



Final Quality Assurance Program Plan

2009

## Screening Study of Bioaccumulation on the California Coast Quality Assurance Program Plan

**May 2009 [Revision 2.1]** 





**Group A Elements: Project Management** 

**Element 1. Title and Approval Sheets** 

## QUALITY ASSURANCE PROJECT PLAN

# SCREENING STUDY OF BIOACCUMULATION ON THE CALIFORNIA COAST

The Bioaccumulation Oversight Group (BOG)

Surface Water Ambient Monitoring Program

**May 2009** 

Program Title SWAMP Bioaccumulation Oversight Group Coastal Study

**Lead Organization** Marine Pollution Studies Lab

California Department of Fish and Game

7544 Sandholdt Road Moss Landing, CA 95039

Mark Stephenson, Project Manager Autumn Bonnema, Project Coordinator

**Primary Contact** Jay Davis, Lead Scientist

San Francisco Estuary Institute

7770 Pardee Lane

Oakland, CA 94621-1424

(510) 746-7368

Mark Stephenson, Project Manager Marine Pollution Studies Lab

California Department of Fish and Game

7544 Sandholdt Road Moss Landing, CA 95039

(831) 771-4177

Effective Date This Quality Assurance Project Plan (QAPP) is effective from May

2009 to March 2011 unless otherwise revised, approved and

distributed accordingly at an earlier date.

Citation for QAPP Bonnema, A. 2009. Quality Assurance Project Plan: Screening

Study of Bioaccumulation on the California Coast. Moss Landing

Marine Labs. Prepared for SWAMP BOG, 53 pages plus

appendices and attachments.

## **QAPP Preface**

This Quality Assurance Project Plan (QAPP) document defines procedures and criteria that will be used for this project conducted by SWAMP Bioaccumulation Oversight Group (BOG) in association with the California Department of Fish and Game Marine Pollution Studies Laboratory (MPSL-DFG), California Dept. of Fish and Game Fish and Wildlife Pollution Control Laboratory (DFG-WPCL), and the San Francisco Estuary Institute (SFEI). Included are criteria for data quality acceptability, procedures for sampling, testing (including deviations) and calibration, as well as preventative and corrective measures. The responsibilities of SFEI, MPSL-DFG, and DFG-WPCL also are contained within. The BOG selects the sampling sites, the types and size of fish, and the number of analyses to be conducted.

This work is funded through the Surface Water Ambient Monitoring Program (SWAMP) fiscal year 08/09 Bioaccumulation funding, with coordination from Southern California Bight

(SCB), Regional Water Quality Control Board 4 (RWQCB4) and the Regional Monitoring Program in the San Francisco Estuary (RMP).

## **Approvals**

The approvals below were submitted separately, preventing their inclusion in this signature block. Instead, they appear in Appendix VII of this document. Originals are kept on file by Autumn Bonnema of MPSL-DFG.

Project Manager/MPSL-DFG Laboratory Direct	or
	Date
Rusty Fairey Contract Manager	
	Date
Jay Davis Lead Scientist	
	Date
Beverly van Buuren SWAMP Quality Assurance Officer	
	Date
Autumn Bonnema Project Coordinator/ MPSL-DFG Quality Assura	ance Officer
	Date
David Crane DFG-WPCL Laboratory Director	
	Date
Loc Nguyen DFG-WPCL Quality Assurance Officer	
	Date

## **Element 2. Table of Contents**

Group A Elements: Project Management	1
Element 1. Title and Approval Sheets	
Element 2. Table of Contents	
Element 3. Distribution List and Contact Information	6
Element 4. Project Organization	7
Element 5. Problem Definition/Background	11
Element 6. Project Description	
Element 7. Quality Indicators and Acceptability Criteria for Measurement Data	26
Element 8. Special Training Requirements/Safety	32
Element 9. Documentation and Records	34
Group B Elements. Data Generation and Acquisition	35
Element 10. Sample Process Design	35
Element 11. Sampling Methods	37
Element 12. Sample Handling and Custody	38
Element 13. Analytical Methods	
Element 14. Quality Control	43
Element 15. Instrument/Equipment Testing, Inspection and Maintenance	44
Element 16. Instrument/Equipment Calibration and Frequency	44
Element 17. Inspection/Acceptance of Supplies and Consumables	46
Element 18. Non-Direct Measures	47
Element 19. Data Management	47
Group C Elements: Assessment and Oversight	48
Element 20. Assessments and Response Actions	48
Element 21. Reports to Management	49
Group D Elements: Data Validation and Usability	49
Element 22. Data Review, Verification and Validation Requirements	49
Element 23. Verification and Validation Methods	50
Element 24. Reconciliation with User Requirements	50
References	51

## LIST OF TABLES

Table 1. Contact Information
Table 2. Positions and duties
Table 3. Bioaccumulation monitoring assessment framework for the fishing beneficial use 13
Table 4. Fish Contaminant Goals (FCGs) for Selected Fish Contaminants Based on Cancer and
Non-Cancer Risk* Using an 8-Ounce/Week (prior to cooking) Consumption Rate (32
g/day)** From Klasing and Brodberg (2008)
Table 5. Advisory Tissue Levels (ATLs) for Selected Fish Contaminants Based on Cancer or
Non-Cancer Risk Using an 8-Ounce Serving Size (Prior to Cooking) (ppb, wet weight).
From Klasing and Brodberg (2008)
Table 6. Compounds summed for comparison with FCGs and ATLs levels
Table 7. Constituents to be Analyzed – Fish Attributes
Table 8. Constituents to be Analyzed – Metals and Metalloids
Table 9a. Constituents to be Analyzed – Organochlorine (OC) Pesticides
Table 9b. Constituents to be Analyzed – Polychlorinated Biphenyls (PCB)
Table 9c. Constituents to be Analyzed – Polybrominated Diphenyl Ethers (PBDE)24
Table 10. Project Schedule Timeline
Table 11. Measurement quality indicators for laboratory measurements
Table 12a. Measurement Quality Objectives – Inorganic Analytes in Tissues
Table 12b. Measurement Quality Objectives – Synthetic Organic Compounds in Tissues 32
Table 13. BOG Coastal Zones
Table 14. Field collection corrective actions
Table 15. Methods for laboratory analyses
Table 16. Trace metal analytical parameters, reporting units, and reporting limits (RL) for tissue
samples
Table 17a. Trace organic analytical parameters, reporting units, and reporting limits (RL) for
tissue samples. Organochlorine Pesticides by EPA 8081BM using GC-ECD 41
Table 17b. Trace organic analytical parameters, reporting units, and reporting limits (RL) for
tissue samples. PCBs by EPA Method 8082M
Table 17c. Trace organic analytical parameters, reporting units, and reporting limits (RL) for
tissue samples. PBDEs by EPA Method 8082M
Table 18. Equipment maintenance and calibration frequency
Table 19. Inspection/acceptance testing requirements for consumables and supplies 47
LIST OF FIGURES
Figure 1. Organizational Chart

## **LIST OF APPENDICES**

Appendix I: List of Associated QAPPs	53
Appendix II: Sampling and Analysis Plan	54
Appendix III: MPSL-DFG SOPs	
Appendix III A: Modifications to EPA 3052	107
Appendix III B: MPSL-101 Sample Container Preparation for Organics and Trace N	
Including Mercury and Methylmercury	108
Appendix III C: MPSL-102a Sampling Marine and Freshwater Bivalves, Fish and C	crabs for
Trace Metal and Synthetic Organic Analysis	
Appendix III D: MPSL-103 Analysis of Mercury in Sediments and Tissue by Flow	Injection
Mercury System (FIMS)	139
Appendix III E: MPSL-104 Sample Receipt and Check-In	145
Appendix III E: MPSL-105 Laboratory Preparation of Trace Metal and Synthetic Or	rganic
Samples of Tissues in Marine and Freshwater Bivalves and Fish	
Appendix IV: DFG-WPCL SOPs	159
Appendix IV A: Procedure for the Management of Samples Received for Chemical	Analysis160
Appendix IV B: SO-TISS Determination of OC and PCB in Sediment and Tissue	
(Modifications to EPA 8081B and 8082)	165
Appendix IV C: Procedure for the Handling, Storage and Disposal of Hazardous and	d General
Laboratory Waste	191
Appendix IV D: Protocol for Corrective Action Procedures	199
Appendix V: MPSL-MLML SOPs	207
Appendix V A: SWAMP SOP Chemistry Data Verification v1.1	
Appendix V B: Validation of BOG Database	209
Appendix VI: SFEI Procedures	210
Appendix VI A: RMP Data Validation	211
Appendix VII: Approval Signatures	216
LIST OF ATTACHMENTS	
Attachment 1: Chain of Custody Forms	221
Attachment 2: Field Data Sheets	
Attachment 3: Analysis Authorization Forms	231
Attachment 4: Laboratory Data Sheets	233
Attachment 4. Laboratory Data Sheets	233

## **Element 3. Distribution List and Contact Information**

A copy of this Quality Assurance Project Plan (QAPP), in hardcopy or electronic format, is to be received and retained by at least one person from each participating entity. At least one person from each participating entity (names shown with asterisk\*) shall be responsible for receiving, retaining and distributing the QAPP to their respective staff within their own organization. Contact information for the primary contact person (listed first) for each participating organization also is provided below in Table 1.

### **Table 1. Contact Information**

Name Agency, Company or Organization
SAN FRANCISCO ESTUARY INSTITUTE

Jay Davis\* SFEI

7770 Pardee Lane

Oakland, CA 94621-1424 Phone: (415) 746-7368 Email: jay@sfei.org

**CALIFORNIA DEPARTMENT OF FISH AND GAME** 

FISH AND WILDLIFE WATER POLLUTION CONTROL LABORATORY

David Crane DFG-WPCL Loc Nguyen\* 2005 Nimbus Road

Rancho Cordova, CA 95670 Phone: (916) 358-2859 Email: dcrane@ospr.dfg.ca.gov

MARINE POLLUTION STUDIES LAB

CALIFORNIA DEPARTMENT OF FISH AND GAME

Mark Stephenson MPSL-DFG

Gary Ichikawa 7544 Sandholdt Road Autumn Bonnema\* Moss Landing, CA 95039

Phone: (831) 771-4177

Email: mstephenson@mlml.calstate.edu

MOSS LANDING MARINE LABORATORIES

**QUALITY ASSURANCE RESEARCH GROUP** 

Beverly van Buuren\*
Amara Vandervort

Will Hagan
Eric von der Geest

QA Research Group, MLML
c/o: 4320 Baker AVE NW
Seattle, WA 98107
Phone: (206) 297-1378

Email: <u>bvanbuuren@mlml.calstate.edu</u>

SOUTHERN CALIFORNIA COASTAL WATER

RESEARCH PROGRAM

Ken Schiff\* SCCWRP

Shelly Moore 3535 Harbor Blvd., Suite 110

Costa Mesa, CA 92626 Phone: (714) 755-3200 Email: kens@sccwrp.org

## **Element 4. Project Organization**

The lines of communication between the participating entities, project organization and responsibilities are outlined in Table 2 and Figure 1.

