or Petite Ponar sampling dredge. The approximate locations of sediment sample collection will be denoted by symbol on the aerial view sketch drawn on the back of the Field Data Sheet.

8. Bioassessment samples will be collected prior and subsequent to pesticide applications. The normal sampling interval will be preapplication, two weeks post application and six weeks post application. The procedures are derived from other documents (Barbour 1999; Hayworth and Siemering 2003; WIDNR 2003).
    a. Epiphytic macroinvertebrate will be collected with a dip net. Two transects will be established running perpendicular to the long axis of the pesticide application zone. Transects will run from near the shoreline out to the long axis of the application zone and will be marked by GPS coordinates only. Water depth will be recorded at intervals along each transect. Transects should represent similar habitat for the average conditions in the area of interest. Approximate locations of each transect will be denoted on the aerial view sketch drawn on the back of the Field Data Sheet.
    b. Benthic macroinvertebrates will be collected using a Van Veen Ponar or Petite Ponar dredge within the immediate vicinity of pesticide application. After collecting a sample, the material will be placed into a 0.5 mm mesh sieve bucket, large debris removed and cleaned of invertebrates (which are added back to the sample), and fine sediments washed from the sample. The material in the sieve will be washed directly into a sample jar using a wash bottle and transferred by forceps or hand, and excess water in the sample jar will be drained. Ethanol (95% v/v) will be added to the jar to achieve 30 % material and 70% ethanol (approximate, by volume). The approximate locations of sample collection will be denoted by symbol on the aerial view sketch drawn on the back of the Field Data Sheet.
    c. Phytoplankton will be collected only at lake/reservoir sites within the pesticide application zone. One sample per station will be collected pre and post application. Phytoplankton will be collected with site water from a Kemmerer grab sample bottle lowered to mid-water column. The sample will then be preserved with 2.5 mL of Lugol's solution and placed in a cooler, taking care to limit sample exposure to sunlight. The approximate locations of phytoplankton sample collection will be denoted by symbol on the aerial view sketch drawn on the back of the Field Data Sheet.

Field sample handling and shipping procedures

1. Samples for all chemical and toxicological analysis (sediment and water) will be maintained on ice in coolers and checked periodically to ensure that samples are appropriately protected and ice is added as needed. Container lids are checked for tightness and sealed with tape if necessary. Immediately upon return, the samples will be packed with more ice and protective wrapping, and then shipped by overnight express to the respective analytical laboratories. If samples are held overnight, they will be stored in a refrigerator at 4ºC, with the exception of Chlorophyll a, which is placed in the freezer.
2. All field biological samples (macroinvertebrates and phytoplankton) will be stored in coolers with no ice. On return, sample jar lids are checked for tightness and additional ethanol is added to macroinvertebrate samples as needed. The samples will be packed with protective wrapping and shipped to the appropriate lab.

3. All shipped samples will be accompanied by a 'Chain of Custody' form that indicates the pertinent sample identification information and analyses requested for each sample. A copy of the COC is maintained by the APMP.

Analysis plan

Physical parameters and conventional parameters measured by the APMP in water, sediment, and biological samples are listed in Table 1. Measurements of the physical parameters are needed to characterize turnover times of water bodies and other processes that dilute, disperse, degrade, or remove the pesticides of interest. The measured water and sediment quality parameters can affect the toxicity and persistence of chemical pesticides through acid-base reactions, complexation, competitive uptake, adsorption, or other chemical reactions (e.g., pH, DOC, calcium, TSS, respectively). Additionally, many of the water and sediment quality characteristics, independently of chemical pesticides, may affect survival when conditions exceed an organism's range of tolerance (e.g., low dissolved oxygen, high temperature, high salinity). Even when these parameters are not in a range resulting in outright mortality of organisms, they may be additional stressors that exacerbate the effects of chemical pesticides.

Physical characteristics of sampling sites will be monitored by APMP staff in the field, and recorded in field logs for subsequent entry in the APMP database. Samples collected in the field will be placed in containers and stored under conditions appropriate for the analyses to be performed. Any unusual sample characteristics or circumstances preventing normal sample handling will also be noted in the field log. On return from the field, the sampling crew will prepare samples for immediate shipping to analytical laboratories or store them under appropriate conditions for subsequent shipping (within the hold times recommended by the analytical laboratories). Documentation of the chain-of-custody will be maintained.

Aquatic pesticides measured by the APMP are listed in Table 2. The appropriate sample bottle types are listed in Table 1b. Additional parameters may be added to these lists for future monitoring. Currently, there are not water quality criteria for most of the monitored pesticides, but Table 3 lists concentrations of pesticides that may be suitable benchmarks for evaluating potential effects and developing future guidelines or criteria. The lowest relevant effects concentrations (EC_{50}, LC_{50}, LOEC, and/or NOEC) are provided for the most sensitive species found in a review (SFEI 2003) of published literature.

Bioassessment parameters used in evaluating effects of chemical pesticides, listed in Table 4, will focus on communities that are widely recognized as good biological indicators of perturbation: aquatic invertebrates, macrophytes, and algal communities (USEPA 2003). Due to the diverse nature of the target pesticides and water-body types studied, the type of bioassessments conducted will be specifically tailored for each pesticide sampling event.

Table 1. Parameters measured in the APMP.

Physical Parameters	**units**
Cloudiness	Approximate
Air Temperature	ºC
Water depth	M
Sediment collection depth	cm
Geometric profiles of water body	Cross-sections/ diagrams
Flow Rate (lotic systems)	Cfs (ft^3/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

Conventional Water Quality Parameters	**units**
Conductivity	µmho
Dissolved Organic Carbon	µg/L
Dissolved Oxygen (DO)	mg/L
Hardness (when salinity is < 5 $^0/_{00}$)	mg/L ($CaCO_3$)
Salinity	psu (‰)
pH	pH
Temperature	°C
Total Chlorophyll a	mg/m^3
Total Phosphorous	mg/L – P
Total Nitrogen	mg/L – N
Total Suspended Solids	mg/L
Alkalinity	mg/L ($CaCO_3$)
Dissolved Calcium	mg/L
Dissolved Magnesium	mg/L
Dissolved Sodium	mg/L
Turbidity	NTU

Sediment Quality Parameters	**units**
% 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 (*Hyallela azteca*)	% survival, growth
Rainbow trout (*Oncorhynchus mykiss*)	% survival
Fathead Minnow (*Pimephales promelas*)	% survival
Zooplankton (*Ceriodaphnia dubia*)	% survival, reproduction
Phytoplankton (*Selenastrum capricornutum*)	% survival
Midge larvae (*Chironomus tentans or riparus*)	% survival, reproduction
Cattail seed germination (*Typha spp.)*	% seed germination, shoot length

Table 2. Trace elements and organic chemicals measured in the APMP.

