Delta Regional Monitoring Program

Quality Assurance Project Plan

for Fiscal Year 2020–2021 Monitoring

Version 6.4

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Prepared by

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San Francisco Estuary Institute-Aquatic Science Center

SFEI | AQUATIC SCIENCE CENTER

1. Title and Approval

For

PROJECT NAME: Delta Regional Monitoring Program, Fiscal Year 2020-2021

Date: June 4, 2021

NAME OF RESPONSIBLE ORGANIZATION: San Francisco Estuary Institute – Aquatic Science Center (SFEI-ASC)

1.1 Approval Signatures

Title:	Name:	Signature:	Signature Date:
MLJ Environmental Interim RMP Manager	**Melissa Turner**		
SFEI-ASC Project Manager / Contract Manager	Jamie Yin	DocuSigned by: Jamie Yin 25D167D71CBE437...	6/15/2021
SFEI-ASC QA Officer	Donald Yee		
SFEI-ASC Data Manager	Michael Weaver	DocuSigned by: Michael Weaver 9B7EBD9FA0E8419...	6/15/2021
Assistant Deputy Director SWRCB Office of Information Management and Analysis	Melissa Morris		
SWAMP QA Officer	Tessa Fojut		
State Water Board QA Officer	Andrew Hamilton		
USGS Biogeochemistry Group Principal Investigator	Tamara Kraus	DocuSigned by: Tamara Kraus C7B35016F7434E3...	6/15/2021
MPSL QA Officer	Autumn Bonnema		
USGS Project Chief (pesticides)	Jim Orlando		
PER Project Director	Stephen Clark	DocuSigned by: STEPHEN CLARK C4D43551B2BC478...	6/15/2021
Delta RMP Steering Committee co-Chair	Adam Laputz		

Delta RMP Steering Committee co-Chair	Debbie Webster		

2. Table of Contents

Appendices

2.1 List of Tables

Links are to online tables in Google docs. Tables are also attached at the end of the PDF version of this document.

2.2. List of Figures

2.3 Acronyms and Abbreviations

Acronyms and abbreviations used in this document are listed in Table 2.1.

3. Distribution List

The organizations and persons listed in Table 3.1 will receive a copy of the approved Quality Assurance Project Plan (QAPP) and any subsequent revisions.

In addition, copies of the QAPP will be posted on the Delta Regional Monitoring Program (Delta RMP) website and made publicly available via the internet at http://sfei.org/DeltaRMP/.

Previous versions of this document, covering monitoring conducted from 2014 - 2019, can be found on the project website, http://sfei.org/DeltaRMP/.

4. Project Task/Organization

This Quality Assurance Project Plan (QAPP) has been prepared for the monitoring of surface water quality in the Sacramento-San Joaquin River Delta (the Delta) by the Delta Regional Monitoring Program (Delta RMP) in fiscal year 2020/2021 (FY 20-21; July 1, 2020 to June 30, 2021). This section of the QAPP describes how the project will be managed, organized and implemented.

The responsible agency for this surface water monitoring program is the San Francisco Estuary Institute-Aquatic Science Center (SFEI-ASC), acting as the fiscal agent and implementing entity for the Delta RMP. The Delta RMP is managed by a Steering Committee and advised by a Technical Advisory Committee (TAC). SFEI-ASC staff contracts with, and partners with, several agencies and laboratories to carry out monitoring activities. Roles and responsibilities are shown in Figure 4.1 and described in more detail in the following sections.

Figure 4.1 Delta Regional Monitoring Program organization chart, FY20-21.

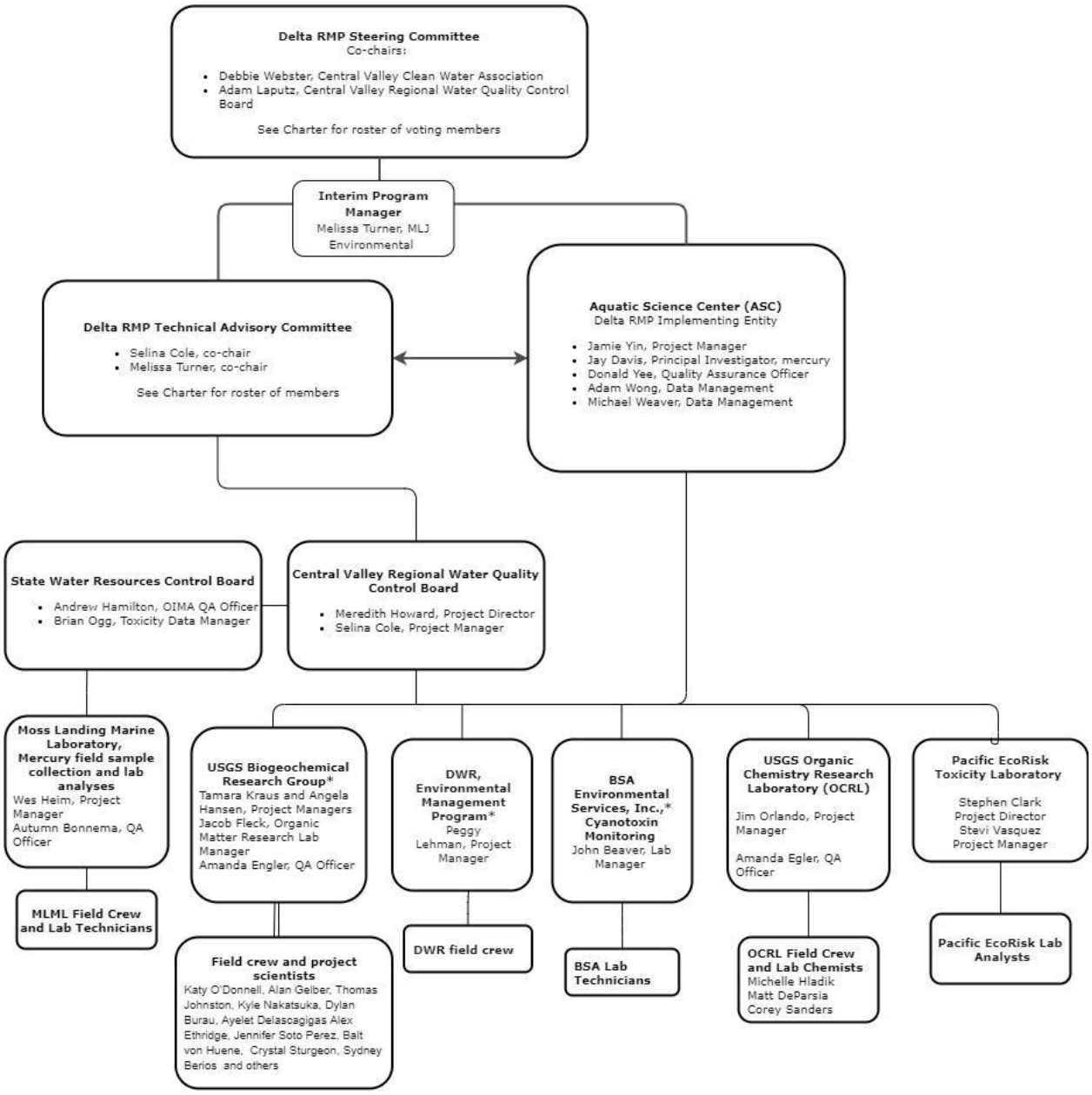


Figure 4.1 Delta Regional Monitoring Program organization chart.

*Conducting cyanotoxin study that is not covered by this QAPP but is described briefly in Section 6.1

See high-resolution image here.

4.1. Principal Data Users and Stakeholders

Principal data users include internal (program participants) and external stakeholders (other Delta managers and policymakers, local scientists and the scientific community at large, and the public). Participants include regulatory agencies, resource agencies, water supply, coordinated monitoring programs, wastewater treatment plants, stormwater municipalities, irrigated agriculture coalitions, and dredgers (Appendix A).

Funding for the Delta RMP is provided by the wastewater treatment plants, stormwater municipalities, irrigated agriculture coalitions, and dredgers listed in Appendix A. The Central Valley Regional Water Quality Control Board (CVRWQCB) and the State Water Resources Control Board provide funding via the Surface Water Ambient Monitoring Program (SWAMP).

4.2. Project Team

An organizational chart, with monitoring responsibilities noted, is provided in Figure 4.1. An abridged description of the Delta RMP staff and leadership is provided here. Detailed information on the governance of the Delta RMP, along with a roster of voting members, can be found in the program's Charter.

4.2.1. Program Leadership

The Delta RMP Steering Committee is the decision-making body of the Delta RMP. The Steering Committee is responsible for establishing the Delta RMP's strategic direction and the policies and procedures that govern its operation. The Steering Committee may direct Delta RMP staff and advisory committees to assist in meeting program objectives and may delegate day-to-day functions of the Delta RMP to the Delta RMP's implementing entity. The Steering Committee is made up of representatives from both the regulated and regulatory community, including organizations and agencies involved in agriculture, dredging, wastewater treatment, stormwater, water supply, and flood control and habitat restoration. An up-to-date list of Steering Committee members can be found online as an appendix to the Delta RMP Charter.

The Steering Committee authorizes the implementation of agreements among the participating members and, specifically:

1. Directs the fiscal/operating agent to request and receive federal, state, local, and private funds from any source and to expend those funds to accomplish the Delta RMP's goals.
2. Approves budgets and expenditures.

3. Directs the fiscal/operating agent to enter into partnerships, contracts, and other legal agreements on behalf of the Delta RMP, as necessary to fulfill the Delta RMP's mission.
4. Approves Delta RMP work products and any other plans, products, or resolutions of the Delta RMP.
5. Sets priorities and oversees the activities of the TAC.
6. Establishes and oversees the implementation of policies and procedures necessary to the day-to-day functioning of the Delta RMP.

The Delta RMP is in the process of establishing a new governance structure which is anticipated to take effect in FY21-22. The role of the Steering Committee will most likely change under the new governance structure.

Under the direction of the Steering Committee, the TAC provides technical oversight of the Delta RMP. The TAC also has a number of technical subcommittees representing different focus areas, such as pesticides, nutrients, and mercury. An up-to-date roster of TAC members can be found online as an appendix to the Delta RMP Charter.

4.2.2. Implementing Entities

Melissa Turner of MLJ Environmental is serving as Interim Program Manager for the Delta RMP for FY20-21. The Interim Program Manager is responsible for overseeing and coordinating individual monitoring elements, and communicating issues or problems to the appropriate Delta RMP committees and proposing solutions.

The San Francisco Estuary Institute – Aquatic Science Center (SFEI-ASC) also manages and operates those monitoring elements of the program covered in this document. The SFEI-ASC Project Manager (Jamie Yin) is responsible for coordinating monitoring components of this project including the organization of field sampling, interactions with the contract laboratories, and managing laboratory subcontracts. The SFEI-ASC Project Manager reports to the Program Manager.

The SFEI-ASC Regional Data Center Manager (Michael Weaver) coordinates the SFEI-ASC Data Services Team, which performs data review and verification to ensure that data submitted by subcontractor labs are timely, complete, and properly incorporated into the Regional Data Center database.

SFEI-ASC's Quality Assurance Officer's (QAO, Donald Yee) role is to provide Quality Assurance oversight and to review and approve the quality assurance and quality control (QA/QC) procedures found in this QAPP, which include field and laboratory activities. The

SFEI QAO will work with the Quality Assurance Officers for contracted analytical laboratories, reviewing and communicating all QA/QC issues contained in this QAPP to the laboratories.

The project QA officer position is independent of data generation.

Many of the data deliverables will be submitted in the new fiscal year when a new implementing entity will be in place. There will be a new governance structure and revised process for reviewing data.

4.2.3. Field Crews and Laboratories

Laboratories contracted by the Delta RMP provide analytical services and will act as a technical resource to Delta RMP staff and management. Laboratories are listed in Table 4.3.

Mercury

Mercury monitoring elements are managed, reviewed, and reported to CEDEN by the SWAMP Unit and reviewed by the State Board for FY20-21 but QA for the work is described in this document. Because SWAMP is funding the mercury analyses and managing these data, SWAMP IQ will upload the Delta RMP data to CEDEN and make it publicly available without the SC review and approval steps that some other Delta RMP datasets are subject to.

The Marine Pollution Studies Lab (MPSL) at Moss Landing Marine Laboratory (MLML) will analyze fish tissue and water samples for mercury and related measurements. Note that sediment was monitored during the 2017 - 2018 fiscal year (FY17-18), but not monitored in the years before or after.

Autumn Bonnema will serve as the MPSL Project Coordinator. She will 1) review, evaluate, and document project reports, and 2) verify the completeness of all tasks. She may also assist field crew in preparation and logistics. Her duties will also be to ensure that laboratory technicians have processing instructions and that all laboratory activities are completed within the proper timelines. She is also responsible for sample storage and custody at MPSL.

Billy Jakl of MPSL is in charge of directing fish and water collection for mercury monitoring. He will 1) oversee preparation for sampling, including vehicle maintenance, and 2) oversee sample and field data collection.

Wes Heim will serve as the project manager for the MPSL component of this project. His specific duties will be to 1) review and approve the QAPP, 2) provide oversight for mercury analyses to be done for this project, 3) ensure that all MPSL activities are completed within the proper timelines, and 4) oversee data validation, management, and reporting.

Pesticides

Jim Orlando is the project manager at the USGS Organic Chemistry Research Laboratory (OCRL). His duties will be to ensure that all project elements meet the guidelines established in the QAPP and project contract. He is responsible for the final review of all project analytical results produced by the OCRL. He serves as the primary contact between the Delta RMP and the OCRL.

Michelle Hladik is the Chief Chemist at the USGS OCRL and supervises all laboratory activities. Her duties will be to ensure that laboratory technicians have processing instructions and that all laboratory activities are completed following established guidelines (project specific

QAPP and OCRL Standard Operating Procedures [SOPs]). She is responsible for sample analyses and initial data review, and provides data to the USGS project manager for review.

Corey Sanders is the chemist/database manager for the USGS OCRL. His duties will be to ensure that all sample collection information and analytical results are entered into the OCRL internal database and that this information is subsequently formatted and transferred to the USGS National Water Information System (NWIS) database. He is also responsible for sample storage and custody at OCRL.

Matt DeParsia is the OCRL field technical lead for the project. His duties will be to ensure that water quality sampling is conducted following documented procedures (as described in the USGS *National Field Manual*, and this project-specific QAPP). He is also responsible for the initial processing of water samples at the OCRL and for shipping samples to the USGS National Water Quality Laboratory in Denver for additional chemical analyses not performed at the OCRL in Sacramento, and to Pacific EcoRisk for Aquatic Toxicity testing.

Aquatic Toxicity

Stephen Clark is the Project Director for Pacific EcoRisk (PER). His duties will include ensuring all toxicity data produced by the laboratory meets the guidelines established in the QAPP and project contract, as well as reviewing case narratives and project contracts. He will serve as the primary contact between PER and the Delta RMP and will attend quarterly Delta RMP meetings to provide written and verbal updates on the toxicity testing results.

Stevi Vasquez will serve as the PER Project Manager. Her duties will be to ensure that aquatic toxicity testing is conducted following documented procedures outlined in this document, SWAMP Measurement Quality Objectives (MQOs), and laboratory-specific SOPs. She is also responsible for overseeing calculation and compilation of the toxicity data and providing these data to the data managers at SFEI-ASC. Additionally, she will provide reporting data (such as copies of bench sheets and reference toxicity control charts) to SFEI-ASC to share with the TAC.

For FY20-21, SFEI-ASC is responsible for data management for Delta RMP toxicity data. This includes data processing, QA/QC review, and data upload to the California Environmental Data Exchange Network (CEDEN). Responsible parties for SFEI-ASC include Jamie Yin (SFEI-ASC Project Manager), Michael Weaver (Data Manager), and Donald Yee, (QA Officer).

In the event there are changes to the data *after* it has been published, they will be communicated to data users in a timely manner.

4.3. Persons Responsible for QAPP Update and Maintenance

Changes and updates to this QAPP may be made by the RMP Program Manager and SFEI-ASC's Quality Assurance Officer (QAO), after they review the evidence for change, and with the concurrence of the TAC. SFEI-ASC's QAO will be responsible for making the changes, submitting drafts for review, preparing a final copy, and submitting the final QAPP for signatures. Changes and updates to the QAPP will require approval by the Central Valley Water Board in order for the Delta RMP to continue as a Central Valley Water Board approved regional monitoring program. Minor changes not affecting operational procedures (e.g., changes in staff, addresses, phone numbers, etc.) may be made to an Interim version without re-signing, and will be finalized in the next version after receiving approval signatures. The QAPP will be reviewed on an annual basis. Changes are expected year to year in the early years of any new Delta RMP monitoring plan.

5. Problem Definition and Background

The Delta RMP was initiated in 2008 by the Central Valley Regional Water Quality Control Board (CVRWQCB) with the primary goal of tracking and documenting the effectiveness of beneficial use protection and restoration efforts through comprehensive monitoring of water quality constituents and their effects in the Delta. The development of the Delta RMP was initially prompted by the collapse of the populations of several species of fish in the early 2000s, an event that triggered new inquiries into the potential role of contaminants in what is now termed the Pelagic Organism Decline (POD). However, these inquiries highlighted shortcomings of existing monitoring efforts to address questions at the scale of the Delta. Recognition that data from current monitoring programs were inadequate in coverage, could not easily be combined, and did not support a rigorous analysis of the role of contaminants in the POD, persuaded regulatory agencies to improve coordination across multiple monitoring programs.

In addition, the Delta RMP reflects an increasing desire among water quality and resource managers throughout the state for more integrated information about patterns and trends in ambient conditions across watersheds and regions. Many stressors to beneficial uses are interrelated and must be addressed more holistically. The Delta RMP complements existing larger-scale collaborative monitoring efforts throughout the state that attempt to address questions and concerns about regional conditions and trends (e.g., San Francisco Bay RMP, Southern California Bight Monitoring Program, Surface Water Ambient Monitoring Program).

The Delta RMP Steering Committee decided at its December 3, 2012 meeting that the initial Delta RMP would focus on mercury, nutrients, pathogens, and pesticides, since these

constituents represent high priority issues for management that are shared concerns of represented participant groups. The TAC subsequently developed monitoring designs for these priorities to address the Delta RMP management questions (Appendix B) and priority assessment questions for each constituent (Appendix C).

Pesticides monitoring began in 2015 to characterize the spatial and temporal variability of pesticides concentrations and toxicity to aquatic organisms.

Mercury monitoring began in 2016 to address the highest priority information needs related to implementation of the Methylmercury Total Maximum Daily Load (TMDL).

Nutrients are associated with excessive growth of nuisance aquatic vegetation that interferes with navigation and recreation, and can block water supply intakes. It is also suspected to contribute to harmful algal blooms (HABs) that can produce toxins that kill fish, wildlife, and domestic animals, and are detrimental to drinking water quality and human health. Finally, nutrients play an important role in ecosystem health, for example by affecting the primary productivity of algae which form the base of the food chain. Water managers seek to better understand these factors in order to better manage ecosystems and craft more effective plans for the conservation and recovery of threatened and endangered species in the Delta. Nutrient monitoring began in 2017 with a one-year special study to assess spatial variability of nutrients and related water quality constituents in the Delta at the landscape scale. Delta RMP nutrient monitoring is continuing in FY20-21 with two studies: 1) "Cyanotoxin Monitoring in the Delta: Leveraging existing USGS and DWR field efforts to identify cyanotoxin occurrence, duration, and drivers" led by Tamara Krause of USGS and 2) "Source Tracking of the Cyanobacteria Blooms in the Sacramento-San Joaquin Delta" led by Ellen Preece of Robertson-Bryan, Dr. Tim Otten of Bend Genetics, and Dr. Janis Cooke of the Central Valley Regional Water Board. Quality assurance documentation and methods for the cyanotoxin study are provided in other documents (see Section 6.1 for a list).

The Source Tracking of the Cyanobacteria Blooms study is funded as a Supplemental Environmental Project and per Steering Committee direction a QAPP is not required.

5.1. Core Management Questions

5.1.1. Pesticides and Aquatic Toxicity

A better understanding of the effects of contaminants in the apparent decline of Delta ecosystems is a priority for regulators and stakeholders. Pesticide use in the Delta and Central Valley is one of the potential drivers of these effects. Constantly changing pesticide use presents a challenge for environmental scientists, resource managers, and policy makers trying to

understand whether these contaminants are impacting aquatic systems and if so, which pesticides are the biggest problem. Less than half of the pesticides currently applied in the Central Valley are routinely analyzed in monitoring studies and new pesticides are continually being registered for use. Therefore, baseline monitoring of ambient surface water for both aquatic toxicity and a broad list of current use pesticides is needed to understand whether current use pesticides contribute to observed toxicity in the Delta.

The monitoring is intended to provide useful information to state and federal water quality regulators. Important regulatory drivers are described below.

Water Quality Control Plan for the Sacramento River and San Joaquin River Basin **(Basin Plan, link)**

According to the State Water Board, the Basin Plan is "the Board's master water quality control planning document. It designates beneficial uses and water quality objectives for waters of the State, including surface waters and groundwater. It also includes programs of implementation to achieve water quality objectives."

The Central Valley's Basin Plan states that, "in addition to numerical water quality objectives for toxicity, the Basin Plan contains a narrative water quality objective that requires all surface waters to '...be maintained free of toxic substances in concentrations that are toxic to or that produce detrimental physiological responses to human, plant, animal, and aquatic life.' To check for compliance with this objective, the CVRWQCB initiated a biotoxicity monitoring program to assess toxic impacts from point and nonpoint sources in Fiscal Years 1986 - 1987" (CVRWQCB 2016, IV-32.08). The plan states that the Regional Board "will continue to impose toxicity testing monitoring requirements in NPDES [National Pollutant Discharge Elimination System] permits. The focus of ambient toxicity testing will continue to be the Delta and major tributaries." In other words, the Board is interested in verifying that there are "no toxics in toxic amounts" in waterways, and will continue to require aquatic toxicity testing as a key means of making this determination.

Organophosphate TMDL

In 2006, the CVRWQCB identified Delta waterways as impaired under the federal Clean Water Act Section 303(d) due to elevated concentrations of the organophosphate pesticides, diazinon and chlorpyrifos, and created a plan for their allowable discharge to the Delta referred to as the Total Maximum Daily Load (TMDL). Under this plan (CVRWQCB 2006), the board put in place a number of new rules and requirements. One of these stated that new discharge permits (or

WDRs) for runoff from fields and orchards draining to Delta Waterways must include monitoring to meet a number of goals, the most relevant being:

- Determine attainment of the diazinon and chlorpyrifos water quality objectives and Load Allocations (additivity target).
- Determine whether alternatives to diazinon and chlorpyrifos are causing surface water quality impacts.
- Determine whether the discharge causes or contributes to a toxicity impairment due to additive or synergistic effects of multiple pollutants

In addition, there are nearly identical requirements for agricultural dischargers to the Sacramento and San Joaquin River under those TMDLs (Daniel McClure, personal communication).

Control Program for Diazinon and Chlorpyrifos

In 2014, the Central Valley Water Board published an additional amendment to the Basin Plan containing a control program for discharges of diazinon and chlorpyrifos (CVRWQCB 2014). The control plan created new pollution control requirements for waterways designated as supporting both warm and cold freshwater habitats. Under these requirements, agricultural, municipal stormwater, and wastewater dischargers in the Sacramento and San Joaquin River basins below major reservoirs are required to monitor in order to:

- Determine compliance with established water quality objectives applicable to diazinon and/or chlorpyrifos.
- Determine whether alternatives to diazinon and/or chlorpyrifos are being discharged at concentrations that have the potential to cause or contribute to exceedances of applicable water quality objectives.

In addition, agricultural dischargers are also required to monitor water quality in order to:

- Determine whether the discharge causes or contributes to a toxicity impairment due to additive or synergistic effects of multiple pollutants

Pyrethroids Basin Plan Amendment

In 2017, the Regional Board determined that more than a dozen waterways are impaired due to elevated concentrations of pyrethroid pesticides under the Clean Water Act, section 303(d). In response, the regional board adopted a Basin Plan Amendment (CVRWQCB 2017) which includes a pyrethroid pesticide control program for the Sacramento and San Joaquin River Basins. This Basin Plan Amendment was adopted by the regional board in June 2017 and it is

expected to be fully approved by Stater Water Board, the Office of Administrative Law, and EPA by the end of 2018.

The amendment contains requirements for monitoring of pyrethroids, pyrethroid alternatives, and aquatic toxicity to the invertebrate *Hyalella* in discharges and/or receiving water in order to:

- Determine if the pyrethroid concentration goals are being attained through monitoring pyrethroids either in discharges (monitoring requirements apply to wastewater treatment plants or publicly-owned treatment works, POTWs) or in receiving waters (monitoring requirements apply to municipal separate storm sewer systems [MS4s] and agricultural dischargers).
- Determine whether pyrethroid pesticides are causing or contributing to exceedances of the narrative water quality objectives for toxicity – through toxicity testing with *Hyalella* in water column of receiving waters (POTWs, MS4s, and agricultural dischargers) or receiving waters water column and bed sediments (agricultural dischargers and MS4s)

This monitoring must be completed two years from the February 2019 effective date of the Basin Plan Amendment (BPA). After that two-year period, dischargers will also be required to monitor for alternative insecticides that could be having water quality impacts.

Assessment Questions Addressed

The study of pesticides and toxicity is designed to help answer the core Delta RMP Management and Assessment Questions,

> Is water quality currently or trending towards adversely affecting beneficial uses of the Delta?
>
> **Status & Trends (S&T) Assessment Questions**
>
> S&T 1 - To what extent do current use pesticides contribute to observed toxicity in the Delta?
>
> S&T 1.1 - If samples are toxic, do detected pesticides explain the toxicity?
>
> S&T 1.2 - What are the spatial and temporal extent of lethal and sublethal aquatic and sediment toxicity observed in the Delta?
>
> S&T 2 - What are the spatial/temporal distributions of concentrations of currently used pesticides identified as possible causes of observed toxicity?