Table 2. Positions and duties

Position	Name	Responsibilities
Contract Manager	Rusty Fairey MPSL-MLML	Approve reports and invoices for payment.
Project Manager	Mark Stephenson MPSL-DFG	Project management and oversight.
Lead Scientist	Jay Davis SFEI	Advisory Roll; Data reporting
Project Coordinator	Autumn Bonnema, MPSL-DFG	Generation of a QAPP, Project coordination; ensures all laboratory activities are completed within proper timeframes.
Program QA Officer	Beverly van Buuren QA Research Group, MLML	Approve QAPP and oversee SWAMP projects' QA/QC
Laboratory QA Officer	Loc Nguyen DFG-WPCL Autumn Bonnema, MPSL-DFG	Ensures that the laboratory quality assurance plan and quality assurance project plan criteria are met through routine monitoring and auditing of the systems. Ensure that data meets project's objective through verification of results.
Sample Collection Coordinator	Gary Ichikawa MPSL-DFG	Sampling coordination, operations, and implementing field-sampling procedures.
Laboratory Director	David Crane DFG-WPCL Mark Stephenson MPSL-DFG	Organizing, coordinating, planning and designing research projects and supervising laboratory staff; Data validation, management and reporting
Sample Custodian	Stephen Martenuk MPSL-DFG Laurie Smith DFG-WPCL additional staff	Sample storage. Not responsible for any deliverables.
Technicians	Technical staff MPSL-DFG DFG-WPCL	Conduct fish tissue dissection, digestion, and chemical analyses. Not responsible for any deliverables.

## 4.1. Involved parties and roles

Rusty Fairey of Marine Pollution Studies Lab - Moss Landing Marine Laboratories (MPSL-MLML) will be the Contract Manager (CM) for this project. The CM will approve reports and invoices for payment.

Mark Stephenson of MPSL-DFG will serve as the Project Manager (PM) for the project. The PM will 1) review and approve the QAPP, 2) review, evaluate and document project reports, and 3) verify the completeness of all tasks.

Jay Davis of San Francisco Estuary Institute (SFEI) is the Lead Scientist (LS) and primary contact of this project. The LS will 1) generate the Sampling and Analysis Plan (SAP), 2) approve the QAPP, and 3) provide the BOG with a final report on completion of this project.

Autumn Bonnema of MPSL-DFG is the Project Coordinator (PC). The PC will 1) prepare the QAPP, 2) ensure that laboratory technicians have processing instructions and 3) ensure all laboratory activities are completed within the proper timelines. In addition, the PC may assist field crew in preparation and logistics.

Gary Ichikawa of MPSL-DFG is in charge of directing fish collection for this project. He will 1) oversee preparation for sampling, including vehicle maintenance and 2) oversee sample and field data collection.

Stephen Martenuk is responsible for sample storage and custody at MPSL. His duties will be to oversee compositing of tissue samples. Laurie Smith will do the same for samples processed at DFG-WPCL.

David Crane will serve as the Laboratory Director (LD) for the DFG-WPCL component of this project. His specific duties will be to 1) review and approve the QAPP, 2) provide oversight for all organic chemical analyses to be done for this project, and 3) ensure that all DFG-WPCL activities are completed within the proper timelines.

Mark Stephenson will also serve as the Laboratory Director (LD) for the MPSL-DFG component of this project. His specific duties will be to 1) review and approve the QAPP, 2) provide oversight for all trace metal analyses to be done for this project, and 3) ensure that all MPSL-DFG activities are completed within the proper timelines.

The following serve in an advisory role and are not responsible for any deliverables: Terry Fleming (EPA), Bob Brodberg (Office of Environmental Health Hazard Assessment (OEHHA)), Karen Taberski (RWQCB2), Mary Adams (RWQCB3), Michael Lyons (RWQCB4), Chris Foe (RWQCB5), Cassandra Lamerdin (MPSL-MLML), Jennifer Doherty (State Water Resources Control Board (SWRCB)), Billy Jakl (MPSL-DFG), Dylan Service (MPSL-DFG), Ken Schiff (SCCWRP) and Aroon Melwani(SFEI).

### 4.2. Quality Assurance Officer (QAO) Role

The Laboratory Quality Assurance Officers fulfill the functions and authority of a project quality assurance officer (QAO). Autumn Bonnema is the MPSL-DFG QAO and Loc Nguyen is the DFG-WPCL QAO. The role of the Laboratory QAO is to ensure that quality control for sample processing and data analysis procedures described in this QAPP are maintained throughout the project. The Program QAO (Beverly van Buuren, MLML) acts in a consulting

role to the Laboratory QAOs and ensures the project meets all SWAMP QA/QC criteria (Puckett, 2002).

The Laboratory QAOs will review and assess all procedures during the life of this project against QAPP requirements, and assess whether the procedures are performed according to protocol. The Laboratory QAOs will report all findings (including qualified data) to the Program QAO and the PM, including all requests for corrective action. The Laboratory and Program QAOs have the authority to stop all actions if there are significant deviations from required procedures or evidence of a systematic failure.

A conflict of interest does not exist between the Laboratory QAOs and the work outlined in this QAPP as neither Laboratory QAO participates in any of the chemical analyses of the project. There is not a conflict of interest with one person fulfilling the roles of Laboratory QAO and Project Coordinator (PC), as laboratory decisions are not made by the PC and no other duties overlap. The role of the PC is detailed above.

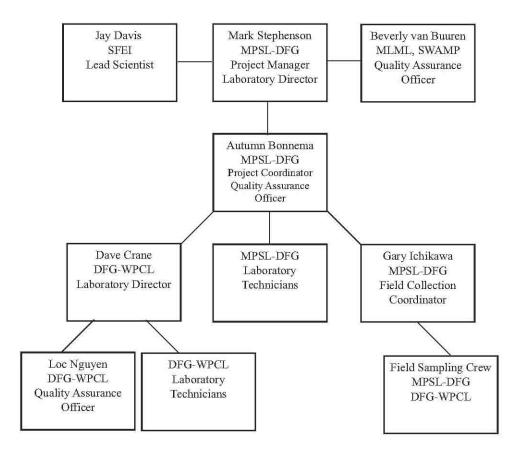
## 4.3. Persons responsible for QAPP update and maintenance

Revisions and updates to this QAPP will be carried out by Autumn Bonnema (PC), with technical input of the PM and the Laboratory and Program QAOs. All changes will be considered draft until reviewed and approved by the PM and the SWAMP QAO. Finalized revisions will be submitted for approval to the SWAMP QAO, if necessary.

Copies of this QAPP will be distributed to all parties involved in the project. Any future amended QAPPs will be held and distributed in the same fashion. All originals of these first and subsequent amended QAPPs will be held on site at SFEI, DFG-WPCL and MPSL.

## 4.4. Organizational chart and responsibilities

Figure 1. Organizational Chart



Element 5. Problem Definition/Background

## 5.1. Problem statement

## 5.1.1. Addressing Multiple Beneficial Uses

Bioaccumulation in California water bodies has an adverse impact on both the fishing and aquatic life beneficial uses (Davis et al. 2007). The fishing beneficial use is affected by human exposure to bioaccumulative contaminants through consumption of sport fish. The aquatic life beneficial use is affected by exposure of wildlife to bioaccumulative contaminants, primarily piscivorous species exposed through consumption of small fish. Different indicators are used to monitor these different types of exposure. Monitoring of status and trends in human exposure is accomplished through sampling and analyzing sport fish. On the other hand, monitoring of status and trends in wildlife exposure can accomplished through sampling and analysis of wildlife prey (small fish, other prey species) or tissues of the species of concern (e.g., bird eggs or other tissues of juvenile or adults of the species at risk).

Over the long-term, a SWAMP bioaccumulation monitoring is envisioned that assesses progress in reducing impacts on both the fishing and aquatic life beneficial uses for all water bodies in California. In the near-term, however, funds are limited, and there is a need to demonstrate the value of a comprehensive statewide bioaccumulation monitoring program through successful execution of specific components of a comprehensive program. Consequently, with funds available for sampling in 2007 (\$797,000) and additional funds of a similar magnitude anticipated for 2008, the BOG has decided to focus on sampling that addresses the issue of bioaccumulation in sport fish and impacts on the fishing beneficial use. This approach is intended to provide the information that the Legislature and the public would consider to be of highest priority. Monitoring focused on evaluating the aquatic life beneficial use will be included in the Project when expanded funding allows a broader scope.

## **5.1.2.** Addressing Multiple Monitoring Objectives and Assessment Questions for the Fishing Beneficial Use

The BOG has developed a set of monitoring objectives and assessment questions for a statewide program evaluating the impacts of bioaccumulation on the fishing beneficial use (Table 3). This assessment framework is consistent with frameworks developed for other components of SWAMP, and is intended to guide the bioaccumulation monitoring program over the long-term. The four objectives can be summarized as 1) status; 2) trends; 3) sources and pathways; and 4) effectiveness of management actions.

Over the long-term, the primary emphasis of the statewide bioaccumulation monitoring program will be on evaluating status and trends. Bioaccumulation monitoring is a very effective and essential tool for evaluating status, and is often the most cost-effective tool for evaluating trends. Monitoring status and trends in bioaccumulation will provide some information on sources and pathways and effectiveness of management actions at a broader geographic scale. However, other types of monitoring (i.e., water and sediment monitoring) and other programs (regional TMDL programs) are more appropriate for addressing sources and pathways and effectiveness of management actions.

In the near-term, the primary emphasis of the statewide bioaccumulation monitoring program will be on evaluating Objective 1 (status). The reasons for this are:

- 1. a systematic statewide assessment of status has not been performed to date and is urgently needed;
- 2. we are starting a new program and establishing a foundation for future assessments of trends;
- 3. past monitoring of sport fish established very few time series that are useful in trend analysis.

## Table 3. Bioaccumulation monitoring assessment framework for the fishing beneficial use.

## D.1. Determine the status of the fishing beneficial use throughout the State with respect to bioaccumulation of toxic pollutants

- D.1.1 What are the extent and location of water bodies with sufficient evidence to indicate that the fishing beneficial use is at risk due to pollutant bioaccumulation?
- D.1.2 What are the extent and location of water bodies with some evidence indicating the fishing beneficial use is at risk due to pollutant bioaccumulation?
- D.1.3 What are the extent and location of water bodies with no evidence indicating the fishing beneficial use is at risk due to pollutant bioaccumulation?
- D.1.4 What are the proportions of water bodies in the State and each region falling within the three categories defined in questions D.1.1, D.1.2, and D.1.3?

## D.2. Assess trends in the impact of bioaccumulation on the fishing beneficial use throughout the State

- D.2.1 Are water bodies improving or deteriorating with respect to the impact of bioaccumulation on the fishing beneficial use?
  - D.2.1.1 Have water bodies fully supporting the fishing beneficial use become impaired?
  - D.2.1.2 Has full support of the fishing beneficial use been restored for previously impaired water bodies?
- D.2.2 What are the trends in proportions of water bodies falling within the three categories defined in questions D.1.1, D.1.2, and D.1.3 regionally and statewide?

## D.3. Evaluate sources and pathways of bioaccumulative pollutants impacting the fishing beneficial use

- D.3.1 What are the magnitude and relative importance of pollutants that bioaccumulate and indirect causes of bioaccumulation throughout each Region and the state as a whole?
- D.3.2 How is the relative importance of different sources and pathways of bioaccumulative pollutants that impact the fishing beneficial use changing over time on a regional and statewide basis?

## **D.4.** Provide the monitoring information needed to evaluate the effectiveness of management actions in reducing the impact of bioaccumulation on the fishing beneficial use

- D.4.1 What are the management actions that are being employed to reduce the impact of bioaccumulation on the fishing beneficial use regionally and statewide?
- D.4.2 How has the impact of bioaccumulation on the fishing beneficial use been affected by management actions regionally and statewide?

## **5.1.3.** Addressing Multiple Habitat Types

SWAMP has defined the following categories of water bodies:

- lakes and reservoirs;
- bays and estuaries;
- coastal waters;
- large rivers;
- wadeable streams; and
- wetlands.