Applied Pesticides	Sample Bottle Type*	units in water; sediment; tissue
Acrolein	Glass	µg/L; NA; NA
Copper (copper sulfate and chelated copper)	Polyethylene	µg/L; µg/kg; µg/kg
2,4-D	Glass	µg/L; µg/kg; µg/kg
Diquat dibromide	Polyethylene	µg/L; NA; NA
Fluridone	Polyethylene	µg/L; µg/kg; µg/kg
Glyphosate	Polyethylene	µg/L; NA; NA
Malathion	Glass	µg/L; NA; NA
Methoprene	Glass	µg/L; µg/kg; µg/kg
Surfactants	Glass	µg/L; NA; NA
Triclopyr	Glass	µg/L; µg/kg; NA

NA=Not applicable

* Determined by scientific literature review and discussion with manufacturers.

Table 3. Pesticide minimum effect concentrations (test & non-target species)

Pesticide	Water
2,4-D	8.3 µg/L (NOEC Grass shrimp)
	0.3 mg/L (4-day LC_{50} Chinook salmon)
Acrolein	0.04 µg/L (5-day LOEC *Skeletonema costatum*)
Copper (copper sulfate, chelated copper)	0.04 mg/L (4-day LOEC *Ceriodaphnia dubia*)
	0.03 mg/L (4-day NOEC *Ceriodaphnia dubia*)
Diquat dibromide	5.4 µg/L (32-day LOEC *Fundulus heteroclitus*)
Fluridone	0.8 mg/L (4-day NOEC Walleye)
	200 µg/L (Coho salmon alevin)
Glyphosate	42 mg/L glyphosate (NOEC fathead minnow)
	1.0 mg/L surfactant (4-day LC_{50} fathead minnow)
Malathion	0.5 µg/L (4-day LC_{50} *Gammarus lacustris*)
Methoprene	2 µg/L (life cycle LOEC *Mysidopsis bahia*)
Triclopyr	260 µg/L (Coho Salmon Alevin LC50)

Table 4. Bioassessment parameters measured in the APMP.

Metric	Unit

Benthic Macroinvertebrates

Abundance	***Total Number***
Richness	Total Number of Individual Taxa
Diversity	Shannon-Weaver Index
EPT Taxa	%
Intolerant Organisms*	%
Tolerant Organisms*	%
Dominant Taxa	%
Collector	%
Filterer	%
Scraper	%
Predators	%
Shredders	%
Diptera Richness	%
Chironomidae Richness	%
Oligochaeata Richness	%

*=tolerances are derived from sensitivity to organic pollutants

Epiphytic Macroinvertebrates

Abundance/ Sweep	***Total Number***
Richness	Total Number of Individual Taxa
Diversity	Shannon-Weaver Index
EPT Taxa	%
Intolerant Organisms*	%
Tolerant Organisms*	%
Dominant Taxa	%
Functional Feeding Group	%
Diptera Richness	%
Oligochaeata Richness	%

*=tolerances are derived from sensitivity to organic pollutants

Macrophytes

Abundance	***Total # of occurrences***
Frequency of Occurrence	# intercepts/total intercepts for each species
Coverage	Interval area / total transect area for each species (areas estimated)
Species Diversity	Average number of species per interval
Dominant Taxa	% Present
Invasive Taxa	% Present
Occurrence by Structural Morphology	%

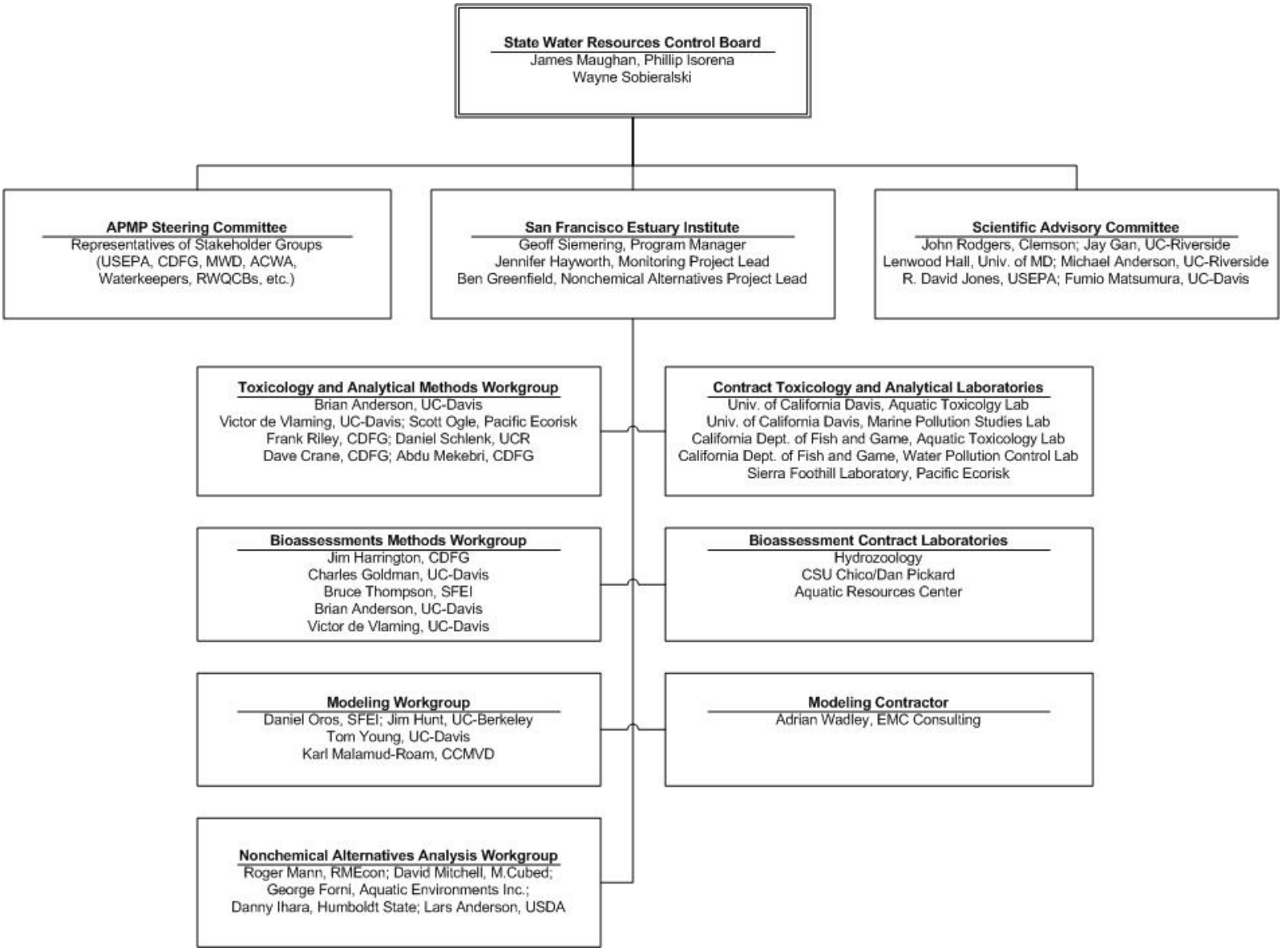
Phytoplankton

Abundance	***Total Number***
Diversity	Total Number of Individual Taxa
Richness	Shannon-Weaver Index

APMP Organization

An APMP organizational chart is provided in Figure 1.