The study objectives are to:

- Collect water samples from a variety of locations across Delta subregions and analyze them for a broad suite of current use pesticides, and for toxicity to aquatic organisms.
- Test whether pesticides in ambient water samples exceed aquatic life benchmarks.
- Test for the co-occurrence of pesticides and observed aquatic toxicity.

Example Information Applications

The examples below show ways that information from the Delta RMP study of pesticides and toxicity could be used by scientists, water managers, and regulators. Example information applications include, but are not limited to:

- The Delta RMP may use this information to determine what percentage of Delta waters exhibit toxicity to aquatic organisms or have concentrations of pesticides that exceed screening values.
- State water quality regulators may use this information to help evaluate if waterways should be classified as impaired under Section 303(d) of the Clean Water Act. Regulators will be able to evaluate particular stream segments and parameters for signs of impairment, and, after several years of monitoring, may be able to track changes in impairment over time.
- If certain compounds are found to have adverse impacts on the aquatic environment that prevent attainment of beneficial uses, regulators may require the development of a management plan to prevent or mitigate pesticide contamination of waterways or, when warranted, adopt restrictions to further protect surface water from contamination.

5.1.2. Mercury

The Delta Methylmercury TMDL is the embodiment of management decisions for methylmercury in the Delta, establishing goals for cleanup and calling for a variety of control studies and actions. The Delta Methylmercury TMDL (aka Delta Mercury Control Program) was adopted in 2010 as a Basin Plan Amendment and includes a control program to reduce methylmercury and inorganic mercury in the Delta. The Delta Mercury Control Program emphasizes studies and pilot projects to develop and evaluate management practices to control methylmercury in the Delta. Currently, responsible entities are implementing methylmercury control studies to assess methods of limiting methylmercury entering Delta waterways. The studies encompass a variety of source types, including municipal wastewater treatment plants, urban and industrial stormwater discharges, dredging operations, tidal wetlands, open water habitats, and seasonal wetlands.

With providing information to support TMDL implementation in mind, the Mercury Subcommittee carefully considered the assessment questions articulated by the Steering Committee and TAC for mercury.

The Delta RMP management and assessment questions addressed by each of the methylmercury monitoring elements are indicated in Table 5.1. In addition, the combination of water and fish monitoring addresses a critical data need for management not captured in the current set of questions for the Program: data to strengthen the linkage analysis that is a key component of the technical foundation for the TMDL.

Monitoring of subregional trends in bass is addressing questions relating to Status and Trends, Forecasting, and Effectiveness Tracking. Status and Trends Question 1A in Table 5.1 (Are trends over time in MeHg in sport fish similar or different among Delta subareas?) is a high priority for managers that relates to the TMDL, and is a primary driver of the sampling design for subregional bass trend monitoring. Annual monitoring of mercury in sport fish (bass) is needed to 1) firmly establish a baseline for each Delta subregion and 2) to characterize the degree of interannual variation, which is essential to designing an efficient monitoring program for detection of long-term trends. In addition to addressing status and trends, this monitoring will provide an essential foundation for Forecasting Scenarios (past trends are a starting point for projecting future conditions) and Effectiveness Tracking (evaluating whether water quality is improving at the subregional scale as a result of management actions).

Monitoring of subregional trends in water is addressing all of the major categories of Delta RMP management questions (Status and Trends; Sources, Pathways, Loadings, and Processes [SPLP];

Forecasting Scenarios; and Effectiveness Tracking). Data on concentrations of methylmercury in water are valuable as an indicator of Status and Trends as they can be compared to the TMDL implementation goal of 0.06 ng/L of unfiltered aqueous methylmercury. The use of water data to update the mass budget addresses SPLP Question 1A and is a key element of the TMDL. Aqueous methylmercury concentrations are essential input and validation data for the models that DWR and USGS are developing for the Delta that will elucidate the processes affecting methylmercury patterns and allow forecasting and testing of various water management scenarios. Water concentration data will also be valuable in Effectiveness Tracking, allowing assessment of status relative to the implementation goal and of changes in loading in the context of the overall mass budget for the Delta.

Monitoring of subregional trends in bass and water will also provide information on the influence of climate, hydrology, and ecology. For example, the first two years of monitoring have already spanned the end of a prolonged drought and a high flow year, providing an opportunity to examine the impact of extreme variation in flow on methylmercury concentrations in fish and water.

Restoration monitoring will address questions relating to SPLP, Forecasting Scenarios, and Effectiveness Tracking. The basic concern with restoration projects is that they may enhance net methylmercury production within the Delta ecosystem, and represent an internal source that increases as the projects proceed (SPLP Question 1B) – restoration monitoring will track whether this occurs or not. Restoration monitoring will yield insights into which types of projects, if any, impact net methylmercury production and food web accumulation (Forecasting Scenarios Question 1) and whether internal loadings change and ambient water quality shows net improvement as a result of restoration projects (Effectiveness Tracking).

5.2 Beneficial Uses and Water Quality Goals

Two water quality control plans apply to the Sacramento-San Joaquin Delta: the *Water Quality Control Plan for the Sacramento River and San Joaquin River Basins* (CVRWQCB, 2011.) This is frequently referred to as the *Central Valley Basin Plan* or simply, the *Basin Plan*. The *Basin Plan* is the Central Valley Regional Water Quality Control Board's regulatory reference for meeting the state and federal requirements for water quality control established under the federal *Clean Water Act* and California's Porter-Cologne Water Quality Control Act. The *Basin Plan* establishes numeric and narrative objectives for water quality aimed at protecting beneficial uses of water in the Sacramento River and San Joaquin River Basins, including the Sacramento-San Joaquin River Delta (Chapter III: Water Quality Objectives).

The second water quality control plan that applies to the Delta is the *Bay-Delta Water Quality Control Plan* (SWRCB 2006), commonly referred to as the *Bay-Delta Plan*. The State Water Resources Control Board adopted the Bay-Delta Plan to establish water quality objectives for the Bay-Delta Estuary related to flow and water project operations.

Table 5.2 provides an overview of beneficial uses that are relevant to the prioritized assessment questions of each of the individual monitoring elements. The full list of Delta RMP assessment questions can be found in Appendix B.

Table 5.3 summarizes existing numeric water quality criteria and aquatic life benchmarks for target analytes of pesticide monitoring. This information is useful for determining whether the lab's analytical methods are sensitive enough to detect pesticides at relevant concentrations. We make this determination by comparing the lab's detection limits to relevant screening values. For the majority of the pesticide analytes, there are no regulatory screening values. Exceptions are chlorpyrifos and diazinon, for which water quality objectives (WQOs) were set by the CVRWQCB. Other screening values are drawn from the literature. In order to determine whether contaminants are present in waterways at concentrations that are ecologically relevant, i.e., those which may cause harm to aquatic biota, scientists compare observed concentrations with screening values for aquatic toxicity gathered from the literature. The presence of a compound above a screening value is not necessarily evidence that harm is taking place, but rather it is a first step in a process for interpreting the data and evaluating relative ecological risk

The screening values listed in Table 5.3 include:

- Water Quality Objectives for California's Central Valley (Central Valley Water Board 1998, 2007)
- EPA Office of Water (OW) Aquatic Life Ambient Water Quality Criteria (EPA 2000, 2015a, 2015b, website link)
- EPA Office of Pesticide Programs (OPP) Aquatic Life Benchmarks (link).
- California Department of Pesticide Regulation's Aquatic Life Benchmark Alternatives (Luo et al. 2013)

Table 5.4 lists the water quality objectives for methylmercury that will be used in evaluations of Delta RMP data. In addition to these water quality objectives, the Methylmercury TMDL includes implementation goals for largemouth bass (0.24 mg/kg in 350 mm largemouth bass) and unfiltered methylmercury in water (0.06 ng/L).

6. Project Tasks Description

6.1 Water Quality Monitoring Overview

The Delta RMP is one of several ongoing water-quality monitoring programs in the Delta. In terms of budgets, it represents less than 10% of all Delta monitoring (Jabusch and Gilbreath, 2009). Therefore, the Program seeks to complement existing programs and address gaps in existing monitoring, rather than to comprehensively address every water quality challenge described above.

The Delta RMP collects water quality data to address high-priority management decisions identified in Section 5.1. The current Delta RMP monitoring design is predominantly aimed at understanding the status and trends or impacts of three classes of pollutants: (1) pesticides and aquatic toxicity, (2) mercury, and (3) nutrients (nitrogen and phosphorus).

The pesticides monitoring element includes chemical analyses and toxicity testing. The chemical analyte groups for this monitoring element include several classes of chemicals that are referred to throughout this document as pesticides, including insecticides, herbicides, fungicides, and other compounds in products that are licensed and sold to farmers and residents in California.

Mercury monitoring includes sampling of sport fish, water, and prey fish, and addresses the highest priority information needs related to the implementation of the Methylmercury TMDL.

Nutrient monitoring in FY20-21 consists of two studies: 1) “Cyanotoxin Monitoring in the Delta: Leveraging existing USGS and DWR field efforts to identify cyanotoxin occurrence, duration, and drivers” and 2) “Source Tracking of the Cyanobacteria Blooms in the Sacramento-San Joaquin Delta.” Quality assurance documentation for the cyanotoxin study is provided in other documents as follows:

Determination of Cyanotoxins SOPs

- Streptavidin Amplification Enhanced Sensitivity Enzyme-Linked Immunosorbent Assay for the Congener-Independent* Determination of Microcystins and Nodularins in Water Samples
- Enzyme-Linked Immunosorbent Assay for the Determination of Anatoxin-a* in Water Samples
- Enzyme-Linked Immunosorbent Assay for the Determination of Cylindrospermopsin in Water Samples
- Enzyme-Linked Immunosorbent Assay for the Determination of Saxitoxin (PSP) in Water and Contaminated Samples

- Method 545: Determination of Cylindrospermopsin and Anatoxin-a in Drinking Water by Liquid Chromatography Electrospray Ionization Tandem Mass Spectrometry
- (LC/ESI-MS/MS)
- Method 544: Determination of Microcystins and Nodularin in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/ESI-MS/MS)
- Standard Operating Procedure for Solid Phase Adsorption Toxin Testing (SPATT) Assemblage and Extraction of HAB Toxins

DWR SOPs

- DWR EMP Field and Laboratory Manual
- QAPP for the Phytoplankton Monitoring of the EMP

The Source Tracking of the Cyanobacteria Blooms study is funded as a Supplemental Environmental Project and per Steering Committee direction a QAPP is not required.

Table 6.1 provides a complete list of target constituents for the current implementation of the Delta RMP.

6.2. Constituents to be Monitored and Reported

Table 6.1 lists the water quality constituents that will be measured in mercury and pesticide monitoring by the Delta RMP in FY20-21.

Some pesticides that the Program monitored from 2015–2017 were *dropped* from the analyte list from October 2018 onward. The Organic Chemistry Research Laboratory (OCRL) decided to remove several compounds from their methods list that had not been detected in any of their monitoring in 2015-2017, and which were not present in actively registered products with EPA in the period. The following 13 compounds were removed as of October 2018 (this list includes the Chemical Abstracts Service Registry Number, or CASRN, for reference).

1. Alachlor, CASRN: 15972-60-8
2. Azinphos methyl, CASRN: 86-50-0
3. Azinphos methyl oxon, CASRN: none
4. Bromuconazole, CASRN: 116255-48-2
5. Butylate, CASRN: 2008-41-5
6. Fenarimol, CASRN: 60168-88-9
7. Fenthion, CASRN: 55-38-9
8. Flusilazole, CASRN: 85509-19-9
9. Methidathion, CASRN: 950-37-8

10. Molinate, CASRN: 2212-67-1
11. Pebulate, CASRN: 1114-71-2
12. Tetradifon, CASRN: 116-29-0
13. Thiazopyr, CASRN: 117718-60-2

We have kept these old analytes in Table 5.3 as a reference to the data developed by the Program.

The OCRL also *added* new analytical capabilities beginning in October 2018. The lab added 20 current use pesticides that are permitted for use nationally and in California, and were regularly applied in 2015-2017, according to the California Department of Pesticide Regulation's Pesticide Use Reporting (PUR) database. The *new* analytes are (see Table 5.3 for ecotoxicological screening values and Table 7.3(b) for detection limits and methods):

1. Acetochlor, CASRN: 34256-82-1
2. Benzovindiflupyr, CASRN: 1072957-71-1
3. Carboxin, CASRN: 5234-68-4
4. Chlorfenapyr, CASRN: 122453-73-0
5. Dichlorvos, CASRN: 62-73-7
6. Etoxazole, CASRN: 153233-91-1
7. Flubendiamide, CASRN: 272451-65-7
8. Fluopyram, CASRN: 658066-35-4
9. Flupyradifurone, CASRN: 951659-40-8
10. Imidacloprid urea, CASRN: 120868-66-8
11. Indaziflam, CASRN: 950782-86-2
12. Isofetamid, CASRN: 875915-78-9
13. Oxathiapiprolin, CASRN: 1003318-67-9
14. Penthiopyrad, CASRN: 183675-82-3
15. Pyriproxyfen, CASRN: 95737-68-1
16. Sulfoxaflor, CASRN: 946578-00-3
17. Tebufenozide, CASRN: 112410-23-8
18. Thiamethoxam Degradate (CGA-355190), CASRN: 902493-06-5
19. Thiamethoxam Degradate (NOA-407475), CASRN: NONE
20. Tricyclazole, CASRN: 41814-78-2

6.3. Geographical and Temporal Setting

The geographic scope of the Delta RMP encompasses the legal Delta (as defined by Section 12220 of the Water Code), as well as water bodies that directly drain into the Delta, the Yolo

Bypass, and Suisun Bay (Figure 6.1). The Delta Primary Zone encompasses approximately 500,000 acres of waterways, levees, and farmed lands, including the Yolo Bypass. Most of Yolo Bypass is located within the Primary Zone. The Secondary Zone includes approximately 250,000 acres that are surrounding the Primary Zone and are subject to increasing urban and suburban development. Suisun Marsh on the northern side of Suisun Bay consists of approximately 110,000 acres of managed wetlands. The southern side of the Suisun Bay shoreline encompasses additional tidal wetlands as well as urban, suburban, and industrial areas.

Water dynamics in the Delta and Suisun Bay are governed by inflows from the Sacramento and San Joaquin watershed, tidal exchange with the Pacific Ocean, and water withdrawals for municipal and agricultural use. The main tributaries are the Sacramento River and the San Joaquin River. Additional tributaries include the Mokelumne River, Cosumnes River, Calaveras River, Bear Creek, Marsh Creek, Cache Creek, Putah Creek, and Ulatis Creek. Flows from the Sacramento River, San Joaquin River, and other tributaries are transported across the Delta through a complex network of rivers, channels, and flooded islands, before entering Suisun Bay or the intakes of the federal and state water projects. Flows in the Delta are highly seasonal and peak in the spring and early summer when snowmelt waters from the upper watersheds arrive.

Important human activity and land use impacts in the Delta and Suisun Bay include the presence of urban and agricultural contaminants throughout the system, habitat loss, and alterations to the amount, duration, direction, and timing of water flows. In addition, more than 200 intentionally or accidentally introduced non-native species are residing in the project area.

6.3.1. Delta Subregions for Pesticides and Toxicity Sampling

For monitoring of pesticides and aquatic toxicity, all samples will be collected from within the legal boundaries of the Delta (Figure 6.1).

Previous efforts by both the Delta RMP and the CVRWQCB have divided the Delta into roughly similar subregions based on hydrology and management practices. The Delta RMP has divided the Delta into 6 subregions based on the contribution of source waters, as described in the 2018 report *Modeling to Assist Identification of Temporal and Spatial Data Gaps for Nutrient Monitoring* (Jabusch, Trowbridge, Heberger, and Guerin 2018). The rotating basin monitoring design for pesticides and toxicity includes monitoring random points selected within waterways in each of the 6 subregions shown in Figure 6.2. Geographic data files (shapefiles) of the subregions are available upon request to the SFEI-ASC project manager, Jamie Yin, jamiey@sfei.org.

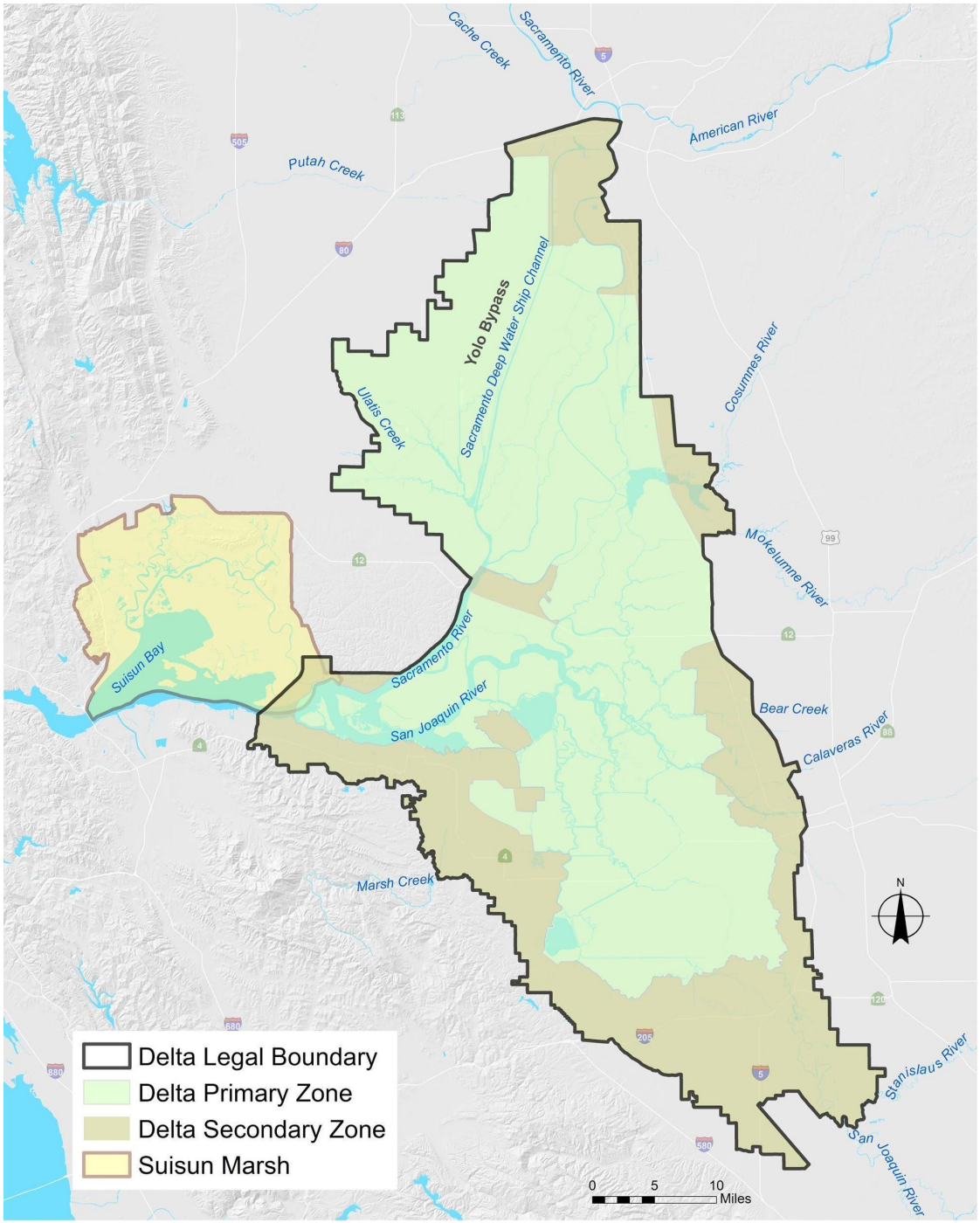


Figure 6.1 T he geographic scope of the Delta RMP encompasses the legal Delta (as defined by section 12220 of the Water Code), including water bodies that directly drain into the Delta, Yolo Bypass, and Suisun Bay.

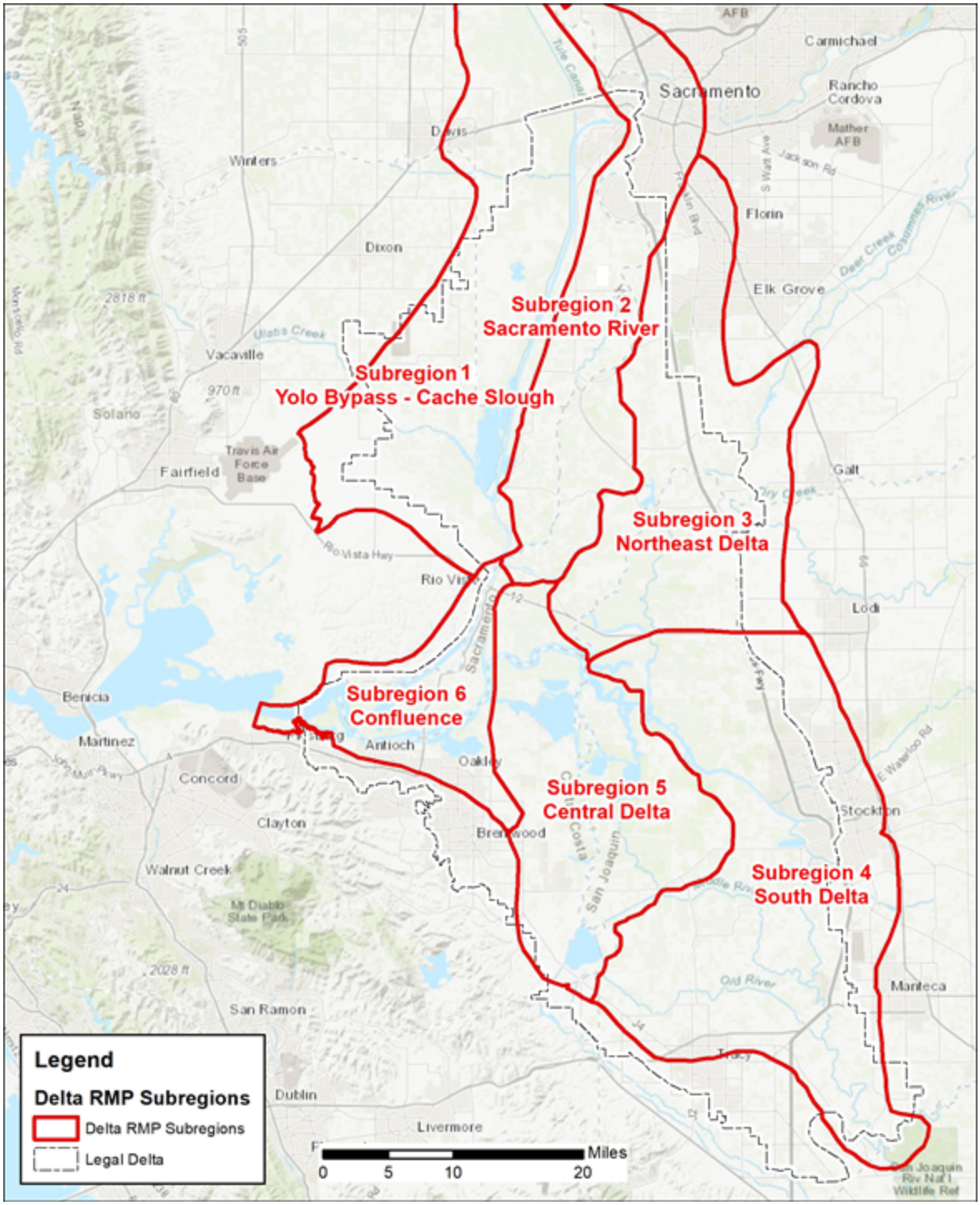


Figure 6.2 Map of Delta RMP subregions for pesticides and toxicity sampling.

6.3.2. Temporal Scope

Delta RMP Status & Trends monitoring is ongoing. Budgets are approved annually by the Steering Committee. A first phase of monitoring of mercury in sport fish and water was conducted through 2019, in order to inform a re-opening of the Methylmercury TMDL. The second phase will include continued monitoring of mercury in largemouth bass, continued monitoring of water but at a lower level of effort than the first phase, and will add monitoring of the impacts of wetland restoration projects on accumulation of mercury in prey fish and largemouth bass.

The monitoring design for pesticides and toxicity was planned to occur over a 4-year cycle with year 1 beginning in October 2018 and ending in September 2019 (Water Year 2019). Surface water samples for toxicity testing and pesticide analyses are collected in 6 sampling events during each water year. Samples are collected over the course of 2 to 3 days during each monitoring event. These events represent times of interest such as high agricultural and/or urban irrigation, periods of high flow, or following storms when pollutants are flushed from land surfaces into waterways via overland flow and drains. The specific timing for sampling events for pesticides and toxicity testing has been planned in collaboration with Delta RMP Pesticides Subcommittee and Delta RMP science advisors as documented in Section 6.4.3.

6.4. Monitoring Design

Delta RMP monitoring covered by this document includes separate "projects" covering (1) mercury and (2) pesticides and toxicity. The monitoring design for each constituent group is described below.

6.4.1. Mercury

The sport fish samples for mercury analyses are collected annually from fixed stations that represent different subareas of the Delta. Surface water samples for mercury analyses are collected from fixed stations that generally align with the Delta RMP sport fish monitoring stations. The schedule for monitoring has varied from one year to the next based on budgets and priorities, as shown in Table 6.2b and Table 6.2c.

The Central Valley Regional Water Quality Control Board has divided the Delta into eight subregions for assessing and managing methylmercury impairment (shown in Figure 6.3a). The sampling design was developed with consideration given to distributing stations throughout these subregions, and comparing trends across the subregions.

Planned mercury sampling stations are shown in Figures 6.3a,b,c and listed in Table 6.2a. The mercury monitoring element includes sport fish sampling and water sampling in open waters, and sport fish and prey fish monitoring of wetland restoration projects. The chemical analyte groups for this monitoring element include mercury and methylmercury and ancillary parameters for water such as chlorophyll *a*, dissolved organic carbon (DOC), total suspended solids, and volatile suspended solids.