Due to their vast number, high fishing pressure, and a relative lack of information on bioaccumulation (Davis et al. 2007), lakes and reservoirs were identified as the first priority for monitoring. Coastal waters have been selected as the next priority, due to their importance for sport fishing and a relative lack of past monitoring. A Coastal Fish Contamination Monitoring Program was in initiated in 1998 (Gassel et al. 2002). This program was developed to assess the health risks of consumption of sport fish and shellfish from nearshore waters along the entire California coast. The CFCP was considered to be a critical component of a comprehensive coastal water quality protection program, and an important opportunity to build a long-term coastal monitoring database for water quality and contaminants in fish. However, the CFCP, along with the other two major state bioaccumulation monitoring programs (the Toxic Substances Monitoring Program and the State Mussel Watch Program) were discontinued in 2003 as plans for SWAMP began to take shape. Systematic monitoring of bioaccumulation in fish on the coast was therefore only in place for a few years. Given the extensive area, multiple habitats (coastline, bays and estuaries), diversity of species to be covered, and the amount of funding available (\$500,000 of SWAMP funds for sampling and analysis), the coastal waters survey is also going to be a two-year effort spanning 2009 and 2010. In 2011, SWAMP will monitor bioaccumulation in California rivers and streams. In 2012, the long-term plan calls for beginning another five-year cycle of monitoring, with another two-year lake survey.

In summary, focusing on two closely associated habitat types (the coast and bays and estuaries), one objective (status), and one beneficial use (fishing) will allow us to provide reasonable coverage and a thorough assessment of bioaccumulation in California's coastal waters over a two-year period.

### 5.2. Decisions or outcomes

Three management questions have been articulated to guide the 2009-2010 survey of the status of bioaccumulation in sport fish on the California coast. These management questions are specific to this initial screening effort.

One major difference between this set of questions and the questions for the lakes survey is that the question regarding 303(d) listing is not included here. The 303(d) question was a major driver of the design of the lakes survey. On the coast, however, 303(d) listing is not a high priority for the Water Boards.

## 5.2.1. Management Question 1 (MQ1): Status of the Fishing Beneficial Use

For popular fish species, what percentage of popular fishing areas have low enough concentrations of contaminants that fish can be safely consumed?

Answering this question is critical to determining the degree of impairment of the fishing beneficial use across the state due to bioaccumulation. This question places emphasis on characterizing the status of the fishing beneficial use through monitoring of the predominant pathways of exposure – the popular fish species and fish areas. This focus is also anticipated to enhance public and political support of the program by assessing the resources that people care most about. The determination of percentages captures the need to perform a statewide assessment of the entire California coast. The emphasis on safe consumption calls for: a positive message on the status of the fishing beneficial use; evaluation of the data using thresholds for safe consumption; and performing a risk-based assessment of the data.

The data needed to answer this question are average concentrations in popular fish species from popular fishing locations. Inclusion of as many popular species as possible is important to understanding the nature of impairment in any areas with concentrations above thresholds. In some areas, some fish may be safe for consumption while others are not, and this is valuable information for anglers. Monitoring species that accumulate high concentrations of contaminants ("indicator species") is valuable in answering this question: if concentrations in these species are below thresholds, this is a strong indication that an area has low concentrations.

## 5.2.2. Management Question 2 (MQ2): Regional Distribution

What is the distribution of contaminant concentrations in fish within regions?

Answering this question will provide information that is valuable in formulating management strategies for observed contamination problems. This information will allow managers to prioritize their efforts and focus attention on the areas with the most severe problems. Information on regional distribution will also provide information on sources and fate that will be useful to managers.

This question can be answered with different levels of certainty. For a higher and quantified level of certainty, a statistical approach with replicate observations in the spatial units to be compared is needed. In some cases, managers can attain an adequate level of understanding for their needs with a non-statistical, non-replicated approach. With either approach, good estimates of average concentrations within each spatial unit are needed.

## 5.2.3. Management Question 3 (MQ3): Need for Further Sampling

Should additional sampling of bioaccumulation in sport fish (e.g., more species or larger sample size) in an area be conducted for the purpose of developing consumption guidelines?

This screening survey of the entire California coast will provide a preliminary indication as to whether many areas that have not been sampled thoroughly to date may require consumption guidelines. Consumption guidelines provide a mechanism for reducing human exposure in the short-term. The California Office of Environmental Health Hazard Assessment (OEHHA), the agency responsible for issuing consumption guidelines, considers a sample of 9 or more fish

from a variety of species abundant in a water body to be the minimum needed in order to issue guidance. It is valuable to have information not only on the species with high concentrations, but also the species with low concentrations so anglers can be encouraged to target the low species. The diversity of species on the coast demands a relatively large effort to characterize interspecific variation. Answering this question is essential as a first step in determining the need for more thorough sampling in support of developing consumption guidelines.

## 5.2.4. Overall Approach

The overall approach to be taken to answer these three questions is to perform a statewide screening study of bioaccumulation in sport fish on the California coast. Answering these questions will provide a basis for decision-makers to understand the scope of the bioaccumulation problem and will provide regulators with information needed to establish priorities for both cleanup actions and development of consumption guidelines.

It is anticipated that the screening study may lead to more detailed followup investigations of areas where consumption guidelines and cleanup actions are needed. Funding for these followup studies will come from other local or regional programs rather than the statewide monitoring budget.

### 5.2.5. Coordination

Through coordination with other programs, SWAMP funds for this survey are going to be highly leveraged to achieve a much more thorough statewide assessment than could be achieved by SWAMP alone. Details on coordination with the Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP), the Southern California Bight (SCB) and the Regional Water Quality Control Board 4 (RWQCB4) can be found in the Sampling and Analysis Plan (SAP) (Appendix II, p 8).

#### **5.3.** Fish tissue contamination criteria

Threshold levels for determining impairment of a body of water based on pollutants in fish tissue are listed in Tables 4 and 5. Fish Contaminant Goals (FCGs), as described by Klasing and Brodberg (2008), are "estimates of contaminant levels in fish that pose no significant health risk to humans consuming sport fish at a standard consumption rate of one serving per week (or eight ounces [before cooking] per week, or 32 g/day), prior to cooking, over a lifetime and can provide a starting point for OEHHA to assist other agencies that wish to develop fish tissue-based criteria with a goal toward pollution mitigation or elimination. FCGs prevent consumers from being exposed to more than the daily reference dose for non-carcinogens or to a risk level greater than  $1 \times 10^{-6}$  for carcinogens (not more than one additional cancer case in a population of 1,000,000 people consuming fish at the given consumption rate over a lifetime). FCGs are based solely on public health considerations without regard to economic considerations, technical feasibility, or the counterbalancing benefits of fish consumption." For organic pollutants, FCGs are lower than Advisory Tissue Levels (ATL)s.

BOG Coastal QAPP Revision 2.1 September 2009 Page 17 of 234

ATLs, as described by Klasing and Brodberg (2008), "while still conferring no significant health risk to individuals consuming sport fish in the quantities shown over a lifetime, were developed with the recognition that there are unique health benefits associated with fish consumption and that the advisory process should be expanded beyond a simple risk paradigm in order to best promote the overall health of the fish consumer. ATLs provide numbers of recommended fish servings that correspond to the range of contaminant concentrations found in fish and are used to provide consumption advice to prevent consumers from being exposed to more than the average daily reference dose for non-carcinogens or to a risk level greater than  $1 \times 10^{-4}$  for carcinogens (not more than one additional cancer case in a population of 10,000 people consuming fish at the given consumption rate over a lifetime). ATLs are designed to encourage consumption of fish that can be eaten in quantities likely to provide significant health benefits, while discouraging consumption of fish that, because of contaminant concentrations, should not be eaten or cannot be eaten in amounts recommended for improving overall health (eight ounces total, prior to cooking, per week). ATLs are but one component of a complex process of data evaluation and interpretation used by OEHHA in the assessment and communication of fish consumption risks. The nature of the contaminant data or omega-3 fatty acid concentrations in a given species in a water body, as well as risk communication needs, may alter strict application of ATLs when developing site-specific advisories. For example, OEHHA may recommend that consumers eat fish containing low levels of omega-3 fatty acids less often than the ATL table would suggest based solely on contaminant concentrations. OEHHA uses ATLs as a framework, along with best professional judgment, to provide fish consumption guidance on an ad hoc basis that best combines the needs for health protection and ease of communication for each site."

Thresholds for Total PCBs, DDTs, and Chlordanes are based on the summation of concentrations from the compounds listed in Table 6. The summations will be compared with the threshold values in Tables 4 and 5, and may lead to the identification of species which meet the beneficial uses of MQ1.

Table 4. Fish Contaminant Goals (FCGs) for Selected Fish Contaminants Based on Cancer and Non-Cancer Risk\* Using an 8-Ounce/Week (prior to cooking) Consumption Rate (32 g/day)\*\* From Klasing and Brodberg (2008).

	FCGs (ppb, wet weight)
	(PPs)
Contaminant	
Cancer Slope Factor	
(mg/kg/day) <sup>-1</sup>	
Chlordane (1.3)	5.6
DDTs (0.34)	21
Dieldrin (16)	0.46
PCBs (2)	3.6
Toxaphene (1.2)	6.1
Contaminant	
Reference Dose	
(mg/kg-day)	
Chlordane (3.3x10 <sup>-5</sup> )	100
DDTs (5x10 <sup>-4</sup> )	1600
Dieldrin (5x10 <sup>-3</sup> )	160
Methylmercury (1x10 <sup>-4</sup> ) <sup>S</sup>	220
PCBs (2x10 <sup>-3</sup> )	63
Selenium (5x10 <sup>-3</sup> )	7400
Toxaphene (3.5x10 <sup>-4</sup> )	1100

<sup>\*</sup>The most health protective Fish Contaminant Goal for each chemical (cancer slope factor- versus reference dose-derived) for each meal category is bolded.

Tabled values are rounded based on laboratory reporting of three significant digits in results, where the third reported digit is uncertain (estimated). Tabled values are rounded to the second digit, which is certain. When data are compared to this table they should also first be rounded to the second significant digit as in this table.

<sup>\*\*</sup>g/day represents the average amount of fish consumed daily, distributed over a 7-day period, using an 8ounce serving size, prior to cooking.

<sup>&</sup>lt;sup>S</sup>Fish Contaminant Goal for sensitive populations (i.e., women aged 18 to 45 years and children aged 1 to 17 years.)

Table 5. Advisory Tissue Levels (ATLs) for Selected Fish Contaminants Based on Cancer or Non-Cancer Risk Using an 8-Ounce Serving Size (Prior to Cooking) (ppb, wet weight). From Klasing and Brodberg (2008).

Approximation and the second s				
Contaminant	Three 8-ounce Servings* a Week	Two 8-ounce Servings* a Week	One 8-ounce Servings* a Week	No Consumption
Chlordane <sup>c</sup>	≤190	>190-280	>280-560	>560
DDTs <sup>nc**</sup>	≤520	>520-1,000	>1,000-2,100	>2,100
Dieldrin <sup>c</sup>	≤15	>15-23	>23-46	>46
Methylmercury (Women aged 18-45 years and children aged 1-17 years) <sup>nc</sup>	≤70	>70-150	>150-440	>440
Methylmercury (Women over 45 years and men) <sup>nc</sup>	≤220	>220-440	>440-1,310	>1,310
PCBs <sup>nc</sup>	≤21	>21-42	>42-120	>120
Selenium <sup>nc</sup>	≤2500	>2500-4,900	>4,900-15,000	>15,000
Toxaphene <sup>c</sup>	≤200	>200-300	>300-610	>610

cATLs are based on cancer risk

Tabled values are rounded based on laboratory reporting of three significant digits in results, where the third reported digit is uncertain (estimated). Tabled values are rounded to the second digit, which is certain. When data are compared to this table they should also first be rounded to the second significant digit as in this table.

nc ATLs are based on non-cancer risk

<sup>\*</sup>Serving sizes are based on an average 160 pound person. Individuals weighing less than 160 pounds should eat proportionately smaller amounts (for example, individuals weighing 80 pounds should eat one 4-ounce serving a week when the table recommends eating one 8-ounce serving a week).

<sup>\*\*</sup>ATLS for DDTs are based on non-cancer risk for two and three servings per week and cancer risk for one serving per week.