Figure 1. APMP Organizational Chart



In addition to overall program management, SFEI is responsible for field sampling and data management for the APMP. The Principal Investigator and Program Manager for SFEI on this program is Geoff Siemering, who is responsible for overall administration of the program, including contracting. Jennifer Hayworth manages the chemical pesticide monitoring aspects of the program, and Ben Greenfield leads the portion of the program evaluating non-chemical alternatives. The Quality Assurance Officer for SFEI on this program is Donald Yee, whose

responsibilities include maintainence of this QAPP document and review of APMP data for conformance to program DQCs. The Data Manager for SFEI is Cristina Grosso, who ensures that data submitted by subcontractor labs are timely, complete, and properly incorporated into the APMP database. Contact information for these staff are listed below:

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Sub-contractor laboratories and the analyses they perform for APMP are listed below:

Oncorhynchus Mykiss, Ceriodaphnia dubia, Pimephales promelas, and *Selenastrum capricornutum* toxicity tests, definitive *Ceriodaphnia dubia and Pimephales promelas* toxicity tests:
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California Department of Fish and Game
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(916) 685-1880

Dissolved Organic Carbon, Chlorophyll A, general water quality criteria:

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Ceriodaphnia dubia, Pimephales promelas, and *Selenastrum capricornutum* toxicity tests:
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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:

- 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.

- 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).
- 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.
- Sample containers will be pre-cleaned and of the recommended type for minimizing contamination for the analytes measured.

Recommended preservation conditions and holding times for samples for chemical analyses are listed in Table 5.

For bioassessments (listed in Table 4), all samples should initially be preserved with 95% ethanol in the field. Field preserved samples in 95% ethanol should be transferred to 70% ethanol between 2 to 3 days after collection. Samples should be processed within 5 months after collection. Processed samples needing longer storage for QA and other reanalysis (e.g., remnant examination) should be supplemented with 10% glycerol to help reduce sample deterioration.

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.

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:

- Written protocols for the analytical methods to be employed for sample analysis will be submitted to the Program for review,
- Method detection limits (MDLs) and the procedures for determining them will be provided for each analyte,
- An initial calibration curve will be established for each analyte, the calibration curve shall include a low calibration point set at three to five times the MDL and include a minimum of five calibration points for trace organics,
- Acceptable performance will be shown on known or blind reference material (see section Laboratory Quality Control Procedures, Initial Demonstration of Capability), and

- 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:

- The laboratory will participate in an on-going series of inter-laboratory comparison exercises and provide results,
- Calibration checks will be performed during analyses, and
- Analysis of QA samples including laboratory method blanks, replicates, and certified reference materials and/or fortified samples (matrix spikes) will be made with field samples analyzed (see section Laboratory Quality Control Procedures, Ongoing Demonstration of Capability).

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.

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.

Reporting turnaround times for submission of results from sample analyses are specified in contracts with the analytical laboratories. These (reporting) turnaround times are independent of holding time requirements for samples; in all cases samples should be extracted and analyzed within the holding times specified for the analytical methods used. Turnaround time requirements specified in subcontracts are generally 60 days or less. The final sampling in October 2003 will allow sufficient time for report preparation and submittal in February 2004.

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. Data are checked for conformance to APMP DQCs by SFEI personnel. Verification of all individual quantitative results submitted by analytical laboratories will not be undertaken due to the high level of effort that would be required. However, analytical results will be spot checked for consistency and validity between laboratory hardcopy/electronic reports and the APMP database via verification of sums, range checking, and other aggregating methods. Anomalies in data sets received will be identified and reported to the lab as needed for correction.

4. FIELD QUALITY ASSURANCE AND QUALITY CONTROL

The quality of samples collected in the field is addressed through a number of procedures in the APMP. Proper selection of equipment and supplies and training for use of those items ensures that samples collected are minimally or not affected by collection procedures and materials. Collection and analyses of appropriate quality control samples allows measurement and assessment of artifacts or influences of sampling on sample characteristics, to differentiate uncertainties and variability introduced by the sampling process from those inherent in the monitored system. This section will describe quality assurance and quality control procedures implemented in the APMP.

Field Sample Collection Quality Assurance Procedures

Personnel using the field collection equipment must be trained on their use and care prior to field use. Sample containers appropriate to the matrices being sampled and the analyses to which they will be subjected will be chosen. Container preparation includes nonphosphate detergent washing, multiple tap water and ASTM Type I deionized water rinses, and 1:1 HNO_3 (Nitric Acid) rinses. Containers are oven dried. All containers meet and exceed the required detection limits established by the USEPA in SPECIFICATIONS AND GUIDANCE FOR CONTAMINANT-FREE SAMPLE CONTAINERS. Pre-cleaned bottles for sampling organic contaminants will be stored empty, dry, and tightly capped. Eliminating leachable plastics (e.g., non-Teflon® 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. Chemical resistant nitrile gloves will be worn and care taken not to touch objects other than the exterior of sample containers and equipment when possible to minimize contamination, and cleaning procedures of sampling equipment are employed to minimize cross-contamination between samples for the parameters of interest. Storage conditions of samples should be chosen to minimize changes in the parameters to be measured caused by reaction or interaction with the environment, the sample container, or other components of the collected sample.

Water sample collection

Water samples will be collected at one meter depth or mid-water column (if water body is less than 2 m deep) at each sampling site. For collection of water samples (for chemical analyses and toxicity testing) all tubing must be cleaned prior to use at each sampling location. 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. The inlet of the sampling pump tubing will be attached to an extendable sampling pole and deployed upstream (and upwind if possible) of the boat, away from the engine. A sufficient volume of water is collected to fill all necessary sample containers and the water homogenized by briefly stirring before individual containers are filled. Before filling sample containers, tubing should be flushed with site water for at least two minutes. Each sample container should be double rinsed with site water unless the container contains a preservative. If there is any question of whether a container contains preservative, refer to the sample plan for clarification. The outlet tubing of the water sampling pump should be positioned at the mouth of the sample container, being careful not to touch the inside of the container or the lid with the tubing. Fill the container completely to eliminate any headspace. Care should be

taken to minimize exposure of samples to sunlight. Immediately after collection, close the container and place on ice in a cooler.

Sediment sample collection

The dredge will be operated as described in the appropriate equipment manuals. Gloves will be worn. Prior to use at each site and between each station, the dredge and stainless steel bowl and spoon will be washed with detergent (e.g. Alconox) solution and rinsed with deionized water three times. Multiple dredge pulls will usually be necessary to obtain enough sediment sample for all the analyses. After the dredge is dropped to the sediment and retrieved, the spoon will be used to carefully scoop out the top 2-3 cm of sediment from each dredge pull. On one of the pulls, prior to removing the top sediment layer, the oxidation reduction potential (ORP) probe from the multimeter will be inserted into the top 2-3 cm to collect a soil redox potential reading. The upper sediment layer will be placed into the bowl and once enough sediment is collected, the sample is composited by mixing. The sample will then be placed into the appropriate pre-cleaned containers and placed on wet ice in coolers.