In FY20-21 sport fish monitoring is occurring at 7 core monitoring stations and 5 wetland restoration monitoring stations in September and prey fish will be sampled at 8 stations in May. A list of the target fish species and other fish collection details are included in Section 11.1.2.3. Table 6.2d provides details and rationale on the stations selected for restoration monitoring.

In reviewing the design of the prey fish monitoring, TAC members questioned whether stations in the northern Liberty Island area are too close together to show differences in mercury bioaccumulation. Particle tracking models and isotope studies have found this "stair step" region to be "hydrodynamically detached" from the rest of the northwest Delta, with low mixing and long residence times (Downing et al. 2016). This raised concerns about whether the prey fish stations in this area could be considered discrete stations that could show different patterns in fish mercury concentrations (specifically, stations 4, 5, and 6 on Figure 6.3[b}). Resource Management Associates (RMA) conducted a particle tracking simulation to investigate the hydraulic connectivity between the three sampling sites in question (Stephen Andrews and John DeGeorge, RMA, personal communication). Groups of "virtual particles" were released from each station at two-hour intervals over a day in the simulation, in order to average over the tidal conditions during each drop. Qualitative information about station hydraulic connectivity was assessed by creating an animation showing particle movement in the area, and cumulative distributions of particles impacting adjacent stations were assessed (Figure 6.3[e]). The simulation suggests there is relatively low connectivity between the stations. Particles originating from the Wildlands restoration impact other stations the most, with 13% of all particles released impacting the Liberty Island station within 5 days of release. This suggests these stations are independent enough of one another to justify sampling at all three sites. This is further supported by a study that found differences in zooplankton community composition between nearby sites in this area (Liberty Island, Stairstep and Shag Slough sites in Kimmerer et al. [2018]).

Sediment was sampled in FY17/18, but there are no plans for continued sediment sampling.

In FY20-21, three monthly sampling events for water are planned (September 2020, March 2021, and April 2021) at seven stations (Table 6.2a). The timing of the March and April events may be adjusted (in consultation with the Mercury Subcommittee) to capture the effect of floodplain inundation in the watershed during high flow years. Scientists at Moss Landing will choose the exact dates for water sampling in collaboration with ASC Principal Investigator Dr. Jay Davis and the Delta RMP Mercury Subcommittee. Any changes to planned sample dates shall be communicated to ASC staff in a timely manner.

The overall sampling schedule is shown in Tables 6.2(a) through (c).

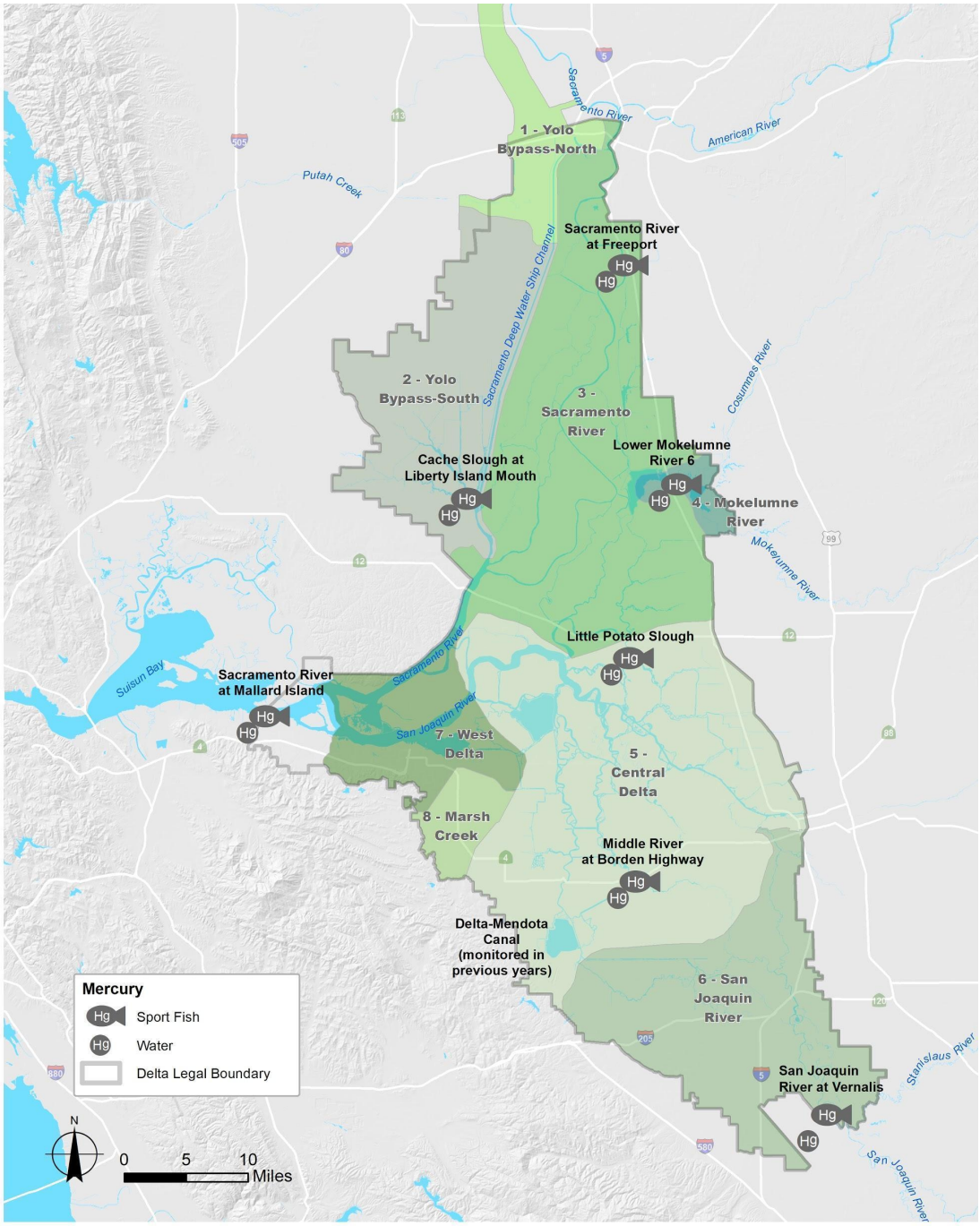


Figure 6.3 (a) Map of mercury monitoring stations: sport fish and water.

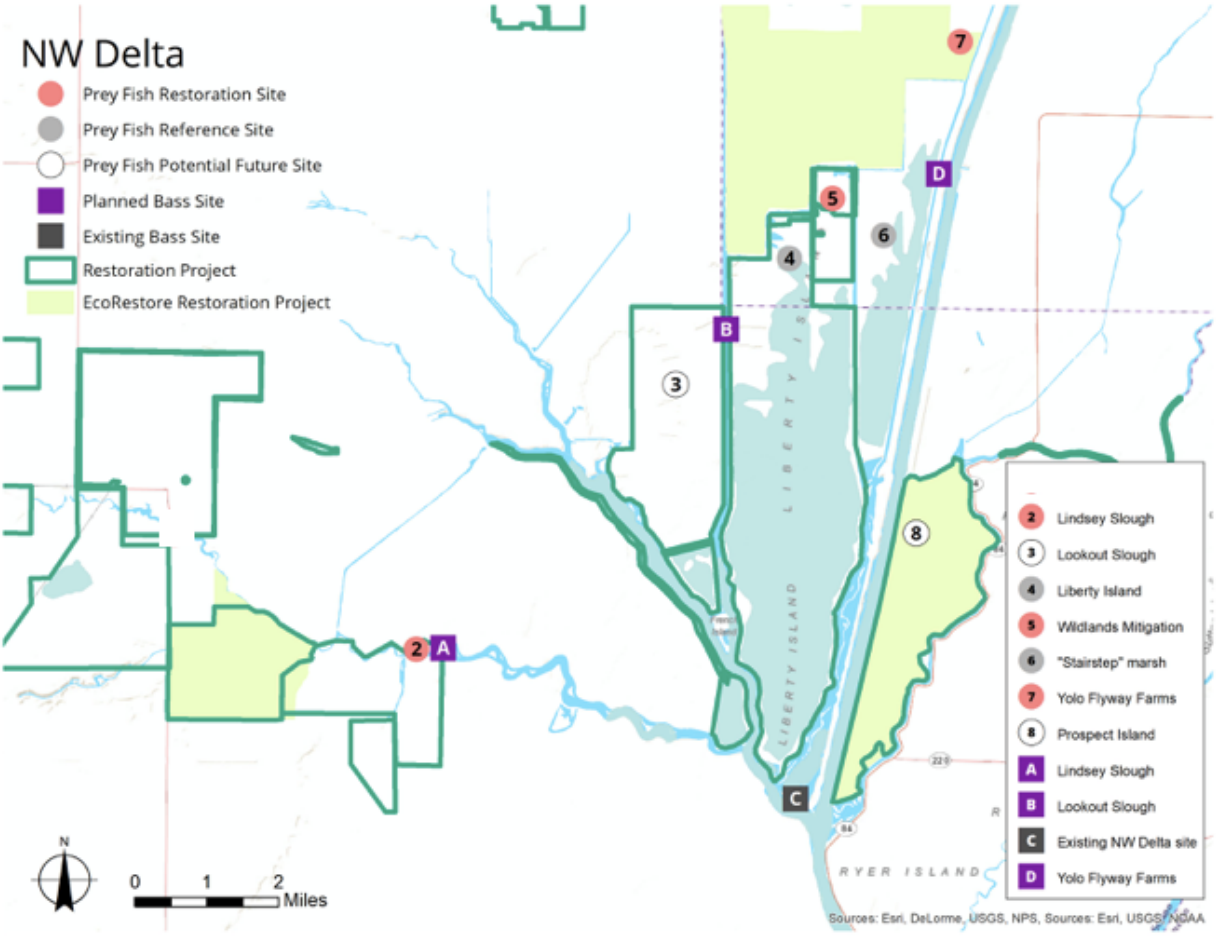


Figure 6.3(b) Map of mercury monitoring stations: restoration stations in the northwest Delta.

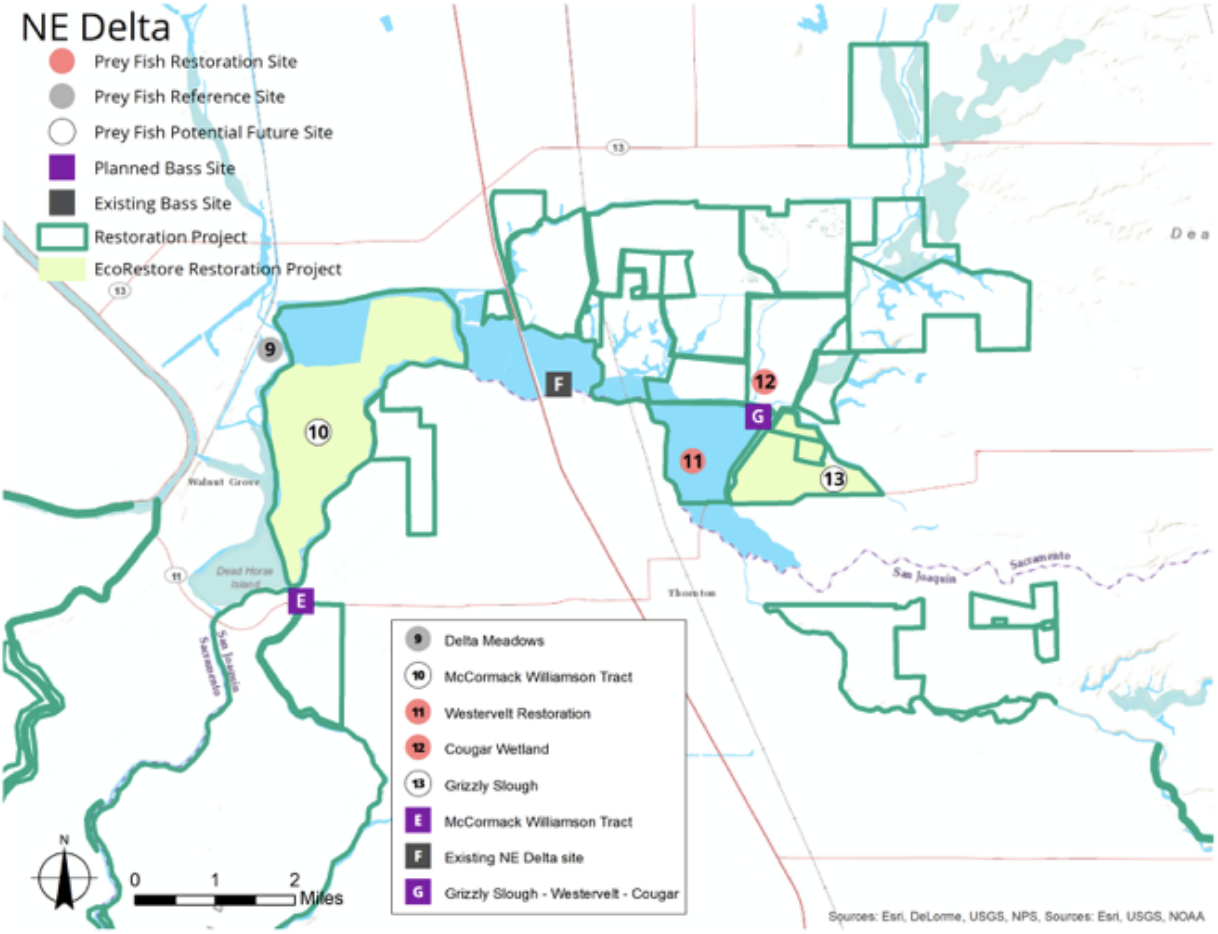


Figure 6.3(c) Map of mercury monitoring stations: restoration stations in the northeast Delta.

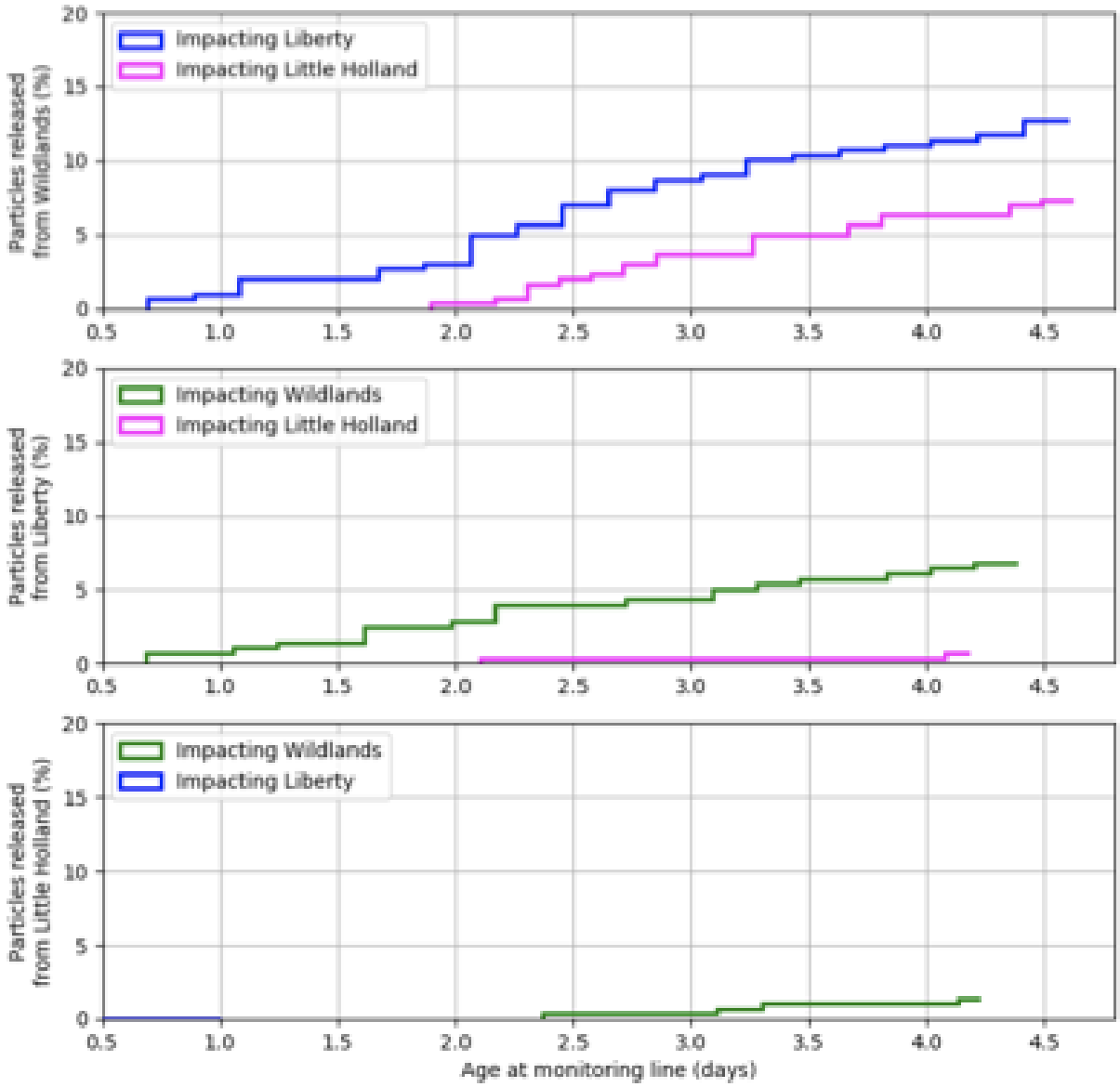


Figure 6.3(e) Plots of model hydrodynamic results showing the cumulative impact of particles at restoration stations other than their release location. Impact is shown as a percent of particles released from a station reaching each of the other two stations. Particles released from the Wildlands stations are shown in the upper plot, those from the Liberty station in the middle plot, and those from the Little Holland station in the lower plot.

6.4.3. Pesticides and Aquatic Toxicity

A "rotating basin" probabilistic monitoring design was chosen for the purpose of understanding the spatial extent of toxicity and pesticide concentrations (Table 6.3). In this instance, the "basins" are 6 Delta subregions. Under the rotating basin monitoring design, crews will collect enough samples in each subregion to adequately characterize the mean and variance of pesticide concentrations and toxicity in each subregion. Samples will be collected by boat at randomly-selected locations within each subregion. The locations and timing of sampling are described in more detail below.

In addition, the monitoring design calls for continued monitoring 6 times per year at two fixed sites. Both sites, Ulatis Creek at Brown Road and San Joaquin River at Buckley Cove, are locations where aquatic toxicity has been observed by Delta RMP monitoring in the past (see locator map in Figure 6.5). For more information on the first year of Delta RMP pesticides monitoring, see recent reports by the USGS (De Parsia et al. 2018) and SFEI-ASC (Jabusch, Trowbridge, Heberger, Orlando, et al. 2018). Fixed site monitoring allows us to detect temporal trends at these two sites as well as analyzing relationships between observed pesticide concentrations and aquatic toxicity. Sampling at the same location repeatedly holds a greater number of factors constant in comparison to the rotating basin component of the monitoring design. Any relationship between pesticides and toxicity may have less variability (i.e., less noise) and be easier to identify at fixed locations than between parameters at locations that change.

Environmental water samples will be analyzed for a suite of current-use pesticides and for chronic toxicity to 5 organisms as shown in Table 6.1.

The original monitoring design involved collecting 48 ambient surface water samples in each water year from 2019 to 2022 resulting in 24 samples being collected from each of the 6 Delta subregions after 4 years of monitoring. However, due to the COVID-19 pandemic and constraints with sampling in the spring and summer of 2020, the original sampling design that began in the 19/20 water year has been extended into the 20/21 water year to pick up in spring 2021 where the 19/20 monitoring stopped. Therefore, to complete the entire monitoring design, monitoring will occur through 2023. The monitoring design will allow project scientists to make inferences about water quality conditions across the Delta, as well as to detect differences among the subregions. If the monitoring design is continued in the future, scientists may be able to draw inferences about trends or changes over time. However, trend detection is not an emphasis of the rotating basin component of the design.

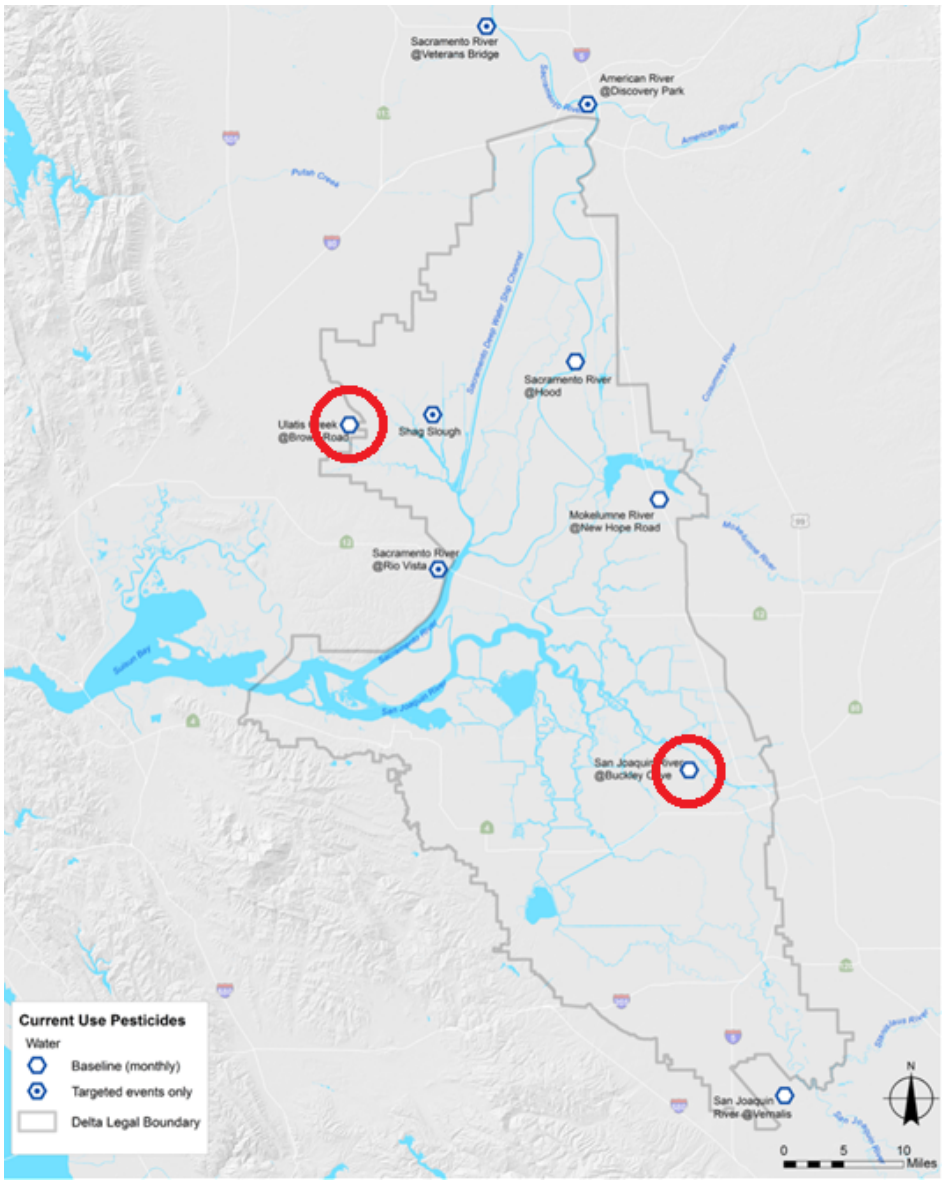


Figure 6.5 Map of Delta RMP "integrator" sites monitored for pesticides and aquatic toxicity from 2015 to 2017, highlighting the two fixed stations selected for continued sampling beginning in Water Year 2019.

Sampling Locations

Table 6.4 contains information about the sampling locations, such as the siteID (a unique identifier assigned to each location), subregion, and latitude and longitude coordinates. If a site is inaccessible, field crews will cross this site off the list, and sample the next "oversample" site on the list. Field crews should communicate this to the Program Manager.

These sampling points were created by performing five Generalized Random Tessellation Stratified (GRTS) draws using the R software. The project team selected draw #3, which looked the most "reasonable" with points reasonably spaced, and no samples appearing too close to one another. Further, it included sample points in waterways that our technical advisors deemed important such as Discovery Bay, Miner Slough, Steamboat Slough, and the Stairstep.

Before sampling, the field crew chief will inspect each point against aerial photos, and make sure it can be safely reached by boat. If in doubt, the field crew should reject the site and choose the next site on the "oversample" list.

The order of visiting sampling sites during each sampling event does not matter. Field crews should aim to collect all samples in one day, to minimize the hold times and to ensure that the toxicity tests can all be initiated in a single batch. If samples are collected on two days, separate batches may be needed for toxicity testing. The field crew may sample sites in the order that is most efficient in terms of time, fuel, and other logistical factors.

If the field crew determines that a sampling site is inaccessible or unsafe, a sample should be taken within 100 meters of the target coordinates if possible and only if there is not some obvious change in the environment, such as moving downstream of an outfall, a change in water clarity, etc. If not possible to sample within 100 m, the crew should choose the next site on the "oversample" list shown in Table 6.4.

The monitoring design calls for sampling in 2 subregions each year. Sampling began in regions 1 and 2 in Water Year 2019: (1) Yolo Bypass-Cache Slough, and (2) Sacramento River. In Water Year 2019, field crews collected a total of 24 samples in the first subregion, and 12 samples in the second subregion. In other words, the second subregion is sampled at "half intensity," with sampling split across two consecutive years. After four years, crews will have collected the desired number of samples (n = 24) in each of the 6 subregions. For subregions sampled at an intensity of n = 12 each year, crews will collect 2 samples during each of the 6 sampling events described in the following section.The detailed plan for how many samples to collect in each subregion is outlined in Table 6.5.

