

## Delta RMP Special Study Proposal

### Aquatic Toxicity and Current Use Pesticides Monitoring Using a Rotating Basin Probabilistic Design, Water Year 2019

#### Executive Summary

**Estimated Cost:**

**Delta RMP Funds:** \$248,352 or \$255,933 (depending on monitoring design chosen)

**SWAMP Funds** (in-kind contribution): \$311,120

**USGS In-kind contribution:** \$18,022

**Oversight Group:** Delta RMP Pesticides Subcommittee

**Proposed by:** SFEI-ASC, USGS

This proposal requests funding from the Delta RMP Steering Committee for Year 1 of a 4- to 5-year study of current-use pesticides and aquatic toxicity in the Sacramento-San Joaquin Delta. Two options are proposed: 1) a rotating basin monitoring design and 2) a hybrid design that adds monitoring at 2 fixed sites selected based on previous monitoring history. Both options include a statistical survey of subregions of the Delta and include analysis of the same constituents. Year 1 monitoring would begin in October 2018 and continue through September 2019 (2019 Water Year); years 2–4 would continue to be based on a water year. A key to the success of a status and trends monitoring program is that it be sustained over a long time. This proposal describes a 3 to 4 year monitoring program covering the Delta. During year 4, an interpretive report is planned, from which lessons may be drawn to adaptively manage and improve future monitoring.

Under this “rotating basin” monitoring design, the Delta is split into 6 subregions (established by prior analytical work by the Delta RMP) and 2 subregions are monitored each year. All 6 subregions are monitored over a 3-year cycle. Within each subregion, sampling points are randomly selected using the Generalized Random-Tessellation Stratified (GRTS) method. Subregions will be further stratified or divided into two water body types, representing 1) large river channels and open water lakes, and 2) smaller, shallower streams and sloughs. An advantage of this random or “probabilistic” design is that it allows the use of standard statistical methods to make inferences about Delta waterways as a whole, and to calculate the uncertainty for estimates in terms of confidence intervals. A key output of the study will be to determine what percent of Delta waterways exhibit toxicity to aquatic organisms or have concentrations of pesticides that exceed a water quality threshold or aquatic life benchmark.

During Year 1 of the study, 48 water samples will be collected by boat from 2 Delta subregions by field crews from the USGS California Water Science Center in Sacramento. Samples will be analyzed for a suite of 174 Current Use Pesticides (CUP) by the USGS Organic Chemistry Research Laboratory (OCRL). Compounds include fungicides, herbicides, insecticides, and their degradation products. In addition, crews will measure field parameters (water temperature, pH, conductivity, dissolved oxygen, turbidity), and document conditions at the field site. The USGS National Water Quality Laboratory will analyze samples for copper and ancillary parameters (total nitrogen, total particulate carbon, particulate organic carbon, and dissolved organic carbon).

The Aquatic Health Program Laboratory at UC Davis will analyze the toxicity of water samples for a suite of test organisms based on EPA (2002, 2000) and SWAMP (2008) methods:

- *Ceriodaphnia dubia*, a daphnid or water flea (survival, reproduction) – sensitive to organophosphate pesticides
- *Hyalella azteca*, an aquatic invertebrate (survival) – sensitive to pyrethroids
- *Selenastrum capricornutum* (also known as *Raphidocelis subcapitata*), a single-celled algae (growth) – sensitive to herbicides
- *Chironomus dilutus*, midge larvae (formerly *Chironomus tentans*) - sensitive to fipronil and more sensitive in chronic exposures to imidacloprid than *C. dubia*.
- *Pimephales promelas* (growth, survival) – chronic and acute effects on whole organism growth and survival

If toxicity exceeding a certain threshold is found in a water sample, we may instruct the lab to conduct follow-up investigations to determine the cause of toxicity, by performing a Toxicity Identification Evaluation (TIE). As in past years of monitoring, the discussion of whether to conduct a TIE will be triggered when significant toxicity is observed exceeding a pre-determined threshold, and decided upon by a subcommittee of stakeholders and technical experts.

A hybrid option (Option B) is included in this proposal. It reduces the number of probabilistic samples collected each year in order to continue monitoring at two fixed sites (Ulati Creek at Brown Road and San Joaquin River at Buckley Cove) where aquatic toxicity has been observed in the past. This “hybrid” option includes the capability of detecting trends at these two sites over a longer period of continuous data and may provide additional opportunities to test for associations between pesticides and toxicity at these locations. However, under Option B we would collect fewer random samples in each subregion each year, requiring one extra year to obtain the number of samples estimated for the desired statistical power of the study.

This proposal was developed with the collaboration of the Delta RMP Pesticides Subcommittee and with the input of a consulting statistician. During the proposal development process, we sought to follow the recommendations of the 2016 Independent Panel Review (Raimondi et al. 2016). The key recommendations were to: (1) engage the services of a professional

environmental statistician, (2) consider a random sampling to expand beyond monitoring at fixed sites only and expand capability to draw inferences about more areas of the Delta, and (3) clearly define quantities to be observed or estimated from measurements. We have responded to the first two recommendations during the planning of this monitoring design by engaging an environmental statistician with experience in randomized sampling design to analyze the first two years of Delta RMP pesticides and toxicity data, perform power analyses, and advise us on the monitoring design. A report by our consulting statistician is provided in Appendix 3. We responded to (3) by following the EPA's Data Quality Objectives (DQO) process, stating *a priori* the information to be collected, the analytical approach to be used to evaluate data, and tolerable limits on decision errors. More information on this is provided in the section Data Analysis and Presentation on page 35.

There are tradeoffs involved in designing a monitoring program due to budget and practical constraints. The strengths and limitations of the proposed monitoring designs are listed in more detail on page 24.

The Steering Committee is being asked to commit funding for the first year of this 4-year plan. However, this proposal is not intended to lock us into an inflexible program. The program should be open to "adaptively manage" and make changes to the monitoring design. For instance, we have recently hired a contractor to analyze the data on pesticides and toxicity from the first two years of monitoring from 2015 to 2017. We may wish to make changes to the monitoring design based on the results of data analysis and interpretation, and as our knowledge and priorities change over time.

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## Acronyms and Abbreviations

AHPL	Aquatic Health Program Laboratory at UC Davis
ASC	Aquatic Science Center
BLM	biotic ligand model
BPA	Basin Plan Amendment
CAWSC	USGS California Water Science Center
CC	chief chemist
CDF	cumulative distribution function
CEDEN	California Environmental Data Exchange Network
CUP	Current Use Pesticides
CVRWQCB	Central Valley Regional Water Quality Control Board
DDD	dichlorodiphenyldichloroethane
DDE	dichlorodiphenyldichloroethylene
DDT	dichlorodiphenyltrichloroethane
DM	Database manager
DMS	Data management staff
DQO	Data quality objectives
DWR	Department of Water Resources
EC	electrical conductivity
EPA	Environmental Protection Agency
FY	Fiscal year (July 1 – June 30)
GC/MS	Gas chromatography/mass spectrometry
GIS	Geographic Information System
LC50	Lethal concentration (that kills 50% of the test organisms during the observation period)
GRTS	Generalized Random-Tessellation Stratified (sampling method)
LC/MS	Liquid chromatography/mass spectrometry
MDL	Method detection limit
MQO	Measurement quality objective
NA	Not applicable
NHD	National Hydrography Dataset
NOAA	National Oceanic and Atmospheric Administration
NPDES	National Pollutant Discharge Elimination System
NWIS	USGS National Water Information System
NWQL	National Water Quality Laboratory
NWQMC	National Water Quality Monitoring Council
OCRL	Organic Chemistry Research Laboratory
OFR	USGS Open File Report
OPP	USEPA Office of Pesticides Programs
PD	Project director
PTI	Pesticide Toxicity Index
QA	Quality Assurance
QAO	Quality assurance officer

QAPP	Quality Assurance Program Plan
QC	Quality control
RL	Reporting limit
RMA	Resource Management Associates
RMP	Regional Monitoring Program
S&T	Status & Trends
SFEI	San Francisco Estuary Institute
SJR	San Joaquin River
SWAMP	Surface Water Ambient Monitoring Program
TAC	Technical Advisory Committee
TIE	Toxicity identification evaluation
TMDL	Total Maximum Daily Load
USGS	U.S. Geological Survey

## Background and Motivation

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 generally 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 appear to be 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.

## Regulatory Drivers

The proposed 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 Central Valley Basin (Basin Plan)

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 Basin Plans 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 Regional Water Board initiated a biotoxicity monitoring program to assess toxic impacts from point and nonpoint sources in FY 86-87” (CVRWQCB 2016, IV-32.08). The plan states that the Regional Board “will continue to impose toxicity testing monitoring requirements in National Pollutant Discharge Elimination System (NPDES) 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 Central Valley Water Board 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 contain 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 are nearly identical requirements for agricultural dischargers to the Sacramento and San Joaquin River under those TMDLs, respectively (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 Sac -SJR 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 which 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 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 the discharge (POTWs) or discharge or receiving water (MS4s and Ag dischargers)
- Determine whether pyrethroid pesticides are causing or contributing to exceedances of the narrative water quality objective for toxicity – through toxicity testing with *Hyalella* in water column of receiving waters (POTWs) or receiving waters water column and bed sediments (Ag and MS4s)

This monitoring must be completed two years from the effective date of the Basin Plan Amendment (BPA), expected December 2018. In the long term after that two-year period, dischargers will also be required to monitor for alternative insecticides that could be having water quality impacts.

### Objectives of the Delta RMP Current Use Pesticides Monitoring Program

The overall objectives of the Delta Regional Monitoring Program's (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 (Table 1). 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 current proposed 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 status and trends of pesticide concentrations and toxicity in the Delta.

Proposed Delta RMP CUP monitoring includes the collection of samples for aquatic toxicity testing and analyzing pesticide concentrations in water samples at multiple randomly-chosen sampling locations within subregions of the Delta. One or more of these areas would be assessed each year over the rotation cycle.

### Applicable Management and Assessment Questions

Table 1 shows the Delta RMP Management and Assessment Questions that this study can help answer. The table also shows the objectives of the project and examples of how the information collected by the project can be used by water managers and water quality regulators.

Table 1 Delta Regional Monitoring Program Management and Assessment Questions

Relevant Management and Assessment Questions	Study Objectives	Example Information Application
<p><b>Management Question</b> Is water quality currently, or trending towards adversely affecting beneficial uses of the Delta?</p> <p><b>Assessment Questions</b> S&amp;T 1 - To what extent do current use pesticides contribute to observed toxicity in the Delta? S&amp;T 1.1 - If samples are toxic, do detected pesticides explain the toxicity? S&amp;T 1.2 - What are the spatial and temporal extent of lethal and sublethal aquatic and sediment toxicity observed in the Delta? S&amp;T 2 - What are the spatial/temporal distributions of concentrations of currently used pesticides identified as possible causes of observed toxicity?</p>	<p>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.</p>	<p>The Delta RMP can use this information to determine what percentage of Delta waters exhibit toxicity to aquatic organisms or have concentrations of pesticides that exceed thresholds. 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 be having adverse impacts on aquatic environment that prevent the obtainment 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.</p>

## Technical Approach

The Delta RMP will collect ambient surface water samples to be analyzed for pesticide concentrations and toxicity to established aquatic test species during multiple sampling events in the Sacramento-San Joaquin Delta from October 2018 to September 2019. The sampling program is based on a “rotating basin” monitoring design. This design is widely used to assess water bodies on a large geographic scale, repeated at regular intervals, while allowing resources to be focused on smaller geographic areas in any given year (NWQMC 2017). To implement the

design, the resource (in our case, Delta waterways) is divided into smaller geographic areas, referred to in this proposal as “subregions,” and one or more of these areas is assessed each year over the rotation cycle. A rotation cycle is typically five or more years in length. In our case, we have divided the Delta into 6 subregions, and propose to monitor 2 subregions per year over a cycle of 3 or 4 years.

The rotating basin design allows us to assess pesticide and toxicity conditions in individual subregions of the Delta and in the Delta as a whole. The goal is to collect a minimum of 24 samples from 24 different locations in each subregion. This will allow for an assessment of the condition of the subregions over a 3- to 4-year period. Due to the constraints of the budget it is not possible to monitor all subregions within a single year. The proposed monitoring design allows for spatial representation and increases the statistical power to be able to detect differences among the subregions.

Further stratifying regions by water body type ensures that the entire Delta is adequately represented in the sampling design and that we can draw inferences about different types of water bodies, such as large fast-flowing river channels to smaller creeks and sloughs. More details on when and where we propose to monitor, and how the sampling locations will be chosen, are provided in the following section.