Bioassessment sample collection

Epiphytic macroinvertebrate collection

At consistent intervals along each sampled transect, three composite samples will be collected in both the treatment area and in the control (untreated) area using a standard 0.5 mm mesh D-frame dip net. A composite sample consists of three, one minute sweeps within the submerged/emergent pelagic vegetation and within the littoral vegetation up to the shoreline along each transect. After the three sweeps are done, all large vegetation and debris in the dip net will be removed after rinsing, inspecting for, and removing clinging organisms. "Clean" site water, free of vegetation and organisms, will be used for rinsing. Any organisms clinging on discarded debris will be removed with forceps and placed in the sample container. The remaining material in the dip net will be transferred to a sample container, preserved with 95% ethanol in the (approximate) ratio of 30% material to 70% ethanol. Remaining organisms clinging to the net will be removed with forceps. The outside of the container will be labeled with sample information (sample identification code, date, water body name, and initials of the sample collector) with the preservative noted. If more than one container is needed for a sample, each container label should contain all the sample information and should be numbered. This information will be recorded on the chain of custody form for shipping to the appropriate biological laboratory.

Benthic macroinvertebrate collection

Benthic macroinvertebrates will be collected using a Van Veen, Ponar, or Petite Ponar dredge within the immediate vicinity of pesticide application. One Petite Ponar grab is considered one sample. Three samples will be collected from each station. With the Van Veen, one grab will be collected each site and split among containers as three separate samples after sieving. After collection, the sediment will be placed into a 0.5 mm mesh sieve bucket. Any large debris in bucket will be removed from the sample and cleaned (invertebrates removed and added back to the rest of the sample). The sample will then be washed through the sieve over the side of the boat or in a tub with site water until no more fine sediment washes through the mesh. Care will be taken to not allow site water into the bucket from the top as this could allow non-sample

organisms to contaminate the sample. The material remaining in the bucket will then be washed directly into the sample jar using a wash bottle or transferred by forceps or hand. Ethanol (95% v/v) will be added to the container as a preservative to achieve a ratio of 30% material and 70% ethanol. Sample information (site, date, preservative, etc) will be written on a sample label. This information will be recorded on the chain of custody form prior to shipping to the appropriate biological laboratory. The approximate locations of sample collection will be denoted by symbol on the aerial view sketch drawn on the back of the Field Data Sheet.

Phytoplankton collection

Phytoplankton will be collected only at lake/reservoir sites within the pesticide application zone. One sample per station will be collected pre and post application. Phytoplankton in site water will be collected with a Kemmerer grab sample bottle, at a minimum from mid-water column. A 250 mL sample will be preserved with 1% (v/v, 2.5 mL) of Lugol's solution and placed in a cooler (without ice), taking care to limit sample exposure to sunlight. The approximate locations of phytoplankton sample collection will be denoted by symbol on the aerial view sketch drawn on the back of the Field Data Sheet.

Performance Measurement Samples: 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.

- Source Solution Blanks: These account for any pre-existing contamination in the water or preservatives used to prepare the sample containers.
- Bottle Blanks: These account for contamination in sampling containers, in addition to any contamination due to the source solution.
- 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.
- Equipment Blanks: These account for contamination introduced by the field sampling equipment in addition to the above sources.
- 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.
- 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 methods, and any sediment field replicate samples collected will mainly be used to evaluate reproducibilty 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. Sample containers will be cleaned according to the same procedures used to clean all sample bottles. 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 programs, bottle blanks that were generated showed that the "pre-cleaned certified" 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. The correct bottle type for each pesticide is listed in Table 2.

Travel blanks will not always be 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 or Petite Ponar grab sampler, but equipment blanks will not be taken for sediments. If tissue samples are hand collected then equipment blanks are not taken.

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 straight-forward, 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 fully 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 (such as positioning the sampling inlet upstream and upwind of the vessel) this potential problem will be taken.

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; Bewers 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).

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, petite Ponar, or Eckman dredge 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 deionized water to avoid any carryover contamination from one station to another. Sampling, compositing, and homogenization will be conducted with gloved hands, and the homogenate will be placed into the appropriate bottle type for analysis. 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® foil.

5. LABORATORY QUALITY ASSURANCE AND CONTROL

APMP Chemical Analysis Laboratory Requirements

The APMP requires all laboratories to demonstrate capability continuously through:

- Strict adherence to common QA/QC procedures.
- Routine analysis of certified reference materials (CRMs)[1].
- 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.

[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).

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., low parts per quadrillion and parts per billion) analysis of organic and inorganic contaminants in water or sediments. Methods used by the APMP were all validated USEPA analytical methods. While other more sensensitive methods may exist, these USEPA validated methods have adequate detection limits (well below published LOEC and NOEC values).

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 program. Laboratories are expected to conduct operations in a manner that includes:

- A program of scheduled maintenance of analytical balances, microscopes, and other laboratory equipment and instrumentation.
- Routine checking of analytical balances using a set of standard reference weights (American Society of Testing and Materials (ASTM) Class 3, NIST Class S-1, or equivalents).
- Checking and recording the composition of fresh calibration standards against the previous lot. Acceptable comparisons differ < 2 percent from the previous value.
- Recording all analytical data in bound (where possible) logbooks, with all entries in ink, or electronic format.
- Monitoring and documenting the temperatures of cold storage areas and freezer units daily.
- Verifying the efficiency of fume hoods.
- 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 μmhos/cm.
- Labeling all containers used in the laboratory with date prepared, contents, initials of the individual who prepared the contents, and other information as appropriate.
- Dating and safely storing all chemicals upon receipt. Proper disposal of chemicals when the expiration date has passed.
- Having QAPPs, SOPs, analytical methods manuals, and safety plans readily available to staff.
- Having raw analytical data, such as chromatograms, accessible so that they are available upon request.

Laboratories will 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 Program 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 program, 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 program 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 program officials:

- Laboratory QA Plan: Clearly defined policies and protocols specific to a particular laboratory, including personnel responsibilities, laboratory acceptance criteria and corrective actions to be applied to the affected analytical batches, qualification of data, and procedures for determining the acceptability of results.

- Laboratory Standard Operating Procedures (SOPs): Containing instructions for performing routine laboratory procedures.
- Laboratory Analytical Methods Manual: Step-by-step instructions describing exactly how a method is implemented in the laboratory for a particular analytical procedure. Contains all analytical methods utilized in the particular laboratory for the APMP.
- 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.
- 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.

Appendix D contains copies of laboratory methods, SOPs, and QA plans current at the time of publication of this document . Some laboratory methods and SOPs may be edited to exclude proprietary details about the analyses. Quality assurance documents are reviewed conformance to program needs by the APMP Program Manager and QA Officer or their designees.

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 at a minimum on a biennual basis. Review of current NELAP and/or state ELAP certification of a laboratory for the analyses performed for APMP may be accepted in some cases in lieu of an on-site audit. 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. Results of analyses of QA samples are to be reported with results of field samples. Minimum frequencies and other performance requirements for analyses of QA samples are indicated in Tables 6-11.