Table 6. Compounds summed for comparison with FCGs and ATLs levels.

Pollutant	Components	Reference
Total PCBs	Sum of all congeners analyzed	
Total PCB Aroclors	PCB AROCLOR 1248	SWRCB 2000
	PCB AROCLOR 1254	
	PCB AROCLOR 1260	
Total Chlordanes	Chlordane, cis-	USEPA 2000
	Chlordane, trans-	
	Nonachlor, cis-	
	Nonachlor, trans-	
	Oxychlordane	
Total DDTs	DDD(o,p')	USEPA 2000
	DDD(p,p')	
	DDE(o,p')	
	DDE(p,p')	
	DDT(o,p')	
	DDT(p,p')	
Total PBDEs	Sum of all congeners analyzed	

## **Element 6. Project Description**

## 6.1. Work statement and produced products

The survey is being conducted over two years to allow thorough coverage of the entire coast with available funds. The study is being phased to facilitate coordination and continuing demonstration of successful monitoring by placing a priority on generating information that is of maximum value to regulators and the public.

In year 1, sampling will focus on the SCB (Water Board regions 4, 8 and 9 – see Figure 1) and San Francisco Bay and adjacent coastal areas (Region 2). This will allow for coordination with Bight '08 and the RMP, which are scheduled for 2009. This will also provide a basis for a report on year 1 that describes bioaccumulation in the most populated and heavily fished areas in the state near San Francisco and Los Angeles.

Sampling in year 2 will cover the other coastal regions (1 and 3) and any other remaining areas not covered in year 1. The second year report will present the data for these areas and also provide a comprehensive assessment of the entire two-year dataset.

## 6.2. Constituents to be analyzed and measurement techniques.

A detailed Sampling and Analysis Plan (SAP) is in Appendix II. Chemistry analytical methods are summarized in Section B13. Constituents to be analyzed are summarized in Tables 7-9a,b,c. All chemistry data will be reported on a wet weight basis.

Past studies have calculated PCB as Aroclors for comparison with older data sets and health thresholds. OEHHA no longer intends to use these data, and they will not be reported in SWAMP reports. The BOG agrees that these calculations are not as valuable as individual congener data, and will therefore cease reporting these calculated values. If necessary, these values can be calculated at a later time by the data management team using the provided congener data.

In the SWAMP Lakes Study (conducted in 2007 and 2008), PBDE data were provided at a screening level only as a free service from the analytical lab. These compounds are important emerging contaminants and will be analyzed in the Coastal Study on a subset of the samples. Two of the five species collected will be chosen for PBDE analysis. White croaker or other high lipid fish will be used.

Table 7. Constituents to be Analyzed – Fish Attributes

Fish Attributes
Total Length (mm)
Fork Length (mm)
Weight (g)
Sex
Moisture (%)
Lipid Content (%)

Table 8. Constituents to be Analyzed – Metals and Metalloids

Analyte	Analytical Method
Total Mercury	EPA 7374
Total Selenium	EPA 200.8

Table 9a. Constituents to be Analyzed - Organochlorine (OC) Pesticides

Organochlorine Pesticides (by EPA 8081BM using GC-ECD)		
Group	Parameter	
Chlordanes	Chlordane, cis-	
	Chlordane, trans-	
	Heptachlor	
	Heptachlor epoxide	
	Nonachlor, cis-	
	Nonachlor, trans-	
	Oxychlordane	
DDTs	DDD(o,p')	
	DDD(p,p')	
	DDE(o,p')	
	DDE(p,p')	
	DDMU(p,p')	
	DDT(o,p')	
	DDT(p,p')	
Cyclodienes	Aldrin	
	Dieldrin	
	Endrin	
HCHs	HCH, alpha	
	HCH, beta	
	HCH, gamma	
Others	Dacthal	
	Endosulfan I	
	Hexachlorobenzene	
	Methoxychlor	
	Mirex	
	Oxadiazon	
	Tedion <sup>1</sup>	

<sup>&</sup>lt;sup>1</sup>Tedion has been removed from the analyte list. This compound was discontinued from use in 1985 and has a very short residence time. Furthermore, it is a compound that is not bioaccumulated.

Table 9b. Constituents to be Analyzed – Polychlorinated Biphenyls (PCB)

Polychlorinated Biphenyl (PCB) Congeners (by EPA Method 8082M)		
PCB 008	PCB 128	
PCB 018	PCB 137	
PCB 027	PCB 138	
PCB 028	PCB 141	
PCB 029	PCB 146	
PCB 031	PCB 149	
PCB 033	PCB 151	
PCB 044	PCB 153	
PCB 049	PCB 156	
PCB 052	PCB 157	
PCB 056	PCB 158	
PCB 060	PCB 169	
PCB 064	PCB 170	
PCB 066	PCB 174	
PCB 070	PCB 177	
PCB 074	PCB 180	
PCB 077	PCB 183	
PCB 087	PCB 187	
PCB 095	PCB 189	
PCB 097	PCB 194	
PCB 099	PCB 195	
PCB 101	PCB 198/199	
PCB 105	PCB 200	
PCB 110	PCB 201	
PCB 114	PCB 203	
PCB 118	PCB 206	
PCB 126	PCB 209	

Table 9c. Constituents to be Analyzed – Polybrominated Diphenyl Ethers (PBDE)

Polybrominated Diphenyl Ethers (PBDEs) (by EPA Method 8081BM)				
PBDE 017				
PBDE 028				
PBDE 047				
PBDE 066				
PBDE 085				
PBDE 099				
PBDE 100				
PBDE 138				
PBDE 153				
PBDE 154				
PBDE 183				
PBDE 190				

## 6.3. Project schedule and number of samples to be analyzed.

Key tasks in the project and their expected due dates are outlined in Table 10.

Five species will be collected from each of 69 zones over two years, resulting in 350 composites analyzed for the constituents found in Tables 8 and 9a, b and c.

**Table 10. Project Schedule Timeline** 

Item	Activity and/or Deliverable	<b>Deliverable Due Date</b>	
1	Contracts		
	Subcontract Development	March 2009	
2	Quality Assurance Project Plan & Monitoring Plan		
2.1	Draft Monitoring Plan	March 2009	
2.2	Final Monitoring Plan	April 2009	
2.3	Draft Quality Assurance Project Plan	March 2009	
2.4	Final Quality Assurance Project Plan	April 2009	
3	Sample Collection	Yr1 April-November 2009 Yr2 April-November 2010	
4	Sample Selection and Chemical Analysis		
4.1	Selection of Tissue for Analysis	Yr1 May-November 2009 Yr2 May-November 2010	
4.2	Creation of Sample Composites	Yr1 May-December 2009 Yr2 May-December 2010	
4.3	Chemical Analysis  Yr1 June 2009-March 20 Yr2 June 2010-March 20		
5	Interpretive Report		
5.1	Draft Report	Yr1 June 2010 Yr2 June 2011	
5.2	Final Report	Yr1 September 2010 Yr2 September 2011	

## 6.4. Geographical setting and sample sites

California has over 3000 miles of coastline that spans a diversity of habitats and fish populations, and dense human population centers with a multitude of popular fishing locations. Sampling this vast area with a limited budget is a challenge.

The approach being employed to sample this vast area is to divide the coast into 69 spatial units called "zones" (SAP Figure 2, Appendix II). The use of this zone concept is consistent with the direction that OEHHA will take in the future in development of consumption guidelines for coastal areas. Advice has been issued on a pier-by-pier basis in the past in Southern California, and this approach has proven to be unsatisfactory. All of these zones will be sampled, making a probabilistic sampling design unnecessary.

The sampling will be focused on nearshore areas, including bays and estuaries, in waters not exceeding 200 m in depth, and mostly less than 60 m deep.

Details on the determination of zone boundaries can be found in the SAP (Appendix II, p. 9).

## 6.5. Constraints

All sampling must be completed by the end of the current year's sampling season in order to meet analysis and reporting deadlines set forth in Table 10.

Ultimately, additional zones may be sampled pending time remaining in the sampling season and available funding within the project once cost savings from analysis has been determined.

## **Element 7. Quality Indicators and Acceptability Criteria for Measurement Data**

Data quality indicators for the analysis of fish tissue concentrations of analytes will include accuracy (bias), precision, recovery, completeness and sensitivity. Measurement Quality Indicators for analytical measurements of organics and metals in tissue are in Table 11.

Previously collected data will not be utilized in this study, therefore specific acceptance criteria are not applicable.

Table 11. Measurement quality indicators for laboratory measurements.

Parameter	Accuracy	Precision	Recovery	Completeness	Sensitivity
Trace	CRM 75% - 125%	Duplicate RPD	Matrix Spike	90%	See Table
metals		<25%; n/a if	75% - 125%		16
(including		concentration of			
mercury)		either sample			
		<mdl matrix<="" td=""><td></td><td></td><td></td></mdl>			
		Spike Duplicate			
		RPD <25%			
Synthetic	Certified	Duplicate RPD	Matrix spike	90%	See Tables
Organics	Reference	<25%; n/a if	50% - 150% or		17a,b,c
(including	Materials (CRM,	concentration of	control limits		
PCBs,	PT) within 70-	either sample	control limits		
pesticides,	130% of the	<mdl< td=""><td>based on 3x the</td><td></td><td></td></mdl<>	based on 3x the		
and PBDEs)	certified 95% CI		standard		
	stated by provider		deviation of		
	of material. If not		laboratory's		
	available then		actual method		
	within 50-150% of		recoveries		
	reference value.				

## 7.1. Accuracy

Evaluation of the accuracy of laboratory procedures is achieved through the preparation and analysis of reference materials with each analytical batch. Ideally, the reference materials selected are similar in matrix and concentration range to the samples being prepared and analyzed. The accuracy of the results is assessed through the calculation of a percent recovery.

% recovery = 
$$\frac{V_{analyzed}}{V_{certified}} x100$$

Where:

 $v_{analyzed}$ : the analyzed concentration of the reference material  $v_{certified}$ : the certified concentration of the reference material

The acceptance criteria for reference materials are listed in Tables 12a, b.

While reference materials are not available for all analytes, a way of assessing the accuracy of an analytical method is still required. Laboratory control samples (LCSs) provide an alternate method of assessing accuracy. An LCS is a specimen of known composition prepared using contaminant-free reagent water or an inert solid spiked with the target analyte at the midpoint of the calibration curve or at the level of concern. The LCS must be analyzed using the same preparation, reagents, and analytical methods employed for regular samples. If an LCS needs to be substituted for a reference material, the acceptance criteria are the same as those for the analysis of reference materials. These are detailed in Tables 12a, b.

#### 7.2. Precision

In order to evaluate the precision of an analytical process, a field sample is selected and digested or extracted in duplicate. Following analysis, the results from the duplicate samples are evaluated by calculating the Relative Percent Difference (RPD).

$$RPD = \left| \frac{\left( V_{sample} - V_{duplicate} \right)}{mean} \right| x100$$

Where:

 $V_{\text{sample}}$ : the concentration of the original sample digest  $V_{\text{duplicate}}$ : the concentration of the duplicate sample digest mean: the mean concentration of both sample digests

Specific requirements pertaining to the analysis of laboratory duplicates vary depending on the type of analysis. The acceptance criteria for laboratory duplicates are specified in Tables 12a, b.

Upper and lower control chart limits (e.g., warning limits and control limits) will be continually updated at DFG-WPCL; control limits are based on 99% confidence intervals around the mean.

A minimum of one duplicate per analytical batch will be analyzed. If the analytical precision is unacceptable, calculations and instruments will be checked. A repeat analysis may be required to confirm the results.