Field crews will collect one-sixth of the total samples during each event. For subregions being sampled at full intensity, 4 samples will be collected during each event. For subregions being sampled at half intensity, 2 samples will be collected during each event. The number of samples collected during each event is detailed in Table 6.6. This table shows the number of regular environmental samples of ambient water to be collected.

In addition, field crews shall collect field (method) blanks and field duplicate samples at a rate of 1 per 20 samples, as prescribed in Table 14.2. As the study design calls for 48 samples per

year, this translates to 3 field duplicates collected during 6 events. The suggested schedule for field duplicates is as follows:

- 1 at a GRTS site during Event 1
- 1 at San Joaquin River at Buckley Cove during sampling Event 3
- 1 at Ulatis Creek during sampling Event 5.

Adaptive management of the monitoring design is an important component of Delta RMP monitoring. Changes to the schedule described here may be made based on budgets, evolving priorities, or lessons learned from our sampling and data analysis. Changes may be made by the program manager, in consultation with the Pesticides Subcommittee. Major changes shall be subject to review by the TAC and approval by the Steering Committee. Significant changes shall be documented as an amendment to, or revision of this document.

Sampling Events

Sampling for pesticides and aquatic toxicity will be conducted over 6 events during the water year, designed to capture a range of hydrologic conditions and periods of the agricultural calendar. Among the 6 planned events, 3 are for storm sampling, and 3 for dry weather / irrigation season. It is necessary to space sampling events by at least 2 weeks so the labs can process all the samples from the previous round.

Samples will be taken on the ebb tide, if possible.

Planned timing of sampling events is shown in Table 6.7. This table shows how the six events have been designed to capture a variety of hydrologic conditions throughout the year. The timing of sampling events shall be planned by the field crews and scientists at the Organic Chemistry Research Laboratory (OCRL), in collaboration with staff of PER, to ensure that the lab is ready to accept water samples and initiate the toxicity tests. The sampling triggers for storm sampling in Table 6.7 are guidelines and may be adjusted by the project scientists based on their best professional judgment. Scheduling of sampling events and changes to the schedule shall be communicated with ASC staff in a timely manner.

Staff will maintain an online spreadsheet "dashboard" to document the planned and actual monitoring dates as they are established.

6.5. Constraints

There is a constraint related to the timing of sampling for pesticides and toxicity due to the operations of the toxicity testing lab. The monitoring design calls for collecting "split" samples

at the same place and time, and sending a portion of the sample for pesticides chemical analysis, and the other portion to the toxicity testing lab. This sample design is intended to determine whether there is a relationship between pesticides in Delta waterways and harm to aquatic ecosystems. PER will be able to accept samples any day of the week, therefore not constraining sampling time.

The ability to measure some of the target compounds at the ultra-trace levels found in the ambient environment may be constrained by the detection limits routinely achievable by analytical laboratories. Target detection limits in this document represent those achieved by laboratories contracted by the Delta RMP, or levels needed to obtain quantitative measurements of ambient concentrations in a majority of samples.

An inherent limitation of discrete samples is that they represent only a moment in time and may not represent conditions during other time periods.

6.6. Evaluation of Monitoring Data

Data analysis and interpretation in the Delta RMP provide answers to the assessment questions, and ultimately, the management questions (see Section 5.1).

Program participants develop the interpretation collectively in a science-based and collaborative process. With oversight by the TAC, program staff and contracted independent scientists conduct the relevant analyses by evaluating the data against the specific monitoring questions and benchmarks.

6.6.1. Mercury

The mercury monitoring is designed to answer the specific monitoring questions listed in Section 5.1.2 and Table 5.1. Mercury concentrations in largemouth bass will be evaluated for interannual trends in time series and compared to the TMDL implementation goal of 0.24 mg/kg in 350 mm largemouth bass. Water concentrations for unfiltered methylmercury will be compared to the TMDL implementation goal of 0.06 ng/L. Water concentrations for unfiltered and filtered methylmercury and unfiltered and filtered total mercury will be compared to past data to evaluate trends. Concentrations in water will also be related to concentrations in fish in order to update the TMDL linkage analysis. A better understanding of the linkage, or relationship, between aqueous mercury and the concentration in fish tissue is an important goal of this study.

Monitoring of sport fish and prey fish will also be conducted to assess whether wetland restoration projects in the Delta are influencing spatial and temporal patterns in

bioaccumulation. Concentrations in sport fish at stations near restoration projects will be compared to concentrations in sport fish at the core stations and historic data. Concentrations in prey fish at restoration projects will be evaluated relative to concentrations in prey fish at "comparison" stations in nearby wetlands and to historic data at nearby stations. Time series at each station will also provide insight into the influence of the restoration projects.

6.6.3. Pesticides and Aquatic Toxicity

A better understanding of the effects of contaminants in the apparent decline of Delta ecosystems is a priority for regulators and stakeholders. Pesticide use in the Delta and Central Valley is one of the potential drivers of these effects. One of the goals of toxicity testing is to determine whether Delta waterways contain toxic substances in toxic amounts that are impairing the attainment of beneficial uses such as fish and wildlife habitat.

The overall objective of the Delta Regional Monitoring Program's (Delta RMP's) Current Use Pesticide (CUP) monitoring program is to collect ambient surface water samples to answer the program's Management and Assessment Questions (Appendix B and Appendix C). The management and assessment questions are broad and the Delta is large, so addressing them will require a correspondingly large effort over the course of several years. The study design was developed to make the best use of available funding to answer the highest priority Management and Assessment Questions in an initial effort to characterize the status and trends of pesticide concentrations and toxicity in the Delta.

6.7. Products and Reporting

Table 6.8 provides a summary of key products of the Delta RMP. Data from Status and Trends monitoring efforts will be made available annually for download via:

- SFEI's Contaminant Data, Display and Download tool (CD3)
- The California Environmental Data Exchange Network (CEDEN)
- The California Estuaries web portal (link)

Data are planned to be reported in annual data reports and constituent-specific technical reports (i.e., reports on mercury, pesticides/toxicity, or nutrients) (every 2-3 years).

Provisional and final data will be made available for review and public release in a timely manner that will allow the Regional Board to be responsive to water quality concerns.

Technical reports will provide a more in-depth evaluation of monitoring and special study results. These reports will facilitate technical review of Delta RMP studies and are targeted to a

technical audience. The annual reports and 3-year interpretive technical report for mercury will be prepared by staff from ASC and MPSL. Reports for mercury and pesticides will be submitted first to the Mercury and Pesticide Subcommittees, respectively, and then to the TAC for technical review.

6.7.1. QA Summary Report

The Project QA officer or designee shall write a report for each dataset outlining the quality of the data (for disciplines other than toxicity testing). This report highlights any issues that were addressed by the laboratory, project manager, or data management staff. The QA Summary Report includes the following details:

- Lab
- Matrix
- Analyte
- Reporting Issues for Lab to Review
- Formatting Issues for Data Manager to Review
- QA Review:
    - Dataset completeness
    - Overall acceptability
    - MDLs sensitivity
    - Blank sample averages and ranges (lab method blanks, field created blanks)
    - Precision averages and ranges from replicate field samples
    - Accuracy (using a variety of standard reference materials or matrix spike quality assurance recoveries)
    - Comparison of dissolved and total phases
    - Comparison of results to previous year's observations

The QA summary report will be reviewed and approved by the QAO and program manager, and is typically included in a year-end data report as an appendix. These reports are reviewed by the Delta RMP TAC and the Steering Committee.

Annual data reports are planned to describe chemical analyses for each of the focus areas (e.g., pesticides, toxicity, mercury, etc.). Monitoring data (and associated metadata) that meet predetermined MQOs will be made available to the Regional Board and made publicly accessible no more than [one year] after sample collection.

7. Quality Objectives and Criteria

7.1. Data Quality Objectives

Data Quality Objectives (DQOs) aim to support defensible conclusions that address the management and assessment questions in Appendix B and Appendix C.

7.1.1. Pesticides

The overall objectives of the Delta RMP's Current Use Pesticide (CUP) monitoring program are to collect ambient surface water samples to answer the Program's Management and Assessment Questions. The management and assessment questions are broad and the Delta is large, so addressing them will require a correspondingly large effort over the course of several years. The study design was developed to make the best use of available funding to answer the highest priority Management and Assessment Questions in an initial effort to characterize the status and trends of pesticide concentrations and toxicity in the Delta.

The priority questions driving the design for the CUP study are:

ST1. To what extent do current use pesticides contribute to observed toxicity in the Delta?

ST1.1 - If samples are toxic, do detected pesticides explain the toxicity?

ST1.2 - What are the spatial and temporal extent of lethal and sublethal aquatic and sediment toxicity observed in the Delta?

ST2 - What are the spatial/temporal distributions of concentrations of currently used pesticides identified as possible causes of observed toxicity?

Data quality objectives (DQOs) for the pesticides and toxicity monitoring program are shown in Table 7.1. The decision rules in Table 7.1 anticipate that parametric statistical methods will be used. If data are non-normally distributed or regression residuals are non-normal, there may be a need to use nonparametric statistical analysis methods. Nonparametric methods may require larger sample sizes to answer the assessment questions listed in Table 7.1. The table shows tolerable limits on decision errors (referred to by statisticians as *alpha* and *beta*) based on commonly used assumptions in similar scientific studies. The planned study calls for a statistical significance level (alpha) of 0.05 for a one-tailed hypothesis test. For example, suppose you are testing whether more than 1% of river miles have a pesticide concentration exceeding a screening value. With alpha = 0.05, there is a 5% chance of a false positive with hypothesis testing (incorrectly concluding that concentrations in these river miles exceed the screening value.) The choice of beta of 0.2 is the probability of a false negative. Statistical power is 1 – beta

or 0.8. This means, for example, that you have a 20% chance of incorrectly concluding that a predicted pesticide concentration does not exceed a screening value.

Water quality screening values– The simplest and most straightforward way of determining whether a chemical may be causing an adverse impact on a waterway is to compare observed concentrations to a water quality standard or benchmark. When such a value has the force of law, it is referred to as a standard, or in California, a water quality objective. However, state and federal regulators have written standards for only a few current use pesticides. For example, the CVRWQCB has established water quality objectives for chlorpyrifos and diazinon that cover much of the Central Valley including the Delta.[1] For the hundreds of other current use pesticides, there are neither national water quality criteria recommended by the EPA, nor are there state water quality objectives.

Comparing ambient concentrations to other benchmarks, or screening values, is a useful first step in the process for interpreting pesticide data and evaluating relative risk. The choice of a screening value is important. If our monitoring shows that concentrations exceed a conservative screening value, the implication is that there may be a problem. Whereas, chemicals with concentrations below conservative screening values can be determined with confidence that they are not likely to be impairing beneficial uses. The choice of screening values is a complicated technical question. *Project scientists have not explicitly defined screening values for pesticides*, in part because this work is ongoing, as part of an analysis of pesticides and toxicity data contracted by the Delta RMP to the firm Deltares.

Options for setting screening values include aquatic life (AL) benchmarks published by the US EPA Office of Pesticide Programs (OPP). OPP benchmarks were developed by the EPA for use in the agency's risk assessments conducted as part of the decision-making process for pesticide registration. The OPP benchmark values are based on the most sensitive species tested within taxonomic groups (fish, invertebrates, and vascular and non-vascular plants). They represent the lowest toxicity values available from peer-reviewed data with transparent data quality standards. OPP benchmarks may or may not be useful for interpreting Delta RMP toxicity data. However, these values are broadly relevant to protecting aquatic life. It has also been suggested by TAC members that it may be appropriate to divide OPP aquatic life benchmarks by a safety factor of 5 or 10. This would be in line with the precautionary principle.

Handling of non-detects – In the first two years of pesticide monitoring by the Delta RMP, many of the pesticide chemistry results were non-detects. Statistical methods should be chosen

[1] See *Amendments to the 1994 Water Quality Control Plan for the Sacramento River and San Joaquin River Basins* (Central Valley Regional Water Quality Control Board, 2016), Table III-2A, Specific Pesticide Objectives, on page III-6.01. Chronic toxicity is based on the average concentration over a 4-day period.

carefully for handling "censored data" (Helsel 2010). Common methods used in the past, such as substitution of zero or one-half the detection limit for non-detects, are known to introduce bias in data analyses. One of our science advisors has recommended the use of the "Nondetects and Data Analysis (NADA)" package in R created by D. Helsel (USGS). Staff anticipate that useful guidance will also be developed as a part of the Delta RMP-funded interpretive report underway by Deltares. The Delta RMP TAC will continue to evaluate non-detect analysis options and provide guidance for future use of non-detect data in interpretative reports and annual summaries. All non-detects will be coded in CEDEN as less than the MDL.

7.1.2. Aquatic Toxicity

For the Delta RMP, the primary goal of toxicity testing is to determine whether pesticides are potentially causing significant aquatic toxicity in the Delta. Toxicity testing is an integrative tool because it evaluates the combined effects from multiple constituents on biota concurrently in site media, and provides an environmentally relevant understanding of the potential for beneficial use impairment. Chemical analyses are also important for understanding trends and can be compared with paired sample toxicity test data to identify which pesticides (or other parameters) might be contributing to observed effects.

Toxicity Identification Evaluations (TIEs) are an investigative tool that can be used to identify the cause of toxicity. The primary goal of Delta RMP TIE testing is to determine if pesticides (or degradates, or any of the inert ingredients in the formulated product), are contributing to observed effects.

Appendix J describes the protocol the Delta RMP will follow for deciding whether to initiate a TIE. TIEs are planned for Delta RMP samples when there is a ≥ 50 percent adverse effect observed (for *either* chronic or acute tests, at *any* point during the test, and for *all* test organisms and *all* endpoints).

TIEs shall be initiated within 48 hours of the observation of the TIE trigger being met in the initial sample screening. The primary goal of Delta RMP TIE testing is to identify whether pesticides are causing or contributing to observed toxicity, and if so, which pesticides (or degradates, or any of the inert ingredients in the formulated product) are the drivers. Potential toxicity drivers may be determined (via weight of evidence) from the TIE, paired chemistry data, and/or with more advanced TIEs. A secondary goal is to identify other factors (i.e., water quality conditions or other toxicants) contributing to reduced survival, growth, or reproduction.

Table 14.3 and Table 14.4 outline the data quality indicators and MQOs for toxicity testing and water quality measurements associated with the toxicity testing procedures**.** Test methods shall

follow USEPA (2002) and SWAMP guidance (most recent version dated August 22, 2018).[2] Test results will be rejected when test acceptability criteria are not met. However, a sample may be retested and qualified as having exceeded the recommended hold time if the ProgramManager and the Pacific EcoRisk project director and project manager agree on the need for additional testing/retesting.

7.1.3. Mercury

The Delta Methylmercury TMDL uses a tissue-based implementation goal of 0.24 ppm in 350 mm largemouth bass to determine impairment within Delta subregions. Monitoring of mercury concentrations in sport fish tissue as an index of mercury impairment in the Delta and as a performance measure for the TMDL was identified by the Delta RMP as a priority data need.

The priority assessment question driving the design for the methylmercury monitoring is:

ST1. What are the status and trends in ambient concentrations of methylmercury and total mercury in sport fish and water, particularly in subareas likely to be affected by major existing or new sources (e.g., large-scale restoration projects)?

ST1.A. Do trends over time in methylmercury in sport fish vary among Delta subareas?

ST1.B. Do trends over time in methylmercury in water vary among Delta subareas?

The initial and preliminary data quality objective (DQO) for subregional bass trend monitoring is the ability to detect a trend of mercury in 350 mm largemouth bass of 0.040 ppm/yr. This DQO will be refined when additional data are available. MQOs are identical to those used in other mercury studies throughout the state for determinations of impairment and trend detection. These MQOs generally call for indices of accuracy and precision to be within 30% of expected values.

The Delta Methylmercury TMDL describes a statistically significant relationship between the annual average concentration of methylmercury in unfiltered water and average mercury in 350 mm largemouth bass, when data are organized by subarea. The linkage of aqueous methylmercury concentration to fish mercury concentration provides a connection between methylmercury inputs from various in-Delta pathways (e.g., municipal wastewater, municipal stormwater, agricultural drainage, and wetlands) and impairment of beneficial uses. Because of this linkage, the Delta Methylmercury TMDL established an implementation goal of 0.06 ng/L of

[2] https://www.waterboards.ca.gov/water_issues/programs/swamp/swamp_iq/docs/chronic_freshwater_tox_mqo_082218.pdf

unfiltered aqueous methylmercury[3,4]. Monitoring of fish mercury and aqueous methylmercury is needed to: better quantify the fish-water linkage that is the foundation of the TMDL; support development of a mercury model for the Delta; support evaluation of the fish data by providing information on processes and trends; and provide mass balance data for re-evaluation of the Delta Methylmercury TMDL, when it is updated. The aqueous methylmercury data are not intended for use for a rigorous evaluation of interannual trends.

Restoration monitoring with prey fish addresses questions relating to SPLP, Forecasting Scenarios, and Effectiveness Tracking. The basic concern with restoration projects is that they may enhance net methylmercury production within the Delta ecosystem, and represent an internal source that increases as projects proceed (SPLP Question 1B: How do internal sources and processes influence MeHg levels in fish in the Delta?) – restoration monitoring will track whether this occurs or not. Restoration monitoring will yield insights into which types of projects, if any, impact net methylmercury production and food web accumulation (Forecasting Scenarios Question 1: What will be the effects of in-progress and planned source controls, restoration projects, and water management changes on ambient methylmercury concentrations in fish in the Delta?) and whether internal loadings change and ambient water quality shows net improvement as a result of restoration projects (Effectiveness Tracking).

For restoration monitoring with prey fish to answer sub-questions calling for comparisons among stations over time and space, based on data collected for the same target species with the same design in the North Bay Biosentinel Project, ANOVAs to detect differences in means across groups of stations will have high power (> 0.99), and pairwise comparisons will have 80% power to detect a difference of 0.023 between stations or time intervals.

$$\sum_{k} | \ |$$

7.2. Data Quality Indicators

Data Quality Indicators (DQIs) are the quantitative measures and qualitative descriptors used to set limits of acceptable levels of data error. The principal data quality indicators are precision, accuracy/bias, comparability, completeness, and representativeness (SWRCB 2017).

[3] For methylmercury, aqueous samples should be analyzed using USEPA method 1630 with a method detection limit of 0.02 ng/L or less. For total recoverable mercury, aqueous samples should be analyzed with a method detection limit of 0.2 ng/l or less.

[4] The preferred method for total mercury is USEPA Method 1631 Revision E. If quality control objectives are not being met (for example, recoveries in matrix spike samples are outside of expected limits) and matrix interferences are suspected as the cause, USEPA Method 245.7 may be used, if detectable concentrations are within the range of the method's calibration and quality control criteria.

- **Precision** describes how close the agreement is between multiple measurements (SWRCB 2017).
- **Accuracy (Bias)** is the assessment of the closeness of agreement between a measured or determined value and the true value. Bias is the quantitative measure of the difference between those values (NDT 2016).
- **Comparability** expresses the measure of confidence that one dataset can be compared to and combined with another for a decision(s) to be made (US EPA QA/G-5 2002).
- **Completeness** refers to the comparison between the amount of valid data originally planned to be collected, and the actual quantity collected (US EPA QA/G-5 2002).
- **Representativeness** is the degree to which measurements correctly represent the environmental condition, target organism population, and/or watershed to be studied (US EPA QA/G-5 2002).
- **Sensitivity** is the ability of a measurement to detect small quantities and differences in concentration of the measured component.

7.3. Field Quality Control Measurements for Sensors and Sample Collection

7.3.1. Field Measurements

Precision of field measurements is determined by repeated measurement of the same parameter within a single sample, or samples taken in rapid succession (only when conditions are not dynamically variable). The project will address the precision of field measurements by performing replicate measures at the required intervals described in Section 14.1, Field Measurements.

Accuracy of field measurements is established by calibration and tested by periodic measurement of known standards. The project will perform instrument calibration prior to each sampling day or event for user-calibrated instruments (e.g. daily for handheld field meters), or at the manufacturer-specified interval for instruments requiring factory servicing or otherwise incapable of field calibration. All instruments undergo blank and calibration checks as described in Table 14.1.

Instruments will also be visually inspected for fouling at the checkpoints and cleaned if necessary. Fouling and drift of instruments may occur due to electrical, optical, and/or communication issues, but redundant measurements can distinguish such issues from environmental variability. Additionally, grab samples are collected for laboratory analysis to ground-truth environmental measurements.

Completeness of field measurement is evaluated as the percentage of usable measurements out of the total number of measurements desired. The project will ensure that at least 90% of the planned field measurements are collected and are usable. If a lower percentage is achieved for any sampling event or time period, causes shall be investigated and fixed where possible, through instrument maintenance (e.g. defouling), recalibration, repair, or replacement (with the same or different instrument type) as needed. If completeness targets are not achieved, instrument choice, settings, deployment method, maintenance, and/or other activities shall be adjusted to improve measurement reliability before the next sampling event or measurement period.

Comparability of field measurements will be ensured by using protocols (see Section 23) and QA standards that are comparable within the project and to similar monitoring projects in the study area.

Representativeness of field measurements will be ensured by utilizing standardized protocols (Section 23) and selecting representative monitoring sites and underway paths to support the project management questions (Section 5.1). Conditions that may influence the measurements will be noted in the database and measurements may be retaken if necessary.

Sensitivity is most commonly defined as the lowest value an instrument or method can measure with reasonable statistical certainty (SWRCB 2017) as well as the ability of the instrument to detect small changes. Where applicable, the desired sensitivity is expressed as a target detection limit (Section 6.2) and resolution of a deployed sensor. For this project, sensors will be used that meet the DQOs.

7.3.2. Field Sample Collection

Precision of the field sample collection will be evaluated by collecting field duplicates/replicates (for water and sediment samples). Replicate (e.g., duplicate) samples account for variability in the field collection and laboratory analysis combined and are collected at the same time under the same conditions as the original sample. Different ways of collecting replicate field samples are possible, and include different factors contributing to sample variability. For the purposes of this project, we use the following terminology:

- Field split - in CEDEN: “Single sample collected and then split to multiple separate jars.” These are similar to splits made in an analytical lab, with the primary differences being the party performing the splitting, the location where it is done, and the time it is done. For this project, two bottles simultaneously filled from a single pump using a Y-splitter are considered a field split; likewise a cluster of bottles on a sampler rosette all filled at the same time and depth. However, this SampleType has been end-dated by CEDEN

(retained in historical data, but inactive/unusable for new entries), so field splits are distinguished by incrementing the LabReplicate count.

- Field replicate - these do not have a separate code or definition in CEDEN, and just maintain the same SampleType (e.g., Grab, Integrated), incrementing in Replicate count. For this project we use "field replicate" to indicate separate samples collected from the field for a given site and event. These capture not just the heterogeneity of subsampling or splitting the sample matrix, but also the spatial and temporal variation in collection within a given site for a collection event. Sequential filling of sample bottles (if separated by >1 minute in collection time) is considered a field replicate rather than a field split. Similarly, reloading and redeploying a sampler rosette would yield field replicates; however, all the bottles on the rosette for each given deployment would be considered field splits of each other.

Minimum frequencies and target performance requirements for field replicates are described in Table 14.2.

Contamination. In the field, contamination of field samples can be introduced by sampling equipment or personnel during field sample collection, in addition to any contamination already present in the sampling container or blank water used. Naming conventions for blanks will differ among projects, so here we define their usage for this project based upon CEDEN descriptions. Although the CEDEN definitions were made with water analyses in mind, for solid phase samples it will be more appropriate to extract an empty bottle (null matrix), as added laboratory water not in samples will interfere with extraction or introduce contaminants if the laboratory water is not normally used in sample processing.

- Bottle blank - in CEDEN: "An analyte-free water sample prepared in the laboratory and used to evaluate potential contamination due to sample container or laboratory cleaning methods."
- Travel blanks - in CEDEN: "Clean water transported to site, handled like sample (never opened), and returned to laboratory for analysis". These account for contaminants introduced during the transport process between the laboratory and field site, in addition to any contamination from the source solution and container.
- Field (ambient) blank - in CEDEN: "Clean water taken to field, transferred to container, preserved (if appropriate) and treated same as corresponding sample type during the sampling event." These add exposure to the field sampling environment, in addition to those included in travel blanks. The "treated same as" part of the description is interpreted for the purposes of the Delta RMP as applying to steps only after the blank is in the container (i.e., not exposed to or transferred by field sampling equipment). Field

blanks collected using field equipment are instead listed as "(field) equipment blanks" (defined below).

- Equipment blank - in CEDEN: "Clean water pumped through new equipment, cleaned equipment after contamination, equipment for non-surface water, new lot of filters (metals), preserved (if appl.) and analyzed". CEDEN instructs to note in the comments field the equipment type and whether these are done in the lab or field.

To collect a field blank, reagent grade water provided by the analytical lab, shall be transferred into a sample container provided by the analytical laboratory WITHOUT using the usual collection equipment, but treated the same as field samples after collection. Since this does not include any field equipment, a field blank can be collected any time while at a field site.

Any field equipment blanks for equipment used a single time within an event, can be collected at any point during sample collection, but ensure the sample is collected using cleaned or new equipment. For equipment used for multiple sites before replacement or recleaning at a lab, equipment will be field cleaned or flushed as usual between sites, except where site-water is normally used, using blank water instead.

Field blanks (NOT including equipment) will be obtained for each sampling event, unless a lab or principal investigator opts (based on past experience or best professional judgement) to collect field equipment blanks instead. Minimum frequencies and target performance requirements for field (ambient) blanks, travel/bottle blanks, and field equipment blanks are described in Table 14.2.

Neither bottle blanks nor travel blanks are required as part of this project at the present time. The SFEI-ASC QAO may decide to reinstate these other types of blanks in the future, for example when an established procedure is changed or when contamination problems are identified. In some cases, field-generated equipment blanks may be substituted for field blanks, but must be approved by the Delta RMP PM and QAO.