- 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.
- Internal Standards: These account for error introduced by the analysis, and recoveries should be reported for each sample individually.
- 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.

- Replicate Samples: These are replicates of extracted material that measure the instrumental precision.
- Laboratory Replicate Samples: These are replicates of the raw material that are extracted and analyzed to measure laboratory precision.
- Matrix Spike Replicate Samples: These can be 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).
- 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. Results of both field and QA samples will be reviewed by the APMP QA Officer or designees for conformance with APMP reporting and data quality requirements.

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 5-10), 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:

- No process or method changes have been made.
- 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 5). These MDLs have been derived empirically from reported literature or other monitoring and research efforts. Most are considerably lower than water quality criteria or sediment and tissue quality guidelines (Table) 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 three to five 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 ±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 ±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 5-10) 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 5-10); 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.

A minimum of one CRM (or LCM) sample per analyzed batch (minimum one per 20 samples for larger batches) of APMP samples will be analyzed for accuracy. CRM samples in an appropriate matrix (water, sediment, tissue) should be used. The following calculations is used to determine the relative accuracy (in percent) of an analytical process:

$$\text{Accuracy (\%)} = \frac{\text{Laboratory measurement}}{\text{Certified or Consensus Value}} \times 100$$

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 seven 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 5-10 for each analyte of interest. Following are the calculations:

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

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 criteria 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 5-10). For each class of organic analytes, 70% of the individual analytes will be within the certified 65% confidence interval (±1 STDEV of the consensus value); no individual analyte value shall exceed the 99% confidence interval (±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 ±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 5-10), 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 5-10). 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 (in percent) is calculated as follows:

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

Recovery data for the fortified compounds ultimately will provide a basis for determining the prevalence of matrix effects in the samples analyzed during the program. If the percent recovery for any analyte in the MS or MSD is not in recommended range of (within 50 percent of the expected spike in the case of trace organic analyses, within 30 percent for trace elements) , the chromatograms or other 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 or 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

Water quality chemical analyses

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. Accuracy of performance standards (reference materials, matrix spikes) should be within ±5% of the target value. The precision criterion, RPD between duplicates, is 5%.

Other WQ chemical parameters

In addition to samples for DOC, samples for chemical analyses of other water quality parameters will be collected with samples for chemical analyses of biocides. For chemical analyses of other water quality parameters performed in the laboratory (alkalinity (as CaCO3), ammonia, hardness, total nitrogen, total phosphorous, and dissolved sodium, magnesium, and calcium), the recovery criterion for reference materials, matrix spikes, and other performance standards is ±15% of the target value. The precision criterion is 15% RPD for duplicate analyses.

Turbidity

Turbidity meters should be calibrated monthly. Samples to be analyzed for turbidity are acclimated to room temperature in the dark prior to measurement. Replicate measurements are made on one per twenty samples, a minimum of one per analysis batch. The precision criterion is 15% RPD.

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 reference material is available for TSS. Recovery of matrix spikes should be within 15% of the target value. The precision criterion is ±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 ±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 20% RPD for duplicate analyses.

Total Kjeldahl Nitrogen (TKN)

Blanks, reference material or matrix spikes, and duplicates (of matrix spikes or field samples) will be analyzed with each batch of samples. The accuracy criterion for replicate analyses is ±25% of the target value. Precision (RPD) of duplicate analyses should be 20% or less.

Biological 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 toxicity tests

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 for water toxicity should be initiated as soon as possible, within 36 hours after initial sample collection. In rare instances, holding times can be extended if data demonstrating no change in sample toxicity over time are presented, but in no case shall holding times be longer than 72 hours. For sediment toxicity, tests should also be initiated as soon as feasible and within four weeks of collection. If the toxicant of interest has been shown to have rapid degradation

either in the laboratory or the field, recommended maximum holding times should be further reduced.

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 *Pimephales promelas* protocols. Tests with other organisms 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 12. Requirements for considering toxicity tests complete are summarized in Table 13. 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 water flea, *Ceriodaphnia dubia,* reproduction and survival, *Pimephales promelas*, survival and growth, and algae, *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_{50}. Tests should be initiated within two weeks of sample collection.

Sediment toxicity tests

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. When methoprene sediment toxicity is measured, test must be set up within 48 hours of sample collection. Where USEPA standard test species are used (*Hyallela azteca*) should follow the appropriate latest revisions from the USEPA (USEPA 2000), the annual book of ASTM standards, or established academic laboratory procedure.

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.

QA Requirements for Bioassesments

Bioassessment samples can be identified and counted in total or subsampled, depending on the total abundance of organisms in the sample. Organisms will generally be sorted to the genus level, with the exception of chironomids and oligochaetes, which are sorted to the species level. After collected samples are rinsed of preservative, large undecayed items remaining in the sample should be examined. Any clinging or embedded organisms should be carefully rinsed and the debris remnant set aside in a separate remnant jar. Decayed items should be kept and carefully inspected for invertebrates with the aid of a stereo microscope for counting and identification.

If there are a large number of organisms in a sample, it may be subsampled by distributing the sample evenly on a counting grid and counting a subset of the grids. A minimum of 300 organisms should be indentified and counted, and at least three grids should be processed if subsampling is used. Otherwise (e.g., there are fewer than 300 organisms in the sample), all organisms in the sample should be identified and counted. Indentified organisms should be placed in separate glass vials for each taxon. If 300 organisms are counted before a grid is completed, the remainng organisms in that grid are counted but not identified. Remaining sample (uncounted grids, and counted but unidentified organisms) are placed back in a jar labeled for the “original” sample.

In processing samples (or subsamples from grids), the following must not be included in invertebrate counts and should be placed in remnant jars:

1. organisms that were dead before sampling (these can be recognized by their generally decayed “husk-like” and frail appearance, and will often lack one or more body parts).
2. exuviae
3. organisms with incomplete bodies (a head, thorax and most of the abdomen should be present)
4. terrestrial invertebrates
5. semi-aquatic insects including Collembola and surface hemipterans
6. worm fragments - this may depend on the project. If oligochaetes are to be identified to family, only heads should be counted, or count heads and tails and divide by two.
7. empty shells and cases (e.g., gastropods, ostracods, clams, caddisflies, chironomids)

Ten percent of the remnant samples are to be examined by a QC taxonomist for overlooked organisms or other counting errors during subsampling. The number of unpicked benthic macroinvertebrates (if any) and their identity are recorded. For subsamples containing 300 or more organisms, the remnant sample should contain fewer than 10% of the total organisms subsampled. For samples containing fewer than 300 organisms, the remnant should contain fewer than 30 organisms. If these criteria are not met, then corrective actions are initiated,

including a recount of the sample and auditing of future work done by the same analyst until their work consistently meets performance criteria.

Ten percent of the samples from any given project are also checked for quality assurance in taxonomic identification. Misidentifications, counting errors and differences in taxonomic effort are recorded in spreadsheet form and analyzed by statistical software. If a taxonomist is discovered to consistently misidentify a particular taxon, samples processed for the project by that taxonomist will be reexamined, and that person will receive instruction from the QC taxonomist about how to properly identify specimens in that group; all future ID's involving that taxon will be checked until the problem is resolved. Bioassessment acceptability criteria are summarized in Table 7.