Duplicate precision is considered acceptable if the resulting RPD is  $\leq$  25% for analyte concentrations that are greater than the Minimum Level (ML). The U.S. Environmental Protection Agency (EPA) defines the ML as the lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all standard operating procedure (SOP) or method-specified sample weights, volumes, and cleanup procedures have been employed.

## 7.2.1. Replicate Analysis

Replicate analyses are distinguished from duplicate analyses based simply on the number of involved analyses. Duplicate analyses refer to two sample digests, while replicate analyses refer to three or more. Analysis of replicate samples is not explicitly required; however it is important to establish a consistent method of evaluating these analyses. The method of evaluating replicate analysis is by calculation of the relative standard deviation (RSD). Expressed as a percentage, the RSD is calculated as follows:

$$RSD = \frac{Stdev(v_1, v_2, .... v_n)}{mean} x100$$

Where:

Stdev( $v_1, v_2, ..., v_n$ ): the standard deviation of the values (concentrations) of the replicate analyses.

mean: the mean of the values (concentrations) of the replicate analyses.

## **7.3.** Bias

Bias is the systematic or persistent distortion of a measurement process that skews data in one direction. Certified Reference Materials (CRM) and Matrix Spike (MS) samples are used to determine the analyte-specific bias associated with each analytical laboratory. CRMs are used to determine analytical bias, and MS are used to determine the bias associated with the tissue matrix.

A matrix spike (MS) is prepared by adding a known concentration of the target analyte to a field sample, which is then subjected to the entire analytical procedure. If the ambient concentration of the field sample is known, the amount of spike added is within a specified range of that concentration. Matrix spikes are analyzed in order to assess the magnitude of matrix interference and bias present. Because matrix spikes are analyzed in pairs, the second spike is called the matrix spike duplicate (MSD). The MSD provides information regarding the precision of the matrix effects. Both the MS and MSD are split from the same original field sample.

The success or failure of the matrix spikes is evaluated by calculating the percent recovery.

% recovery = 
$$\frac{\left(V_{MS} - V_{ambient}\right)}{V_{spike}} x 100$$

Where:

V<sub>MS</sub>: the concentration of the spiked sample

V<sub>ambient</sub>: the concentration of the original (unspiked) sample

V<sub>spike</sub>: the concentration of the spike added

In order to properly assess the degree of matrix interference and potential bias, the spiking level should be approximately 2-5 times the ambient concentration of the spiked sample. If the MS or MSD is spiked too high or too low relative to the ambient concentration, the calculated recoveries are no longer an acceptable assessment of analytical bias. In order to establish spiking levels prior to analysis of samples, the laboratories should review any relevant historical data. In many instances, the laboratory will be spiking the samples blind and will not meet a spiking level of 2-5X the ambient concentration. However, the results of affected samples will not be automatically rejected.

In addition to the recoveries, the RPD between the MS and MSD is calculated to evaluate how matrix affects precision.

$$RPD = \left| \frac{\left( V_{MS} - V_{MSD} \right)}{mean} \right| x100$$

There are two different ways to calculate this RPD, depending on how the samples are spiked.

1) The samples are spiked with the same amount of analyte. In this case,

V<sub>MS</sub>: the concentration for the matrix spike

 $V_{MSD}$ : the concentration of the matrix spike duplicate mean: the mean of the two concentrations (MS + MSD)

2) The samples are spiked with different amounts of analyte. In this case,

V<sub>MS</sub>: the recovery associated with the matrix spike

 $v_{MSD}$ : the recovery associated with matrix spike duplicate mean: the mean of the two recoveries (recovery<sub>MS</sub> + recovery<sub>MSD</sub>)

The MQO for the RPD between the MS and MSD is the same regardless of the method of calculation. These are detailed in Tables 12a, b.

## 7.4. Contamination assessment – Method blanks

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. At least one laboratory method blank will be run in every sample batch of 20 or fewer field samples. The method blanks will be processed through the entire analytical procedure in a manner identical to the samples. The QC criterion for method blank analysis states that the

blanks must be less than the Reporting Limit (<RL) for target analytes. If blank values exceed the RL, the sources of the contamination are determined and corrected, and in the case of method blanks, the previous samples associated with the blank are re-analyzed. All blank analysis results will be reported. If is not possible to eliminate the contamination source, all impacted analytes in the analytical batch will be flagged. In addition, a detailed description of the contamination sources and the steps taken to eliminate/minimize the contaminants will be included in interim and final reports. Subtracting method blank results from sample results is not permitted, unless specified in the analytical method.

## 7.5. Routine monitoring of method performance for organic analysis – surrogates

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 QC samples, prior to extraction. The reported concentration of each analyte is adjusted to correct for the recovery of the surrogate compound. The surrogate recovery data will be carefully monitored. If possible, isotopically-labeled analogs of the analytes will be used as surrogates. Surrogate recoveries for each sample are reported with the target analyte data. Surrogate is considered acceptable if the percent recovery is within 50-150%.

#### 7.6. Internal standards

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

#### 7.7. Dual-column confirmation

Dual-column chromatography is required for analyses using Gas Chromatography Electron Capture Detector (GC-ECD) due to the high probability of false positives arising from single-column analyses.

### 7.8. Representativeness

The representativeness of the data is mainly dependent on the sampling locations and the sampling procedures adequately representing the true condition of the sample site. Requirements

for selecting sample sites are discussed in more detail in the SAP (Appendix II). Sample site selection, sampling of relevant media (water, sediment and biota), and use of only approved/documented analytical methods will determine that the measurement data does represent the conditions at the investigation site, to the extent possible. The goal for meeting total representation of the site will be tempered by the types and number of potential sampling points (Puckett, 2002).

## 7.9. 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 SWAMP completeness goals of 90% for fish samples when target species (SAP Table 4, Appendix II) are present. Due to the variability and uncertainty of species availability in each zone, this level of completeness may not be attainable.

Laboratories will strive for analytical completeness of 90% (Table 11).

Table 12a. Measurement Quality Objectives – Inorganic Analytes in Tissues

SWAMP Measurement Quality Objectives* - General						
Laboratory Quality Control	Frequency of Analysis	Measurement Quality Objective				
Calibration Standard	Per analytical method or manufacturer's specifications	Per analytical method or manufacturer's specifications				
Continuing Calibration Verification	Per 10 analytical runs	80-120% recovery				
Laboratory Blank	Per 20 samples or per batch, whichever is more frequent	<rl analyte<="" for="" target="" th=""></rl>				
Reference Material	Per 20 samples or per batch, whichever is more frequent	75-125% recovery				
Matrix Spike	Per 20 samples or per batch, whichever is more frequent	75-125% recovery				
Matrix Spike Duplicate	Per 20 samples or per batch, whichever is more frequent	75-125% recovery, RPD ≤25%				
Laboratory Duplicate	Per 20 samples or per batch, whichever is more frequent	RPD <25%; n/a if concentration of either sample <mdl< th=""></mdl<>				
Internal Standard	Accompanying every analytical run when method appropriate	75-125% recovery				

\*Unless method specifies more stringent requirements.

MDL = Method Detection Limit

RL = Reporting Limit

n/a = not applicable

Table 12b. Measurement Quality Objectives – Synthetic Organic Compounds in Tissues

SWAMP Measurement Quality Objectives* - General					
Laboratory Quality Control	Frequency of Analysis	Measurement Quality Objective			
Calibration Standard	Per analytical method or manufacturer's specifications	Per analytical method or manufacturer's specifications			
Continuing Calibration Verification	Per 10 analytical runs	75-125% recovery			
Laboratory Blank	Per 20 samples or per batch, whichever is more frequent	<rl analytes<="" for="" target="" th=""></rl>			
Reference Material	Method validation: as many as required to assess accuracy and precision of method before routine analysis of samples; routine accuracy assessment: per 20 samples or per batch (preferably blind)	70-130% of the certified 95% confidence interval stated by provider of material. If not available then within 50-150% of reference value.			
Matrix Spike	Per 20 samples or per batch, whichever is more frequent	50-150% recovery or control limits based on 3x the standard deviation of laboratory's actual method recoveries			
Matrix Spike Duplicate	Per 20 samples or per batch, whichever is more frequent	50-150% recovery, RPD <25%			
Laboratory Duplicate	Per 20 samples or per batch, whichever is more frequent	RPD <25%; n/a if concentration of either sample <mdl< th=""></mdl<>			
Surrogate or Internal Standard	As specified in method	50-150% recovery			

<sup>\*</sup>Unless method specifies more stringent requirements.

MDL = method detection limit (to be determined according to the SWAMP QA Management Plan)

RL = Reporting Limit

 $n/a = not \ applicable$ 

## Element 8. Special Training Requirements/Safety

## 8.1. Specialized training and safety requirements

Analysts are trained to conduct a wide variety of activities using standard protocols to ensure samples are analyzed in a consistent manner. Training of each analyst includes the use of analytical equipment and conducting analytical protocols, and other general laboratory processes including glassware cleaning, sampling preparation and processing, hazardous materials handling, storage, disposal. All laboratory staff must demonstrate proficiency in all the aforementioned and required laboratory activities that are conducted, as certified by the Laboratory QAO.

## 8.2. Training, safety and certification documentation

Staff and safety training is documented at DFG-WPCL and MPSL-DFG. Documentation consists of a record of the training date, instructor and signatures of completion. The Laboratory QAO will certify the proficiency of staff at chemical analyses. Certification and records are maintained and updated by the Laboratory QAO, or their designee, for all laboratory staff.

## 8.3. Training personnel

The DFG-WPCL or MPSL-DFG Lab Director (LD) trains or appoints senior staff to train personnel. The Laboratory QAO ensures that training is given according to standard laboratory methods, maintains documentation and performs performance audits to ensure that personnel have been trained properly.

## 8.3.1. Laboratory Safety

New laboratory employees receive training in laboratory safety and chemical hygiene prior to performing any tasks in the laboratory. Employees are required to review the laboratory's safety program and chemical hygiene plan and acknowledge that they have read and understood the training. An experienced laboratory employee or the laboratory safety officer is assigned to the new employee to provide additional information and answer any questions related to safety that the new employee may have.

On-going safety training is provided by quarterly safety meetings conducted by the laboratory's safety officer or an annual laboratory safety class conducted by the DFG-OSPR Industrial Hygiene Officers or MLML Chemical Safety Officer.

## 8.3.2. Technical Training

New employees and employees required to learn new test methods are instructed to thoroughly review the appropriate standard operating procedure(s) and are teamed up with a staff member who is experienced and qualified to teach those test methods and observe and evaluate performance. Employees learning new test methods work with experienced staff until they have demonstrated proficiency for the method both by observation and by obtaining acceptable results for QC samples. This demonstration of proficiency is documented and certified by the section leader, Laboratory QAO and the laboratory director prior to the person independently performing the test method. Training records are retained on file for each employee by their supervisor or QAO. On-going performance is monitored by reviewing QC sample results.

## **Element 9. Documentation and Records**

The following documents, records, and electronic files will be produced:

- Quality Assurance Project Plan (submitted to contract manager in paper and electronic formats)
- Monitoring Plan (submitted to contract manager in paper and electronic formats)
- Archived Sample Sheets (internal documentation available on request)
- Chain-of-Custody Forms (exchanged for signatures with chemistry lab, and kept on file)
- Lab Sample Disposition Logs (internal documentation available on request)
- Calibration Logs for measurements of water quality standards (internal documentation available on request)
- Refrigerator and Freezer Logs (internal documentation available on request)
- Quarterly Progress Reports (oral format to contract manager)
- Data Tables (submitted to contract manager in electronic formats)
- Draft Manuscript (produced in electronic format)
- Final Manuscript (in electronic format)
- Data Appendix (submitted to contract manager in paper and electronic spreadsheet formats)

Copies of this QAPP will be distributed by the project manager to all parties directly involved in this project. Any future amended QAPPs will be distributed in the same fashion. All originals of the first and subsequent amended QAPPs will be held at MPSL-DFG. Copies of versions, other than the most current, will be discarded to avoid confusion.