**Adaptive management of the study design** – The TAC has discussed whether it makes sense to commit to a multi-year project before the Pesticides and Toxicity interpretive report and analysis is complete. The TAC concluded that we should plan to “adaptively manage” and change our monitoring design based on the results of data gathering and interpretation. This is in fact, a key expected outcome of the interpretive report that is currently underway by Deltares; the scope of work for the study says that the analysis should “inform decisions about future monitoring for pesticides and toxicity in the Delta.” Therefore, this proposal is not intended to lock us into an inflexible program. On the contrary, the program should remain open to make changes as our knowledge and priorities change over time.

## Geographic and Temporal Scope

### Delta Subregions

Samples will be collected from within the legal boundaries of the Delta. Previous efforts by both the Delta RMP and the Central Valley Regional Water Quality Control Board (CVRWQCB) have divided the Delta into roughly similar regions based on hydrology and management practices.

The Delta RMP has divided the Delta into 7 regions 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 CVRWQCB has also identified regions within the Legal Delta which it uses for the 303(d) list. The boundaries of the subregions are shown in Figure 1. Other monitoring efforts by the Delta RMP are utilizing



the subregions identified in Jabusch et al. 2018 (Delta RMP subregions) including the nutrient monitoring design; therefore, this proposal includes assessing the subregions defined by this effort rather than the 303(d) waterways. The rotating basin monitoring design includes monitoring 6 of the 7 subregions shown in Figure 1, excluding the Suisun Bay subregion, which is outside of the Legal Delta. (Note that the numbers on this figure are only placeholders and are not intended to dictate the order in which subregions are monitored.)

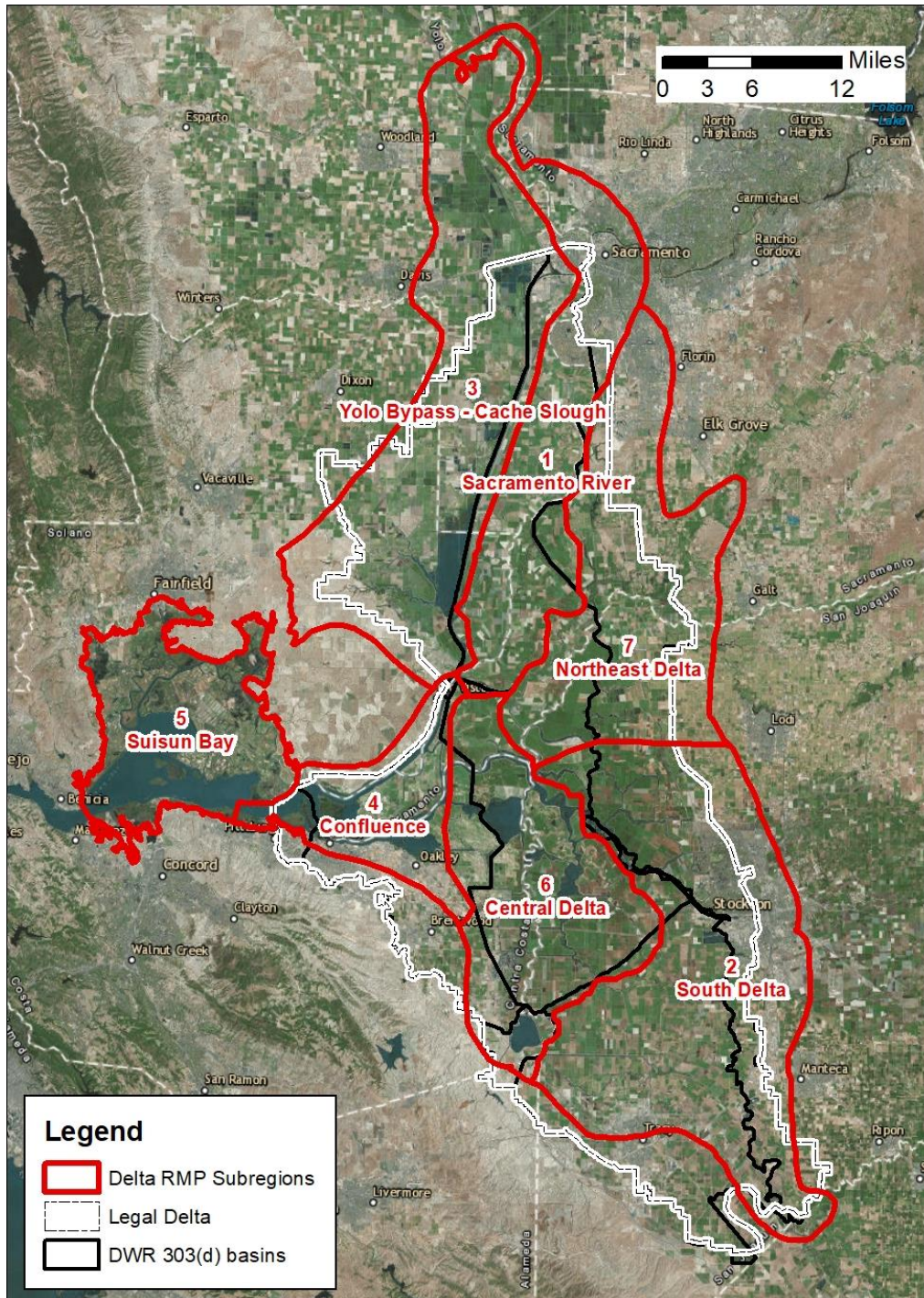


Figure 1 Map of Delta RMP subregions

### Temporal Scope

In this proposal, we are requesting the first year of funding for a proposed monitoring design that will last for 4-5 years depending on the option selected. Year 1 of this effort would begin in October 2018 and end in September 2019.

We propose 6 sampling events during each water year. Samples will be collected over the course of 2 to 3 days at the following during times of interest (high agricultural and/or urban irrigation). Other sampling will occur during periods of high flow or following storms when pollutants are flushed from land surfaces into waterways via overland flow and drains. These events may include the fall “first flush,” a second winter storm, and a period of high flow during spring runoff (snowmelt). Storm triggers are perhaps one of the most significant elements of stormwater sampling.

The specific timing will be planned in collaboration with the Delta RMP Pesticides Subcommittee and our science advisors and will be documented in detail in the Quality Assurance Program Plan (QAPP). This planning will occur from July to September of 2018, and the deliverable will be the detailed sampling and analysis plan included in the revised QAPP. Table 2 shows the sampling event triggers in the Delta RMP 2016 QAPP, which can be adapted or expanded upon for proposed monitoring program. Furthermore, special consideration may be needed in the event of a drought year. We will work with the Pesticides Subcommittee of the TAC to determine a course of action if the storm trigger conditions are not met by a particular date.

Table 2 Sampling event triggers in the Delta RMP 2016 QAPP, to be adapted for proposed monitoring program

Event	Sampling Triggers	Criteria	Notes
<b>Wet</b>			
1 <sup>st</sup> seasonal flush (Water Year)	<ul style="list-style-type: none"> <li>Guidance plots project significant increase (~25%) in flow at four sites: lower Sacramento River, lower American River, San Joaquin River at Vernalis, and Mokelumne River.</li> </ul>	<ul style="list-style-type: none"> <li>Preceded by <math>\geq 30</math> days dry weather (Sacramento R. stormwater criteria).</li> </ul>	<ul style="list-style-type: none"> <li>Sample events to hit all sites in 1 to 2 days.</li> <li>When favorable storm conditions and runoff are forecast coordinate directly with AHP lab.</li> <li>Alert AHPL 7 days in advance of upcoming storm for organism preparation and 2 days in advance about likelihood of adequate precipitation</li> </ul>
Significant winter storm	<ul style="list-style-type: none"> <li>Guidance plots project significant increase (~25%) at four sites: lower Sacramento River, lower American River,</li> </ul>	<ul style="list-style-type: none"> <li>Minimum 2 weeks since 1<sup>st</sup> flush sample event.</li> </ul>	<ul style="list-style-type: none"> <li>If collect more than 1 event sample in the same month, do not sample in following month.</li> </ul>

Event	Sampling Triggers	Criteria	Notes
	San Joaquin River at Vernalis, and Mokelumne River.		<ul style="list-style-type: none"> <li>• When favorable storm conditions and runoff are forecast coordinate directly with AHP lab.</li> <li>• Alert AHPL 7 days in advance of upcoming storm for organism preparation and 2 days in advance about likelihood of adequate precipitation</li> </ul>
<b>Dry</b>			
Early Spring	<ul style="list-style-type: none"> <li>• No triggers, can sample in a particular month (March-April).</li> </ul>	<ul style="list-style-type: none"> <li>• None</li> </ul>	<ul style="list-style-type: none"> <li>• Meant to capture snowmelt but recognize significant impact of upstream dams.</li> <li>• Coordinate sampling schedule with AHP lab 7 or more days in advance.</li> </ul>
1 <sup>st</sup> irrigation season sampling (late spring/ early summer)	<ul style="list-style-type: none"> <li>• No triggers, can sample in a particular month (May-June).</li> </ul>	<ul style="list-style-type: none"> <li>• None</li> </ul>	<ul style="list-style-type: none"> <li>• Meant to capture late winter and spring pesticide applications (post storms).</li> <li>• Account for planting/ pesticide application timing.</li> <li>• Coordinate sampling schedule with AHP lab 7 or more days in advance.</li> </ul>
2 <sup>nd</sup> irrigation season sampling (late summer)	<ul style="list-style-type: none"> <li>• No triggers, can sample a particular month (August).</li> </ul>	<ul style="list-style-type: none"> <li>• None</li> </ul>	<ul style="list-style-type: none"> <li>• Meant to capture summer pesticide applications (rice, etc.).</li> <li>• Account for planting/ pesticide application timing.</li> <li>• Coordinate sampling schedule with AHP lab 7 or more days in advance.</li> </ul>

## Monitoring Design

The two monitoring design options are presented in Table 3. The options involve collecting 48 ambient surface water samples under Option A, or 57 samples under Option B in Water Year 2019. Both monitoring design options would result in 30 samples from each of the 6 Delta subregions after 3 or 4 years of monitoring depending on the design selected. This will allow us to draw conclusions about water quality conditions across the Delta, as well as differences among the subregions.

There were several constraints on designing a pesticides monitoring program in 2018/19. Based on the available budget and laboratory costs, a maximum of around 60 samples can be collected and analyzed per year. Due to logistical constraints involving the toxicity testing laboratory, no

more than 15 samples can be analyzed for planned toxicity tests per sampling event. This number is based on the proposed suite of test organisms, and is based on available bench space, refrigeration, labor to initiate tests, etc.

**Option A**, the “rotating basin” probabilistic monitoring design, is excellent for the purpose of understanding the spatial extent of toxicity and pesticide concentrations. In this instance, the “basins” are our 6 Delta subregions. The rotating basin approach will allow for enough samples in each subregion to characterize the variance of concentrations in the subregion. A weakness of the approach is that subregions will be sampled in different years under different weather conditions. Therefore, comparisons between subregions will be compromised. With Option A, after 3 years, we will have collected data for the whole Delta. Further, we will have collected 30 samples in each of the subregions, which allows us to make statistical comparisons between subregions with a reasonably small margin of error.

Under **Option B**, the “hybrid” design, we keep the rotating basin design but reduce the number of probabilistic samples in order to continue 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 (Figure 2). 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). This “hybrid” option includes the capability of detecting temporal trends at these two sites and an analysis of the correlation between pesticide concentrations and toxicity. By sampling at the same location repeatedly, we are holding more factors constant, which may provide additional opportunities to test for the association between pesticides and toxicity at these locations. However, because of the limited budget, there is a trade-off of collecting fewer random samples in each subregion each year, which means it will take us an additional year to reach the desired 30 samples in each subregion.



Table 3 Rotating Probabilistic Monitoring Design Options with/without 1 fixed site per subregion

Option	Option A (Rotating Basin)	Option B (Hybrid)
Number of random sample locations per subregion	24	24 in first region 12 in second subregion
Subregions evaluated per year	2	2
Number of repeated sample locations per subregion	0	0
Number of fixed sites sampling locations	0	2
Sampling events per year	6	6
Total samples per year	48	36 samples at random locations; 12 samples at 2 fixed sites; 48 samples total
Time (years) to collect 30 samples in all subregions covering the Delta	2 regions evaluated in any given year. 3 years to cover whole Delta with desired margin of error.	One subregion fully evaluated (n = 24) in any given year. Second subregion will be sampled at half the intensity (n=12) with sampling to be continued over two subsequent years to reach the desired number of samples. Based on the lower intensity of sampling, it will take 4 years rather than 3 in order to obtain 24 samples in each subregion and cover the whole Delta with the desired margin of error.