6. DATA MANAGEMENT AND VALIDATION IN THE APMP

After data are submitted and included in the APMP database, APMP staff will examine the data set for completeness (e.g., correct numbers of samples and analyses, appropriate QA sample data included) and accuracy (e.g., in sample IDs), and spot-checked for consistency with hardcopy results reported by the laboratory. The APMP QA Officer or designee will examine submitted QA data for conformance with APMP DQCs. Incomplete or inaccurate data, or data failing DQCs without appropriate explanation will be referred back to the laboratory for correction or clarification.

In addition to contamination and other artifacts introduced by sampling and analytical methods used, errors may arise at many points in the processing and transmittal of data generated for the APMP. Characteristics of reported data will be examined to identify possible problems in the generation and transmission of data. Data submitted to APMP will be compared to values in the literature for comparable environments and from previous APMP monitoring to evaluate their environmental coherence. Simple statistics (e.g., minimum, maximum, mean, median) may be generated to quickly identify data sets or individual data points greatly outside of their expected range. Anomalous individual points will be examined for transcription errors. Unit conversions and sample quantitation calculations may be reviewed to identify larger and systematic errors.

Where groups of analytes or results in different environmental phases are or can be summed to generate totals (e.g., %gravel + sand + fines = 100%, dissolved + particulate = total), data sets or individual samples will be further checked for internal consistency. For example, total water concentrations of contaminants should generally be greater than dissolved concentrations. Gross deviances may be used to identify problems in sampling, analysis, quantitation, or data transcription and transmission. Problems found by APMP staff will be relayed to the appropriate laboratory and field sampling staff to address. However, in some cases (particularly where the differences are on the order of the MDL) dissolved results less than totals may indicate the uncertainty typical for the analytical method, and apparent anomalies will be evaluated on a case-by-case basis.

The APMP Science Advisory Panel will conduct program review four times during the duration of the program. The first review was conducted July 2002, the second review was in February 2003, the third review will be conducted in January 2004, and the final review will be conducted in January 2005.

Table 5. Pesticide Analytical Methods, MDLs, Laboratories, Preservation, and Holding Time.

Lab	Medium	Compound	Method	Target MDL	Preservation	Max Holding Time
CDFG	Water	Acrolein	LC-MS	0.005 µg/L	Glass, pH 4-5, 4°C	14 days (EPA Method 603)
		Copper		1.0 µg/L	HNO_3 pH 2, 4°C	6 months
		2,4-D	HPLC-MS	0.005 µg/L	Amber glass, 4°C	Extract 7 days / Analyze 40 days of Extraction
		Diquat dibromide	HPLC, LC-MS	0.50 µg/L	Amber glass, 4°C	Extract 7 days / Analyze 21 days of Extraction
		Fluridone	SePRO method ELISA HPLC-MS HPLC-Flourescence	0.5 µg/L 0.001 µg/L 0.05 µg/L	Amber glass, 4°C	14 days
		Glyphosate	HPLC-Flourescence	5.00 µg/L	Glass, 4°C	14 days, 18 months if frozen
		Malathion	GC-FPD, GC-MS	0.020 µg/L	Glass, 4°C	Extract 7 days / Analyze 40 days of extraction
		Methoprene	HPLC-MS	0.05 µg/L	Amber glass, 4°C	Extract 7 days Analyze 21 days of Extraction
		Surfactants	HPLC-MS	2.0 µg/L		
		Triclopyr	HPLC-MS	0.020 µg/L	Amber glass, 4°C	Extract 7 days / Analyze 40 days of extraction
	Sediment	Copper	Electrothermal AAS Flame AAS	20 µg/kg 100 µg/kg		6 months
		2,4-D	HPLC-MS	0.1 µg/kg	Glass, 4°C	Extract 7 days / Analyze 40 days of Extraction
		Fluridone	HPLC-MS HPLC- Flourescence	2.00 µg/kg 25.00 µg/kg	Glass, 4°C	14 days
		Methoprene	LC-MS	2.0 µg/kg	Glass, 4°C	Extract 7 days Analyze 21 days of Extraction
		Triclopyr	LC-MS	0.20 µg/kg	Glass, 4°C	Extract 7 days / Analyze 40 days of extraction
	Tissue	Copper	Electrothermal AAS Flame AAS	20 µg/kg 100 µg/kg		6 months
		2,4-D	LC-MS	0.1 µg/kg	Glass, 4°C	Extract 7 days / Analyze 40 days of Extraction
		Fluridone	HPLC-MS	2.00 µg/kg	Glass, 4°C	14 days
		Methoprene	LC-MS	2.0 µg/kg	Glass, 4°C	Extract 7 days Analyze 21 days of Extraction
Ceimic	Sediment	AVS-SEM (copper)	ICP-AES	0.5 mg/ kg		6 months

Table 6. WATER: Quality control criteria for analysis of organic compounds.

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	DATA QUALITY CRITERION	CORRECTIVE ACTION
Method Blank	**Contamination** by reagents, laboratory ware, etc.	1 per 20 field samples, minimum one per batch	< MDL or < 30% 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.	1 per 20 field samples, minimum one per batch	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, minimum one per batch	Recovery within ±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.
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 LCM 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 ± 20% for Pesticides.	Beginning with last sample before failure, recalibrate and reanalyze. Compare RSD and reanalyze.

MDL = method detection limit; RSD = relative standard deviation

Table 7. WATER: Quality control criteria for analysis of trace elements.

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	DATA QUALITY CRITERION	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, minimum one per batch	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.
Replicates: (analytical and/or laboratory) Applies to replicates of field samples, CRMs, matrix spike samples, etc.	**Precision**	1 per 20 field samples, minimum one per batch	RSD < 15%; 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, minimum one per batch	Recovery within ±30% (70-130%)	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.
Laboratory Control Material (LCM; optional)	**Accuracy, Laboratory precision**	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 8. WATER: Quality control criteria for analysis of cognates.

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	DATA QUALITY CRITERION	CORRECTIVE ACTION
Toxicity				
Alkalinity, ammonia, hardness, nitrate/nitrite (total N), phosphorous, silicate, sodium, magnesium, calcium,				
Method Blank	**Contamination** by reagents, laboratory ware, etc.	1 per 20 field samples, minimum 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) or Standard	**Accuracy**	One per batch.	Error < 15% (ammonia, nitrate, phosphate)	Check calculations and instruments. Recalibrate and reanalyze.
Replicates: (analytical and /or laboratory) Applies to replicates, CRMs, matrix spike samples, etc.	**Precision**	1 per 20 field samples, minimum one per batch. NA for TSS	RSD < 15%	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, minimum one per batch	Recovery within ±15%	Review data reports and chromatographs. Check instruments.
Chlorophyll *a*, turbidity, TSS				
Method Blank	**Contamination** by reagents, laboratory ware, etc.	1 per 20 samples, minimum 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) or Standard	**Accuracy**	Once per sample set. NA for chl *a* or TSS	Error < 15%	Check calculations and instruments. Recalibrate and reanalyze.
Replicates: (analytical and /or laboratory) Applies to replicates, CRMs, matrix spike samples, etc.	**Precision**	1 per 20 samples, minimum 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.
Matrix Spike	**Accuracy**	1 per 20 samples, minimum one per batch	Recovery within ±15%	Review data reports and chromatographs. Check instruments.
DOC (Dissolved Organic Carbon)				
Method Blank	**Contamination**	One per batch	< MDL or < 30% of lowest sample	Reanalyze samples
Certified Reference Material (CRM)	**Accuracy**	Once per sample set	Recovery within ±5%	Recalibrate and reanalyze

Replicates	**Precision**	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 9. SEDIMENT AND TISSUE: Quality control criteria for analysis of organic compounds.