The final report will consist of summary data tables and an appendix that contains all project data in electronic SWAMP compatible spreadsheet format. All laboratory logs and data sheets will be maintained at the generating laboratory by the Laboratory Manager for five years following project completion, and are available for review by the Contract Manager or designee during that time. Copies of reports will be maintained at SFEI for five years after project completion then discarded, except for the database, which will be maintained without discarding. Laboratories will provide electronic copies of tabulated analytical data (including associated QA/QC information outlined below) in the SWAMP database format or a format agreed upon by the Contract Manager. All electronic data are stored on computer hard drives and electronic back-up files are created every two weeks or more frequently.

Laboratories will generate records for sample receipt and storage, analyses and reporting.

Laboratories maintain paper copies of all analytical data, field data forms and field notebooks, raw and condensed data for analysis performed on-site, and field instrument calibration notebooks.

The PC will be responsible for sending out the most current electronic copies of the approved QAPP to all appropriate persons listed in Table 1.

## **Group B Elements. Data Generation and Acquisition**

## **Element 10. Sample Process Design**

The project design is described in the Sampling and Analysis Plan (SAP), Section III, pp. 6-17 (Appendix II). Sixty-nine Coastal "zones" will be sampled for 5 fish species each, when possible. Zones are listed in Table 13. Specific details on zone selection, boundaries and target species are found in Section III D and E1-2, pp. 9-13 of the SAP.

Due to the large size of sampling zones, it is not anticipated any zone will become inaccessible. If a particular launch ramp or pier is not accessible, another ramp or pier within the zone will be utilized. Latitude and Longitude will be recorded wherever sampling equipment is deployed to pinpoint collection sites within each zone. Blank field data sheets are in Attachment 1.

Each zone will be sampled within 3 full field days. Potential sampling equipment and methods can be found in MPSL-102a (Appendix III). Samples collected may be stored short-term for up to 1 month prior to delivery to the laboratory for processing. Once samples have been identified for composite creation, they will be shipped to the dissection laboratory for processing and analysis according to the timeline in Table 10.

All measurements and analyses to be performed are critical to address the objectives laid out in Section III of the SAP (Appendix II), with the exception of fish weight, sex, moisture, and lipid content. These parameters may be used to support other data gathered.

**Table 13. BOG Coastal Zones** 

Zone	Region	Station Code	Zone Name	Zone	Region	Station Code	Zone Name
1	9	91001TJNI	TJ to North Island	36	3	30836SMYC	Southern Monterey County Coast
2	9	91202SDSB	SD South Bay	37	3	30837BSUR	Big Sur Coast
3	9	91203SDNB	SD North Bay	38	3	30838CARM	Carmel Coast
4	9	90804PLMA	Pt Loma	39	3	30939MYPG	Monterey/Pacific Grove Coast
5	9	90605PLLJ	Pt Loma to La Jolla	40	3	30940MLMC	Moss Landing/Marina Coast
6	9	90606MISS	Mission Bay	41	3	30641ELKS	Elkhorn Slough
7	9	90407LJSO	La Jolla to San Onofre	42	3	30442SCWB	Santa Cruz Area Wharfs/Beachs
8	9	90208OCNH	Oceanside Harbor	43	2	30443SCCA	Santa Cruz Coast Area
9	8	90109SOCC	San Onofre to Crystal Cove	44	2	30444ANNU	Ano Nuevo Area
10	8	90110DANA	Dana Point Harbor	45	2	20245SMAT	San Mateo Coast
11	8	80111CCSA	Crystal Cove to Santa Ana River	46	2	20246PPTH	Pillar Point Harbor
12	4	80112NWPT	Newport Bay	47	2	20247HMBC	Half Moon Bay Coast
13	4	80113SASB	Santa Ana River to Seal Beach	48	2	20248PACC	Pacifica Coast
14	4	80114ORCO	Orange County Oil Platforms	49	2	20249SSFC	San Francisco Coast
15	4	40515LNGB	Long Beach	50	2	20150FARI	Farallon Islands
16	4	41116SPDB	San Pedro Bay	51	2	20151SMAC	Southern Marin Coast
17	4	40617CATI	Catalina Island	52	2	20152TBAY	Tomales Bay
18	4	40418PVER	Palos Verdes	53	2	20153NMRC	Northern Marin Coast
19	4	40419SSMB	South Santa Monica Bay	54	1	11554BDGA	Bodega Harbor
20	4	40420MSMB	Middle Santa Monica Bay	55	1	11555SSNC	South Sonoma Coast
21	4	40421NSMB	North Santa Monica Bay	56	1	11356NSNC	North Sonoma Coast
22	3	40422PTDU	Pt Dume to Oxnard	57	1	11357PTAR	Point Arena Area
23	3	31623NCHI	Northern Channel Islands	58	1	11358MENC	Mendocino Coast Area
24	3	40124VTRC	Ventura to Rincon	59	1	11359FTBG	Fort Bragg Area
25	3	31525RCGA	Rincon to Goleta	60	1	11360NMCC	North Mendocino County Coast Area
26	3	31526SBCP	Santa Barbara Channel Oil Platform	61	1	11261SHLC	Shelter Cove Area
27	3	31527GPTC	Goleta to Pt Conception	62	1	11262CMEN	Cape Mendocino Area
28	3	31028NSBC	North Santa Barbara County Coast	63	1	11063EURC	Eureka Coast Area
29	3	31029PISM	Pismo Beach Area	64	1	11064HUMB	Humboldt Bay
30	3	31030PTSL	Port San Luis Area	65	1	10865TRIN	Trinidad Area
31	3	31031DIAB	Diablo Canyon Coast	66	1	10866NHCC	North Humboldt County Coast Area
32	3	31032MRBC	Morro Bay Coast	67	1	10367DENC	Del Norte Coast
33	3	31033MRRB	Morro Bay	68	1	10368CRCC	Crescent City Coast
34	3	31034CAMB	Cambria\Cayucos Coast	69	1	10369CCHA	Crescent City Harbor
35	3	31035NSLC	Northern San Luis Obispo County Coast				

## 10.1. Variability

Due to potential variability of contaminant loads in individual tissue samples, samples will be analyzed in composites as outlined in the SAP (Appendix II) and MPSL-DFG SOPs (Appendix III).

## 10.2. Bias

Bias can be introduced by using fish of one particular species and/or total length for chemistry regressions and statistical analyses. The SAP (Appendix II) was reviewed by a Scientific Review Panel which approved of the inclusion of length ranges and multiple target species to reduce the associated bias.

## **Element 11. Sampling Methods**

Fish will be collected in accordance with MPSL-102a, Section 7.4 (Appendix III) except where noted here. Because coastal habitats vary greatly, there is no one method of collection that is appropriate. Field crews will evaluate each fishing site and species targeted to determine the correct method to be employed. Potential sampling methods include, but are not limited to: spear fishing, trawling, seining, gill netting, and hook and line.

Details on targeted fish species, number of individuals and size ranges can be found in the SAP (Appendix II, Tables 4 and 6).

The following adaptation to MPSL-102a, Section 7.4.5 (Appendix III) has been made: Collected fish may be partially dissected in the field. At the dock, the fish is placed on a measuring board covered with clean aluminum foil; fork and total length are recorded. Weight is recorded. Large fish such as sharks will is then be placed on the cutting board covered with a foil where the head, tail, and guts are removed using a clean cleaver (scrubbed with Micro<sup>TM</sup>, rinsed with tap and deionized water). The fish cross section is tagged with a unique numbered ID, wrapped in aluminum foil, and placed in a clean labeled bag. When possible, parasites and body anomalies are noted. The cleaver and cutting board are re-cleaned with Micro<sup>TM</sup>, rinsed with tap and deionized water between fish species, per site if multiple stations are sampled.

Zones are not fully segregated from other zones; therefore no special equipment cleaning will be done between zones.

Further details on sample collection and processing can be found in the SAP, Section III, E-F, pp. 10-17 (Appendix II).

### 11.1. Corrective Action

In the event samples cannot be collected, the Sample Collection Coordinator will determine if corrective actions are appropriate. Table 14 describes action to take in the event of a collection failure.

Table 14. Field collection corrective actions

Collection Failure	Corrective Action
One or more primary target species not present in	Change locations to fish another site within the
fishing site within the zone	zone
After 3 days effort, one or more primary target species	Collect one or more species from secondary
not collected within zone	target list; document the occurrence

## **Element 12. Sample Handling and Custody**

The field coordinator will be responsible for ensuring that each field sampling team adheres to proper custody and documentation procedures. A master sample logbook of field data sheets shall be maintained for all samples collected during each sampling event. A chain-of-custody (COC, Attachment 1) form must be completed after sample collection, archive storage, and prior to sample release.

Fish samples will be wrapped in aluminum foil and frozen on dry ice for transportation to the storage freezer or laboratory, where they will be stored at -20°C until dissection and homogenization. Samples delivered to MPSL-DFG will be logged in according to MPSL-104 (Appendix III). Samples delivered to DFG-WPCL will undergo a similar handling procedure (SAMPMAN\_REV\_Aug08, Appendix IV).

Authorization forms will be provided to each dissecting laboratory detailing the dissection and analysis to be performed (Attachment 3). Samples will be dissected according to MPSL-105 (Appendix III) and data retained on the lab data sheets in Attachment 4.

Lab Homogenates will be frozen until analysis is performed. Frozen tissue samples have a 12 month hold time from the date of collection. If a hold-time violation has occurred, data will be flagged appropriately in the final results.

# **Element 13. Analytical Methods**

Methods and equipment for laboratory analyses are listed in Table 15. EPA methods can be downloaded from <a href="www.epa.gov/epahome/index/nameindx.htm">www.epa.gov/epahome/index/nameindx.htm</a>. EPA method numbers followed by "M" indicate modifications have been made. Modifications and non-EPA SOPs can be found in Appendix III and IV. Method validation data for modifications and SOPs can be obtained by contacting the analytical laboratory (Table 1.)

An AWS brand AMW-DISC digital pocket scale, or similar, is used to weigh fish in the field and is calibrated monthly in the lab with standard weights. Fish lengths are determined using a fish measuring board that does not require calibration. No other field measurements are being taken.

Table 15. Methods for laboratory analyses

Parameter	Method	Instrument
Mercury	EPA 7473	Milestone DMA 80
Selenium	EPA 3052M	CEM MARSXpress Digester
		Perkin-Elmer Elan 9000
	EPA 200.8	ICP-MS
Organochlorine	EPA 8081BM	Agilent 6890 GC-ECD
Pesticides		Varian 3800 GC with Varian
		1200 Triple-Quad MS
Polychlorinated	EPA 8082M	Varian 3800 GC with Varian
Biphenyls		1200 Triple-Quad MS
Polybrominated	EPA 8081BM	Agilent 6890 GC-ECD
Diphenyl Ethers		

Mercury will be analyzed according to EPA 7473, "Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry" (USEPA, 1998) using a Direct Mercury Analyzer (DMA 80). Samples, blanks, and standards will be prepared using clean techniques. ASTM Type II water and analytical grade chemicals will be used for all standard preparations. A continuing calibration verification (CCV) will be performed after every 10 samples. Initial and continuing calibration verification values must be within ±20% of the true value, or the previous 10 samples must be reanalyzed. Three blanks, a certified reference material (DORM-3 or similar), as well as a method duplicate and a matrix spike pair will be run with each analytical batch of samples. Reporting Limits (RL) can be found in Table 16 and Measurement Quality Objectives (MQO) in Section 7, Table 12a.