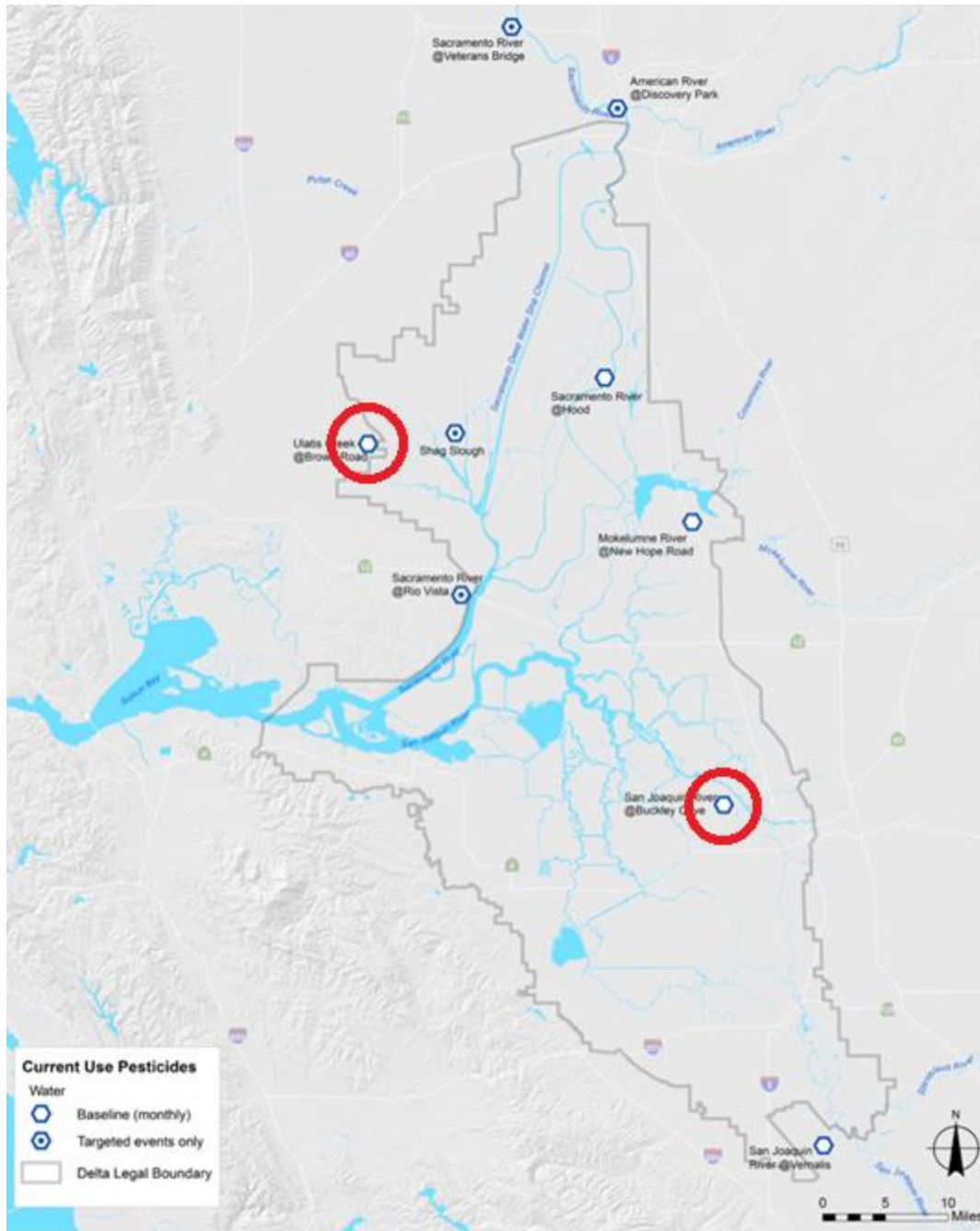


Figure 2 Map of Delta RMP integrator sites monitored 2015-2017, highlighting the two fixed stations where continued monitoring is proposed.

Table 4 shows a schedule of monitoring and deliverables for years 1 through 5 of the proposed monitoring designs. Under both options, sampling will be conducted in two out of six subregions each year. At the end of the 3-year cycle, we will analyze the collected data and determine whether it makes sense to continue the existing monitoring design or to reevaluate. Under Option B, we will continue monitoring into Year 4 in order to obtain our target of 30 samples in each of the 6 subregions.

In terms of reporting and deliverables, the Annual Field Sampling Report will document sample collection methods, target sampling sites, actual sampling sites, how many samples were collected, measurements made using field instruments, and any deviations from the QAPP for field sampling methods. After 3 years of data collection, we will have sampled the entire Delta. In Year 4, a Summary and Interpretive Report will be prepared. Under option B, this report would be prepared in Year 5. This interpretive report will answer the program’s management and assessment questions to the extent possible. Namely, the analysis will determine whether, and to what extent, pesticides contribute to observed toxicity in the Delta. The report will show where and when pesticides and toxicity are observed, prioritize which pesticides should be monitored in the future, and describe gaps in current monitoring programs that limit answering other important management questions.

Table 4 Schedule of monitoring and deliverables for years 1 – 5 of the proposed monitoring designs.

#### Option A Rotating Basin Design only

	Year 1 FY18/19	Year 2 FY19/20	Year 3 FY20/21	Year 4 FY 21/22
<b>Monitoring</b>	24 samples each in Subregions 1, 2 (48 samples total)	24 samples each in Subregions 3, 4 (48 samples total)	24 samples each in Subregions 5, 6 (48 samples total)	
<b>Reporting/ Deliverables</b>	Annual Field Report	Annual Field Report	Annual Field Report	<b>Summary and Interpretive Report</b>

#### Option B Hybrid design: Rotating Basin + 2 fixed sites

	Year 1 FY18/19	Year 2 FY19/20	Year 3 FY20/21	Year 4 FY 21/22	Year 5 FY22/23
<b>Monitoring</b>	24 samples in subregion 1; 12 samples in subregion 2 (50% of n = 24 needed, complete in year 2) 6 samples at each of 2 fixed sites (48 samples total)	12 samples in subregion 2; 24 samples in subregion 3; 6 samples at each of 2 fixed sites (48 samples total)	24 samples in subregion 4; 12 samples in subregion 5 (50% of n = 24 needed, complete in year 4) 6 samples at each of 2 fixed sites (48 samples total)	12 samples in subregion 5; 24 samples in subregion 6; 6 samples at each of 2 fixed sites (48 samples total)	
<b>Reporting/ Deliverables</b>	Annual Field Report	Annual Field Report	Annual Field Report	Annual Field Report	<b>Summary and Interpretive Report</b>

## Rotating Basin - Stratified Probabilistic Sampling Design

The main advantage to using a random sampling design is that it allows us to analyze the data with lower chances of errors. Statisticians have developed procedures for assessing the margin of error or confidence interval of estimates. It lets us draw conclusions about the population we are interested in (in this case, water quality in the Delta) and understand the uncertainty associated with these estimates. By further subdividing the Delta into subregions, it lets us assess whether there are differences in water quality within the Delta, i.e. between one subregion and others.

A pool of potential sample locations will be developed for sample collection. Sample collection locations will be randomly selected from within each of the subregions. Each subregion will be sampled at the frequency and number of samples described below at locations randomly selected from a pool of potential sampling locations. Sampling locations within a subregion will be selected using the Generalized Random-Tessellation Stratified (GRTS) method which identifies monitoring sites based on a stratified random selection process (NPS 2017). These locations will be selected and mapped during the development of the Quality Assurance Project Plan (QAPP) before the beginning of sampling. As is typical with randomized trials, we will “oversample,” identifying more sampling locations than needed in the event where a location is inaccessible or impractical to reach.

## Further Stratification by Hydrographic Features

Stratifying the population helps to ensure that the sampling program is representative of the Delta. Therefore, Delta subregions will be further stratified based on hydrography and water body characteristics. The random sampling algorithm (GRTS) is based on area, and is biased towards placing more sample points in larger water bodies, simply because of their larger surface area. Stratifying by hydrographic characteristics will help ensure that not all of the samples are in large channels and that we also collect samples from smaller sloughs and creeks. Our working hypothesis is that the smaller sloughs and creeks are often closer to sources and have less initial dilution, and less tidal flushing, and thus have the potential for higher pesticide concentrations. These smaller water bodies may also have high habitat value. The sample frame and strata will be planned in collaboration with the Delta RMP Pesticides Subcommittee and field sampling crews and outlined in the Quality Assurance Program Plan (QAPP) from July to September 2018.

In order to draw conclusions with reasonable statistical confidence, we would like to have approximately 30 samples within each of the strata. Therefore, in order to make conclusions about conditions in any of the strata such as “shallow water,” we should collect at least 20% of the samples from within that strata. The Pesticide Subcommittee has had a preliminary discussion where it was suggested to split the number of samples would be 50% in open water (wide river channels and lakes) and 50% in shallow regions (sloughs, tributaries, and backwater reaches). Others have suggested that a ratio like 60/40 or 70/30 would be preferable. This ratio could be based on the available surface area of each water body type in a subregion, their linear

distance, or water volume. Such details will be worked out during the development of the detailed sampling plan and documented in the project QAPP.

One proposed method has been to split Delta waterways into “open water” vs. “shallow water.” A preliminary stratification is shown in Figure 3. The potential sample frame in Figure 3 is based on a GIS datalayer developed by DWR for a similar purpose, to draw sampling points for benthos monitoring (Elizabeth Wells, DWR, personal communication). The data is a polygon layer representing Delta waterways. It was based on the National Hydrography Dataset (NHD) created by the USGS. DWR technicians refined the basic hydrology and also broke the overall areas into Bay-Large, Bay, River, River-Large, Lake, and Slough, in addition to Island (non-target) and identified other inaccessible areas. The data layer was further refined by removing areas that boat captains deemed inaccessible because of hazards or emergent vegetation that makes sampling impractical. To add depth to this datalayer, an SFEI geographer/GIS technician merged this with data that was compiled from a variety of sources previously for the study *A Delta Transformed* (Robinson et al. 2014). Here, we defined “deep water” as greater than as deeper than 2m (6.6 feet). We divided channels where appropriate, but did not cut channels longitudinally. Further refinement of the sample frame will be made in consultation with the USGS field crews, who may be using a smaller boat than the vessel used by DWR and may be able to reach shallower waters.

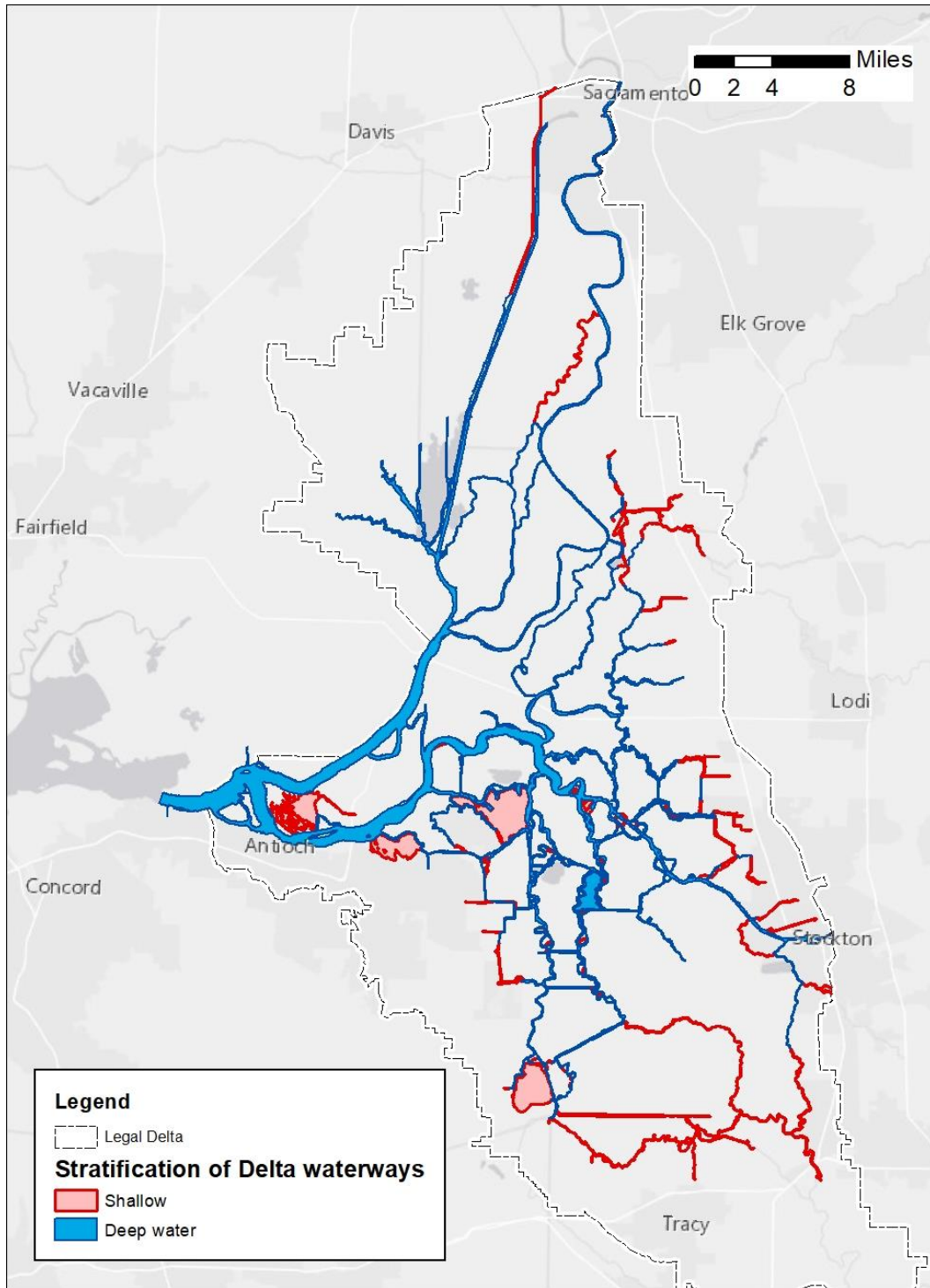


Figure 3 Stratification of Delta waterways into shallow and deep water (>2m)