Accuracy. Field blank or equipment blank contamination discussed previously will also affect the accuracy of measurements, usually causing a high bias in reported concentrations. Matrix interference by various environmental substances will also cause high biases (by being mistaken for target compounds) or low biases (by competition for or consumption of reagents, or attenuating measured signals). Similarly biotic and abiotic reactions in the sample due to improper preservation and/or extended storage will cause loss of some target analytes, or generation of others (e.g. metabolites or degradates). Minimum frequencies and target performance requirements for matrix spike samples are described in Table 14.2.

7.4. Chemistry Laboratory Quality Control Measurements

The discussion in this section reviews the measurements and procedures expected to demonstrate the quality of reported data. Table 7.2 provides an overview of quality control (QC) sample types and their purpose. The quality assessment process that is used after the data have been collected to evaluate whether the Data Quality Objectives (DQOs) have been satisfied is described and illustrated in Section 22, Data Review, Verification, and Validation.

Prior to the initial analyses of samples for the project, each laboratory will demonstrate capability and proficiency for meeting MQOs for the Delta RMP. Performance-based measures for chemical analyses consist of two basic elements: initial demonstration of laboratory capability and on-going demonstration of capability during analysis of project samples. Initial demonstration includes documentation that sample analyses can be performed within the measurement quality objectives and method quality objectives listed in the QAPP (Table 14.2) as well as demonstrate ability to meet the project's required reporting levels. On-going demonstration of capability during analysis of project samples includes routine analyses (e.g., intercomparison studies) that ensure on a continual basis that MQOs and RLs listed in Table 7.3 are met.

7.4.1. Laboratory QC Measurements

Accuracy (Bias) is the assessment of the closeness of agreement between a measured or determined value and the true value. Blank spikes (laboratory control samples or LCSs), matrix spikes/matrix spike duplicates (MSs/MSDs), internal standards, surrogate recoveries, initial calibration, and calibration checks will be employed to ensure accuracy of results.

Sensitivity refers to the capability of a method or instrument to detect a given analyte at a given concentration and reliably quantitate the analyte at that concentration. This project will achieve the desired sensitivity by selecting appropriate analytical methods and the laboratory will demonstrate analytical capability to meet the project DQOs and reporting limits.

Precision is the reproducibility of an analytical measure. Field samples will be utilized to perform laboratory replicates.

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). The goal of the Delta RMP is to achieve >90% completeness for all analyses.

Completeness will be quantified as the total number of usable results divided by the total number of site visits, aggregated by all analytes of interest. However, additional factors may be considered on a case-by-case basis.

Contamination. 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.

Comparability. The Delta RMP adheres to the requirements specified in the SWAMP Quality Assurance Program Plan (QAPrP), for parameters covered by the SWAMP Quality Control and Sample Handling Tables, to facilitate coordination and data integration with other water quality monitoring efforts. Specifically, the Delta RMP adheres to SWAMP requirements for QC and holding times and to California Environmental Data Exchange Network (CEDEN) requirements for data submittal.

Table 7.3 summarizes the reporting limits (RL) and method detection limits (MDL) for all laboratory measurements. Table 7.3(a) lists the RL and MDL for conventional analytes, field parameters, and trace metals. Table 7.3(b) lists the RL and MDL for current use pesticides analyzed by USGS Organic Chemistry Research Laboratory (OCRL).

Laboratory methods for analyses conducted for the Delta RMP are listed in Appendix E.

7.4.2. Laboratory Chemistry QC Samples

Data from USGS OCRL and NWQL (pesticides and ancillary chemistry) and MLML (mercury and related parameters) shall include at least the following QC data:

1. Surrogate recovery (for all environmental and QC samples, where applicable)
2. Method blank (or suitable substitute, e.g., a bottle blank or similar encountering all potential lab generated contamination experienced by samples, but no/minimal field contamination sources).
3. Matrix spike recovery (where applicable)
4. Laboratory replicate precision (environmental samples or CRM, matrix spike, blank matrix spike samples when applicable)
5. Certified/lab reference material (CRM/LRM) recovery (where applicable)

Method blanks shall be run at a minimum frequency of one per analytical batch of up to 20 field samples. Results for laboratory method blanks, combined with those for field equipment blanks, can help identify whether probable causes of sample contamination originated in the field or in laboratory analyses. If both field and lab method blanks have similar levels of contamination, it

is likely primarily from lab procedures. If field equipment blanks have higher contamination, sample collection methods are likely the cause. Results for method blanks shall be reported.

A laboratory control sample (LCS) shall be run at a minimum frequency of one per analytical batch[5] (for analytical batches consisting of up to 20 field samples). At discretion of the SWRCB QA Officer, substitution by other recovery type samples (e.g., CRM or/and MS) at a minimum one per batch frequency may be permitted. Results shall be reported along with the expected values and recoveries (as a percentage of the expected value), where available for target analytes in appropriate matrices.

Matrix spikes (MS) shall be run at a minimum frequency of one per 20 samples. Matrix spike results are to be reported, along with the expected result (unspiked sample concentration + spike concentration), and a recovery estimate. The spiking concentrations should be sufficiently high to quantify recovery (at least 3× the unspiked sample concentration) but also low enough to be a relevant accuracy indicator in the concentration range of field samples (3 - 10x the unspiked sample concentration). In cases where analytes are mostly not detected in unspiked samples, a concentration range of 10× to 100× over the MDL may be appropriate to use instead.

Precision can be determined with all sample types analyzed and reported in replicate. Lab replicates (split and analyzed in the laboratory) of field samples are generally the preferred indicator of precision for typical field samples, as the target analyte concentration range, matrix, and interferences are most similar to previous analyzed samples or samples from nearby sites. However, sometimes field sample concentrations are below detection limits for many analytes and replicate results for CRMs, LRMs, MS/MSDs, or blank spikes (LCSs) may be needed to obtain quantitative precision estimates. These alternative sample types, in particular blank spikes (LCSs), should not serve as the primary or exclusive indicator of measurement precision without prior approval by the Program Manager and QAO. LCSs are often created from a clean laboratory matrix and are likely not representative of the measurement precision routinely achievable in more complex matrices of real field-originated samples. The relative percent difference (RPD) should be calculated as described in Section 7.4.3 and reported for all samples analyzed in replicate.

[5] A batch is a set of samples that are processed together. It does not refer to samples that arrived or were delivered together. Each lab should determine what defines a batch, keeping in mind the factors that lead to significant differences in the analysis. For example, in some processes, it is the extraction that may be more critical than the instrument run/start/stop in terms of defining the method performance. Other factors could include which lab personnel perform sample preparation, temperature of the extraction, which batch of solvent, or who spiked the internal standards or prepped the calibration samples. For certain "finicky" lab instruments, stopping and restarting the instrument may make a difference; in this case, labs should define a batch that way.

7.4.3. Precision

Precision measurements will be determined on field and/or laboratory replicates. If samples other than environmental samples are used to evaluate lab precision, target concentrations should be at least high enough to be quantitative but less than 100 times those in environmental samples, as precision in high concentration samples is not likely representative for much lower ambient samples. When using MS/MSD, samples of a similar matrix are most relevant and thus preferred for evaluating precision.

A minimum of one field duplicate per 20 samples, or no less than 5%, of environmental samples will be collected, processed, and analyzed for precision. In addition, a minimum of one environmental sample (or alternative sample type such as a MS, where sample material is insufficient or target analytes are largely not detected in field samples) per batch of samples submitted to the laboratory (minimum one per 20, or 5%, in large batches) will be processed and analyzed in replicate for precision.[6] Previously analyzed material (e.g. from the same project in prior years, or from other projects) may also be analyzed as replicates to help ensure that results are in a quantifiable range. The RPD among replicate samples should be less than the MQO listed in Table 14.2 for each analyte of interest. RPD is calculated as:

$$RPD = \frac{|X_1 - X_2|}{\left(\frac{X_1 + X_2}{2}\right)} \times 100$$

where X_1 and X_2 are independent measurements of the replicate samples.

When more than two replicate samples are collected, the relative standard deviation (RSD) shall be used as a basis of comparison against the MQOs:

$$RSD = [STDEV\ (all\ replicate\ samples) \div Average\ (all\ replicate\ samples)\ ] \times 100$$

7.4.4. Accuracy

Accuracy is the closeness of a measured result to an accepted reference value. Accuracy shall be measured as a percent recovery. QC analyses used to measure accuracy include standard recoveries, laboratory control samples (LCS), spiked samples (matrix spikes and matrix spike duplicates), internal standards, surrogate recoveries, initial calibration, and calibration checks. The accuracy of lab measurements will be evaluated based on measurement quality objectives (Table 14.2).

For a matrix spike, a known quantity of an analyte added to a sample to test whether the response to a sample is the same as that expected from a calibration curve. These samples are

[6] For example, if there were 61 samples, 4 environmental samples would be processed and analyzed in replicate for precision.

useful for determining whether elements of the matrix (the remainder of the sample other than the analyte) influence the results of the measurement. The percent recovery for spiked samples is calculated using the equation:

$$\%\, recovery = \frac{\left(C_{spiked\ sample} - C_{unspiked\ sample}\right)}{C_{added}} \times 100$$

The percent recovery for LCS and surrogates is calculated using the equation

$$\%\, recovery = \frac{analyzed\ concentration\ of\ LCS\ or\ surrogate}{certified\ concentration\ of\ LCS\ or\ surrogate} \times 100$$

Table 7.4 lists recovery surrogate standards used for pesticide analyses and associated measurement quality objectives.

7.4.5. Contamination

For laboratory chemical analyses, at least one laboratory method blank will be run at a minimum rate of one for each 20 field samples. The method blank will be processed throughout the entire analytical procedure in a manner identical to the samples (i.e., using the same reagents and equipment). The result for a method blanks should be that the analyte concentration is less than the method detection limit (MDL).

A method blank with a measured concentration greater than the MDL for any analyte of interest will require corrective action (e.g., checking of reagents, re-cleaning and re-checking of equipment) to identify and eliminate the source(s) of contamination before proceeding with sample analysis.

If eliminating the blank contamination and reanalysis is not possible, results for all impacted analytes in the analytical batch shall be flagged. In addition, a detailed description of the contamination sources and the steps taken to identify and eliminate/minimize them shall be included in the transmittal letter. The analytical lab may or may not "blank correct" the reported results, depending on the guidelines in the method and/or laboratory SOP. Blank correction involves subtracting the result of the lab method blank from all results. A "LabBatch" comment shall be included in the tabulated data, indicating whether the sample results in that batch are blank corrected or not, and the individual result records will also contain flags (CEDEN QACode) indicating use of blank correction.

7.5. Toxicity Quality Control

Toxicity is being monitored in FY20-21 for the Delta RMP using MQOs previously established and used by the Surface Water Ambient Monitoring Program (SWAMP). The following QC

measures are required for toxicity tests, as excerpted from the 2017 SWAMP QAPrP, https://www.waterboards.ca.gov/water_issues/programs/swamp/qapp/swamp_QAPrP_2017_Final.pdf), with MQOs last updated in January 2020. https://www.waterboards.ca.gov/water_issues/programs/swamp/mqo.html

Reference Toxicants (Toxicity)

Definition: A reference toxicant is a known concentration of a reference material used to evaluate test organism response. Analogous to a positive control, reference toxicant tests assess precision and overall laboratory performance. Laboratories routinely expose toxicity test species to reference toxicants, such as potassium chloride or copper sulfate, in order to evaluate their health and sensitivity and how it changes over time. The results of these tests are plotted on control charts that are used to assess test precision and overall laboratory performance. EPA (2002) toxicity test guidance provides helpful information for interpreting reference toxicity test results. Requirements: See MQOs for frequency of use and acceptance criteria.

Negative Control

Definition: A blank consisting of a sterile form of the environmental matrix sampled, such as laboratory water or control sediment. Negative controls are used to compare the potential toxicity in a sample to a control sample where chemical induced toxicity should occur. The negative control also provides information on stock organism health and the normal variability in survival or growth of those stock organisms. Negative controls may also be used to differentiate between chemical toxicity and toxicity caused by salinity or pH. Primary negative controls consist of standard laboratory water; whereas, additional negative controls match the salinity or pH in the sample. Requirements: A minimum of one negative control per toxicity test batch is required. Toxicity test species used in negative controls must meet the minimum requirements established by the method-specific test acceptability criteria (see MQOs).

Additional Negative Controls

Definition: If sample parameters (e.g., salinity or pH) are outside the ranges established in the appropriate MQO, additional negative controls (also called secondary negative controls, tolerance controls, and conductivity controls) matching these conditions are used to account for any potential effects associated with water quality. Requirements: A conductivity or salinity control must be tested when these parameters are above or below a species' tolerance (see MQOs for tolerance ranges). All other secondary negative controls are utilized on a discretionary basis. Delta RMP Pesticide Subcommittee recommendations for setting up

alternative controls are detailed in Appendix III of the Delta RMP Toxicity Data Management and Quality Assurance Standard Operating Procedures.

Toxicity Test Water Quality Measurements

In addition to toxicity test control samples noted above, required water quality parameters (specific to the test method) must be reported. These may include measurements of initial and final conditions, conditions on water renewal, and additionally minimum and maximum values, or values taken at specified intervals, as required in a given test method. Water quality measurements typically reported include DO, pH, conductivity, ammonia, alkalinity, hardness, and temperature measurement, but may include others parameters with ranges specified or recommended in the test method.

8. Special Training or Certifications

Chemistry and toxicity testing laboratories must have a designated on-site QA Officer for the particular analytical component(s) performed at that laboratory. This individual will serve as the point of contact for the SFEI-ASC QA staff in identifying and resolving issues related to data quality.

To ensure that the samples are analyzed in a consistent manner throughout the duration of the program, key laboratory personnel will participate in an orientation session conducted during an initial site visit or via communications with SFEI-ASC staff. The purpose of the orientation session is to familiarize key laboratory personnel with this QAPP and the Delta RMP QA/QC program. Participating laboratories will be required to demonstrate acceptable performance before analysis of samples can proceed. Laboratory operations will be evaluated on a continuous basis through technical systems audits and by participation in laboratory intercomparison programs. Personnel in any laboratory performing analyses will be well versed in good laboratory practices (GLPs), including standard safety procedures. It is the responsibility of the analytical laboratory manager and/or safety staff to ensure that all laboratory personnel are properly trained. Each laboratory is responsible for maintaining a current safety manual in compliance with Occupational Safety and Health Administration (OSHA) or equivalent state or local regulations. The safety manual will be readily available to laboratory personnel. Proper procedures for safe storage, handling, and disposal of chemicals will be followed at all times. Each chemical will be treated as a potential health hazard and good laboratory practices (GLPs) will be implemented accordingly.

Personnel collecting samples will be trained in the field sampling methods described in the QAPP.

For mercury monitoring, the MPSL project coordinator will be responsible for training the MPSL field staff.

For pesticides monitoring and analysis, the USGS Organic Chemistry Research Laboratory (OCRL) principal investigators will be responsible for training field and laboratory staff.

For aquatic toxicity testing,the PER project director and project manager will be responsible for ensuring training of laboratory staff.

Staff shall maintain a record of field training given. Information will include trainer, trainees, and dates of training. The sign-in sheet of the training can be the documentation of the training.

8.1. Training Certification and Documentation

Contractors performing sampling are responsible for providing training to their staff and maintaining records of all trainings. Those records can be obtained if needed from contractors through their respective QA or Safety Officers.

8.2. Training Personnel

Each contract laboratory's QA Officer and Safety Officer shall provide and/or designate staff to provide training to their respective personnel. All personnel responsible for sampling will be trained in field sample collection and safety prior to the first day they are scheduled to sample for the Delta RMP.

9. Documentation and Records

The main information products and reports planned by the Delta RMP are described in Section 6.7. These include annual data reports, annual QA reports, and occasional interpretive reports. All Delta RMP documents will be provided to the Steering Committee, which includes the Central Valley Regional Water Quality Control Board.

SFEI-ASC will collect records for sample collection, field analyses, and laboratory chemical analyses. Samples sent to analytical laboratories will include a Chain-of-Custody (COC) form. The analytical laboratories will maintain records of sample receipt and storage, analyses, and reported results.

SFEI-ASC will maintain hard copy or scanned files of field notes and measurements as well as documentation and results submitted by laboratories at the SFEI-ASC main office. The SFEI-ASC Data Manager will be responsible for the storage and organization of information.

Contract laboratories will be responsible for maintaining copies of project documentation originating from their respective laboratories, with backup archival storage offsite where possible. All SOPs used for the Delta RMP will be stored indefinitely, in case future review is necessary.

9.1. Quality Assurance Documentation

All laboratories will have the latest revision of the Delta RMP QAPP. In addition, the following documents and information will be current and available to all laboratory personnel participating in the processing of project samples and to SFEI-ASC program staff:

1. **Field Standard Operating Procedures** (SOPs): Containing instructions for fieldwork activities, including procedures for conducting field observations, field measurements, and environmental sample collection. Describes requirements for sample containers, volume, preservation, and storage.
2. **Laboratory Quality Management Plan:** clearly defined policies and protocols specific to a particular laboratory, including policies and objectives, organizational authority, personnel responsibilities, and internal performance measures.
3. **Laboratory Standard Operating Procedures** (SOPs): containing instructions for performing routine laboratory procedures (such as logging, labelling, and storage of samples; cleaning of equipment; checking of reagents) that are not necessarily part of any analytical methodology for specific analytes or analyte types.
4. **Laboratory Analytical Methods**: step-by-step instructions describing exactly how a method is implemented in the laboratory for a particular analytical procedure. Contains all analytical methods utilized in the particular laboratory for services provided to the Delta RMP.
5. **Instrument Performance Information**: information on instrument baseline noise, calibration standard response, analytical precision and bias data, detection limits, etc. This information shall be reported for the periods during which Delta RMP samples are analyzed.
6. **Control Charts**: control charts are useful in evaluating internal laboratory procedures and are helpful in identifying and correcting systematic error sources. Contract

laboratories are encouraged to develop and maintain control charts whenever they may serve in determining sources of analytical problems.

Copies of laboratory methods, SOPs, and QA plans shall be available upon request from the SFEI-ASC QA Officer or Project Manager. Some laboratory methods and SOPs may be edited to exclude proprietary details about the analyses. Quality assurance documents are reviewed to assure conformance to program needs by the Delta RMP Program Manager and QAO or their designees. All methods and SOPs will be provided in unredacted form to the QA Officer for the State Water Resources Control Board (State Board) for review and approval, but the State Board QA Officer will not share them with anyone else.

Handwritten original field sheets, logs, and calibration records will be maintained by the field sample collection teams.

Copies of all records will be maintained at SFEI-ASC and at the laboratory for a **minimum of ten years** after project completion, after which they may be discarded. This excludes electronic databases at SFEI-ASC, which will be maintained without discarding. All data will be backed up and secured at a remote location (i.e., separate from the SFEI-ASC office). As needed, data recovery can be initiated by contacting the back-up facility for restoration and this will be covered through SFEI-ASC overhead.

All participants listed in Table 3.1 will receive the most current version of the Delta RMP QAPP. The Delta RMP Program Manager will be responsible for sharing the latest version of the QAPP. The QAPP will also be posted publicly on the Delta RMP website.

9.2 Standard Operating Procedures (SOPs)

Standard Operating Procedure documents are listed in Appendix E in this QAPP. The QA Officer and Project Manager shall approve any changes in methods.

10. Sampling Process Design

10.1. Study Area and Period

Sample collection points and a justification for site selection and study areas for the different elements are described in the specific designs for each of the Delta RMP monitoring elements (Appendix D). Short Summaries of Delta RMP Monitoring Elements). Delta RMP monitoring occurs in, upstream, and downstream of the Delta.

The monitoring stations for mercury sampling represent different subareas of the Delta (Figure 6.3(a)).

The monitoring stations for pesticides and aquatic toxicity monitoring are shown in Figure 6.5 and Table 6.4.

Sampling timing and frequency varies for the different elements of the monitoring program:

- **Mercury monitoring** includes annual sport fish sampling at 12 stations (7 core stations and 5 restoration area stations) in September, monthly water sampling at 7 stations in March, April, and September, and prey fish monitoring at 8 stations in May.
- **Sampling for pesticides and aquatic toxicity** will be conducted over 6 events during the water year, designed to capture a range of hydrologic conditions and periods of the agricultural calendar at 6 randomized locations within designated subregions and at 2 fixed sites. Among the 6 planned events, 3 are for storm sampling, and 3 for dry weather / irrigation season. It is necessary to space sampling events by at least 2 weeks so the labs can process all the samples from the previous round. Planned timing of sampling events is shown in Table 6.7. Samples will be taken on the outgoing, or ebb, tide, if possible.

The Delta is a highly dynamic and hydrologically complex system. Seasonal and temporal variability of target analytes within the system is shaped by numerous influencing factors, including the relative contributions of source waters and their chemical composition, seasonal and temporal variability in loads, biogeochemical processes within the system, seasonally-varying process rates, flow rates and flow routing, climate variability, and habitat-specific (local) factors. Therefore, study design and data evaluation should always take into consideration co-variance of and potential bias caused by influencing factors.

Collected data are used to evaluate future data needs and adjust the sampling and analysis plan as needed to optimize data collection in an adaptive manner. The program will be continually adjusted to optimize data collection. In addition to this document, monitoring designs are described in Annual Workplans on the project website: http://sfei.org/DeltaRMP/

10.2. Sampling Sites

Mercury monitoring

Table 10.1 summarizes information on sampling sites and schedule for the mercury monitoring project in FY20-21. The field team lead must report any deviations or alterations to the sampling design (such as changes due to an inaccessible site) to Tessa Fojut at SWRCB and to Selina Cole

at CVRWQCB. These deviations will be communicated via email to the Mercury Subcommittee and discussed at the next Mercury Subcommittee meeting if necessary.

Pesticides and aquatic toxicity

For pesticides sampling, occasionally, one of the randomly-selected sampling locations will not be accessible because it is unsafe, on private property, etc. In this case, a sample should be taken within 100 meters of the target coordinates, if possible, and only if there is not some obvious change in the environment, such as moving downstream of an outfall, a change in water clarity, etc. If not possible to sample within 100 m, the crew should choose the next site on the "oversample" list shown in Table 6.4.

11. Sampling (Sample Collection) Methods

11.1. Field Sample Collection

The following sections describe field sampling methods for each component of Delta RMP water quality monitoring.

Table 11.2 shows the sample container type and volume used for each parameter group for collection of water; and target species, number of individuals, and size ranges for collection of fish tissue samples.

11.1.1. Equipment Cleaning and Decontamination Procedures

Mercury Sampling

Equipment cleaning and decontamination procedures are documented in MPSL SOPs MPSL-102b, Section 7, and MPSL-111, Section 7. (See Appendix E for links to download all SOPs referenced in this document.) To avoid cross-contamination, all equipment used in sample collection will be thoroughly cleaned before each sample is processed. Before the next sample is processed, instruments will be washed with a detergent solution (Micro™), rinsed with ambient water, , and finally rinsed with Milli-Q® water. Immediately prior to sample collection, the bucket sampler is rinsed again with ambient water from that site. Waste detergent and solvent solutions must be collected and taken back to the laboratory. Boats, sampler, and personal protection equipment (PPE) will be pre-cleaned with 10% bleach to prevent introducing invasive species from one water body to another water body.

11.1.2. Mercury Sampling

The following sections describe collection of samples for analysis of mercury and methylmercury in water. For trace metals such as mercury, great care must be taken and special sampling methods to avoid contamination during sample collection, transport, and analysis. According to the US EPA (1996):

> Preventing ambient water samples from becoming contaminated during the sampling and analytical process is the greatest challenge faced in trace metals determinations. In recent years, it has been shown that much of the historical trace metals data collected in ambient water are erroneously high because the concentrations reflect contamination from sampling and analysis rather than ambient levels. Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing ambient water samples for trace metals.
>
> There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination during sampling include metallic or metal-containing sampling equipment, containers, labware (e.g. talc gloves that contain high levels of zinc), reagents, and deionized water; improperly cleaned and stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust from automobile exhaust, cigarette smoke, nearby roads, bridges, wires, and poles. Even human contact can be a source of trace metals contamination. For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples that are directly exposed to exhalation.

Field crews and laboratory staff are experienced in ultra-trace methods. Further details about sampling methods for each matrix (water, fish tissue) are described below. To avoid contamination, all material that comes in contact with fish are prepared and cleaned as described in Method MPSL-101, *Sample Container Preparation for Organics and Trace Metals, Including Mercury and Methylmercury*. Sample handling protocols are described in more detail below.

11.1.2.1 Water Sampling

This section describes collection of water samples for analysis of mercury and methylmercury by MPSL field crews. Samples will be collected according to MPSL Field SOP v1.1 (see Appendix E for link) and standard trace metal clean-hands/dirty-hands collection methods (USEPA Method 1669 modified) where appropriate to avoid sample contamination. A

depth-integrated sample will be collected using a bucket sampler following methods described in the MPSL Field SOP v1.1 and MPSL-111).

Briefly, a web of clean C-Flex tubing is used to hold the bottle in place while sampling. Tubing will be replaced prior to each sampling event or sooner, if thought to have come in contact with surfaces known to be possible contamination sources, such as the boat deck. Plastic-covered lead weights are fastened with plastic fasteners to the outside bottom of the bucket to allow sufficient weight to lower the sampler through the water column. A clean polypropylene line is attached to the bucket and used to lower and raise the sampler through the water column.

The sampling bucket and line will be kept clean by storing in new clean plastic bags between uses and not allowing contact with surfaces on the sampling platform that are known to be potential sources of contamination.

A depth-integrated sample will be collected by lowering and raising the 4L bottle through the water column at a sufficient rate so that the bottle is not completely filled upon retrieval. A new pre-cleaned 4L glass bottle (MPSL-101 *Sample Container Preparation for Organics and Trace Metals, including Mercury and Methylmercury*) will be used for each site.