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	DATA QUALITY CRITERION	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 (±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 ±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 10. SEDIMENT AND TISSUE: Quality control criteria for analysis of trace elements.

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	DATA QUALITY CRITERION	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	Within the certified 95% confidence interval (±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.
Replicates	**Precision**	One per batch	RSD < 10%; 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 within ±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.
Laboratory Control Material (LCM; optional)	**Accuracy & Precision**	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 11. SEDIMENT AND TISSUE: Quality control criteria for analysis of cognates (total organic carbon, total nitrogen, and grain size) and ancillary measures (lipids).

QA SAMPLE	QA MEASURE	MINIMUM FREQUENCY	DATA QUALITY CRITERION	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	**Accuracy**	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.
Replicates	**Precision**	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.
Laboratory control material (LCM)	**Accuracy & Precision**	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 12. Chronic and acute toxicity test acceptability criteria

Chronic	Acute
Ceriodaphnia dubia	
(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%.
Pimephales promelas	
(7 day test)	*(96 hr 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%.
Selenastrum capricornutum	
No chronic test	*(96 hr test)*
	Cells 4 - 7 days old at test onset. Control cell density ≥ $2x10^5$ cells/ml with < 20% coefficient of variation among replicates
Amphipod (e.g., Hyallela Azteca)	
(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
Larval bivalve (e.g., Mytilus edulis)	*(48 hr acute test)*
	Larvae < 4 hours old at test onset. Control survival ≥70% oysters, 60% clams
Larval insect (e.g.,Chironomus tentans)	*(10 day test)*
	Organisms 10 day old at test onset, >50% 3rd instar Controls mean survival ≥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
Macrophyte (*Typha ssp*)	(*7 day test*)

Table 13. Chronic and acute toxicity test completeness criteria

For all samples	
pH, conductivity, total hardness, alkalinity determined	
For each toxicity test species:	
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 ≥ 30%, then dissolved oxygen, pH, conductivity, and ammonia must be measured on that sample at the time of renewal.	
Chronic	Acute
Ceriodaphnia dubia	
(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
Pimephales promelas	
(7 day test)	*(96 hr 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
Selenastrum capricornutum	
No chronic test	*(96 hr test)*
	Growth measured at the end of the test 4 replicates with initial cell densities of 10^4cells/ml Controls minimum of 4 replicates with initial cell densities of 10^4cells/ml Controls included for all manipulations
Amphipod (e.g., Hyalella azteca)	
(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
Larval bivalve (e.g., Mytilus edulis)	
	(48 hr acute test)
	Samples and controls 5 replicates with 200-250 larvae Percent normally developed measured at termination
Larval insect (e.g.,Chironomus tentans)	
	(10 day test)
	Growth and mortality measured at end of the test. Minimum 5 replicates (8 preferred) of 10 organisms each
Macrophyte (*Typha ssp*)	(*7 day test*)
	Seed germination and shoot growth measured at end of the test. [UNSURE OF WHAT ELSE NEEDS TO GO HERE]

Table 14. Bioassessment acceptance criteria

QA PROCEDURE	MINIMUM FREQUENCY	ACCEPTANCE CRITERION	CORRECTIVE ACTION
Remant analysis	10% of sample remnants	All Remnant counts <10% of corresponding samples	Recount samples with excess remnant counts. Recount all samples performed by taxonomist with count error.
Sample reanalysis	10% of samples	90% of organisms correctly counted and identified	Recount samples of taxonomist with excessiveerror rate Retrain taxonomist and monitor future work until criteria consistently met.

(CDFG 1999; CDFG 2002)

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APPENDIX A: SAMPLE SITE PRIORITY MATRIX

Estimated Site Sampling Cost	Site # Goal	Pesticide	Water Body Classification [Location Name (Application Entity)]			
			Drinking Water Reservoir / Lakes	**Small Pond (< 5 ac)**	**Irrigation Canal**	**Stormwater Canals / Streams**
Medium	1, 2	2,4-D*				
Low	1	Acrolein			5- Planada Canal (Merced ID)	
Medium	2	**Copper Sulfate***	2- Bon Tempe/ Nicassio/ Lagunitas Reservoirs (Marin Municipal Water District)			
Medium	2	Chelated Copper*		5- Sand Bay Isle (Aquatic Environments, Inc.)	5- Byrnes Canal (Solano ID) 1- East Fork Russian River Irrigation Canals (Potter Valley ID)	
Low	1	Diquat		5- Sand Bay Isle (Aquatic Environments, Inc.)		
Low	0	Endothall	applied in few places, only in combo w/ other pesticides			
High	2	**Fluridone***	8- Big Bear Lake (Big Bear Municipal Water District)	5- Costa Ponds (CA Dept. Food & Ag)		
Low	2	**Glyphosate**			5- Atwater Canal (Merced ID)	4- Doris Drain (Ventura County Flood Control)
Medium	0	Malathion	will be sampled opportunistically as applied			
Medium	1, 2	Methoprene				
??	1, 2	Triclopyr				5- Bear Creek (CA Dept. Food & Ag)
Total Goal Sites	13-16	**Total Actual Sites: 16**				

* Soil-partioning pesticides that should be targeted for pre-season sampling

Pesticides in bold will have repeated, intensive sampling regimes at select sites (i.e. one additional 4-6wk post-application sampling event)