Another method of stratifying Delta waterways has been proposed related to hydrologic connectivity, flow-through and circulation. The working hypothesis is that channel edges can have high habitat value and be areas of high pesticide concentrations due to localized drain inputs. We have not yet gotten to the level of detail in the sampling plan to develop this



datalayer. We may be able to do this using hydrodynamic model outputs that were developed as a part of recent Delta RMP nutrients studies (Guerin 2015). For example, Figure 4 shows the water “age” or exposure time. These data are based on model results by RMP subcontractor Resource Management Associates (RMA). Note that this particular map represents a simulation of June 2011 under a particular set of circumstances (e.g. Delta Cross Channel open, Old River Barrier closed for part of month). We have access to dozens of maps (and the underlying data) for similar simulations, under periods of low, high, and average flow. These data could be used to stratify the Delta into areas of “high” and “low” connectivity. This will require a number of assumptions and requires us to set some arbitrary cutoff for the difference between high and low connectivity. This stratification can be done in collaboration with the Delta RMP’s Technical Advisory Committee and Pesticides Subcommittee who have significant amount of local knowledge of the Delta.

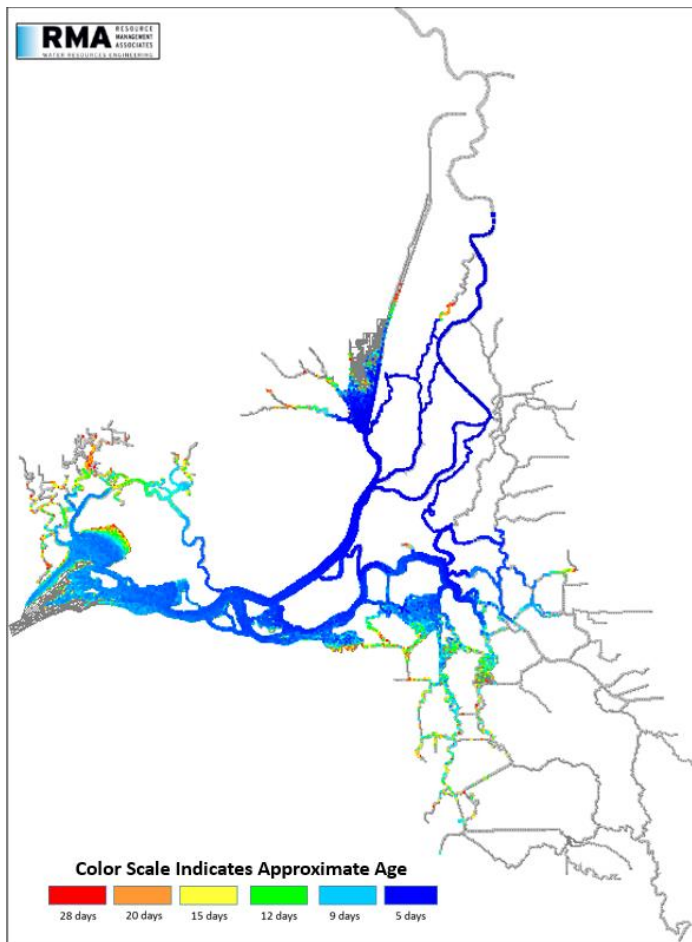


Figure 4 Example fate and age/exposure time map produced by RMA for the Delta RMP 2018 nutrients modeling study.

## Fixed Sites

Option B, the hybrid option, includes sampling at two fixed sites. Some pesticides subcommittee members expressed a strong preference for continuing to monitor at fixed sites. These are “critical to being able to characterize the pesticides in the Delta in terms of the frequency and timing of toxicity, detections and exceedances. All of this is essential to answer Management and Assessment Questions S&T 1.1 and S&T1.2 and the temporal aspect of question S&T2. [See Table 1 on page 11.] The fixed sites proposed are good representatives of areas that receive a mix of urban and agricultural discharges at concentrations of concern in Delta Receiving waters.”

The first of the two sites, San Joaquin River at Buckley Cove is on the main stem of the San Joaquin River, below the influence of the Stockton urban area. It is an integrator site with a variety of land uses upstream. The second site, Ulatis Creek at Brown Road represents agricultural and urban influences in the North Delta discharging to the ecologically significant Cache/Prospect Slough complex. The rationale behind selecting peripheral “integrator” sites is to characterize the spatial and temporal variations in loadings to the inner Delta as a first step. A monitoring design to measure loads of pesticides to the Delta is an appropriate first step toward understanding conditions in the inner Delta.

## Strengths and Limitations of the Proposed Monitoring Designs

Table 5 describes the strengths and limitations of the rotating basin probabilistic design (adapted from NWQMC 2017). Table 6 covers the advantages and disadvantages of fixed site monitoring.



Table 5 Strengths and limitations of the rotating basin probabilistic design (included in both Option A and Option B).

<b>Strengths</b>	<b>Limitations</b>
<p>Estimates the extent and proportion of the population in condition classes (i.e. meeting or not meeting standards) with known levels of precision and documented margin of error.</p> <p>Identifies patterns as well as associations between indicators to broad analysis of stressor/response signals.</p> <p>Focused approach in a smaller geographic areas allowing for a more robust characterization in the years when the subregion is sampled.</p> <p>Travel time to sites during each sampling event is reduced through selection of rotational areas.</p> <p>Smaller geographic scale allows for more detailed analysis of potential sources. Rotating basin designs paired with long-term trend monitoring at “integrator” sites overcome the lack of ongoing data between rotations.</p> <p>The approach is flexible regarding within-basin study designs, and adaptable to a variety of monitoring questions.</p>	<p>Not designed for localized or site specific characterizations, though data at sites sampled supports detailed characterizations.</p> <p>Generally not applied to characterize local, site specific effectiveness assessments (e.g. Total Maximum Daily Loads, TMDLs, Best Management Practices, BMPs).</p> <p>As with all designs, changes detected by repeat surveys must consider hydrologic and other variable factors.</p> <p>It will take 3 years or more to monitor the entire Delta.</p> <p>Annual changes in weather, stream flow, and other variables make it challenging to compare assessments between subregions. Detecting trends within a subregion will take longer with data collected on three-year intervals than it would if samples were collected annually.</p>

Table 6 Strengths and limitations of fixed site monitoring (included in Option B only).

Strengths	Limitations
<p>Provides long-term, in-depth water quality information at specific locations.</p> <p>Supports conclusions about conditions at specific sites or areas or concern.</p> <p>Because it is holding other variables constant by repeatedly sampling the same location, increased power for trend detections at the fixed sampling locations.</p> <p>Ability to determine frequency of exceedance of water quality thresholds, how conditions vary by season or flow regime, and, possibly, the effectiveness of regulatory actions.</p>	<p>Usually biased sites that provide specific information that cannot be extrapolated to make conclusions about the condition of the entire Delta.</p> <p>Under this proposal’s Option B, adding fixed sites reduces the number of samples per year under the rotating basin probabilistic design, meaning this component of the study will take longer and cost more money to complete (4 years rather than 3 years to cover the whole Delta).</p>

### Data Collected

Samples will be collected by boat by crews from the USGS Organic Chemistry Research Laboratory (OCRL). The water quality parameters to be analyzed are described below. Additional samples (around 20% of samples) will be analyzed for quality assurance and quality control purposes. This will include lab and field replicates, matrix spikes, matrix spike replicates, field blanks, filter blanks, method blanks, continuous calibration blanks, initial blanks, and laboratory control samples. Table 13 in Appendix 1 shows the analysis method, reporting limit, and method detection limits for all parameters.

### Conventional Parameters

Basic field measures of water chemistry (dissolved oxygen, pH, temperature, specific conductivity, turbidity) will be made at each monitoring site during each event. Other conventional water quality parameters are analyzed in the lab, including total alkalinity, ammonium as N, hardness.

### Habitat Parameters

The field crew will make a number of observations about the sampling location, and record these on a field sampling data sheet. These observations are somewhat confusingly referred to (by USGS, SWAMP and others) as “habitat parameters,” even though we are not specifically monitoring wildlife habitat. Table 7 shows the elements captured in this form. In the past, Delta RMP CUP 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 we 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.

We may wish to collect additional information to help understand factors affecting each sampling location more than the standard field form describes. This may include upland land use (e.g., urban, ag, native), cover, submerged or emergent aquatic vegetation presence/absence. This data collection element will be discussed by the TAC during the development of the detailed sampling and analysis plan and documented in the QAPP. This is important as it is typically a much greater effort – and more prone to error - to describe each site 1 to 2 years after sample collection when writing an interpretive report, if data are not collected at the time of sampling or soon after.

*Table 7 Habitat parameters recorded by field crews at each sampling location.*

<b>Parameter</b>	<b>Possible responses</b>
Site odor	None, Sulfides, Sewage, Petroleum, Smoke, Other
Sky code	Clear, Partly cloudy, Overcast, Fog, Smoky, Hazy
Other presence	Vascular, Nonvascular, Oily Sheen, Foam, Trash, Other
Dominant substrate	Bedrock, Concrete, Cobble, Boulder, Gravel, Mud, Unknown, Other
Water clarity	Clear (see bottom), Cloudy (>4" visibility), Murky (<4" visibility)
Water odor	None, Sulfides, Sewage, Petroleum, Mixed, Other
Water color	Colorless, Green, Yellow, Brown
Overland runoff (last 24 hours)	None, light, moderate/heavy, unknown
Observed flow	NA, Dry Waterbody bed, No Observed Flow, Isolated Pool, Trickle (<0.1 cfs), 0.1 - 1 cfs, 1-5cfs, 5-20 cfs, 20-50cfs, 50-200cfs, >200cfs
Wadeability	Yes, No, Unknown
Wind speed (Beaufort scale)	
Wind direction	
Precipitation (at time of sampling)	None, Fog, Drizzle, Rain, Snow
Precipitation (last 24 hours)	Unknown, <1", >1"
Occupation Method	Walk-in, Bridge, Other
Starting bank	
Distance from bank	
Stream width	
Water depth	
Location	Bank Thalweg, Mid-channel, Open Water
Hydromodification	None, Bridge, Pipes, Concrete channel, Grade control, Culvert, Aerial zipline, Other

## Current Use Pesticides

Pesticide chemistry analysis will be performed by the USGS Organic Chemistry Research Laboratory (OCRL) in Sacramento. Samples will be analyzed for total and dissolved pesticide concentrations for 174 current use pesticides and degradates. Compounds include fungicides, herbicides, insecticides, degradation products, and “other.” Examples of compounds classified as “other” include pyriproxyfen which is a hormone and insect growth regulator, and piperonyl butoxide, which is a “synergist” which increases the potency of certain other pesticides. Water samples will be processed and analyzed by liquid chromatography tandem mass spectrometry (LC/MSMS) or gas chromatography mass spectrometry (GC/MS). These analysis methods have been previously described in the Delta RMP’s FY15/16 data report (Jabusch, Trowbridge, Heberger, Orlando, et al. 2018). A full list of analytes, methods, and reporting limits is given in Appendix 1.