Field sample handling and shipping procedures are described in Section 12. Further, Table 12.1 provides important information on storage and hold time requirements.

11.1.2.3. Collection of Fish Tissue for Analysis of Mercury and Methylmercury

Sport fish samples for mercury monitoring are collected annually. The appropriate sample collection method may vary by site and will be determined by the MPSL field sample collection team.

Links to Standard Operating Procedures (SOP) documents for fish sample collection are provided in Appendix E.

Fish will be collected in accordance with the SOP MPSL-102a, *Sampling Marine and Freshwater Bivalves, Fish and Crabs for Trace Metal and Synthetic Organic Analysis*. Because habitats may vary greatly, there is no single method of collection that is appropriate. Field crews will evaluate each fishing site to determine the correct method to be employed. Potential sampling methods include but are not limited to: electroshocking, seining, gill netting, and hook and line. Field crew will determine the appropriate collection method based on physical site parameters such as depth, width, flow, and accessibility. Field crew will indicate the collection method on data sheets. The project data sheet is shown in Appendix F. In sport fish sampling using an electroshocking boat, it is frequently necessary to sample over a linear course of 0.5 – 1 mi to obtain an adequate number of fish. A sport fish sampling station in this study can therefore be

thought of as a circle with a diameter of 1 mile. The transects covered by the e-boat are documented in the sampling cruise report. A 1-mile diameter will also be used for prey fish sampling. If the field crew need to extend beyond 0.5 mi this to obtain the target numbers of fish they will inform the principal investigator at ASC and the Delta RMP Program Manager.

For the mercury status and trends study, for annual sport fish monitoring, the targeted fish species is largemouth bass (*Micropterus salmoides*). The goal is to collect 16 individuals spanning a range of total length from 200 to greater than 407 mm at each site. The targeted size range is as follows:

3 × 200–249 mm

3 × 250–304 mm

7 × 305–407 mm

3 × 407+ mm

The target sizes span a wide range to support development of a length:mercury regression at each station, with a primary focus on fish in the legal range that is most commonly caught

Specimens of similar predator species may be collected, if the desired number of individuals of the primary target fish species in the desired size range cannot be collected at a site. Other acceptable sport fish species include, in order of preference:

1. spotted bass, *Micropterus punctulatus*
2. smallmouth bass, *Micropterus dolomieu*

For mercury monitoring at restoration stations, the target fish species is the Mississippi silverside, *Menidia beryllina*, formerly referred to as the inland silverside. The goal is to collect 6 composites of up to 10 fish each in 5 mm increments across the 45–70 mm size range, as shown in Figure 11.1.

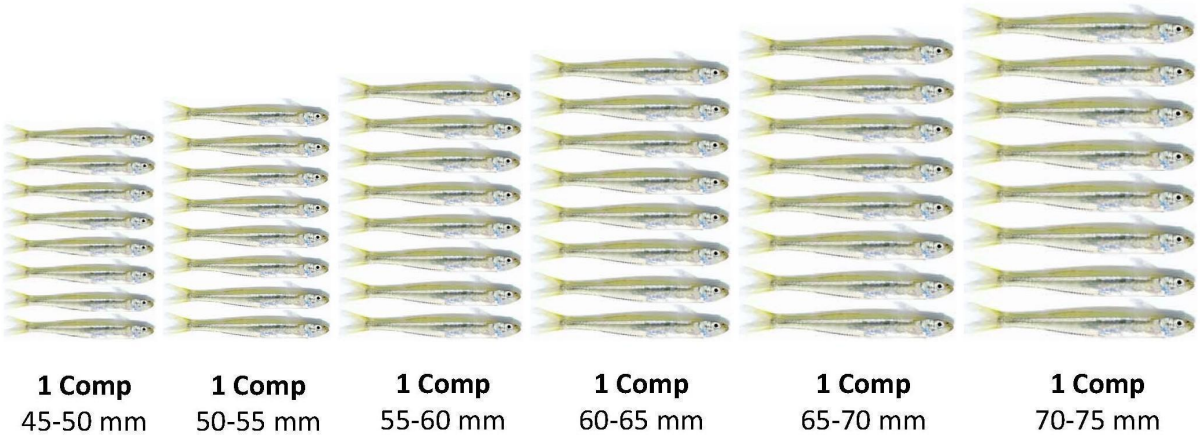


Figure 11.1 Illustration of the target number and size of prey fish to be collected and composited at each of the restoration monitoring stations.

The other primary target prey fish species is young-of-the-year largemouth bass, *Micropterus salmoides*. We will target young-of-the-year (YOY) largemouth in the 50-110 mm range, preparing six composites in 10 mm increments across this range. Other species have not been extensively monitored and would not be as useful for the study.

Section 12.3 provides more information on field sample handling and shipping procedures. Table 12.1 provides information about storage and hold time requirements for each parameter group.)

Fish will be processed according to MPSL- 102a *Sampling Marine and Freshwater Bivalves, Fish and Crabs for Trace Metal and Synthetic Organic Analysis;* except where noted here. 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 or plastic. Fork and total length are recorded. Weight is recorded, if the fish is large enough for the scale. If the fish is too large to fit in the bag, it will then be placed on the covered cutting board, where the head, tail, and guts are removed using a clean cleaver (scrubbed with Micro™, 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™, rinsed with tap and deionized water between fish species. The equipment cleaning procedures will be repeated at each sampling site.

11.1.6. Pesticides and Aquatic Toxicity Sampling

This section describes collection of water samples for pesticides and aquatic toxicity analysis by USGS OCRL field crews. Samples for pesticides and toxicity monitoring shall be collected concurrently as grab samples 0.5 meters below the water surface. All grab samples shall be collected in accordance with the following methods described in the USGS *National Field Manual* (U.S. Geological Survey, variously dated). Relevant sections of the manual include the following chapters:

A1. Preparations for Water Sampling (Version 1.0, 11/2018)

A2. Selection of Equipment for Water Sampling (Version 3.1, 4/2014)

A3. Cleaning of Equipment for Water Sampling (Version 2.0, 4/2004)

A4. Collection of Water Samples (Version 2.0, 9/2006)

The USGS field manual is a dynamic document that has been in constant development since 1991 by the scientists and technicians at the USGS National Water-Quality Laboratory and National Research Program.

The study design calls for grab samples due to the large volume of water (approximately 45 liters or 8 gallons) required for collecting toxicity and pesticide samples concurrently, even in hydrologic conditions that might otherwise dictate integrated sampling techniques.

Samples shall be collected between the high and low tide, or on the ebb tide (for tidally influenced sites) by submerging narrow-mouthed bottles at mid-channel to a depth of 0.5 m. At the two fixed monitoring sites, during low flow conditions, samples may be collected by wading into streams and submerging handheld bottles. In high flow conditions or for sites with difficult bank access, samples shall be collected from bridges using weighted-bottle samplers.

At the probabilistic (random) sites chosen by GRTS, samples will be collected by boat using the weighted bottle sampler. Water samples for pesticide and toxicity analyses will be collected by submerging 1 L baked amber glass bottles (pesticides), 3 L Teflon (copper and dissolved organic carbon or DOC), and 4 L glass (toxicity) to a depth of 0.5 m using weighted bottle samplers. Samples will be collected on an ebb tide if logistically feasible. The sampling boat will be maintained on station at the GRTS site throughout the sample collection process.

Pesticide samples shall be collected in pre-cleaned, baked 1 L glass amber bottles and transported on ice to the USGS OCRL in Sacramento, California for processing and analysis using a combination of liquid chromatography tandem mass spectrometry (LC/MS/MS) and gas chromatography mass spectrometry (GC/MS). Samples for analysis at the USGS NWQL shall be collected in 3-L Teflon bottles, processed at the USGS California Water Science Center, and shipped on ice to the USGS NWQL in Denver, Colorado.

NWQL will analyze the following:

- Copper
- dissolved organic carbon (DOC)
- particulate inorganic carbon (PIC)
- particulate organic carbon (POC)
- total particulate carbon (TPC)
- total particulate nitrogen (TPN)

Toxicity samples shall be collected in pre-cleaned 4-L glass amber bottles provided by PER. Bottles shall be triple rinsed with native water on-site before sample collection. Bottles shall be transported on ice to PER for analysis.

Basic water-quality measurements (water temperature, specific conductance, dissolved oxygen, pH, and turbidity) shall be taken at a depth of 0.5m at mid-channel during each sample collection using a YSI 6920V2 multi-parameter meter. The meter shall be calibrated using appropriate procedures and standards prior to sample collection as described in the USGS National Field Manual (U.S. Geological Survey, variously dated).

11.1.7. Habitat Observations

The field crew collecting pesticides and toxicity water samples shall make a number of observations about the sampling location, and record these on a field sampling data sheet. These observations are referred to (by USGS, SWAMP and others) as "habitat parameters," even though this project is not specifically monitoring wildlife habitat. Table 11.1 shows the elements to be recorded by field crews on the SWAMP field data sheet.[7]

In the past, Delta RMP pesticides monitoring visited the same 5 sites monthly, and therefore each site was well known to us, and there was not much to be gained from these observations. However, as the project will be monitoring dozens of new, randomly-selected locations, it will be important to record conditions at each site, particularly anything out of the ordinary. These observations may be useful for interpreting the pesticide and toxicity results for that station.

11.2. Field Sample Collection Quality Control Samples and Measurement Quality Objectives

Required field sample collection QC samples include field equipment blanks and field duplicates. Each of these types of field QC samples will be collected at a rate of no less than 5% of total field sample count. Field QC samples shall be planned and collected throughout the project to evaluate potential variability sources in the field; including differing environmental conditions, geographic locations, sample collection personnel, and various field sampling protocols employed. Field equipment blanks are required for water sample collection for analysis of field filtered samples collected by MLML: DOC, chl a, dissolved mercury, dissolved methylmercury. Field blanks (no field equipment or processing) are collected by USGS for

[7] Download the SWAMP Water Quality Field Data Sheet: https://drive.google.com/file/d/0B40pxPC5g-D0WTBmZlkzOHE0dnM/view

current use pesticides, and ancillary parameters (DOC, TC, TN) . Field blanks are collected by MLML, for total suspended solids (TSS), volatile suspended solids (VSS), and whole water mercury and methylmercury. Field duplicates are required for all water samples. Field sample quality controls and measurement quality objectives are included in Table 14.1.

11.3. Field Sample Collection Corrective Actions

Table 11.3 lists typical corrective actions that may be taken by the project manager and/or QA Officer in response to issues that arise as a result of field sampling procedures. All necessary steps for corrective action will be documented on the field form and are entered into the electronic version of the Field Sampling Report that is maintained by SFEI-ASC. The individuals responsible for assuring that the field staff are properly trained and implement the Field Sampling SOPs are the Field Collection Coordinators (i.e., MPSL Project Coordinator and USGS Principal Investigators, OCRL Project Chief), SFEI-ASC Project Manager, and the QA Officer.

12. Sample Handling and Custody

This section describes the sample handling and custody procedures from sample collection through transport and laboratory analysis.

Chain of custody (COC) procedures shall be strictly adhered to during sample collection, transportation and laboratory handling to assure the identity of the samples. Proper sample and data handling and appropriate COC procedures help ensure that program data are credible and acceptable, in addition to considerations of accuracy and precision. COC documentation will document the processing of the sample from the time of collection to the time of analysis.

Table 12.1 provides information about storage and hold time requirements for each type of water quality measurement.

12.1. Pesticides

Sample containers will be labeled with the location, date, and time collected and packed in ice chests with sufficient wet ice to maintain sample transport criteria. Field sheets and chain-of-custody forms (COC) will be filled out by the USGS PFRG field crews at the time of collection and will include site ID, site description, collection date/time, container type, sample preservation, field water chemistry measurements, sampler(s) name and requested analyses. All forms will be included with the appropriate samples during shipping.

Samples for pesticide analysis will be delivered to the USGS OCRL laboratory in Sacramento California. If upon arrival at the OCRL samples are found to be warm (ice melted) or if sample

containers are broken the Project Manager and Program Managerwill be immediately notified. Ice chests are examined upon delivery to ensure that samples have been properly chilled (acceptable temperature range = 0 to 6 °C).

Water samples for pesticide analyses will generally be processed to extraction upon arrival at the OCRL. If this is not possible, the samples will be refrigerated at 0 to 6 °C in the dark for a period not to exceed the OCRL holding time requirement of 48 hours between sample collection and extraction. Upon arrival of samples, appropriate laboratory processing forms noting unique laboratory ID, site name, collection time and date, receiving technician's name, requested analysis, and date and time of receipt will be filled out. Signed copies of COCs will be maintained with the appropriate OCRL field and laboratory forms. Prior to pesticide analysis, all water samples will be filtered through pre-weighed, pre-combusted 0.7-micrometer (μm) nominal pore-size glass-fiber filters to remove suspended material. Filter papers containing suspended sediments will be dried at room temperature overnight (in the dark), then stored in a freezer at −20 °C until extraction. The filtered water (dissolved phase) and suspended sediment phase are analyzed for pesticides (as listed in table Table 7.3(b)).

Samples for dissolved copper analysis and DOC/POC analysis will be processed at the USGS OCRL, within 24 hours of collection. Samples for dissolved copper analysis will be filtered using 0.45-micrometer (μm) filters and acidified to a pH less than 2 with 2 mL of 7.5N nitric acid. Samples for DOC analysis will be filtered using 0.7 μm pore size, pre-combusted glass-fiber filters, collected in 125-mL baked amber glass bottles, and acidified using 4.5N sulfuric acid. The 0.7 μm pore size filter holding the retained suspended material will be used for the POC analysis and will be wrapped in an aluminum foil square of appropriate size.

Samples for dissolved copper, DOC, and POC will be placed in a cooler on wet ice and shipped overnight to the USGS NWQL in Lakewood, Colorado.

Receipt temperature and sample condition (broken/compromised containers, incorrect preservatives, holding time exceedance, etc.) will be recorded by receiving laboratories.

12.2. Toxicity Testing

Toxicity test samples will be delivered to the Pacific EcoRisk (PER) Laboratory within 24 hours of sample collection. Upon arrival at PER, toxicity testing samples will be immediately removed from the ice chests and the laboratory staff receiving the coolers will complete the accompanying Chain of Custody form (COC). PER will initiate tests within 48 hours of sample collection, although under rare circumstances, this holding time may be extended to 120 hours for storm events, or when courier delivery schedules on weekends and holidays limit the

availability of test organisms. This, however, is not consistent with the MQOs and will result in a holding time flag. In these instances, PER staff will notify the SFEI-ASC QAO and Delta RMP Program Manager, and associated data will be flagged appropriately for hold time violation.

12.3. Trace Metals - Mercury

12.3.1. Sample Water

Sample containers will be labeled with the location, date, and time collected and packed in ice chests with sufficient wet ice to maintain sample transport criteria. Field sheets and chain-of-custody forms (COC) will be filled out at the time of collection and will include site code, site description, collection date/time, container type, sample preservation, field measurements, sampler(s) name, and requested analyses. All forms will be included with the appropriate samples during shipping. Samples will be delivered to MPSL in Moss Landing, CA. If upon arrival at the laboratory samples are found to be warm (ice melted), or if sample containers are broken, the Project Manager and Principal Investigator will be immediately notified. Ice chests are examined upon receipt to ensure that samples have been properly chilled (acceptable temperature range = 0° to 6° C).

Water samples will be delivered to MPSL within requisite holding times, where laboratory personnel will filter (if not field filtered) and preserve (if not field preserved) water samples following Table 12.1. Receipt temperature and sample condition (broken/compromised containers, incorrect preservatives, holding time exceedance, etc.) will be recorded by receiving laboratories. Upon arrival of samples, appropriate laboratory processing forms noting unique laboratory ID, site name, collection time and date, receiving technician's name, requested analysis, and date and time of receipt will be filled out. Samples for dissolved mercury and dissolved methylmercury analysis will be filtered using 0.45-micrometer (µm) filters and acidified to 0.5% with pre-tested bromine monochloride, BrCl, or 12N hydrochloric acid, HCl, as appropriate within 48 hours of collection.

12.3.2. Fish Tissue

Fish samples will be wrapped in prepared aluminum foil, placed in zipper-closure bags and frozen on dry ice for transportation to the laboratory, where they will be stored at –20°C until dissection and homogenization. To avoid contamination, all material that comes in contact with fish are prepared and cleaned as described in Method MPSL-101, *Sample Container Preparation for Organics and Trace Metals, Including Mercury and Methylmercury*. 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. Holding times for each analyte can be found in Table 12.1.

13. Analytical Methods and Field Measurements

13.1. Field Measurements

The field collection teams for water sampling events will record measurements performed in the field on field sheets (electronic or paper), then enter them into a CEDEN template for subsequent entry in the Delta RMP database by SFEI-ASC. An exception to this is field measurement data from mercury sampling, which will be submitted directly to CEDEN through the CEDEN Data Checker tool.

Data uploading is described in Section 19.3, Data storage/database. Reporting limits (RLs) and method detection limits (MDLs) for field measurements are shown in Table 7.3(a) where applicable.

13.1.1.

13.2. Laboratory Analysis

The following sections list the laboratory analytical methods that will be used in Delta RMP monitoring, and policies for sample archiving and disposal.

Reporting turnaround times for submission of results from sample analyses are generally 90 days or less, but may be specified in contracts with the analytical laboratories. Samples should be extracted and analyzed within the holding times specified for the analytical methods used (Table 12.1).

13.2.1. Analytical Methods

Table 13.1 provides a summary of analytical methods and instruments used by the Delta RMP.

Reporting limits (RLs) and method detection limits (MDLs) are shown in Table 7.3 (a) for conventional analytes, field parameters, and trace metals. Table 7.3(b) shows the RLs and MDLs for pesticide analytes.

All analytical method SOPs can be downloaded from the SFEI-ASC Google Drive. Appendix E provides a list and links to these SOPs.

Detailed descriptions of methods for analysis of pesticides can be found in these publications:

- *Delta Regional Monitoring Program Annual Monitoring Report for Fiscal Year 2015–16: Pesticides and Toxicity* (Jabusch, Trowbridge, Heberger, Orlando, et al. 2018)
- *Pesticide Inputs to the Sacramento-San Joaquin Delta, 2015-2016: Results from the Delta Regional Monitoring Program* (De Parsia et al. 2018)

13.2.2. Toxicity Testing Procedures

Staff of Pacific EcoRisk shall perform aquatic toxicity testing following EPA methods, SWAMP MQOs, and the lab's SOPs as listed in Table 14.4. Additional project-specific requirements are listed below for 3 test species.

Any use of surrogate species must be approved by the QA Officer. Furthermore, it should be discussed by the Pesticides Subcommittee of the Delta RMP TAC and approved by the Steering Committee. Alternative protocols can be proposed to SWAMP and EPA, but tests shall be run per the method for this project.

Ceriodaphnia dubia

Toxicity testing according to SWAMP MQOs describes the recommendation for secondary conductivity controls when an ambient sample conductivity[8] is outside of the physiological range of the test organisms. These can be either high-conductivity controls (i.e., synthetic control waters salted up to match the highest conductivity of the ambient samples collected) or low-conductivity controls (i.e., synthetic control waters diluted with de-ionized water to match the lowest conductivity of the ambient samples collected). The latter will include nutrients (i.e., biotin, sodium selenate, and vitamin B_{12}) added to match the target concentrations in culture water. Secondary controls will be tested as outlined below.

Depending on the range of conductivities observed in ambient sample waters, additional negative controls may be tested to control for water quality near the organisms' tolerance screening value. Figure 13.1 on the following page is a flowchart showing how low-conductivity controls for *C. dubia* toxicity testing should be handled. Part (a) of the figure is a flowchart depicting what controls the lab should prepare based on the range of conductivity in ambient samples. Part (b) is a flowchart showing which control each ambient sample should

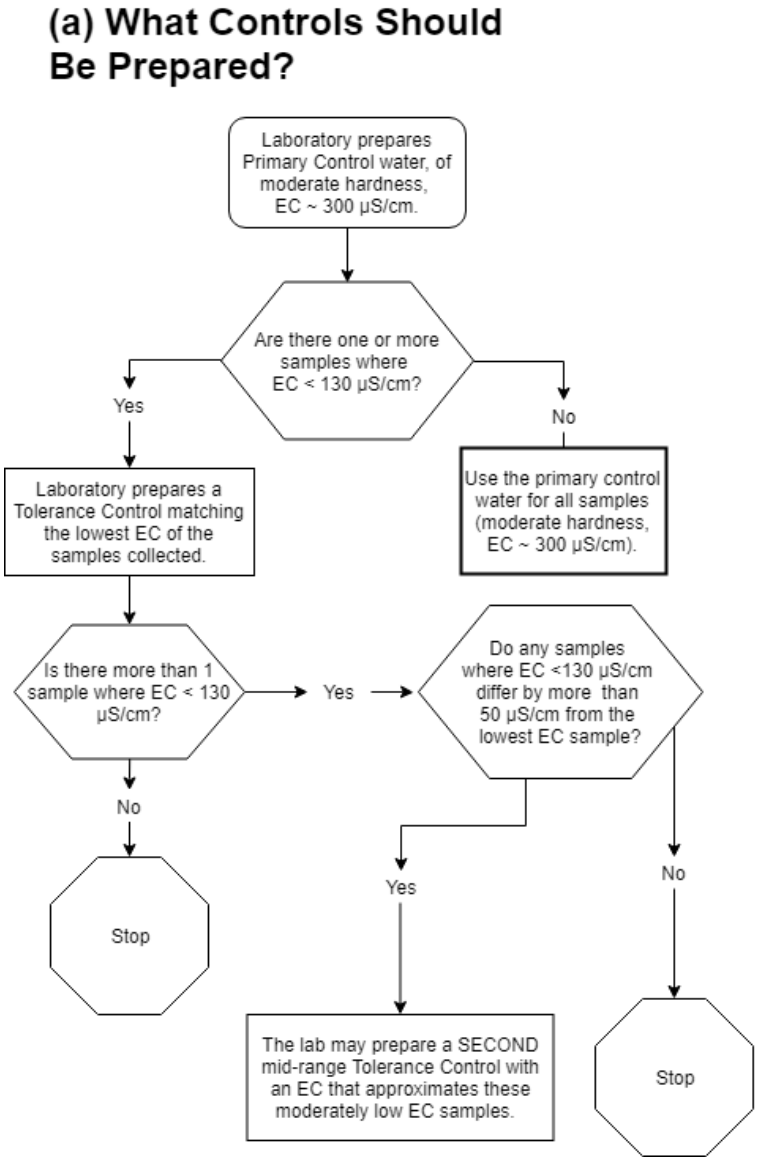
be compared to for performing a t-test, which will result in a binary determination of whether the ambient sample is toxic (i.e., yes/no).

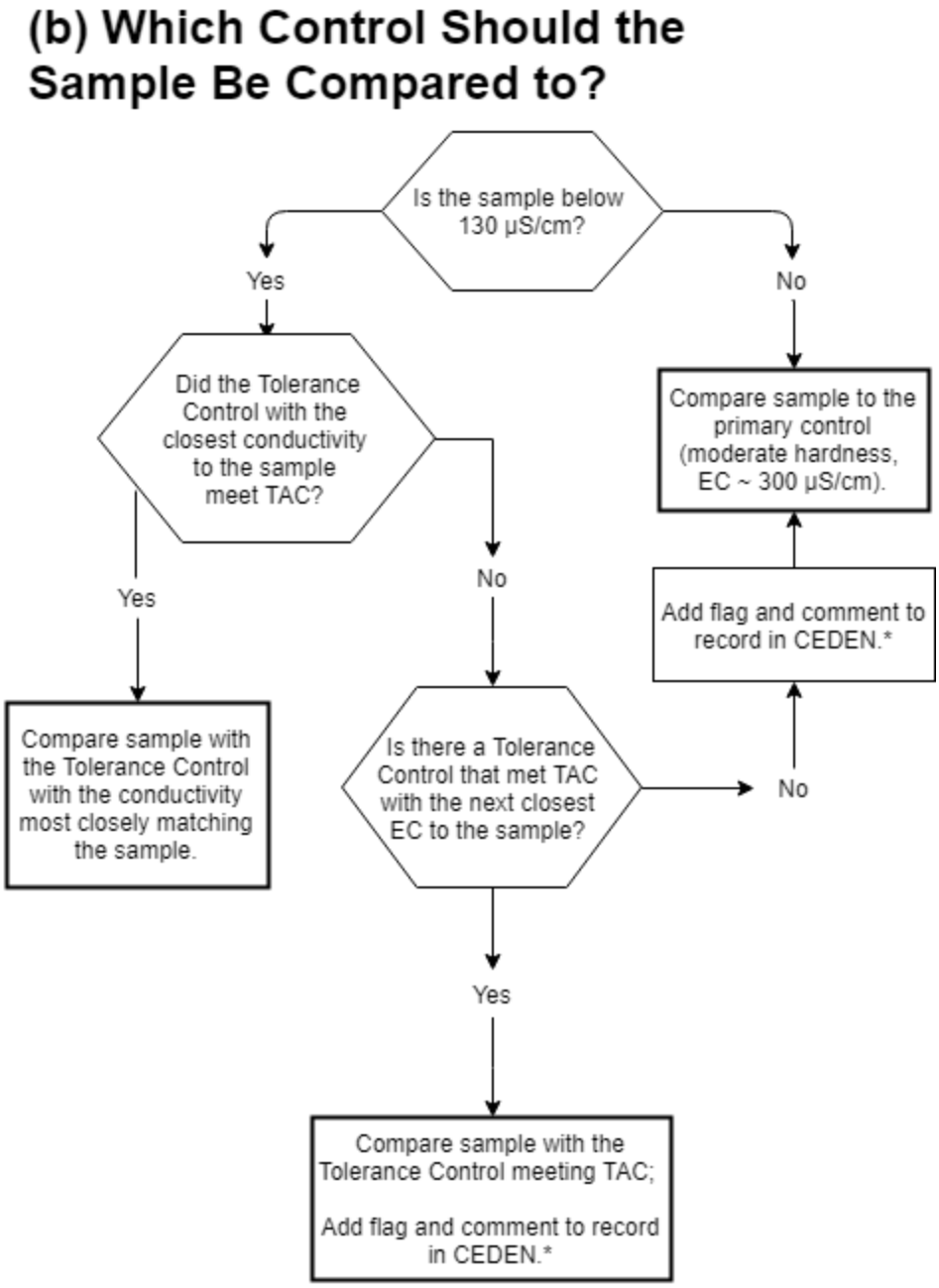
SWAMP guidance states that for *C. dubia* toxicity testing, the sample conductivity should be above 100 µS/cm; although, previous Delta RMP testing found that *C. dubia* reproduction in

[8] Conductivity refers to specific conductance (i.e., conductivity normalized to 25°C).

cultures may be affected by conductivity as high as 127 µS/cm. Therefore, the lab shall run a tolerance control matching the lowest sample conductivity when there are sample(s) with conductivity ≤ 130 µS/cm. The laboratory will also have discretion to run a second tolerance control when there are multiple samples with conductivity ≤ 130 µS/cm (i.e., if samples with conductivity ≤ 130 µS/cm have a difference of at least 50 µS/cm).