Selenium composites will be digested according to EPA 3052M, "Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices" (USEPA, 1996), modified (Appendix III), and will be analyzed according to EPA 200.8, "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry" (USEPA, 1994). Samples, blanks, and standards will be prepared using clean techniques. ASTM Type II water and analytical grade chemicals will be used for all standard preparations. A continuing calibration verification (CCV) will be performed after every 10 samples. Initial and continuing calibration verification values must be within  $\pm 20\%$  of the true value, or the previous 10 samples must be reanalyzed. Two blanks, a certified reference material (2976 or DORM-2), as well as a method duplicate and a matrix spike pair will be run with each set of samples. Reporting Limits (RL) can be found in Table 16 and Measurement Quality Objectives (MQO) in Section 7, Table 12a.

All organic compounds will be extracted following EPA Methods 3545, 3640A, and 3620B. Organochlorine pesticides and PBDEs will be analyzed according to EPA 8081BM, "Organochlorine Pesticides by Gas Chromatography", modified (Appendix IV). PCBs will be analyzed according to EPA 8082M, "Polychlorinated Biphenyls (PCBs) by Gas Chromatography", modified (Appendix IV). Samples, blanks, and standards will be prepared using clean techniques. ASTM Type II water and analytical grade chemicals will be used for all

standard preparations. A continuing calibration verification (CCV) will be performed after every 10 samples. Initial and continuing calibration verification values must be within  $\pm 25\%$  of the true value, or the previous 10 samples must be reanalyzed. One blank, a laboratory control spike (LCS), as well as a method duplicate and a matrix spike pair will be run with each set of samples. Reporting Limits (RL) can be found in Table 17a,b,c and Measurement Quality Objectives (MQO) in Section 7, Table 12b.

Table 16. Trace metal analytical parameters, reporting units, and reporting limits (RL) for tissue samples.

Parameter	Method	RL (µg/g wet wt)	
Mercury	EPA 7473	0.02	
Selenium	EPA 3052M, EPA 200.8	0.40	

Table 17a. Trace organic analytical parameters, reporting units, and reporting limits (RL) for tissue samples. Organochlorine Pesticides by EPA 8081BM using GC-ECD.

Organochlorine Pesticides				
(by EPA 8081BM)				
Group	Parameter	RL (ng/g wet wt)		
Chlordanes	Chlordane, cis-	1		
	Chlordane, trans-	1		
	Heptachlor	1		
	Heptachlor epoxide	0.5		
	Nonachlor, cis-	1		
	Nonachlor, trans-	1		
	Oxychlordane	1		
DDTs	DDD(o,p')	0.5		
	DDD(p,p')	0.5		
	DDE(o,p')	0.5		
	DDE(p,p')	1		
	DDMU(p,p')	1		
	DDT(o,p')	1		
	DDT(p,p')	1		
Cyclodienes	Aldrin	1		
	Dieldrin	0.5		
	Endrin	1		
HCHs	HCH, alpha	0.5		
	HCH, beta	1		
	HCH, gamma	0.5		
Others	Dacthal	0.5		
	Endosulfan I	1		
	Hexachlorobenzene	0.7		
	Methoxychlor	1		
	Mirex	1		
	Oxadiazon	1		
	Tedion <sup>1</sup>	2		

<sup>&</sup>lt;sup>1</sup>Tedion has been removed from the analyte list. This compound was discontinued from use in 1985 and has a very short residence time. Furthermore, it is a compound that is not bioaccumulated.

Table 17b. Trace organic analytical parameters, reporting units, and reporting limits (RL) for tissue samples. PCBs by EPA Method 8082M.

Polychlorinated Biphenyl congeners (by EPA Method 8082M)				
	RL ppb (ng/g	,	RL ppb (ng/g	
PCB	wet wt)	PCB	wet wt)	
PCB 008	0.6	PCB 128	0.6	
PCB 018	0.6	PCB 137	0.6	
PCB 027	0.6	PCB 138	0.6	
PCB 028	0.6	PCB 141	0.6	
PCB 029	0.6	PCB 146	0.6	
PCB 031	0.6	PCB 149	0.6	
PCB 033	0.6	PCB 151	0.6	
PCB 044	0.6	PCB 153	0.6	
PCB 049	0.6	PCB 156	0.6	
PCB 052	0.6	PCB 157	0.6	
PCB 056	0.6	PCB 158	0.6	
PCB 060	0.6	PCB 169	0.6	
PCB 064	0.6	PCB 170	0.6	
PCB 066	0.6	PCB 174	0.6	
PCB 070	0.9	PCB 177	0.6	
PCB 074	0.6	PCB 180	0.6	
PCB 077	0.6	PCB 183	0.6	
PCB 087	0.9	PCB 187	0.6	
PCB 095	0.9	PCB 189	0.6	
PCB 097	0.6	PCB 194	0.6	
PCB 099	0.6	PCB 195	0.6	
PCB 101	0.9	PCB 198/199	0.6	
PCB 105	0.6	PCB 200	0.6	
PCB 110	0.9	PCB 201	0.6	
PCB 114	0.6	PCB 203	0.6	
PCB 118	0.9	PCB 206	0.6	
PCB 126	0.6	PCB 209	0.6	

Table 17c. Trace organic analytical parameters, reporting units, and reporting limits (RL) for tissue samples. PBDEs by EPA Method 8082M.

Polybrominated Diphenyl Ethers (by EPA Method 8081BM)			
PBDE RL ppb (ng/g wet w			
PBDE 017	0.6		
PBDE 028	0.6		
PBDE 047	0.8		
PBDE 066	0.6		
PBDE 085	0.8		
PBDE 099	0.8		
PBDE 100	0.6		
<b>PBDE 138</b>	0.6		
PBDE 153	0.8		
PBDE154	0.6		
PBDE 183	1.2		
PBDE 190	1.8		

### 13.2.1. Corrective Action

It is the responsibility of each analyst to take corrective action upon instrument failure. Corrective action will be conducted according to manufacturer or method specifications. Additional information on corrective actions can be found in Section 20.2.

### 13.2.2. Turn around time

All tissue analyses must be completed within the 1 year hold time. In addition, results need to be reported according to the timeline outlined in Table 10.

## 13.3. Sample Disposal

The laboratories are responsible for complying with all Federal, State and local regulations governing waste management, particularly hazardous waste identification rules and land disposal restrictions. Chemicals must be appropriately neutralized prior to disposal or must be handled as hazardous waste.

# **Element 14. Quality Control**

MPSL-DFG and DFG-WPCL conduct quality control through several activities and methods. These methods of quality control are performed to identify possible contamination problem(s), matrix interference and the ability to duplicate/repeat results. When control limits are exceeded the Laboratory QAO will review with appropriate laboratory staff to ascertain the possible cause

of the exceedance. A review of SOPs will be conducted and any deficiencies will be identified, documented, and corrected. A written report of the corrective action(s) will be provided to the PI and PM via email. The PM will contact the SWAMP QAO as needed. A written report containing all corrective actions will be submitted to the SWAMP QAO on a quarterly basis.

Each aspect of laboratory quality control is listed in Tables 12a and b for frequency as well as Measurement Quality Objectives (MQO) for each.

## Element 15. Instrument/Equipment Testing, Inspection and Maintenance

Laboratory instruments are inspected and maintained in accordance with lab SOPs, which include those specified by the manufacturer and those specified by the method (Tables 16 and 17a, b, and c). These SOPs have been reviewed by each respective Laboratory QAO and found to be in compliance with SWAMP criteria. DFG-WPCL and MPSL-DFG analysts are responsible for equipment testing, inspection, and maintenance. Appendices III and IV list the referenced SOPs. DFG-WPCL SOPs are available upon request from the Laboratory Director by email: <a href="mailto:dcrane@ospr.dfg.ca.gov">dcrane@ospr.dfg.ca.gov</a>. Likewise, MPSL-DFG SOPS are available upon request from the Laboratory QAO by email: <a href="mailto:bonnema@mlml.calstate.edu">bonnema@mlml.calstate.edu</a>.

Electronic laboratory equipment usually has recommended maintenance prescribed by the manufacturer. These instructions will be followed as a minimum requirement. Due to the cost of some laboratory equipment, back up capability may not be possible. But all commonly replaced parts will have spares available for rapid maintenance of failed equipment. Such parts include but are not limited to: batteries; tubes; light bulbs; tubing of all kinds; replacement specific ion electrodes; electrical conduits; glassware; pumps; etc. In some cases, the cost of instruments (i.e., GC-MS, EFD, etc) prohibits the procurement of additional spare parts. However, those instruments are typically maintained and repaired by the manufacturer.

The lead chemist, or designee, is responsible for the testing, inspection, and maintenance of equipment. Each instrument has its own logbook where the results of tests, inspections, maintenance and repairs are documented. When an instrument's test results fail to meet accuracy and/or precision criteria after the lead chemist has performed maintenance, the manufacturer will be contacted.

# Element 16. Instrument/Equipment Calibration and Frequency

Laboratory instruments (listed in Table 18) are calibrated, standardized and maintained according to procedures detailed in laboratory SOPs (Appendices III and IV). Instrument manuals identify step-by-step calibration and maintenance procedures. Instruments and types of calibration required are listed in Table 18. If analytical instrumentation fails to meet performance requirements, the instrument(s) will be checked according to their respective SOP(s) and recalibrated. If the instrument(s) does again does not meet specifications, it will be repaired and retested until performance criteria are achieved. The maintenance will be entered in the instrument log. If sample analytical information is in question due to instrument

performance, the PM will be contacted regarding the proper course of action including reanalyzing the sample(s).

At a minimum all calibration procedures will meet the requirements specified in the US EPA approved methods of analysis. The means and frequency of calibration recommended by the manufacturer of the equipment or devices as well as any instruction given in an analytical method will be followed. When such information is not specified by the method, instrument calibration will be performed at least once daily and continuing calibration will be performed on a 10% basis thereafter except for analysis by GC/MS. It is also required that records of calibration be kept by the person performing the calibration and be accessible for verification during either a laboratory or field audit.

Table 18. Equipment maintenance and calibration frequency.

Instrument	Inspection/Maintenance	Calibration
	Frequency	Frequency
Agilent 6890 Gas Chromatograph equipped with	As needed	At least once prior
micro-ECD detectors and autosamplers using		to each batch
Enviroquant Software (Agilent)		
Varian 3800 Gas Chromatograph with Varian	As needed	At least once prior
1200 Triple Quadrupole Mass Spectrometer		to each batch
equipped with Combi-Pal autosampler		
Perkin-Elmer Elan 9000 Inductively Coupled	As needed	At least once prior
Plasma - Mass Spectrometer		to each batch
Milestone DMA-80 Direct Mercury Analyzer	As needed	At least once
		every 2 weeks

### 16.1. Analytical Instrumentation

### 16.1.1. Instrument calibration

Upon initiation of an analytical run, after each major equipment disruption, and whenever on-going calibration checks do not meet recommended MQOs, 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 of a 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 an R<sup>2</sup> 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 are re-analyzed. All calibration standards will be traceable to a recognized organization for the preparation and certification of QC materials (e.g., National Institute of Standards and Technology, National Research Council Canada, US EPA, etc.).

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

### **16.1.2.** Continuing calibration verification (CCV)

Calibration verification solutions traceable to a recognized organization are inserted as part of the sample stream. The sources of the calibration verification solutions are independent from the standards used for the calibration. Calibration verification solutions used for the CCV will contain all the analytes of interest. The frequency of these verifications is dependent on the type of instrumentation used and, therefore, requires considerable professional judgment. The required frequency for this project is listed in Table 6. All analyses are bracketed by an acceptable calibration verification; all samples not bracketed by an in control CCV should be reanalyzed. If the control limits for analysis of the calibration verification solution are not met, the initial calibration will have to be repeated. All samples analyzed before the calibration verification solution that failed the MQOs will be reanalyzed following the recalibration. Only the re-analysis results will be reported. If it is not possible or feasible to perform reanalysis of samples, all earlier data (i.e., since the last successful calibration control verification) are suspect. In this case, DFG-WPCL will contact the PM to determine proceedings, and will flag the data and note the issue in interim and final reports.