These analytes are the same as those previously monitored during the first phase of the CUP program in 2015 and 2016, plus the addition of 19 new analytes for which the lab has recently developed a method. The new analytes are the following:

Acetochlor	Herbicide
Benzovindiflupyr	Fungicide
Carboxin	Fungicide
Chlorfenapyr	Insecticide
Dichlorvos	Insecticide
Etoxazole	Insecticide
Flubendiamide	Insecticide
Fluopyram	Fungicide
Flupyradifurone	Insecticide
Imidacloprid urea	Insecticide
Isofetamid	Fungicide
Oxathiapiprolin	Fungicide
Penthiopyrad	Fungicide
Pyriproxyfen	Other
Sulfoxaflor	Insecticide
Tebufenozide	Insecticide
Thiamethoxam Degradate (NOA-407475)	Insecticide
Thiamethoxam Degradate (CGA-355190)	Insecticide
Tricyclazole	Fungicide

Some compounds are highly water soluble, while others tend to be adhere to sediments and other particles. In order to gain a full picture of pesticides in the environment, OCRL will measure both the dissolved fraction in water and the fraction associated with suspended sediments. (Note that we are not proposing to measure pesticides in bedded sediment at this

time.) Measuring pesticides that are both dissolved in water and on suspended sediments can help give greater insight into the fate and transport of different compounds. The way chemicals move through and impact the environment can depend strongly on their physical and chemical properties – some are highly soluble in water, while others tend to adsorb strongly to sediments particles. Of the 174 compounds measured in water, the lab is able to analyze 139 compounds in suspended sediment.

## Copper

Copper is an ingredient used in herbicides, and is used in the cultivation of rice, as well as to control aquatic plants and algal blooms, and has been previously suggested as a possible cause of aquatic-biota toxicity in the Delta. However, it is also a natural occurring and ubiquitous trace element that may originate from other sources.

Samples will be sent to the USGS National Water Quality Laboratory (NWQL) in Denver for analysis for copper. Copper will be analyzed at the NWQL using the method described in Techniques and Methods Book 5-B1 (Garbarino, Kanagy, and Cree 2006). It is also important to measure other ancillary parameters in order to interpret whether copper is bioavailable and potentially toxic. Copper has a complex chemistry and its toxicity can vary widely from place to place due to local conditions (e.g., pH, ionic composition, presence of natural organic matter). Hardness-adjusted thresholds provide a simplified approach to address water chemistry and bioavailability but they do not directly consider other water chemistry parameters (e.g., pH and DOC) that affect bioavailability and toxicity of dissolved copper. More complex methods for evaluating copper toxicity take into account additional water quality parameters to estimate bioavailability. For example, EPA’s National Recommended Water Quality Criteria (2017) considers how various water quality parameters affect copper toxicity using the Biotic Ligand Model (BLM). Lab analysis of water samples additional ancillary parameters will help us to interpret the copper measurements using the methods described above.

## Ancillary Parameters

To assist with interpreting the bioavailable fraction of pyrethroid pesticides, samples will also be analyzed for ancillary parameters by the USGS National Water Quality Laboratory (NWQL). Other parameters measured by NWQL are:

<b>Fraction</b>	<b>Water Quality Parameter</b>
Dissolved	Dissolved Organic Carbon
Particulate	Carbon, Total
Particulate	Nitrogen, Total
Particulate	Particulate Organic Carbon
Particulate	Total Inorganic Carbon
Particulate	Total Suspended Solids

Dissolved organic carbon will be analyzed at the NWQL using the method described in OFR 92-480 (Brenton and Arnett 1993). Particulate organic carbon, total particulate inorganic carbon, total particulate nitrogen, and total particulate carbon will be analyzed at the NWQL using EPA method 440.0 (Zimmerman, Keefe, and Bashe 1997).

### Aquatic Toxicity Testing

Under the proposed monitoring design, we plan to test ambient surface water samples for acute and chronic aquatic toxicity with five different organisms shown in Table 8 below. Test organisms were selected based on updated SWAMP guidance (Anderson et al. 2015), past Delta RMP monitoring experience, and input by stakeholders and technical experts.

The use of midge larvae (*Chironomus dilutus*) is new to the Delta RMP. *Chironomus dilutus* has been listed as a valid alternate species for over a decade in EPA’s freshwater acute toxicity test manual (USEPA 2002). EPA and USGS developed species-specific methods that are currently out for review within these agencies. *Chironomus* toxicity data (SWAMP-funded) could support method validation efforts. More information about *Chironomus* is included in Appendix 4. Detailed information on the test methods for the other 4 organisms can be found in the *Delta RMP Current Use Pesticides Year 1 Data Report* (Jabusch, Trowbridge, Heberger, Orlando, et al. 2018).

Table 8 Proposed aquatic toxicity tests

Test organism	Endpoints	Rationale for including
<i>Ceriodaphnia dubia</i> , a daphnid or water flea	survival, reproduction	Sensitive to organophosphate pesticides
<i>Hyalella azteca</i> , an aquatic invertebrate	survival	Sensitive to pyrethroids
<i>Selenastrum capricornutum</i> , a single-celled algae (also known as <i>Raphidocelis subcapitata</i> )	growth	Sensitive to herbicides
<i>Chironomus dilutus</i> (formerly <i>Chironomus tentans</i> ), midge larvae	growth, survival	Sensitive to fipronil and more sensitive in chronic exposures to imidacloprid than <i>C. dubia</i> .
<i>Pimephales promelas</i> , fathead minnow	growth, survival	Chronic and acute effects on whole organism growth and survival

Stakeholders have asked questions about how results from *Chironomus* toxicity data could be used by regulators. Currently all existing *Chironomus* toxicity data in CEDEN is flagged as “screening.” This may change in the upcoming year if the State Water Board publishes method quality objectives (MQOs) for certified labs to follow.

Any data can be used by state regulators to list a water body as impaired under section 303(d) of the Clean Water Act. It is the Regional Board's decision whether or not to use data for a particular purpose. Staff may use any and all data, regardless of whether it is flagged as "screening" "survey" or has any other QA flag attached. If a group (i.e. regulated entity) wants to invalidate data for some reason, it would be incumbent upon them to contact the 303(d) unit at the appropriate Regional Board and make the case that data should not be used. In brief, anything in CEDEN may be used for regulatory purposes, regardless of flags/QA codes, and it is up to the Regional Board to make the decision what they use. Also, some Regions have begun using data from sources other than CEDEN.

**Rainbow trout** - It has been suggested to add rainbow trout (*Oncorhynchus mykiss*) to the suite of test organisms. This would be a useful test organism as it is more closely related to threatened and endangered species in the Delta. However, this test is not covered under the SWAMP contract with the testing lab. We have held discussions with NOAA fisheries, who have indicated that they will consider funding beginning in the *next* fiscal year, FY19/20.

### Toxicity Identification Steps

Consistent with monitoring and assessment question S&T1.1A ("If samples are toxic, do detected pesticides explain the toxicity?"), a Toxicity Identification Evaluation (TIE) is triggered when the sample experiences a 50% reduction in the endpoint (e.g., survival) compared to the control. A TIE is an investigative process that uses laboratory modifications of test sample chemistry and resulting changes in toxicity to identify the constituent group (e.g., organophosphates) that are the likely cause(s) of toxicity.

This proposal includes a budget to conduct up to 4 TIEs during the water year. The decision to conduct a TIE is based upon consideration of multiple factors such as the magnitude of toxicity. magnitude of toxicity present in the sample matrix is an important consideration because a moderate to high level of toxicity typically yield results that are more successful.

### Data Management and Quality Assurance

Data will be reviewed for overall quality/usability according to SWAMP and EPA data validation procedures. SWAMP program staff will be responsible for managing the toxicity data and performing quality assurance. SWAMP is working to identify additional QA or Corrective Actions that will be done in 2018/19 to address past deviations or errors. This may include, for example, performing an independent QC check on 10% of toxicity bench sheet calculations that would trigger a more thorough audit and corrective actions by the lab if errors are found.

SWAMP's QA program is described in its *Quality Assurance Program Plan* (2017). SWAMP has created measurement quality objectives (MQOs) establishing requirements and recommendations for the various tests and measurements used for SWAMP's water-quality monitoring projects. SWAMP's MQOs can be found on the [SWAMP Wiki](#) and the [SWAMP webpage](#).

SWAMP managers have indicated that they will *not* be providing data analysis, reporting services, or QA summary/narratives for this project. We have added a small amount of budget (10 hours total) for ASC staff to review the toxicity data and prepare a brief QA summary of the toxicity data. To prepare the toxicity QA summary, ASC staff will download the toxicity data from CEDEN, run standard QA/QC analyses, and write a short memo describing whether the measurement quality objectives (MQOs) described in the Quality Assurance Program Plan (QAPP) were met, and describing any deviations from the QAPP. ASC will not be adding any new QA flags to the data, nor will we describe deficiencies identified by the SWAMP Quality Assurance Officer, or corrective actions that were taken.

Delta RMP stakeholders have expressed a strong interest in receiving detailed updates regarding any deficiencies by the laboratories, communications, and corrective actions. The SWAMP QA Officer has indicated that SWAMP staff are able to provide us with a “simple summary statement from SWAMP including the following: ‘issues were detected, a correction action report was completed and approved, and laboratory performance will be assessed regularly.’ Discussing the details of what steps were taken with stakeholders is not appropriate. Nor will we allow for additional requests to be made of our Contractor [the UC Davis toxicity lab]” (Melissa Morris, personal communication, June 27, 2018).

In addition, we have arranged for AHPL to submit provisional electronic data and documentation of their processes and controls after each and every monitoring round. These submittals will be in lieu of an annual lab report, which they have provided in years 1 and 2 of pesticide monitoring. ASC’s Data Management and Quality Assurance team will do a brief review of the submitted data, and we will distribute the information to TAC and Pesticides subcommittee members so that those who are interested can review this information.

The Aquatic Science Center (ASC)’s Data Services team (DS) will be responsible for handling and reviewing data generated by field crews and for chemical analyses by the USGS labs. The staff of the OCRL performs certain QA checks on the data before submitting it to ASC. For more information about QA performed by the USGS lab, see Appendix 2. ASC’s Quality Assurance Officer (QAO) and staff independently recalculate any QC metrics reported by the lab, as an additional layer of verification of the results.

The review process consists of ASC’s DS team checking that results are received for all samples collected and that the lab reported results for the analytes requested in the contracts. Staff will check in the data as it arrives, and perform a partial analysis of the data to verify that it is complete and meets certain minimum acceptability criteria. This will help us to identify any potential problems in a timely manner and make any necessary corrective actions. For more information, see the *Delta RMP Data Management and Quality Assurance Standard Operating Procedures* (Franz et al. 2018).

Data is standardized by ASC’s DS team using California Environmental Data Exchange Network (CEDEN) templates, controlled vocabulary, and business rules. Data is reviewed by



ASC's QA officer or designee (under the supervision of the QA Officer) to ensure sufficient laboratory control samples are analyzed in order to evaluate whether samples are meeting Measurement Quality Objectives (MQO) as stipulated in the Quality Assurance Project Plan (QAPP). These processes are necessary to ensure data are usable by project staff, regulatory agencies and members of the public.

Five evaluations make up the core of the QA-review process:

1. **Data completeness:** Has the lab submitted all expected data, including the correct number of QA samples? Were contract and QAPP expectations met?
2. **Sensitivity:** Were the analytical methods sensitive enough to get detectable results?
3. **Contamination:** Was there contamination present in any of the sample batches?
4. **Accuracy:** Did the lab reliably measure known concentrations?
5. **Precision:** Was the lab able to consistently obtain the same result in its analysis of replicate or duplicate samples?

Deliverables for this step include a tabular summary of the data (typically in an Excel spreadsheet), and a memo from ASC's QA officer summarizing the quality assurance (QA) review. The QA review will begin after we receive final dataset from the laboratories, typically about 3 months after the last samples are collected, planned for December 2019. The QA memo will be written in the spring of 2020 and sent to TAC members in the first quarter of 2020. A timeline of planned deliverables is shown in Table 10 on page 44.

### QAPP Modifications Needed

Several important details have been left open-ended, to be developed in the future. It is important that these details be set before monitoring begins in October 2018. This proposal follows a similar process that SEFI-ASC scientists have used successfully over the last 20 years: first we draft a proposal that outlines a monitoring program, and then develop a more detailed "sampling and analysis plan" after funding is approved. This is appropriate because developing this plan requires an investment of time and money that would not be well spent in the proposal stage. Because the Delta RMP has a detailed Quality Assurance Program Plan (QAPP), it is appropriate to add these details to this document. Some of the important details to be included in the QAPP are described below.

The QAPP will include measurement quality objectives for all parameters. The current Delta RMP Quality Assurance Program Plan (QAPP version 3.5, dated March 14, 2018) does not include a description of monitoring of pesticides and toxicity, as the program took a hiatus from monitoring these parameters in FY17/18. Previous versions of the QAPP (version 2.2, dated September 30, 2016) described pesticides and toxicity monitoring. Much of this information is still useful and relevant; however, certain updates and modifications will need to be made to the QAPP following approval of this monitoring plan. We expect to draw heavily on the QAPP from FY16/17, and to update it as necessary.