Figure 13.1 Flowchart illustrating procedure for handling low-conductivity controls for *C. dubia* toxicity testing.





*In cases like these for *C. dubia* toxicity testing, where sample conductivity is low, but the low-conductivity tolerance control does not meet test acceptability criteria, the sample is compared to the regular, medium-hardness control which has higher EC. In cases like these, the result of the statistical comparison may indicate that the sample is toxic, but it may not be (entirely) due to toxic contaminants, but rather due to a deficiency of ions that *C. dubia* need in order to thrive. Therefore, a comment may be added to the CEDEN database field ToxTestComments (limit 255 characters) as follows: “Tolerance control based on sample conductivity did not meet test acceptability criteria; percent effect based on comparison with

standard control. Effects may include response to low EC in sample." In addition, it is also appropriate to add a "TW" flag to the field ToxResultQACode. This code means, "Water quality parameters outside recommended test method ranges."

If the conductivity is less than 130 µS/cm, field crews should ensure sufficient volume is collected for all testing, and possible TIEs. (The PER project manager has indicated that the planned volume is sufficient, but staff should continue to track this and adjust if necessary, for example, if larger volumes of water are required for TIEs.)

Ceriodaphnia dubia will **not** be tested in samples with specific conductance > 2,500 µS/cm, which is outside of the maximum tolerance of this test species. SWAMP MQOs state that *Hyalella azteca* can be used as a surrogate for *C. dubia* in this case. The Delta RMP is already testing with *H. azteca*.

Nutrient addition in low-conductivity samples

This paragraph describes additional testing for research purposes, with the intent of understanding if nutrient additions to low conductivity samples will increase *C. dubia* reproduction as has shown it does in the tolerance controls (Stillway and Irvine 2018). If there is at least one sample with conductivity ≤ 130 µS/cm in a batch, the lab shall use water from one low-conductivity environmental sample to run an additional test. In this sample, the lab will treat the environmental sample by adding the standard blend of nutrients (i.e., biotin, sodium selenate, and vitamin B_{12}). The amount of nutrients added should match the amount added to the lowest conductivity tolerance control. The results of the research treatments will be compared to the secondary controls with the most closely matching conductivity, and also with the untreated sample. These data may inform the Delta RMP if background water quality and/or nutrients affect the test organism response. At this time, a minimum sample size has not been identified.

Hyalella azteca

Feeding during toxicity tests will follow the SCCWRP method where food is given two hours prior to water changes (Schiff and Greenstein 2016). This approach is consistent with SWAMP MQOs and reduces the potential for contaminants to sorb to food where they may be less bioavailable to the organism and bias the results.

Chironomus dilutus

Chronic toxicity testing is recommended by the CUP TAC to assess the potential for effects from imidacloprid and fipronil, to which the midge is sensitive. SWAMP MQOs for this 10-day

chronic survival and growth test were published in August 2018, and Delta RMP sample testing with this midge commenced in late 2018.

Selenastrum capricornutum[9]

Micronutrient stock solution should NOT contain ethylenediaminetetraacetic acid (EDTA), as EDTA is known to chelate metals and therefore the presence of EDTA in the algal growth test can mask metal toxicity.

13.2.3. Sample Retesting

When a test fails to meet test acceptability criteria, the Delta RMP project team may request a re-test. Therefore, retesting samples may require using samples that have exceeded the 48 hour hold time. Decisions to retest samples need to be made as quickly as possible by the testing lab in consultation with the Delta RMP Program Manager and TIE Subcommittee (see Appendix J). The laboratory will notify the Delta RMP Program Manager and TIE Subcommittee by email of the possible need to retest immediately upon identifying an invalid test or, if possible, when the control is exhibiting a poor or irregular survival or reproduction pattern that causes the laboratory staff to anticipate that Test Acceptability Criteria may not be met. In this notification, the laboratory will describe the concern and could provide a recommendation for retesting or continued monitoring of the results.

Within 24 hours of test result notification from the toxicity laboratory, the TIE Subcommittee will review the laboratory notification, discuss (i.e., over email or a conference call), and make a consensus decision regarding whether to retest a sample. The Program Manager, who will be a part of the TIE Subcommittee communications, will inform the laboratory of the decision on retesting. The laboratory will initiate the retest of the previously collected sample within 24 hours of notification from the subcommittee (i.e., within ~48 hours of the lab notification).

If the TIE Subcommittee does not respond within 24 hours, then the laboratory will implement its recommendation. In the event that retesting is delayed beyond this timeline (e.g., organisms need to be ordered from a supplier or samples need to be recollected), such delays will be communicated to the TIE Subcommittee and documented. Any issues contributing to an invalid test and its resolution will also be documented and submitted to the Delta RMP QA Officer and to the Delta RMP Program Manager to inform adaptive management of the Delta RMP.

[9] Currently accepted scientific name for this algae species is *Raphidocelis subcapitata*. Also formerly known as *Pseudokirchneriella subcapitata*. Nevertheless, it is still widely referred to as *Selenastrum* by the aquatic toxicity testing community.

The potential need for resampling or retesting may also arise if, for example, samples are accidentally lost or destroyed in whole or in part. The bioassay laboratory will immediately notify the TIE Subcommittee, the Program Manager, the SFEI/ASC project manager, and the USGS analytical lab with a description of the problem so that a decision to resample can be made by the project team.

13.2.4. Statistical Analyses

Statistical analysis of laboratory toxicity test data will be consistent with standard single concentration statistical protocols (EPA 2002; Appendix H, page 306-308). This approach compares each sample with the appropriate control and calculates the test result according to standardized statistical methods used in aquatic toxicology. Statistics for toxicity data will be made with the software application Comprehensive Environmental Toxicity Information System™ (CETIS; Tidepool Scientific, McKinleyville, CA, USA).

Samples will be compared with the appropriate negative control. This will be the negative control (i.e., primary or tolerance control) with water quality (i.e., specific conductance) most closely matching the sample when multiple negative controls are included as part of a toxicity test. See the SWAMP 2018 Memo: "Use of Additional Controls in SWAMP Toxicity Tests."[10] Statistical analyses shall follow the method and SWAMP memo for additional controls. Specifically:

- Samples with conductivity > 130 µS/cm will be compared with the primary control.
    - If the primary control does not meet Test Acceptability Criteria then results are rejected. Retesting the sample and control can be considered.
- Samples with conductivity ≤ 130 µS/cm will be compared with the tolerance control. If there is more than one tolerance control then samples with ≤ 130 µS/cm will be compared with the tolerance control with water quality (i.e., conductivity) most closely matching the sample.
    - If the tolerance control with water quality (i.e., conductivity) most closely matching the sample does not meet Test Acceptability Criteria then either:
        - 1) Compare the sample with the other tolerance control if the other tolerance control meets Test Acceptability Criteria. Add a flag and a comment to the record in CEDEN.*.
        - 2) Compare the sample with the primary control if there was no other tolerance control that met Test Acceptability Criteria. Add a flag and a comment to the record in CEDEN.* .

[10] https://www.waterboards.ca.gov/water_issues/programs/swamp/swamp_iq/docs/swamp_toxicity_test_control_water_memorandum.pdf

*A comment may be added to the CEDEN database field **ToxTestComments** (limit 255 characters) as follows: "Tolerance control based on sample conductivity did not meet test acceptability criteria; percent effect based on comparison with standard control. Effects may include response to low EC in sample." In addition, it is also appropriate to add a "TW" flag to the field **ToxResultQACode**. This code means, "Water quality parameters outside recommended test method ranges."

A flowchart illustrating the steps above is shown in Figure 13.1.

Sample comparisons with the primary control will generally determine toxicity due to contaminants in the sample when the sample is not outside or near the organisms' limit of tolerance. Likewise, comparing samples outside or near an organism's tolerance limit with the appropriate tolerance control accounts for possible background water quality effects to indicate effects due to contaminants. These comparisons will help answer the Delta RMP Assessment Question 1 (Status and Trends) "To what extent do current use pesticides contribute to observed toxicity in the Delta?" by identifying toxicity effects due to contaminants (e.g., pesticides).

When a tolerance control fails to meet Test Acceptability Criteria, it is an indication that the background water quality does not support the test organism and that the toxicity endpoint is not a reliable indicator of the effects due to contaminants in samples with similar water quality. Background water quality effects may be included in the observed effects when comparisons are made between a sample at or near an organism's tolerance limit and the primary control when the tolerance control fails to meet test acceptability criteria. This may describe the 'absolute toxicity' of a sample (i.e., difference between the sample performance and the maximum potential performance in its normal culture water conditions), but the result may reflect effects of the background water quality.

Lab analysts shall use the software application *Comprehensive Environmental Toxicity Information System*™ (CETIS; Tidepool Scientific, McKinleyville, CA, USA) to calculate Effect Concentration and Lethal Concentration values (EC_{25} for sublethal endpoints and LC_{50} for survival endpoints) for reference toxicant tests.

Delta RMP samples will be compared with the control (either primary or secondary/tolerance control) with the most similar water quality conditions, measured by specific conductivity. This group or 'batch' will be analyzed independently of other batches. If the negative control for a batch does not meet Test Acceptability Criteria, then the test organism health is compromised in those water quality conditions. There is not a valid benchmark for comparing the toxicity endpoint in samples associated with a negative control that does not meet Test Acceptability Criteria. Samples may be retested once. Sample results will remain invalid if a batch control fails

to meet Test Acceptability Criteria in a retest. The potential cause(s) of repeated control failures will then be investigated and corrective actions identified.

13.2.5. Toxicity Identification Evaluation (TIEs)

This section provides guidance for when, and under what conditions, the toxicity testing laboratory should conduct a Toxicity Identification Evaluation (TIE). A TIE is an investigative process that uses laboratory modifications of test sample chemistry and resulting changes in toxicity to identify the constituent groups (e.g., organophosphates) that are the likely cause(s) of toxicity.

The trigger for a TIE shall be a ≥ 50% reduction in the organism response compared to the appropriate lab control. This trigger shall apply to all test organisms and all endpoints (acute and chronic). The decision on whether or not to perform a TIE will be made by the toxicity testing laboratory in consultation with a Delta RMP TIE subcommittee. Decisions to perform a TIE are event-specific and dependent on the degree of effects observed in baseline testing, what is known about the sample (e.g., location, previous effects and toxicants, relevant pesticide applications), test species, and the available funding to conduct the TIE. The TIE Subcommittee and testing lab shall quickly decide whether to conduct TIEs (the Subcommittee should be notified within 24 hours of the TIE trigger, and the TIE should begin less than 72 hours after the TIE trigger), and whether to conduct any follow-up study (e.g., additional TIE treatments, supporting analytical chemistry).

This description is intended to be a starting point to inform the discussion and interpretation of any TIEs that are conducted on Delta RMP samples. TIEs may provide additional information that lead to other approaches to identify the cause of effects that are not identified here.

Phase 1 TIEs attempt to characterize the physical and chemical properties of the possible toxicant(s) in the sample. Information is gained regarding the physical/chemical properties of the toxicant(s) when the toxicity endpoint effect is reduced in the treated sample, adding to the weight of evidence regarding the class of contaminants that may have caused the toxicity. Phase 2 TIEs attempt to identify specific constituents causing or contributing to toxicity through chemical analyses or additional TIE treatments. Multiple TIE methods are presented in EPA guidance documents (USEPA 1991, 1992, 1993a, 1993b). Other approaches may be adopted from the peer-reviewed literature (e.g., Wheelock et al., 2004) or developed to address study-specific questions.

TIEs should be initiated as soon as possible (e.g., within 96 hours) after exceeding the TIE trigger and following approval of the TIE Subcommittee. **All TIEs should be chronic tests, even when observed toxicity is acute.** The laboratory must also conduct a preliminary validation of

the initial toxicity test results by confirming that basic water quality parameters (e.g., conductivity, dissolved oxygen) were within acceptable ranges for the affected test species and that test acceptability criteria were met, unless sufficient acute effects provide clear direction on the need for retesting. Follow-up investigations (e.g., Phase 2 or 3 TIEs) may also be considered.

Delta RMP TIE testing has the primary goal of identifying whether pesticides are causing or contributing to observed toxic effects. A secondary goal may be to identify (or exclude) other factors (i.e., water quality conditions or other toxicants) contributing to reduced survival, growth, or reproduction. A phased TIE approach will be used, to the extent possible, to achieve these goals by initially focusing on treatments that identify major classes of contaminants that could include pesticides:

- EDTA (evidence of metals toxicity; minimum of 2 EDTA concentrations will be tested)
- Solid-phase extraction column (e.g., C-8 or C-18; evidence of toxicity due to non-polar organics, organic-metal chelates, and some surfactants)
- Centrifugation (evidence of toxicity due to particulate-bound contaminants such as chlorpyrifos and pyrethroids; use with turbid samples or at the discretion of the TIE subcommittee)
- Piperonyl Butoxide (PBO) (evidence of toxicity due to a substance that is metabolized by the CYP450 enzyme system; evidence of OP insecticides if toxicity is reduced and of pyrethroid insecticides if toxicity is potentiated)
- Carboxylesterase addition (evidence of toxicity due to a contaminant with an ester bond, such as pyrethroid insecticides)
- Baseline (confirms if the toxicity is persistent)

If the cause of an observed effect is not clear after initial TIE testing, or if further detail describing the type or specific toxicant is desired, then the TIE Subcommittee may choose to have the laboratory conduct additional TIE treatments. Considerations for additional TIEs could include the level of available funding, magnitude of toxicity (TIE treatment effectiveness is easier to determine when there is a strong toxicity signal), species tested, and other data (e.g., potential sources, initial TIE results, and the likelihood that pesticides will be identified). As examples, the following TIE treatments could be selected to assess factors contributing to the observed effect:

- Low temperature – evidence of toxicity due to a contaminant that is metabolized, so lower temperatures slow the organisms' metabolism; increases the toxicity of pyrethroid insecticides
- Aeration – evidence of toxicity due to volatile, sublatable, or oxidizable compounds including surfactants
- Non-polar organic solid-phase extraction (SPE) column – evidence of toxicity due to a relatively polar organic contaminant

- pH 3/11 – evidence of toxicity due to hydrolysable/pH-dependent compounds (and filtration to assess/remove/control for settleable/coagulated toxicants and particulates).
- $Na_2S_2O_3$ – evidence of toxicity due to oxidants
- Cation Exchange – removes metals and other divalent cations
- Chemical analysis of cyanotoxins (to be compared with species-specific toxicity values). This would require freezing a subsample of the freshly collected sample for potential analysis if toxicity is observed from a location with known or potential cyanobacteria bloom.

The specific TIE treatments will depend on the test species. Salinity/conductivity is an important factor affecting toxicity test results for some species in the Delta, and TIEs in some samples with species sensitive to conductivity may require appropriate low-specific conductance or high-specific conductance secondary controls in addition to laboratory culture water controls treatments as indicated in SWAMP MQOs.

13.2.6. Sample Archive and Disposal

Project samples shall not be disposed of until all analyses are complete and analytical and QC results have been reviewed and approved by the Program Manager and the SFEI-ASC QAO.

14. Quality Control

14.1. Field Measurements

Prior to use in the field (typically within 24 hours prior to sampling), handheld water quality instruments will be calibrated against appropriate standards and, if possible, checked against a standard from a different source. For some measurements such as dissolved oxygen, probes are often calibrated to ambient conditions rather than to known standards. In such cases, the field staff should verify appropriate qualitative instrument response (e.g., in water deoxygenated by sparging, sodium sulfite addition, or other means). All calibrations are documented on a calibration checklist on the individual instrument or its case with date, time, and operator name. If an instrument cannot be calibrated or is not reading correctly, a backup instrument will be used to measure water quality parameters.

For single or multi-parameter water quality meters, the following standards will be used to calibrate:

1. **pH** – commercially available standards pH 4, 7, 10. Perform a 2-point calibration covering the range of expected measurements. Use the 3rd pH standard (or standard supplied by another manufacturer) as a check standard to verify calibration accuracy.

2. **Specific Conductance** – perform a single-point calibration in the middle of the expected environmental range and use two check standards (KCl solution) bracketing the expected measurement range.
3. **Dissolved oxygen** – use calibration procedure recommended by manufacturer, typically in 100% air saturation.
4. **Temperature** – check against thermometer of known accuracy before each deployment. An ice water bath of approximately 0°C can be used to semi-quantitatively verify temperature probe response but may vary due to uncontrolled factors such as container size and geometry, ice/water disequilibrium, or the presence of melting point-lowering contaminants.

If failure of an instrument should occur, a backup instrument should be checked and calibrated. All sampling and measurement modifications or failures that occur in the field due to instrument malfunction will be recorded in the Field Form and the Field Reference Sheet. The Field Collection Coordinators, Program Manager, and the SFEI-ASC QAO will be responsible for ensuring that staff document all deviations from planned operations and schedule repairs and/or additional training as needed.

14.2. Laboratory Analysis

For all participating labs, the Laboratory Project Manager must demonstrate and document that the methods performance meets the data quality requirements of the project. Two separate factors are involved in demonstrating method applicability: first, demonstrating that the laboratory can perform the method properly in a clean matrix with the analytical system under control, and second, demonstrating that the method selected generates “effective data” in the matrix of concern. The former addresses lab or operator training and proficiency, while the latter demonstrates that the selected method performs with the appropriate selectivity, sensitivity, accuracy, bias and precision, in the actual analytical matrix, to achieve project goals.

ASC’s Quality Assurance Officer or delegated staff member will assign quality assurance data flags (QACodes) to results that fail to meet the measurement quality objectives (MQOs). The screening value for assigning rejection Quality Assurance flags for each analyte to all environmental results on a project or dataset level is set by ASC at **twice the acceptance limit**. More information on how ASC performs QA and applies flags to data can be found in the Data Management and Quality Assurance SOP and Toxicity Data Management and Quality Assurance SOP.

14.2.1. Measurement Quality Objectives

Laboratory Performance Measurements for Laboratory Analyses

Laboratory performance measurements are included in the QA data review to check if measurement quality objectives are met. Results of analyses of QC samples are to be reported with results of field samples. Minimum frequencies and target performance requirements for QC measures of reported analytes are specified in Table 14.2.

QC measures typically used for evaluation of laboratory and field sampling performance include the following:

1. **Lab method blanks**: samples of a clean or null (e.g., empty container) matrix taken through the entire analytical procedure, including preservatives, reagents, and equipment used in preparation and quantitation of analytes in samples, to assess contamination introduced in lab processes.
2. **Field (ambient) blanks**: samples of a clean or null matrix transferred to the sampling sampling container, then analyzed much like an ordinary field sample to assess ambient contamination introduced in the field superimposed on any existing lab method blank contamination. Field blanks (as defined for this project) do not include contributions from field sampling equipment.
3. **Field equipment blanks:** samples of a clean or null matrix transferred to the sampling sampling container using all the normal procedure and equipment used in sample collection, then analyzed much like an ordinary field sample to assess ambient contamination introduced in the field, and originating from the sample equipment, superimposed on any existing lab method blank contamination.
4. **Laboratory replicates**: replicate sub-samples of field samples, taken through the full analytical procedure including all lab processes combined, to measure analytical precision. Although standard reference materials, lab reference materials, matrix spike samples, or laboratory control samples can also be analyzed in replicate, references to those are usually prefaced by their sample type name, e.g., “matrix spike duplicates”.
5. **Field replicates**: samples collected identically to the primary field samples at a site, used to assess spatial or temporal heterogeneity in the sampled matrix, superimposed on any existing laboratory analytical variation.
6. **Surrogate standards**: analytes introduced to samples prior to sample extraction to monitor sample extraction method recoveries.
7. **Internal standards**: analytes introduced after the last sample-processing step prior to analysis, to measure and correct for losses and errors introduced during analysis, with

recoveries and corrections to reported values generally reported for each sample individually.

8. **Laboratory control samples:** samples of a clean or null matrix spiked with target analytes, then analyzed much like an ordinary field sample, used to assess accuracy of the analytical method.
9. **Matrix spike samples/duplicates**: field samples to which known amounts of target analytes are added, indicating potential analytical interferences present in field samples, and errors or losses in analyses not accounted for by surrogate correction.
10. **Certified Reference Materials:** natural matrix samples with externally validated expected "certified" concentrations of analytes of interest, usually obtained from commercial or government vendors (e.g., NIST, which calls them "SRMs" (standard reference materials)). Often analyzed across multiple analytical batches, to track drift or shifts in analytical accuracy and precision.
11. **Lab reference materials**: materials collected, bought, or created by a laboratory as internal reference samples, to track performance across batches. ASC uses the term “lab reference material” only for natural matrix samples (e.g. archived material previously analyzed, diluted natural matrix CRMs, etc), instead using the term “lab control sample” for control samples from a clean or blank lab matrix

MQOs for Aquatic Toxicity Testing

Required Lab QC samples required by SWAMP were described in Section 7.5. In addition, although not a standard part of SWAMP requirements, as shown in Table 14.2, the study design calls for a rate of field duplicates of 1 per 20 field samples for aquatic toxicity testing. The field duplicate sample should be handled the same as for all other samples, and the full suite of toxicity tests should be run using the same species as the primary sample for the site and event duplicated.

The water quality measurements specifically coupled to toxicity tests are intended to help interpret toxicity test data. Quality control practices and MQOs for toxicity testing and water quality measurements parallel those used for field meter instrumentation. Meters are calibrated at the beginning of each day and calibration checks are performed when measurements for the day exceed 20 readings for each meter. Meters are recalibrated when drift exceeds the MQO for accuracy in Table 14.3. Quality control samples are expected to fall within the precision MQOs below and data are qualified in instances when these are exceeded.

14.2.2. Corrective Actions Procedures

If chemical analytical laboratory results fail to meet the MQOs, the corrective actions in Table 14.5 will be taken. Corrective actions will be documented, resolved, and followed-up on following the process for corrective actions that is outlined by SWAMP. The process is based on the SWAMP Corrective Action Form and is applied to sample results that fail to meet the technical and non-technical requirements of SWAMP and its associated projects.

If toxicity laboratory results fail to meet the MQOs, PER will proceed with their internal corrective action protocol. Corrective actions start with assessment of the cause of the problem (i.e., causal analysis). PER uses an "Evaluation of Non-Conforming Data" report to document and track investigations of non-conforming work and, where necessary, as documentation of implementation and monitoring of corrective actions. The PER QA Manager and their designees are responsible for initiating corrective actions on routine data reviews where a non-conformance is found that could reoccur or where there is doubt about the compliance of the laboratory to its own policies and procedures. All deficiencies are investigated, and a corrective action plan is developed and implemented if determined to be necessary. The PER QA Manager and their designees monitor the effectiveness of corrective actions.

A description of corrective actions taken will be provided to the Delta RMP TAC and other interested parties as a part of the QA Report accompanying the datasets produced in each focus area (mercury and pesticides).

Any significant changes to the monitoring design described in this QAPP should be documented using the Delta RMP QAPP Deviations Form. The purpose of this form is to clearly document deviations from a project plan; this includes workplans, Sampling and Analysis Plans and/or the Quality Assurance Project Plan (QAPP). It is also meant to document corrective actions, or steps that have been taken to prevent recurrence of a problem. Another goal of this process is to provide timely notification to stakeholders of important issues, rather than waiting for a QA summary at the end of the year. The Program Manager will share the completed forms with the Delta RMP TAC and other interested parties. Completed forms will also be included in quarterly progress reports to the Steering Committee. Finally, the forms may be included in year-end monitoring reports or QA summaries.

15. Instrument/Equipment Testing, Inspection, and Maintenance

15.1. Field Equipment

Field equipment such as boats, nets, and traps are inspected prior to each sampling event and are maintained throughout the field season and prior to storage during the off-season. Minimum equipment for the respective project elements includes:

Mercury - Fish

Boats (electro-fishing and/or for setting nets)

Bone saw, gill nets (various sizes), filet knives, fish picks, shackles, pliers, sharpening stone

Rod and reels, tackle box, landing net, live bait container

Plastic ice chests, inflatable buoy, floats, anchor chains, anchors, patch kit

Otter trawls

Blocks

Measuring boards, tape measure, id keys, Teflon cutting boards

Coolers

Mercury - Water

Collection devices appropriate for site

Field meters

Coolers

Pesticides and Aquatic Toxicity

Boat

collection devices

field meter

bottles

coolers and ice

15.2. Laboratory Equipment and Supplies

Contract laboratories maintain equipment in accordance with their respective SOPs, which include those specified by the manufacturer and those specified by the method.

Laboratories maintain internal SOPs for inspection and quality checking of supplies. Under a performance-based measurement system approach, these procedures are presumed to be effective unless field and QC data from analyses indicate otherwise. SFEI-ASC will then work with the laboratory to identify the causes and address deficiencies in the SOPs that resulted in those problems. If the problem is serious and cannot be corrected by the laboratory, the Program Manager and QAO will discuss and identify alternatives, including changing the sampling materials and methods, the extraction and analytical methods, the laboratory, or any combination of these.