APPENDIX B: SAMPLE MATRIX

Pesticide [1]	Sample Location/ Applicator Entity	Sampling Metrics								
		Water Chemistry Sample Frequency [2,3]	Number of Stations	Sediment Chemistry Sample Frequency	Number of Stations	Toxicity Testing [4]	Sample Frequency	Bio-assessments [5]	Sample Frequency [6]	Special Studies [7]
2,4-D (S)	Stone Lake/ USFWS	Pre, 1-24 hrs post	1	Pre & 2wks post	2	W- EPA 3 species tox; S- Hyallela	same frequency as water & sed collection	B, EI	Pre, 2wks Post	none
Acrolein (C)	Livingston Canal/ Merced ID	Pre, 1-24 hrs post	2	NA	NA	NA	NA	NA	NA	AM
Copper Sulfate (C)	Bon Tempe/Lagunitas/ Nicassio Reservoirs/ Marin MWD	Pre, 1-24 hrs post; Nicassio also 1 wk post	Bon Tempe/Lag unitas - 1; Nicassio - 2	Pre, 2wks, 4-6wks post; Nicassio not 4-6wks	Bon - 6; Lag - 1; Nic - 5	W- cerio, juvi rainbow trout; S- Hyallela	same frequency as water & sed collection	B, PP	Pre, 2wks, 4-6wks Post; Nicassio not 4-6wks	none
Chelated Copper (C)	Byrnes Canal/ Solano ID	Pre, 1-24 hrs post	3	Pre & 2wks post	2	W- cerio, juvi rainbow trout; S- Hyallela	same frequency as water & sed collection	B, EI	Pre & 2wks post	M
	East Fork Russian River Irrigation Canals/ Potter Valley ID	Pre, 1-24 hrs post	2	Pre & 2wks post	1	W- cerio, juvi rainbow trout	same frequency as water collection	B	Pre & 2wks post	none
Diquat (C)	San Bay Isle/ Aquatic Env. Inc.	Pre, 1-24 hrs post	1	Pre & 2wks post	2	W- EPA 3 species tox; S- Hyallela	same frequency as water & sed collection	B, EI	Pre & 2wks post	none
	7 Mile Slough/ DBW	Pre, 1-24 hrs post	1	1-24 hrs post & 2wks post	1	W- EPA 3 species tox; S- Hyallela	same frequency as water & sed collection	B, EI	1-24 hrs post & 2wks post	none
Mixed Site - Diquat & Copper	San Bay Isle/ Aquatic Env. Inc.	none	none	Pre & 2 day post	2	none	none	B	Pre & 2 day post	none
Fluridone (S)	Costa Ponds/ CDFA	Pre, 1-24 hrs post	2	Pre,2wks, 6wks Post	5	W- EPA 3 species tox; S- Hyallela & Typha	same frequency as water & sed collection	B, EI	Pre,2wks, 6wks Post	M
	Big Bear Lake/ Big Bear MWD	none	none	Pre & 2wks post	6	S- Hyallela & Typha	same as sed collection	B, EI	Pre, 2wks Post	none
Glyphosate (S)	Stone Lake/ DBW	Pre, 1-24 hrs post	2	1-24 hrs post, 4wk post, 8wk post	3	W- EPA 3 species tox	same frequency as water collection	B, EI	1-24 hrs post, 4wk post, 8wk post	none
	Atwater Drain/ Merced ID	Pre, 1-24 hrs post	2	none	none	W- EPA 3 species tox	same as water collection	EI	Pre, 1-24 hrs post	none
	Doris Drain/ Ventura Flood Control	Pre, 1-24 hrs post	1	Pre, 1-24 hrs post	1	W- EPA 3 species tox	same as water collection	B, EI	Pre, 1-24 hrs post	none
Methoprene (C)	Swanton's Marsh/ Contra Costa VCD	Pre, 1-24 hrs post	3	Pre & 96hrs post	3	S- Hyallela & Chironomid	same as sed collection	none	none	IST

APPENDIX C: FIELD REFERENCE SHEET

Physical Parameters		units		
Air Temperature		°C		
Water depth		M		
Sample collection depth		M		
Geometric profiles of water body		Cross-sections/ diagrams		
Flow Rate (lotic systems)		Cfs (ft3/s)		
Inflow & Outflow Volumes (lotic systems)		Cubic ft		
Flow Diversions		Describe		
Current from wind action (lentic systems)		Qualitative – none, mild, moderate, strong		
Anthropogenic activities/ alterations		Describe		
Wildlife presence		Describe		
Volume / Bottle Type	**Conventional Water Quality Parameters**	**units**	**Field Blank / Dups**	**Toxicity / Dups**
Meter	Conductivity	µmho/ cm	One per site (2L Poly) / One Duplicate (DOC, Pesticide, Chem) per event	2.5gal Poly – unless copper, need additional 10L / One per site
Meter	Dissolved Oxygen (DO)	mg/L		
Meter	Turbidity	NTU		
Meter	pH	pH		
Meter	Temperature	°C		
Meter	Salinity (in Bay & Delta systems only)	psu (‰)		1L Poly for matrix spike per event
250mL Amber Glass	Dissolved Organic Carbon	µg/L		
Filter	Total Chlorophyll a	mg/m^3		
2L Poly: all below	Total Phosphorous	mg/L – P		
	Total Nitrogen	mg/L – N		
	Total Suspended Solids	mg/L		
	Alkalinity	mg/L ($CaCO_3$)		
	Hardness	mg/L ($CaCO_3$)		
	Dissolved Calcium – only for Copper	mg/L		
	Dissolved Magnesium – only for Copper	mg/L		
	Dissolved Sodium – only for Copper	mg/L		
Conducted by Tox Lab	Dissolved Ammonia *Note on COC for lab to report data	mg/L - N		
1L – Glass or Poly, depends on pesticide *	Pesticide	µg/L		
1L – Poly	Non-ionic Surfactant – For Glyphosate, Diquat, 2,4-D, Triclopyr sample events only	µg/L		
Volume / Bottle Type	**Sediment Quality Parameters**	**units**	**Field Blank / Dups**	**Toxicity / Dups**
125ml (100g) Poly: all grain size	% gravel (> 2 millimeters)	% dry weight	One per site for all / One Duplicate all per event	1L Poly / 2-4 per station – depends on tox tests: 2L per tests type and number (10 day, 28 day, Dup)
	% sand (2 mm > 62 µm)	% dry weight		
	% fines (< 62 µm)	% dry weight		
500mL (500g) Poly: five below	Nitrate-Nitrogen *Note on COC to archive portion until Sept	mg/kg		
	Total Nitrogen *Note on COC to archive portion until Sept	mg/kg		For Typha test, 250mL sed collected for PacEcoRisk / one
	% solids	% dry weight		
	% moisture	% dry weight		

	Non-ionic Surfactant – For Glyphosate, Diquat, 2,4-D, Triclopyr sample events only	µg/L		Dup
250mL Glass	Total Organic Carbon	mg/kg		
250mL Poly or Glass (DOP)	Pore Water Pesticide Concentration	mg/l or µg/L		
100mL Glass	SEM-AVS - For copper treatments only	SEM-AVS Ratio		
Meter	Eh	mV		

APPENDIX D: LABORATORY METHODS AND SOPS

The latest versions of analytical SOPs for laboratory analyses of the following compounds are attached:

CDFG WPCL

2,4-D

Cu in tissue

Diquat/paraquat in soil

fluridone in sediment and tissue

Ceimic (proprietary, based on EPA draft method attached)

AVS-SEM (EPA 821)

Sierra Foothill

chlorophyll a

DOC

TKN? and other WQ

California Laboratory Services

Sediment quality criteria

The latest versions of laboratory toxicity test methods are attached:

CDFG ATL

UC Davis ATL

PERL

The latest versions of field and laboratory bioassessment procedures are attached:

Aquatic Resources Center

CSU Chico

Still need: Wayne Fields Hydrozoology
Phytoplankton sample analysis Ecoanalysts, Inc.