Budget to update the QAPP was approved by the Steering Committee as part of the FY18/19 Workplan. The sampling and analysis plan will rely heavily on standardized methods for data/sample collection and analysis. A QAPP will describe these specific activities and be sufficiently robust to achieve the study goals. As shown in the schedule of deliverables (Table 10 on page 44), QAPP updates will be done from July to September 2018.

ASC staff will work closely with the pesticides subcommittee and our science advisors as we develop additional guidance and documentation to include in the QAPP. In addition, the draft QAPP will be made available to the TAC and external stakeholders for review (planned for August 2018), and their comments and input solicited. At least two meetings with the pesticides subcommittee will be held from July to September to discuss the detailed sampling plan and QAPP amendments. New elements to be added to the QAPP include the following items:

**Sample location selection and pool of possible locations** - Development of the final geographic datalayer of Delta waterways to form the basis of our population or the “sample frame” from which random sampling locations will be drawn. Stratification of Delta waterways, as described above on page 20. Selection of sample locations using the GRTS method.

**Additional EC-based control and data interpretation protocols for *Ceriodaphnia dubia* toxicity tests** - In the first two years of Delta RMP monitoring, it was noted by technical reviewers that there may be an interference with toxicity testing of *C. dubia* when sample water had had unusually low levels of salinity/conductivity, as indicated by measurements of electrical conductivity (EC). *C. dubia* reproduction is known to be sensitive to low conductivity. The Delta RMP Pesticides subcommittee has been discussing this issue with the SWAMP QA team and the UC Davis aquatic toxicity lab manager. Our goal is to put in place revised procedures in the form of Measurement Quality Objectives (MQOs) that will increase the reliability of the test in low-EC waters, most likely by adding an additional control batch when EC is in the range of 100 – 200  $\mu\text{S}/\text{cm}$ , and establishing protocols for performing statistical comparisons to the most appropriate control. It is our current understanding that Bryn Phillips of the UC Davis Granite Canyon lab is currently drafting a tech memo for SWAMP that will provide guidance on this issue. For additional information on this issue, see the tech memo from the Jan 9, 2018 Pesticides Subcommittee meeting (available upon request or on the TAC workspace website.)

**Toxicity test methods for *Chironomus dilutus*** – There are at present no standardized test methods for water-only testing with midge larvae (*Chironomus dilutus*). We will work with the lab, SWAMP and our technical advisors to determine the most appropriate methods with a view to making test results reliable, repeatable, and comparable with results obtained by others. For more detailed information on method development for water-only toxicity testing with *Chironomus*, see Appendix 4.

## Data Analysis and Presentation

The goal of Delta RMP monitoring is to help answer the management and assessment questions shown in Table 1. As a part of the Data Quality Objectives (DQO) process, the Pesticide Subcommittee has worked to convert these questions into hypotheses, or specific, quantitative decisions to be made based on the data collected. The next step in the DQO process is to “Specify tolerable limits on decision errors.” Data quality objectives (DQOs) for the monitoring program are shown in Table 9. The decision rules in Table 9 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. Non-parametric methods may require larger sample sizes to answer the assessment questions listed in Table 1. In the table, we set the parameters for tolerable limits on decision errors (referred to by statisticians as *alpha* and *beta*) based on commonly used assumptions in science. We chose a significance level (alpha) of 0.05 for a one-tailed hypothesis test. For example, suppose we are testing whether more than 1% of river miles have a pesticide concentration exceeding a threshold. With alpha = 0.05, there is a 5% chance of a false positive with hypothesis testing (incorrectly concluding that concentrations in these river miles exceeds the threshold.) 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 we have only a 20% chance of incorrectly concluding that a predicted pesticide concentration does not exceed a threshold.

**Water quality thresholds** – 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 threshold or benchmark. When a threshold 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 Central Valley Regional Water Quality Control Board has established water quality objectives for chlorpyrifos and diazinon that cover much of the Central Valley including the Delta.<sup>1</sup> 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 benchmarks is a useful first step in the process for interpreting pesticide data and evaluating relative risk. The choice of a threshold is important. If our monitoring shows that concentrations exceed a threshold, the implication is that there is a problem. Yet, the choice of a threshold is a complicated technical question. *We have not explicitly defined thresholds in this proposal*, 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.

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<sup>1</sup> 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.

Options for setting thresholds include aquatic life (AL) benchmarks published by the US EPA Office of Pesticide Programs (OPP). OPP benchmarks were developed by the U.S. 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, 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 thresholds 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, and consistent with the CVRWQCB's Basin Plan, which states that standards will be based on the lowest LC50 divided by 10.<sup>2</sup>

**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 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 is 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). We anticipate that useful guidance will also be developed as a part of the Delta RMP-funded interpretive report underway by Deltares.

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<sup>2</sup> See Amendments to the 1994 Water Quality Control Plan for the Sacramento River and San Joaquin River Basins (2016), page IV-35: “Where valid testing has developed 96 hour LC50 values for aquatic organisms (the concentration that kills one half of the test organisms in 96 hours), the Board will consider one tenth of this value for the most sensitive species tested as the upper limit (daily maximum) for the protection of aquatic life. Other available technical information on the pesticide (such as Lowest Observed Effect Concentrations and No Observed Effect Levels), the water bodies and the organisms involved will be evaluated to determine if lower concentrations are required to meet the narrative objectives.”

Table 9 Analytic approach, decision rule, and data quality objectives

**Spatial extent of pesticides and toxicity (included in Options A and B)**

Questions to Answer with Delta RMP Pesticide Data	Analytic Approach	Decision Rule	Data Quality Objectives	Power Analysis
<p><b><i>Spatial extent of pesticide, toxicity occurrence</i></b></p> <p>For what percent of the subregion was aquatic toxicity and co-occurrence of pesticides greater than risk-based thresholds observed?</p> <p>Over what percentage of the subregion does a pesticide concentration exceed a threshold?</p> <p>Secondary objective that can be evaluated qualitatively:</p> <p>Identify spatial patterns in aquatic toxicity and pesticide concentrations within the subregion to inform decisions about sensitive habitats, sources, and strata for future designs.</p>	<p>1. Metric for toxicity: Binary variable (0/1 or True/False) indicating whether toxicity was observed, by species (as determined by a statistically significant reduction in an endpoint compared to control, to be described in greater detail in the QAPP).</p> <p>2. Metric for pesticides:                      -Individual pesticide concentrations in water and suspended sediment                      - Individual pesticide frequency of exceedance of aquatic life benchmark.                      - Cumulative frequency of exceedance</p> <p>3. Metric for determining cause of toxicity: outcome of Toxicity Identification Evaluations (TIEs)</p>	<p>Population estimates will be made using open source R software ('spsurvey').<sup>3</sup></p> <p>Population estimates are not a statistical test. There is no null hypothesis. The result will be a percent of subregion water area meeting a certain condition such as:</p> <ul style="list-style-type: none"> <li>-Percent of subregion with statically significant aquatic toxicity</li> <li>-Percent of subregion with pesticide concentrations above risk based thresholds</li> <li>-Percent of subregion with significant toxicity AND pesticide concentrations above risk based thresholds</li> </ul>	<p>The sample size for each subregion should be large enough to be able to estimate the percent of subregion's water area with a certain condition with error bars of <math>\pm 10\%</math>.</p> <p>Assume a Type 1 error of <math>&lt;0.05</math> and a Type 2 error of <math>&lt;0.2</math> (80% statistical power).</p>	<p>Because we are employing a random sampling design, a standard probability distribution known as the binomial distribution can be used to estimate of the upper and lower bounds of confidence intervals. The relationship between sample size and the confidence intervals around the cumulative distribution function are shown in Appendix 3 Figure 7 (see notes for assumptions). A sample size of <math>n = 24</math> gives a 90% confidence interval of around <math>\pm 13\%</math>. (This is acceptably close to our objective of <math>\pm 10\%</math>.)</p> <p>More details on the power analysis presented in Appendix 3.</p>

<sup>3</sup> <https://cran.r-project.org/web/packages/spsurvey/spsurvey.pdf>

## Co-Occurrence of Pesticides and Toxicity (included in both Options A and B)

Questions to Answer with Delta RMP Pesticide Data	Analytic Approach	Decision Rule	Data Quality Objectives	Power Analysis
<p><b>Causes of toxicity</b> Evaluate the co-occurrence of aquatic toxicity and pesticides.</p>	<p><b>Metrics for toxicity:</b></p> <ol style="list-style-type: none"> <li>1. Binary variable (0/1, or True/False) indicating whether significant toxicity was observed (stratified by species, and possibly by endpoint)</li> <li>2. Continuous variable - Percent effect observed for individual toxicity tests: reduction in organism survival, reproduction, or growth compared to control.</li> </ol> <p><b>Metrics for pesticides:</b></p> <ol style="list-style-type: none"> <li>1. Continuous variable: Observed concentration of individual pesticides, in ng/L</li> <li>2. Binary variable (0/1 or True/False) Individual pesticide observations exceeding a risk threshold.</li> <li>3. Frequency with which individual pesticides exceed a threshold.</li> <li>4. Cumulative frequency of exceedance (for one or all pesticides)</li> <li>5. Cumulative frequency of exceedance for classes of pesticides grouped by type or mode of action (organophosphate and pyrethroids)</li> <li>6. Pesticide Toxicity Index*</li> </ol>	<p><b>Statistical Test:</b></p> <ul style="list-style-type: none"> <li>-Logistic Regression</li> <li>-Multivariate linear regression</li> </ul> <p>All data from all sites will be pooled for the test if and/or sites to be analyzed individually based on a statistical analysis of their similarity using Generalized Linear Models or Principal Components Analysis.</p> <p>Null hypotheses:</p> <p>Ho: Toxicity is not related to exposure to pesticides. (There is no relationship between pesticide levels and toxicity.)</p> <p>Ha: There exists a relationship between pesticide exposure and the toxicity.</p>	<p>The test should be able to detect a 5% effect** of pesticide exposure with a Type 1 error of &lt;0.1 and a Type 2 error of &lt;0.2 (80% power).</p>	<p>For the site on the San Joaquin River at Buckley Cove, to detect an effect size = 0.03 would require around 60 samples. In this context, an effect size of 0.03 is equivalent to a 3% increase in toxicity to macroinvertebrates for each unit increase in the Pesticide Toxicity Index (PTI). Requires 36 new samples at each site, or 6 years (i.e., collecting 6 samples per year at this fixed location). See Appendix 3 for more details on the power analysis.</p>

\* The Pesticide Toxicity Index (PTI) is a screening tool to assess potential aquatic toxicity of complex pesticide mixtures by combining measures of pesticide exposure and acute toxicity in an additive toxic-unit model. For more information, see "Pesticide Toxicity Index—A tool for assessing potential toxicity of pesticide mixtures to freshwater aquatic organisms" (Nowell et al. 2014).

\*\* An effect size of 5% means that a unit increase of the PTI would result in a 5% reduction in a toxicity endpoint such as reproduction, survival, or growth. In general, large effect sizes (e.g. 50% reduction in survival) are easier to detect with smaller sample sizes, while small effect sizes (5% reduction in survival) are more difficult to differentiate from random chance and need a much larger number of samples to detect.)

### Co-Occurrence of Pesticides and Toxicity (included in both Options A and B)

A goal of the proposed program is to better understand the role that contaminants play in contributing to toxicity in the Delta.<sup>4</sup> A statistical analysis of the first two years of Delta RMP monitoring data, described in more detail in Appendix 3, included an evaluation of power to detect statistical relationships between pesticide concentrations and toxicity across a range of sample sizes. In brief, an examination of data from the first two years of sampling did not find a statistically significant relationship between pesticide concentrations and observed toxicity. However, with two years of monthly data, collected under a variety of flow conditions, we now have a better estimate of the variability in predictor variables (pesticide concentrations) and response variables (toxicity endpoints such as percent reductions in survival or reproduction compared to a control).

The variability of these parameters is a key input into the power analysis. What the power analysis allows us to say is, if there is a relationship among these variables of a certain strength (or “effect size”), how many samples would be needed to recognize this relationship statistically, given a certain risk tolerance for a false conclusion? It was concluded that, based on the historically measured variability, and certain assumptions on the effect size we wish to detect and desired statistical power, that a total of 60 samples would be required. As we already have 24 samples at each fixed site to date, we need 36 additional samples giving us the ability to detect a correlation between pesticide concentrations and toxicity. Under this proposal, we would collect 6 samples per year at each of the fixed stations. Therefore, we would be able to detect such a correlation after another 6 years of sampling. For more details on the statistical power analysis, see Appendix 3.