16. Instrument/Equipment Calibration and Frequency

16.1. Field Instruments/Equipment

Whenever an environmental water sample is collected, field crews shall collect basic water quality measurements using handheld measurement devices. Instruments for field data collection are described in Section 14.1, Field Measurements.

16.2. Laboratory Equipment

All laboratory instruments involved in analyses of Delta RMP samples shall be inspected, maintained, calibrated (as applicable) and tested prior to use. Laboratory instruments are calibrated, standardized, and maintained following procedures detailed in laboratory Quality Assurance Plans (QAPs) and Standard Operating Procedures (SOPs), adopted herein by reference, and listed in Appendix E.)

At a minimum, calibration procedures shall meet the requirements specified in the approved method, e.g. from USEPA or Standard Methods. Calibration procedures are described briefly below.

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 (e.g., a certified solution). The calibration curve is acceptable if it has an R^2 of 0.995 or greater for all analytes present in the calibration mixtures. If not, the calibration standards, as well as all the samples in the batch, must be re-analyzed. All calibration standards will be traceable to an organization that is recognized for the preparation and certification of QA/QC materials (e.g., NIST, NRCC, U.S. EPA).

Calibration curves will be established for each analyte and batch analysis from a calibration blank and a multi-point calibration (as described or required in the method), covering the range of expected sample concentrations. Only data within the working calibration range (above the MDL) should be reported (i.e., extrapolation is not acceptable). Samples outside the calibration range will be diluted as appropriate and reanalyzed.

Table 14.1 lists the project requirements for the frequency of calibration and type of calibration for field instruments. The required rate of calibration verification samples for laboratory instruments is listed in Table 14.2. A variety of sample types is used to check the accuracy and precision of lab instruments, including calibration verification samples, laboratory blanks, and lab duplicates.

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) again does not meet specifications, it will be serviced 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).

17. Inspection/Acceptance for Supplies and Consumables

All supplies shall be examined for damage as they are received. Laboratory personnel will review all supplies as they arrive to ensure the shipment is complete and intact. Laboratory staff shall log in all chemicals to the appropriate logbook and dated upon receipt. All supplies shall be stored appropriately following manufacturer recommendations. Chemicals and reference standards shall be discarded upon expiration date or if there is evidence that the material is degraded or damaged. Table 17.1 indicates items that should be considered for accuracy, precision, and contamination. If these items are not found to be in compliance with the acceptance criteria, they will be discarded or returned to the manufacturer.

17.1. Field Supplies

All containers should meet or exceed the required trace limits established by the U.S. EPA in the document EPA/540/R-93/051, Section 10, *Specifications and Guidance for Contaminant-Free Sample Containers*. Chemical-resistant powder-free nitrile and polyethylene gloves shall be worn.

At a minimum, the following supplies are required for the respective project elements:

Mercury - Fish

- Waterproof labels
- Bait
- Heavy-duty aluminum foil (prepared), zipper-closure polyethylene bags
- Field sheet (see Appendix F)
- Ice
- Chain-of-custody form (see Appendix G)

Mercury -Water

- Sampling containers and labels
- Powder-free nitrile gloves
- Deionized water squirt bottle
- Field sheet (see Appendix F)
- Ice
- Chain-of-custody form (see Appendix G)

Pesticides and Toxicity Sampling

- Safety gear; personal flotation devices; wet-weather gear if necessary
- GPS unit; mobile phone and/or radio
- Sampling containers and labels
- Collection devices appropriate for site
- Powder-free nitrile gloves
- Field meters
- Deionized water squirt bottle
- Field sheet (see Appendix F)
- Coolers and ice
- Chain-of-custody forms (see Appendix G)

18. Non-direct Measurements

Non-Delta RMP data (e.g., from Irrigated Lands Regulatory Program) may be used in determining ranges of expected concentrations in field samples, characterizing average conditions (e.g., temperature, barometric pressure) for calculations, and other purposes. These data will be reviewed against the measurement quality objectives and used only if they meet all of the specified criteria (See Section 14.2.1, Measurement Quality Objectives). Data not meeting Delta RMP quality objectives should be used only in a qualitative manner for developing conceptual models and prioritizing future data needs.

Hydrologic data (stage, flow, etc.) will be obtained from existing gauges and recorders located at or near designated monitoring locations. Only fully QA-reviewed hydrologic data will be used in analysis and reporting. Acceptable sources include the USGS National Water Information System (NWIS, https://waterdata.usgs.gov/nwis) and the DWR Water Data Library (WDL, http://wdl.water.ca.gov/waterdatalibrary/). Provisional data and modeled/forecasted data may be used for planning sampling events, for example determining whether there is sufficient rainfall and runoff forecasted to meet one of the event triggers described in Table 6.7.

19. Data Management

This section provides a brief overview of how project staff manage data generated by the project's sampling and analysis. For more detailed information, refer to SFEI-ASC's *Data Management and Quality Assurance Standard Operating Procedures* document, included as

Appendix H, and for toxicity data, the *Toxicity Data Management and Quality Assurance Standard Operating Procedure*s, included as Appendix I.

All raw and statistical analysis data are subject to review before upload, with ~10% spot-checked for accuracy by the SFEI-ASC QAO and Laboratory QAOs. Data are analyzed and proofread for accuracy, and then QA checked against the QAPP and project criteria before being entered into the CEDEN database. Original hard copies of the data are stored securely 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.

SFEI and cooperators shall update computer hardware and software as recommended by the manufacturer or as needed. Regular testing of individual components is not required, other than verifying day to day functionality. Each entity is responsible for the necessary updates or upgrades, whether provided regularly through an Information Technology department or otherwise.

19.1. Entering and formatting of sampling and QA data results

19.1.1. Laboratory reporting of results

Chemical-analytical data shall be reported by labs in CEDEN's Water Quality (WQ) or Tissue templates (see section 19.1.2. for Toxicity data procedures). Tabulated data will include the following information for each sample (when applicable):

1. **Sample identification**: Unique sample ID, site code, site name, collection date, collection time, analysis date, sample type (field or QC types), and matrix.
2. **Analytical method**s: Preparation, extraction, and quantitation methods (codes should reference SOPs submitted with the data submission package). Also include preparation, extraction, and analysis dates.
3. **Analytical results**: Analyte name, fraction, result, unit, method detection limit (MDL), and reporting limit (RL) for all target parameters. The appropriate data qualifiers should be submitted with the results.
4. **Batch and result comments**: Lab comments must be applied to any batch when any QA code was applied to a result in the batch that may affect data use. A brief explanation of the issue shall be included.

Required additional data include:

- Lab replicate results (and field replicates, when sent for analysis).
- Quality assurance information for each analytical chemistry batch.

- CRM or LRM results: absolute concentrations measured, certified value, and percent recovery relative to certified or expected value.
- Matrix (or blank) spike results: include expected value (native + spike) for each analyte, actual recovered concentrations, calculated per recovery, and RPD.
- Method blank sample results in units equivalent to field sample results (e.g., if the field samples are reported as ng/g, method blanks are given in the same units). Lab replicate results and calculated RPD or RSD.

Documentation containing definitions, field length, field requirement, and associated lookup lists (if applicable) for each field is available on the CEDEN website at http://www.ceden.org/ceden_datatemplates.shtml.

Fields requiring controlled vocabulary can be identified by hovering over the field name in the template and referring to the lookup list that is referenced. Lookup lists are available on the CEDEN website at http://www.ceden.org/CEDEN_Checker/Checker/LookUpLists.php.

Batches must be reviewed for QC completeness and any deviation in QC results should be documented in the accompanying case narrative. The required fields will be identified in the template in green font. Each laboratory shall establish a system for detecting and reducing transcription and calculation errors prior to reporting data.

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

Reporting turnaround times for submission of results from sample analyses are specified in contracts with the analytical laboratories. However, samples should be extracted and analyzed within the holding times specified for the analytical methods used (Table 12.1). Turnaround time requirements specified in subcontracts are generally 90 days or less.

19.1.2. Toxicity data

Delta RMP toxicity collection agencies and laboratories will provide toxicity data to ASC in accordance with the ASC contract requirements. ASC will assume all data management responsibilities for Delta RMP toxicity data. This includes data processing, QA/QC review, and data uploading to the California Environmental Data Exchange Network (CEDEN). Data will be reviewed by ASC data managers under the supervision of the ASC QA Officer, following the Delta RMP *Toxicity Data Management and Quality Assurance Standard Operating Procedures*. The ASC project manager will distribute the provisional toxicity data to the TAC for review as

Electronic Data Deliverables (EDDs) are received from the toxicity lab (after verifying that all expected results for the sampling event have been provided), and will distribute the final toxicity data and QA summary to the Delta RMP TAC for review upon completion of QA/QC review of the data (and prior to the data's public release). The data will be made publicly available through CEDEN's Advanced Query tool in a timely manner that will allow the Regional Board to be responsive to water quality concerns.

19.1.3. Mercury data

The Delta RMP mercury collection laboratory will provide water and tissue data to the data managers at the State Water Resources Control Board's Information Management & Quality Assurance Center unit (SWAMP IQ) in accordance with the Water Board's contract requirements. The SWAMP IQ unit will assume all data management responsibilities for Delta RMP mercury data. This includes data processing, QA/QC review, and data uploading to the California Environmental Data Exchange Network (CEDEN). Data will be reviewed by the State Water Resources Control Board Office of Information Management and Analysis (OIMA) data managers under the supervision of the SWAMP QA Officer, following the SWAMP Chemistry Data Verification Standard Operating Procedures. The data will be made publicly available through CEDEN's Advanced Query tool.

19.1.4. Pesticides Chemistry Data

Pesticides chemistry is analyzed by the USGS Organic Chemistry Lab (OCRL) in Sacramento. The handling of these data is different from other Delta RMP datasets due to the nature of our cooperation with the USGS, which is not simply a contract lab, but a federal science agency with its own long-standing policies and procedures. According to USGS policy, results from their labs shall be included in the National Water Information System (NWIS). This is an online database where results are freely available to the public.

OCRL staff perform a quality assurance review of the results generated in their lab, and then upload provisional data to the NWIS database. Afterwards, OCRL transmits the data to ASC in the CEDEN data template format. ASC staff format these data and perform a thorough and independent QA review. As with other datasets, if serious issues arise, ASC will communicate with OCRL to resolve these issues. This would include, for example, missing or duplicate data, data that appear to have been reported incorrectly, results outside of the expected range, incorrect units, serious deviations from the measurement quality objectives, or any other issue identified that could indicate problems with the lab analysis.

As a part of ASC's QA review, the ASC QA Officer may flag records which did not meet MQOs, or reject results that are considered unacceptable by the QA officer. The QA officer writes a short memo summarizing the findings of the QA review, and summarizing the quality of the data. This memo describes whether the results received from the lab are complete and accurate and whether there is any evidence of contamination or other problems. The audience for the QA memo is both internal (the ASC project manager and staff) and external (stakeholders with an interest in reviewing the data and findings of the QA review).

The ASC project manager will distribute the provisional pesticides chemistry data and QA summary to the Delta RMP TAC for review. ASC data analysts upload these data to CEDEN, and they are made viewable by the public once approved by the Delta RMP Steering Committee. Note that this data release process is under review by Regional Board staff and under discussion by the new RMP governance structure. Therefore, changes may be implemented in 2021 based on the outcomes of these discussions and to be consistent with California's open data laws (AB1755) and State Water Resources Control Board Resolution No. 2018-0032.

19.2. Laboratory data report package information

Analytical results, including associated quality control samples (see Section 14.2.1 Measurement Quality Objectives), will be provided to SFEI-ASC or OIMA by the analytical laboratories. The laboratories analyze samples according to the hold times listed in the Delta RMP QAPP. The final report may be finalized for review up to 90 days after samples are received from the laboratory. Exceedances of the standard turnaround time should be discussed with and approved by the Delta RMP Program Manager and SFEI-ASC QAO.

Laboratory personnel will verify, screen, validate, and prepare all data, including QA/QC results, and will provide (upon request) detailed QA/QC documentation that can be referred to for an explanation of any factors affecting data quality or interpretation. Any detailed QA/QC data not submitted as part of the reporting package should be maintained in the laboratory's database or files for future reference.

Laboratories will provide electronic copies of the tabulated analytical data in a format agreed upon with the Program Manager, SFEI-ASC Data Manager, or a designee or in accordance with the Water Board's contract requirements for mercury data.

Results should be flagged by the laboratory for exceedances of Delta RMP MQOs for completeness, sensitivity, precision, and accuracy, using data quality codes as defined by CEDEN's list of QA codes, which have been adopted by the Delta RMP for reporting data. The

data quality codes should be provided in the LabResult table in the ResQualCode and QACode fields. A list of commonly used result qualifier codes is shown in Table 23.1. The most commonly used QA codes are shown in Table 23.2. A complete list of codes is available online at CEDEN's Controlled Vocabulary web page.

For a detailed description of the measurements and procedures that are used by the lab QA Officer, SWAMP QA Officer, and ASC QA Officer to demonstrate the quality of reported, see Section 7, Quality Objectives and Criteria.

19.3. Data storage/database

With the exception of mercury data managed by SWRCB, data are managed by SFEI-ASC Data Services staff under the supervision of the Data Services Manager and the SFEI-ASC Quality Assurance Officer. Upon completion of QA/QC review and data validation, data are compiled into the SFEI-ASC RDC database and distributed to the project managers.

Data that are approved for public release by the Delta RMP Steering Committee are made available through SFEI-ASC's Contaminant Data Display and Download website (CD3), usually within one year of sample collection. Data will also be made available through CEDEN's Advanced Query Tool webpage. Additionally, pesticide chemistry data will be added to the National Water Information System (NWIS) online database by USGS OCRL staff.

Delta RMP mercury data are managed by OIMA staff under the supervision of the SWAMP QA Officer. Upon completion of QA/QC review and data validation, data are compiled into the SWAMP RDC database. Because SWAMP is funding the mercury analyses and managing these data, the SWAMP IQ unit will make the data publicly available through CEDEN's Advanced Query Tool webpage, without the same review and approval steps that govern the release of other Delta RMP datasets, as outlined in the Communications Plan.

20. Lab Assessment and Response Actions

Before a new monitoring project is initiated, an initial desktop or on-site performance audit will be performed by the QAO and designated staff to determine if each laboratory can meet the requirements of the QAPP and to assist the laboratory where needed. Additional audits may be conducted at any time during the scope of the study. The QAO will review every data file submitted as part of these audits and ensure that QC issues will be addressed as soon as they are detected. Results will be reviewed with participating laboratory staff and corrective action

recommended and implemented, where necessary. Furthermore, laboratory performance will be assessed on a continual basis through laboratory intercomparison studies (or "round robins") where available, such as those conducted by the National Institute of Standards and Technology (NIST).

If data quality issues are identified, a preliminary meeting will be held between SFEI-ASC's QAO, the Program Manager, and the lab QAO to discuss possible solutions. If necessary, a corrective action plan will be developed in consultation with the appropriate lab(s), the corrective actions taken, and the issue and its resolution summarized in a brief report or memorandum. A summary of these issues will be maintained in the project files and will be noted in any reporting that includes affected data.

21. Reports to Management

The Implementing Entity of the Delta RMP (currently SFEI-ASC) will produce Annual Monitoring Reports for each of the focus areas, which documents the activities of the program each year that summarizes monitoring results and synthesizes the information they provide; and technical reports that document specific studies and synthesize information from diverse sources in relation to specific topics and prioritized assessment questions. Reporting products and schedules are described in more detail in Section 6.6.

The Annual Monitoring Reports and/or QA Reports for each of the focus areas will present the results of the previous July-June fiscal year of sampling. The main purpose of these reports is to summarize the final data and results of the QA review. The QAO is responsible for summarizing potential QA issues with reported data and communicating those issues to the Program Manager. The QAO also reviews any SFEI-ASC analyses and reports generated from the data, to ensure that QA issues are appropriately acknowledged in the presentation and interpretation of data. The QAO will prepare a QA memo for each monitoring element (mercury, nutrients, etc.) annually, after completion of the QA review.

Any significant changes to the monitoring design described in this QAPP should be documented using the Delta RMP QAPP Deviations Form. The purpose of this form is to clearly document deviations from a project plan; this includes workplans, Sampling and Analysis Plans and/or the Quality Assurance Project Plan (QAPP). It is also meant to document corrective actions, or steps that have been taken to prevent recurrence of a problem. Another goal of this process is to provide timely notification to stakeholders of important issues, rather than waiting for a QA summary at the end of the year. The Program Manager will share the completed forms with the Delta RMP TAC and other interested parties. Completed forms will also be included in

quarterly progress reports to the Steering Committee. Finally, the forms may be included in year-end monitoring reports or QA summaries.

22. Data Review, Verification, and Validation

Delta RMP mercury data are managed by SWAMP IQ unit staff, and are reviewed following the SWAMP Chemistry Data Verification Standard Operating Procedures. All other Delta RMP data undergo review and evaluation by SFEI-ASC to ensure that the data conform to quality criteria identified in this document (particularly Section 7) and other project-specific criteria. In addition, data are assessed to determine usability and whether the data support their intended use. Review of the data consists of three discrete but highly interlinked processes: verification, and validation, described in the next section, and assessment, in the last section.

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

23. Verification and Validation Methods

This section describes at a high level SFEI-ASC's process for verification and validation of reported environmental data. SFEI staff, working under the supervision of the SFEI QA Officer, perform data verification and validation following methods described in the Data Management and Quality Assurance Standard Operating Procedures. The latest version of this document is in Appendix H. See the Delta RMP Toxicity Data Management and Quality Assurance Standard Operating Procedures for information on verification and validation of Delta RMP toxicity data.

23.1. Data Verification

In EPA guidance (EPA QA/G-8, USEPA 2000), data verification is defined as "the process of evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual requirements." Data are evaluated as meeting or failing MQOs, first by the laboratory, and again by the project QA Staff. In addition to contamination and other artifacts introduced by sampling and analytical methods, errors may arise at many points in the processing and transmittal of data generated for the Delta RMP. Characteristics of reported data are examined to identify possible problems in the generation and transmission of data.

Before submitting data, the contract laboratory's QA Officer (QAO) checks all of its records and the laboratory's Director or Project Manager will recheck 10%. All checks by the laboratory may be reviewed by SFEI-ASC. Issues are noted in a narrative list and communicated to the field or laboratory teams as needed to correct any problems found (e.g. unanalyzed samples left in storage, transcription errors).

Data are submitted to SFEI-ASC in electronic form. Labs send the results to ASC after each round of analysis, typically within 30 days after sample receipt. ASC verifies the completeness of the submittal. Data verification for chemistry results will be done after each submittal. The Quality Assurance Officer will prepare the QA summary for external distribution after each year's monitoring is complete.

After data are submitted to SFEI-ASC, SFEI-ASC staff will verify the data set for completeness (e.g., correct numbers of samples and analyses, appropriate QC sample data included) and accuracy (e.g., in sample IDs, using CEDEN vocabulary), and spot-check for consistency with hardcopy results reported by the laboratory. The SFEI-ASC QAO or designee will examine submitted QA data for conformance with MQOs, specified previously (Section 14.2.1). Data that are incomplete, inaccurate, or failing MQOs without appropriate explanation will be referred back to the laboratory for correction or clarification. The Project Manager and QAO will discuss data failing MQOs with laboratory staff to determine corrective actions and whether the samples need to be re-collected. If problems cannot be readily corrected (insufficient sample, irremovable interferences, or blank contamination), results outside the MQOs will be flagged using CEDEN codes appropriate for the specific deviations to alert data users to uncertainties in quantitation. Table 23.1 shows the CEDEN controlled vocabulary for result qualifiers. Table 23.2 shows the most frequently used CEDEN QA codes. A full list of QA codes that may be applied can be found online at CEDEN's Controlled Vocabulary web page.

Data are further assigned a batch verification code on a batch level. See Table 23.4 for batch verification codes. When measurement quality objectives (MQOs) are not met, verification codes from the Batch Verification Look -up and/or QA Code Lookup tables may be applied by ASC staff or QA Officer and entered into the database. These codes are preceded by a "V" in the "Batch Verification Code" or "QA Code" fields. Individual records for field data and taxonomy, and laboratory batches for chemistry, tissue and toxicity will be coded "VAC" once verification is complete. This code is contained in the Batch Verification Code field. If deviations from the MQOs are detected by ASC staff that were not detected by the laboratory, the data is coded " VAC, VMD. " If some QC information is missing, the data will be coded with "VAC,VQI." If all QA data were expected to be reported and none are available, then the data are coded as "VQN". When batches are determined to be missing some or all QC required information, ASC

staff will initiate communication with the lab to obtain this information, and will recommend corrective action so this information is included in future data deliverables. When MQOs do not exist for certain data types, the data are coded as "NA" ("Not Applicable").

Data from the first group of samples analyzed for each matrix will be reported as completed, to establish that all sampling, analysis, and reporting processes are performing as planned; after the first sampling group, data may be reviewed at a lower frequency as warranted (e.g., if no corrective actions appear likely necessary moving forward). However, new issues identified by the field or lab teams will be reviewed and addressed by SFEI-ASC's Program Manager and QAO mid-project as needed.

23.2 Data Validation

EPA (in EPA QA/G-8, USEPA 2000) defines data validation as "an analyte- and sample-specific process that extends the evaluation of data beyond method, procedural, or contractual compliance (i.e., data verification) to determine the analytical quality of a specific data set." Data verification evaluates the quality of reported data at a more granular level, for example, as individual batches provided by the analytical laboratory. In data validation, the results in field and lab samples are considered in aggregate across batches to assess the overall quality of the reported data.

In addition to verification of performance on required QC measures and samples (i.e., MDLs, blanks, matrix spikes, CRM, and replicates), data are also examined for internal and external consistency to ensure that reported values are realistic and representative for the locations and matrices of collected samples. This review may include but is not limited to:

1. Comparison of reported values to those from previous monitoring to evaluate if they are within the expected range of values for a given study. Simple statistics (e.g., minimum, maximum, mean, median) may be generated to quickly identify data sets or individual data points greatly outside of their expected range. Anomalous individual points will be examined for transcription errors. Unit conversions and sample quantitation calculations may be reviewed to identify larger and systematic errors. However, large differences from previously reported values may not necessarily indicate analytical issues and may simply reflect natural spatial and temporal variability of the ecosystem.
2. Comparison of reported values to those in the published literature, where available – differences from other regions and/or species may merely indicate differences in resident species and ecosystem structure, but very large (e.g. 2-3 orders of magnitude) differences may sometimes help identify errors in analysis or reporting (e.g. unit conversions).
3. Internal checks of relative analyte abundance. Variations in concentrations of one compound or isomer are often tightly linked to those of related compounds, such as its

degradation products, manufacturing byproducts, or other compounds from the same group of chemicals (e.g., congeners of the same class of chemicals within a commercial mixture). Deviations in these relative abundances can sometimes indicate matrix interferences or other analytical problems, although care should be taken to not disregard results that might reveal atypical sources and/or ecosystem processes.

The results of performance on QC samples reviewed in the previous section on data verification is considered together with the comparability of the project's new data to that previously generated by the project, and/or in other studies, to evaluate the uncertainty in the quantities reported for field samples. At the completion of the QA review by the QAO, results are assigned a compliance code on an individual record level. See Table 23.3 for compliance codes. Results from the data review (both verification and validation) will be summarized in the annual QA Report.

24. Data Assessment and Reconciliation with User Requirements

EPA (in EPA QA/G-9, USEPA 2000) defines data quality assessment (DQA) as "the scientific and statistical evaluation of data to determine if data obtained from environmental data operations are of the right type, quality, and quantity to support their intended use." Procedures used to evaluate the uncertainty of the reported validated data are described in Sections 7, 14, and 20-23. Limitations on data use will be reported to the data users as validation and verification QA codes and comments in the CEDEN database (Section 23) and in Annual Monitoring Reports (Section 21). The monitoring reports are also central to the data quality assessment, as they report the results in the full context of the data needs of the program.

Measurement quality objectives listed previously (Section 14.2.1) establish targets to be routinely achieved by the analytical laboratory. Data verification checks conformance to these targets, as well as achievement of project goals by field and lab teams in completeness and conformance to project protocols of collection of samples and reporting of data. Data validation uses the provided information to report on the overall accuracy or uncertainties in the data.

In data assessment, the project team reports the results in the context of the questions and other data needs for which the project was designed, However, it is uncertain whether obtained data, even when meeting all stated MQOs, will be sufficient to answer the Delta RMP management questions with sufficient certainty, as the relative contributions of environmental variability and analytical uncertainty to cumulative uncertainty (e.g. for use in modeling, comparisons to guidelines, or other functions) cannot be known *a priori* before sufficient data have been collected. However, as Delta RMP studies proceed, the ability of collected data to answer these

management questions should be periodically re-evaluated for study design and budget planning in subsequent years.

Limitations on data use shall be reported to data users in the form of flags or qualifiers in the CEDEN electronic database. Further, program staff and contractors will describe important limitations on the use and interpretation of program data in reports. Program staff, working under the supervision of SFEI's Quality Assurance Officer (QAO), write quality assurance summaries for each dataset produced by the Delta RMP. These are reviewed and approved by the QAO and program manager, and are typically attached to year-end data reports as an appendix. These reports are reviewed by the Delta RMP TAC and approved by the Steering Committee prior to being published.

For example, one of the goals of the initial phase of Delta RMP fish mercury monitoring is to obtain robust information on interannual variation to support future power analysis. The power to detect interannual trends in mercury in largemouth bass on a per site basis will be reevaluated when 3-5 years of monitoring data are available. It will be discussed then, whether the DQO needs to be refined and/or whether the monitoring design should be modified (e.g. increase or decrease the number of fish to be collected at each site).

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