## Element 17. Inspection/Acceptance of Supplies and Consumables

All supplies will be examined for damage as they are received. Laboratory ordering personnel will review all supplies as they arrive to ensure the shipment is complete and intact. All chemicals are logged in to the appropriate logbook and dated upon receipt. All supplies are stored appropriately and are discarded upon expiration date. Table 19 indicates items that are considered for accuracy, precision, and contamination. If these items are not found to be in compliance with the acceptance criteria, they will be returned to the manufacturer.

Table 19. Inspection/acceptance testing requirements for consumables and supplies.

Project-Related Supplies (source)	Inspection / Testing Specifications	Acceptance Criteria	Frequency	Responsible Individual
Certified pre-cleaned glass (I-Chem/Fisher Scientific or similar)	Carton custody seal is inspected	Carton custody seal intact	At receipt date of shipment	MSPL-DFG or DFG- WPCL personnel
Nitrile Gloves (Fisher Scientific or similar)	Carton seal is visually inspected for damage or tampering	Carton is intact and gloves within are clean and intact	At receipt date of shipment	MSPL-DFG or DFG- WPCL personnel
Polyethylene Gloves (Fisher Scientific or similar)	Carton seal is visually inspected for damage or tampering	Carton is intact and gloves within are clean and intact	At receipt date of shipment	MSPL-DFG or DFG- WPCL personnel
Analytical Standards (Perkin-Elmer, VWR, Fisher Scientific or similar)	Solution bottles are inspected to verify factory seal	Manufacturer's seal intact	At receipt date of shipment	MSPL-DFG or DFG- WPCL personnel

### **Element 18. Non-Direct Measures**

Data will not be used from non-direct measures in this study.

## Element 19. Data Management

Field data will be entered into the SWAMP Database version 2.5 upon return to the lab. Original field sheets (Attachment 1) will be retained in a log book, and copies of the COCs (Attachment 2) will be kept by each receiving laboratory. SWAMP Authorization forms will also accompany samples sent to each laboratory (Attachment 3).

All data generated by DFG-WPCL will be maintained as described in DFG-WPCL SOPs (Appendix IV) and the DFG-WPCL Quality Assurance Manual (Appendix I). The DFG-WPCL QAO will be responsible for oversight of the collection of all organic chemical analysis data and entering QA-checked data into the SWAMP database.

Likewise, all MPSL-DFG data will be generated and maintained according to the Marine Pollution Studies Laboratory Quality Assurance Plan (Appendix I). The MPSL-DFG QAO will be responsible for oversight of the collection of all dissection and metals analysis data and entering QA-checked data into the SWAMP database.

All data collected will be entered into electronic spreadsheets that are SWAMP compatible. Each data element is checked at a minimum by the technician that entered the data and verified by the technician's signature on the data sheet. Tissue data will be provided to the PC in Microsoft Excel spreadsheets. Data will be reviewed to ensure they are consistent with the format of the database and other data records.

All raw and statistical analysis data are subject to a 100% check for accuracy by the PM and Laboratory QAOs. Data are analyzed and proofread for accuracy, and then QA checked against the QAPP and SWAMP criteria before being entered into the SWAMP database. Original hard

copies of the data are filed in a secure cabinet until requested by the PM and/or inclusion into the Final Report. Electronic copies are stored and backed up by each analyst and respective laboratory internal project manager.

Hardware and software will be updated as recommended by the manufacturer or as needed. Testing of each component is not required on a regular basis aside from day to day functionality. Each entity is responsible for the necessary updates or upgrades, whether provided regularly through an Information Technology department or otherwise.

Data management checklists are not required. Analytical completeness will be tracked through the SWAMP Database version 2.5.

# **Group C Elements: Assessment and Oversight**

## Element 20. Assessments and Response Actions

### **20.1.** Audits

All reviews of QA data will be made by the QAO of each laboratory prior to submission of each batch to SWAMP Tissue Database 2.5. Reviews of the sampling procedures will be made by the Field Collection Coordinator and the Project Coordinator in case problems occur. As SOPs are updated and refined, additional reviews will be made. Each data technician is responsible for flagging all data that does not meet established QA/QC criteria.

Project data review established for this project will be conducted once all data sets have been received, and includes the following:

- Initial review of analytical and field data for complete and accurate documentation, chain of custody procedures, compliance with analytical holding times, and required frequency of laboratory QA samples.
- Comparison of all spike and duplicate results with the MQOs in tables 12a and b.
- Assigning data qualifier flags to the data as necessary to reflect limitations identified by the process.

If a review discovers any discrepancy, the QAO will discuss it with the personnel responsible for the activity. The discussion will include the accuracy of the information, potential cause(s) leading to the deviation, how the deviation might impact data quality and the corrective actions that might be considered.

Assessments will be oral; if no discrepancies are noted and corrective action is not required, additional records are not required. If discrepancies are observed, the details of the discrepancy and any corrective action will be reported and appended to the report.

All assessments will be conducted in accordance with the timeline in Table 10.

### 20.2. Deviations and corrective actions

Analyses are conducted according to procedures and conditions recommended by the US EPA and described in laboratory SOPs (Appendices III and IV), with the exception of those reported herein. Beyond those identified, deviations from these recommended conditions are reported to the Laboratory QAO. The PM will be notified within 24 hours of these deviations.

In the event of a SOP/QAPP deviation or corrective action, a deviation/corrective action form will be prepared, completed, signed and the PM notified. Best professional judgment will be used in interpretation of results obtained when deviations in the test conditions have occurred. All deviations and associated interpretations will be reported in interim and final reports. Protocol amendments will be submitted to the Laboratory QAO and PM. Upon approval, protocol amendments will be employed.

This study strives for 90% analytical data completeness. If this goal cannot be achieved, various corrective actions can be undertaken as described in Section D24.

## **Element 21. Reports to Management**

The following products are to be delivered to PM:

- Each LD shall regularly brief the PC, LS and PM on the progress of all on-going chemical analyses in monthly emails or conference calls. When deemed necessary for decision making, other BOG participants will also be notified of progress.
- o The LS will provide a draft final report and a final report to the PM in accordance with the dates listed in Table 10.

# **Group D Elements: Data Validation and Usability**

## Element 22. Data Review, Verification and Validation Requirements

Data generated by project activities will be reviewed against the measurement quality objectives (MQOs) in Tables 12a and 12b, Section 7. Furthermore, the final dataset as a whole will scrutinized for usability to answer the three Management Questions.

## **Element 23. Verification and Validation Methods**

All data reported for this project will be subject to a 100% check for errors in transcription, calculation and computer input by the laboratory internal project manager and/or laboratory QAO. Additionally, the Laboratory QAO will review sample logs and data forms to ensure that requirements for sample preservation, sample integrity, data quality assessments and equipment calibration have been met. At the discretion of the LD, data that do not meet these requirements will either not be reported, or will be reported with qualifiers which serve as an explanation of any necessary considerations.

Reconciliation and correction will be decided upon by the Laboratory QAO and LD. The Laboratory QAO will be responsible for informing data users of the problematic issues that were discussed, along with the associated reconciliations and corrections. DFG-WPCL checklists and forms are in Attachment 5. MPSL-DFG does not have specific forms; comments are made on original data sheets and reports.

Data will be reported electronically to the Project Coordinator, then to the SWAMP Database Management Team (DMT) for inclusion in the SWAMP Database version 2.5. The DMT will follow SWAMP SOP Chemistry Data Verification V1.1 (Appendix V).

Data will be validated by Stacey Swenson of the DMT according to RMP Data Validation (Appendix VI) with the modifications to adjust for SWAMP requirements as in Validation of BOG Database (Appendix V). A QA narrative will be produced to be incorporated in the BOG Coastal Report. This narrative will summarize the data set from a QA standpoint. Validated data will be made available to users via the SWAMP Database 2.5 provided by the DMT on the State Water Resources Control Board website (<a href="http://www.swrcb.ca.gov/water\_issues/programs/swamp/">http://www.swrcb.ca.gov/water\_issues/programs/swamp/</a>).

# **Element 24. Reconciliation with User Requirements**

Data will be reported in the SWAMP Database version 2.5. Data that do not meet with the Measurement Quality Objectives in Tables 11a and b will be flagged accordingly as discussed in Section D23. Rejected data will not be included in data analyses while data flagged as estimated will be evaluated for inclusion on a case-by-case basis in conjunction with the associated QA data and program objectives.

The project needs sufficient data, as represented by the completeness objective (Table 10, Section 7), to address the management questions laid out in Section 5; specifically MQ1 and MQ2. A failure to achieve the number of data points cited could mean an inability to answer these questions.

To address MQ1, the concentrations from all composites will be compared with the BOG adopted thresholds presented in Tables 4 and 5. Mercury will be calculated as laid out on p.14 of the SAP (Appendix II).

In order to answer MQ2 the analytical results will be compared to the BOG adopted thresholds as described in the previous paragraph. For each analyte the percent of zones that have fish that exceeded the threshold will be calculated.

Those zones with analyte results greater than the OEHHA FCGs or ATLs in Tables 4 and 5 will be called to the attention of the California Regional Water Quality Control Boards in the technical report. It will be up to each Region to compare the measured chemistry results of this study with the appropriate regional 303(d) list requirements and to determine if further sampling is needed (MQ3).

Since this study is a screening study with primarily the two management questions as objectives, complex statistical analysis is not anticipated except as mentioned above. The data collected by this study is not intended to be used with traditional statistics.

## References

Davis, J.A., J. L. Grenier, A.R. Melwani, S. Bezalel, E. Letteney, and E. Zhang. 2007. Bioaccumulation of pollutants in California waters: a review of historic data and assessment of impacts on fishing and aquatic life. Prepared for the Surface Water Ambient Monitoring Program, California Water Resources Control Board, Sacramento, CA.

Klasing, S. and R. Brodberg. 2008. Development of Fish Contaminant Goals and Advisory Tissue Levels for Common Contaminants in California Sport Fish: Chlordane, DDTs, Dieldrin, Methylmercury, PCBs, Selenium, and Toxaphene. California Office of Environmental Health Hazard Assessment, Sacramento, CA.

Stanley, T. W., and S. S. Verner. 1985. The U. S. Environmental Protection Agency's quality assurance program. pp 12-19 In: J. K. Taylor and T. W. Stanley (eds.). Quality Assurance for Environmental Measurements, ASTM STP 867. American Society for Testing and Materials, Philadelphia, Pennsylvania.

State Water Resources Control Board (SWRCB). 2003. 2002 California 305(b) Report on Water Quality [prepared as required by Federal Clean Water Act section 305(b)]. Sacramento, CA: State Water Resources Control Board.

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

US Environmental Protection Agency. 1994. Method 200.8. Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry. Revision 5.4. US Environmental Protection Agency, Washington, DC.

BOG Coastal QAPP Revision 2.1 September 2009 Page 52 of 234

US Environmental Protection Agency. 1996. Method 3052. Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices. Revision 0. US Environmental Protection Agency, Washington, DC.

US Environmental Protection Agency. 1996. Method 8081B. Organochlorine Pesticides by Gas Chromatography. Revision 1. US Environmental Protection Agency, Washington, DC.

US Environmental Protection Agency. 1996. Method 8082. Polychlorinated Biphenyls (PCBs) by Gas Chromatography. Revision 0. US Environmental Protection Agency, Washington, DC.

US Environmental Protection Agency. 1998. Method 7473. Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry. Revision 0. US Environmental Protection Agency, Washington, DC.

US Environmental Protection Agency. 2000. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories: Volume 1, Fish Sampling and Analysis, Third Edition. EPA 823-R-93-002B-00-007. US Environmental Protection Agency, Office of Water, Washington, DC.