Both monitoring design options can test for the co-occurrence of aquatic toxicity at measured pesticide concentrations using samples collected throughout the Delta. While toxicity might be found at any sample location in the Delta, the fixed sampling locations included in Option B had elevated toxicity in the past sampling years. Therefore, a similar frequency of toxicity is expected from the fixed monitoring stations under Option B to inform the co-occurrence analysis over the long term. The stratified probabilistic design would include surface water samples from areas with less dilution of pesticides (i.e., small tributaries), which could result in samples with a higher magnitude of toxicity than previously encountered. This would potentially allow for more TIEs to identify the causes of observed toxicity than was done in 2015-2017 Delta RMP sampling.

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<sup>4</sup> Note however that under the “independent applicability policy” in water quality regulation, the cause of toxicity does not need to be demonstrated in order for regulators to list a water body as impaired. The toxicity water quality objective is a separate standard. However, it is desirable to determine which toxicant(s) are contributing to or causing toxicity.

## Spatial Extent of Pesticides and Toxicity (Included in Options A and B)

With the data from the probabilistic design, we would like to know the percentage of each subregion where a pesticide concentration exceeds a benchmark, has observed toxicity, or where elevated concentrations of pesticides and toxicity co-occur. Using sample data from each of the subregions, we can construct cumulative distribution functions (CDFs) that show the distribution of a variable within that region. The CDF shows the percentage of stream miles that are less than or equal to each possible value of a variable. A hypothetical example is shown in Figure 5. In this case, the CDF could describe the concentration of a particular pesticide, the value of the Pesticide Toxicity Index (PTI), or the value of a toxicity endpoint. The CDF is useful for describing the overall condition of the resource being sampled, and lets you answer a number of questions, some of which are of interest to us. The important point is that with a larger number of samples, we will have smaller confidence intervals around the empirical CDF. We cannot do a conventional power analysis for the probabilistic design. However we can *a priori* estimate the size of the confidence intervals around the CDF, using the binomial distribution, and making some assumptions. Having “tighter” error bounds around the CDF is desirable for when we’ll use it as a tool to make any kind of estimation.

A recent report from Oregon (DeGasperi and Stolnack 2015) which used GRTS to evaluate the status and trends of aquatic habitats describes how CDFs derived from sample data can be used to make inferences about the sampled populations:

A CDF plot for a particular target sample population sampled in a particular year establishes a baseline against which future surveys (using the same probabilistic design) can be compared. Change over time (or between subpopulations of the target sample frame) can be detected not only in some measure of central tendency such as the mean or median value of a particular metric, but in certain portions of the CDF via visual comparison of the two (or more) CDF plots. Depending on the expected response of a particular metric to environmental stressors or to restoration measures, the CDF will be expected to shift to the left or right. Confidence intervals for each CDF provide a statistical basis for assessing change.



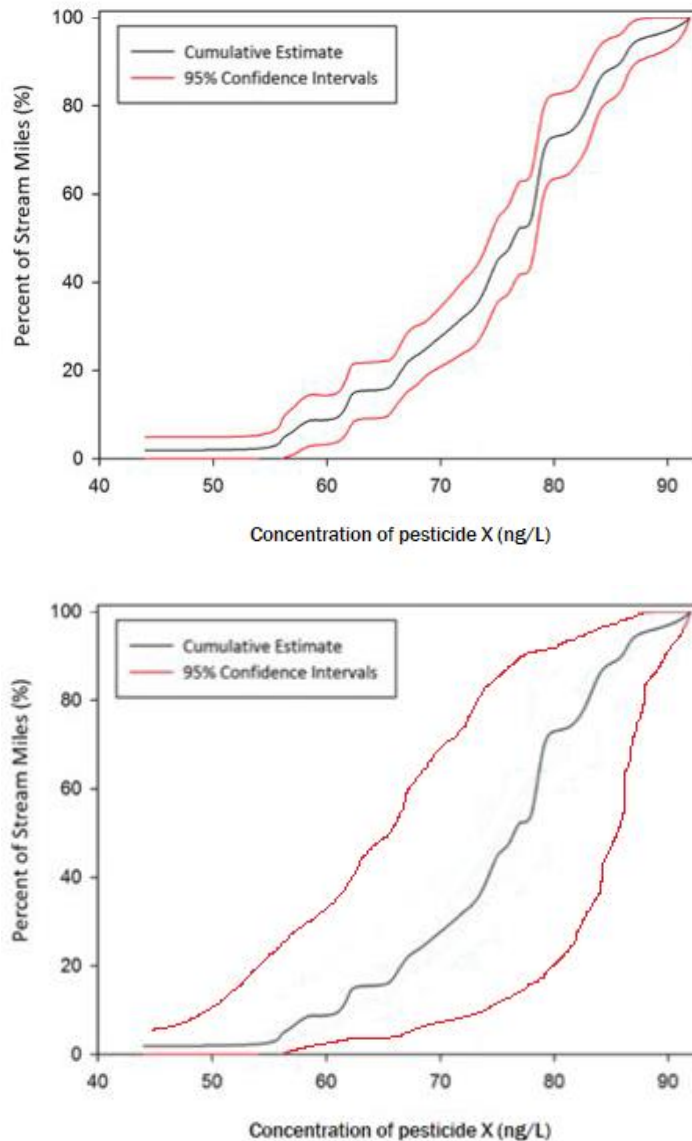


Figure 5 Hypothetical cumulative distribution functions for pesticide concentration in a Delta subregion.

In the hypothetical example in Figure 5, suppose we are seeking to answer the question, what percent of stream miles have a pesticide concentration < 75 ng/L. In the top figure, with more samples and smaller confidence intervals, the answer is 30% to 40%. In the bottom figure, with fewer samples and large confidence intervals, the answer is 15% to 80%. This is a made-up example, but it demonstrates that a larger number of samples lets us make better estimations about the condition of the waterway.

In other words, we wish to make the confidence intervals as small as possible in order to make more reliable estimates about the sampled population. This means collecting a larger the number of samples, however there are constraints in terms of budget. No explicit guidance on the recommended sample size for GRTS survey designs exists. Budgetary and logistical

constraints of individual study designs often dictate the level of effort employed. That said, probabilistic designs incorporating GRTS often aim to determine an estimate of a proportional extent, and thus refer to the binomial distribution to evaluate precision. In the scenarios analyzed in Appendix 3, a sample size of 30 would result in an estimated confidence interval of  $\pm 12\%$ . A sample size of 24 gives only a slightly larger confidence interval of around  $\pm 13\%$ . Increasing the sample size would not significantly impact on the size of the confidence interval, while fewer than 24 samples would increase the confidence interval substantially. Consequently, a sample size of 30 can be considered an “industry standard”, and has, in the experience of our consulting statistician, been selected as a default sample size in order to make statistical inferences about condition, with a relatively low degree of error. A sample size of 24 is only slightly worse, and fits within available budget. Under Option A, this target sample size of 24 will be reached after 3 years. Under Option B, the number will be reached after 4 years. For more details, see the power analysis in Appendix 3.

Option B, which includes fewer random samples to add sampling at 2 fixed sites, can answer all of the same questions, although it may take longer to achieve the desired level of statistical power due to the smaller number of samples collected each year. However, it also adds the ability to detect trends at two locations in the Delta by repeatedly sampling at these two fixed sites. Further, fixed site sampling can be better at identifying associations among different water quality parameters, as we are holding more potentially confounding factors constant by sampling repeatedly at the same location.

Monitoring data can also be used to identify spatial patterns in aquatic toxicity and pesticide concentrations within the subregion to inform decisions about sensitive habitats, sources, and strata for future designs. The goal of most sample surveys is to estimate the proportion of a resource that is degraded. In this case, we will be able to estimate the percentage of each subregion in which a pesticide concentration exceeds a threshold.<sup>5</sup>

Numeric water quality standards exist for only a few current use pesticides. Therefore, we will compare observed pesticide concentrations to U.S. Environmental Protection Agency aquatic life (AL) benchmarks.<sup>6</sup> Benchmark values will be used as a first step in a process for interpreting

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<sup>5</sup> Not all Pesticide Subcommittee members agreed on the usefulness of assessing differences in water quality within or among subregions of the Delta. One member wrote, “I am less interested in the variation of pesticide concentration from one subregion to another sub region. There may be underlying reasons like different crop, climatic change, and pest patterns and therefore different pesticides used from one year to the next year. The overarching management question, ‘Is there a problem or are there signs of a problem?’ and the rotating basin design does not help to answer this. Especially, since we are only evaluating 2 subregions each year. If we find there is a problem, we will not return to that that sub-region again until another 3 years, and that is problematic.”

<sup>6</sup> OPP benchmarks were developed by the U.S. 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, vascular and non-vascular

pesticide data and evaluating relative risk. Aquatic life benchmarks may or may not be useful determining the cause of toxicity. However, these thresholds are broadly relevant to protecting aquatic life. The USGS OCRL's reporting limits are lower than the lowest benchmark for every analyte, as shown in Appendix 1. This appendix has a table showing all of the analytes to be measured, and lists the analysis method, method detection limit, and lowest aquatic life benchmark.

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plants). They represent the lowest toxicity values available from peer-reviewed data with peer-reviewed data quality objectives.

## Proposed Deliverables and Timeline

Table 10 Timeline of proposed activities and deliverables.

	2018						2019												2020				2021				2022									
	Jul	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4						
Task 0: QAPP Update	■	d	f																																	
Task 1A: Year 1 Sampling				■	■	■	■	■	■	■	■	■	■	■	■		d		f																	
Task 1B: Year 1 Data mgmt and QA						■												d	f																	
Task 2A: Year 2 Sampling																				■		d	f													
Task 2B: Year 2 Data mgmt and QA																					■	d	f													
Task 3A: Year 3 Sampling																																	d	f		
Task 3B: Year 3 Data mgmt and QA																																d	f			
Task 4: Analysis and interpretation																																			d	f

D = Draft deliverable  
 f = Final deliverable  
 ■ = Activity

### Deliverables:

- Task 0: Amended QAPP, including detailed sampling and analysis plan
- Tasks 1A, 2A, and 3A: Year- end monitoring reports by USGS and AHPL
- Tasks 1B, 2B, 3B: QA Officer Memo, data uploaded to CEDEN
- Task 4: Detailed interpretive report including findings of 3-year sampling program and recommendations for future monitoring

**Note:** Option B (hybrid design) looks similar but adds a 4<sup>th</sup> year of monitoring from Oct. 2021 – Sept. 2022 and delays interpretive report by 1 year to 2023.

## Budget and Principal Investigators

*The budget for proposed monitoring in Table 11 below covers year 1 of the proposed 4-year study.*

Table 12 shows a multi-year planning budget. Note that the Option B extends over 4 years of monitoring. Even though monitoring activities remain essentially the same from year to year, we assumed a cost escalation of 3% per year. We also assume that the Option B data analysis and interpretation would require somewhat more effort, as it involves analyzing two classes of data from separate sampling designs, and could include an analysis of pesticide and toxicity trends over time. The average annual cost of Option A (not adjusted for inflation) is \$218K per year, while Option B averages \$238K per year.

Participants in the study include:

- San Francisco Estuary Institute – Aquatic Science Center (ASC)
- Aquatic Health Program Laboratory at UC Davis (AHPL)
- U.S. Geological Survey Organic Chemistry Research Laboratory (OCRL)
- USGS National Water Quality Laboratory (NWQL)

All field work will be done by staff of the USGS OCRL at Sacramento State. They will also perform the pesticides chemical analyses. The USGS lab has a unique capability to test 170+ analytes, low detection limits, and a competitive cost when compared to commercial labs. In addition, the USGS has offered a 10% cost share on labor and travel. Water samples will be processed and analyzed by liquid chromatography tandem mass spectrometry (LC/MSMS) or gas chromatography mass spectrometry (GC/MS). These analysis methods are documented in a series of USGS reports and have been previously described in the Delta RMP's FY15/16 data report. See Appendix 1 for the planned analysis method for each analyte.

USGS OCRL will produce an informal data report for the Delta RMP. After some discussion, the project PI and staff agreed it was not worth the extra effort and expense to produce a formal USGS Open File Report, as we did in Years 1 and 2. A report like this would not add a great deal of new information to the literature. Further, a formal report would be less timely, as it typically takes several extra months to publish due to the USGS' editing and approval process. The report will contain describe sample collection and analysis methods, monitoring results, and a summary of data quality assurance.

Toxicity analyses are funded as an in-kind contribution by the State Water Resources Control Board, through the SWAMP program. SWAMP has a contract with AHPL, the UC Davis toxicity lab, which covers toxicity testing and reporting of results, but nothing else. In the past, lab staff have provided us with a number of *pro bono* "extras," such as participation in meetings, presentations of preliminary results, and a detailed year-end report. The contract manager at SWAMP has indicated that they are not willing to pay for these extras under their contract,

which is to cover lab analyses only. If we would like to continue having these extra services, we will need to pay for them out of the Delta RMP budget.

The estimated cost of these extra services from AHPL is \$15,063. This covers preparing and sending provisional data and information on the labs internal processes and controls, in addition to having the lab manager attend Delta RMP meetings to give updates. Note that we have not budgeted for a formal year-end report as in years past in order to reduce costs. However, the lab manager understands that there may be substantive comments on the data, and that staff may need to prepare a detailed response to comments and make revisions to deliverables.

The first task in the list should be considered essential. Provisional results of toxicity testing is required for the Delta RMP TAC to identify samples on which to perform TIEs.

The budget for data management and quality assurance is \$40,998, as shown in Table 11. This budget is somewhat more than was budgeted in years 1 and 2 of Delta RMP pesticides monitoring, but more in line with actual expenses. This task was budgeted in FY16/17 at \$37,400 and projected to go over budget by approximately \$5,000. The previous budgets were not adequate for the task. In brief, we encountered problems with missing and incorrect data that has required a great deal of troubleshooting and correspondence with the labs. In addition, some work has had to be repeated with corrected data, for example the database queries that we run as a part of the QA process. For this proposal, the level of effort and budgets have been adjusted to meet these expectations. ASC and USGS have assessed the “lessons learned” from the first two years of CUP monitoring and are confident that previous data management challenges will be minimized.

Table 11 Budget for proposed Delta RMP Monitoring of Current-Use Pesticides and Toxicity

Contractor	Item	Number	Unit Cost	Option A Cost	Option B Cost
<b>USGS</b>	<b>Field sample collection and lab analysis</b>				
				\$19,350	\$19,350
				\$22,659	\$30,993
				\$7,445	\$7,445
				\$82,587	\$82,587
				\$59,804	\$59,804
				\$11,025	\$11,025
				\$6,691	\$6,691
		USGS Cost share (10% of labor and travel)			-\$17,269
			<b>\$217,645</b>	<b>\$192,292</b>	
<b>AHPL</b>	<b>Toxicity Reporting</b>				
			<b>\$15,063</b>	<b>\$15,063</b>	
<b>ASC</b>	<b>Data Management and Quality Assurance</b>				
				\$6,900	
				\$16,485	
				\$7,904	
				\$4,600	
				\$1,520	
				\$3,589	
			<b>\$40,998</b>	<b>\$40,998</b>	
			<b>Total</b>	<b>\$248,352</b>	<b>\$255,933</b>
				(Option A)	(Option B)



Toxicity Analysis Budget (in-kind contribution by SWAMP)

AHPL	Toxicity Lab Analysis	Number	Unit Cost	Total Cost
	<i>Ceriodaphnia</i> 7-day test	60	\$1,160	\$69,600
	<i>Hyalella</i> 10-day test	60	\$1,160	\$69,600
	<i>Selenastrum</i> (algae) 96-hr test	60	\$960	\$57,600
	<i>Chironomus</i> (midge larvae) 10-day test	60	\$1,160	\$69,600
	<i>Pimephales</i> (fathead minnow) 7-day test	60	\$1,200	\$72,000
				<b>\$270,720</b>
	<b>Toxicity Identification Evaluations (TIEs)*</b>			
	Phase I TIE	4	\$6,600	\$26,400
	Phase II TIE	1	\$14,000	\$14,000
				\$40,400
	<b>Toxicity testing total (same for Option A &amp; B)</b>			<b>\$311,120</b>

\*May not be necessary, pending results of initial toxicity testing

Table 12 Multi-year planning budget for pesticides and toxicity monitoring in the Delta.

Item	Option A	Option B
Year 1 Monitoring	\$250K	\$256K
Year 2 Monitoring	\$258K	\$264K
Year 3 Monitoring	\$265K	\$272K
Year 4 monitoring	-	\$280K
Interpretive Report	\$100K	\$120K
<b>Project Total</b>	<b>\$873K</b>	<b>\$1,190K</b>

## References

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## Appendix 1 Water Quality Measurements, Methods and Reporting Limits

In Table 13 below, methods are referred to by the following codes.

- 1 Hladik, M.L., Smalling, K.L., and Kuivila, K.M., 2009, Methods of analysis—Determination of pyrethroid insecticides in water and sediment using gas chromatography/mass spectrometry: U.S. Geological Survey Techniques and Methods 5–C2, 18 p. <https://pubs.usgs.gov/tm/tm5c2/tm5c2.pdf>
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- 4 Hladik, M.L., and McWayne, M.M., 2012, Methods of analysis—Determination of pesticides in sediment using gas chromatography/mass spectrometry: U.S. Geological Survey Techniques and Methods 5–C3, 18 p. Available at <http://pubs.usgs.gov/tm/tm5c3>
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Table 13 Summary of method, Reporting Limits (RL) and Method Detection Limits (MDL) for monitored constituents.

Constituent	Matrix	Reporting group	RL	MDL	Unit	Lab	Note	Method	Min. OPP Aquatic Life Benchmark (ng/L)	Benchmark Category
Oxygen, Dissolved	Water	Field Parameters	0.5	0.5	mg/L	USGS Field crew		NFM-A6		
pH	Water	Field Parameters	NA	NA	NA	USGS Field crew		NFM-A6		
Specific Conductivity	Water	Field Parameters	10.0	10.0	uS/cm	USGS Field crew		NFM-A6		
Temperature	Water	Field Parameters	NA	NA	NA	USGS Field crew		NFM-A6		
Turbidity	Water	Field Parameters	1.0	1.0	FNU	USGS Field crew		NFM-A6		
Alkalinity as CaCO <sub>3</sub>	Water	Conventional	12.0	4.0	mg/L	AHPL		SM 2320B		
Ammonia as N	Water	Conventional	0.2	0.1	mg/L	AHPL		SM 4500-NH3F		
Hardness as CaCO <sub>3</sub>	Water	Conventional	6.0	2.0	mg/L	AHPL		SM 2340C		
Dissolved Organic Carbon	Water	Conventional	0.2	0.2	mg/L	USGS NWQL		OFR-94-480		
Particulate Organic Carbon	Water	Conventional	0.1	0.1	mg/L	USGS NWQL		EPA 440		
Copper, dissolved	Water	Trace Metals	0.8	0.8	ug/L	USGS NWQL		TM-5-B1		
3,4-Dichloroaniline	Water	Herbicide	3.2	3.2	ng/L	OCRL		3	--	--
3,4-Dichloroaniline	Suspended Sediment	Herbicide	8.3	8.3	ng/L	OCRL		2	--	--
3,5-Dichloroaniline	Water	Herbicide	7.6	7.6	ng/L	OCRL		3	--	--
3,5-Dichloroaniline	Suspended Sediment	Herbicide	7.6	7.6	ng/L	OCRL		2	--	--
Acetamiprid	Water	Insecticide	3.3	3.3	ng/L	OCRL		2	2,100	Invertebrates - Chronic
Acetochlor	Water	Herbicide	1.5	1.5	ng/L	OCRL		2	1,430	Nonvascular plants - Acute
Acetochlor	Suspended Sediment	Herbicide	1.5	1.5	ng/L	OCRL		1	1,430	Nonvascular plants - Acute
Acibenzolar-S-methyl	Water	Fungicide	3.0	3.0	ng/L	OCRL		2	--	--
Acibenzolar-S-methyl	Suspended Sediment	Fungicide	3.0	3.0	ng/L	OCRL		2	--	--
Alachlor	Water	Herbicide	1.7	1.7	ng/L	OCRL		2	1,640	Nonvascular plants - Acute
Alachlor	Suspended Sediment	Herbicide	1.7	1.7	ng/L	OCRL	New in 2018	2	1,640	Nonvascular plants - Acute

Constituent	Matrix	Reporting group	RL	MDL	Unit	Lab	Note	Method	Min. OPP Aquatic Life Benchmark (ng/L)	Benchmark Category
Allethrin	Water	Insecticide	1.0	1.0	ng/L	OCRL		2	1,050	Invertebrates - Acute
Allethrin	Suspended Sediment	Insecticide	1.0	1.0	ng/L	OCRL		2	1,050	Invertebrates - Acute
Atrazine	Water	Herbicide	2.3	2.3	ng/L	OCRL		1	1,000	Nonvascular plants - Acute
Atrazine	Suspended Sediment	Herbicide	2.3	2.3	ng/L	OCRL		2	1,000	Nonvascular plants - Acute
Azinphos-methyl	Water	Insecticide	9.4	9.4	ng/L	OCRL		2	80.0	Invertebrates - Acute
Azinphos-methyl	Suspended Sediment	Insecticide	9.4	9.4	ng/L	OCRL		2	80.0	Invertebrates - Acute
Azinphos-methyl oxon	Water	Insecticide	9.4	9.4	ng/L	OCRL		2	11.0	Invertebrates - Chronic
Azinphos-methyl oxon	Suspended Sediment	Insecticide	9.4	9.4	ng/L	OCRL		2	11.0	Invertebrates - Chronic
Azoxystrobin	Water	Fungicide	3.1	3.1	ng/L	OCRL		2	8,000	Invertebrates - Chronic
Azoxystrobin	Suspended Sediment	Fungicide	3.1	3.1	ng/L	OCRL		3	8,000	Invertebrates - Chronic
Benefin (Benfluralin)	Water	Herbicide	2.0	2.0	ng/L	OCRL		2	1,900	Fish - Chronic
Benefin (Benfluralin)	Suspended Sediment	Herbicide	2.0	2.0	ng/L	OCRL		3	1,900	Fish - Chronic
Benzovindiflupyr	Water	Fungicide	3.4	3.4	ng/L	OCRL	New in 2018	3	950	Fish - Chronic
Benzovindiflupyr	Suspended Sediment	Fungicide	3.4	3.4	ng/L	OCRL	New in 2018	2	950	Fish - Chronic
Bifenthrin	Water	Insecticide	0.7	0.7	ng/L	OCRL		2	1.3	Invertebrates - Chronic
Bifenthrin	Suspended Sediment	Insecticide	0.7	0.7	ng/L	OCRL		2	1.3	Invertebrates - Chronic
Boscalid	Water	Fungicide	2.8	2.8	ng/L	OCRL		2	116,000	Fish - Chronic
Boscalid	Suspended Sediment	Fungicide	2.8	2.8	ng/L	OCRL		2	116,000	Fish - Chronic
Bromoconazole	Water	Fungicide	3.2	3.2	ng/L	OCRL		3	--	--
Bromoconazole	Suspended Sediment	Fungicide	3.2	3.2	ng/L	OCRL		2	--	--
Butralin	Water	Herbicide	2.6	2.6	ng/L	OCRL		3	--	--
Butralin	Suspended Sediment	Herbicide	2.6	2.6	ng/L	OCRL		3	--	--
Butylate	Water	Herbicide	1.8	1.8	ng/L	OCRL		2	105,000	Fish - Acute
Butylate	Suspended Sediment	Herbicide	1.8	1.8	ng/L	OCRL		1	105,000	Fish - Acute
Captan	Water	Fungicide	10.2	10.2	ng/L	OCRL		2	105	Invertebrates - Acute
Captan	Suspended Sediment	Fungicide	10.2	10.2	ng/L	OCRL		1	105	Invertebrates - Acute
Carbaryl	Water	Insecticide	6.5	6.5	ng/L	OCRL		3	500	Invertebrates - Chronic
Carbaryl	Suspended Sediment	Insecticide	6.5	6.5	ng/L	OCRL		1	500	Invertebrates - Chronic
Carbendazim	Water	Fungicide	4.2	4.2	ng/L	OCRL		2	990	Fish - Chronic
Carbofuran	Water	Insecticide	3.1	3.1	ng/L	OCRL		2	860	Fish - Chronic
Carbofuran	Suspended Sediment	Insecticide	3.1	3.1	ng/L	OCRL		2	860	Fish - Chronic
Carboxin	Water	Fungicide	4.5	4.5	ng/L	OCRL	New in 2018	3	370,000	Nonvascular plants - Acute



Constituent	Matrix	Reporting group	RL	MDL	Unit	Lab	Note	Method	Min. OPP Aquatic Life Benchmark (ng/L)	Benchmark Category
Chlorantraniliprole	Water	Insecticide	4.0	4.0	ng/L	OCRL		3	6,360,000	Fish - Chronic
Chlorfenapyr	Water	Insecticide	3.3	3.3	ng/L	OCRL	New in 2018	1	20,000	Nonvascular plants - Acute
Chlorfenapyr	Suspended Sediment	Insecticide	3.3	3.3	ng/L	OCRL	New in 2018	3	20,000	Nonvascular plants - Acute
Chlorothalonil	Water	Fungicide	4.1	4.1	ng/L	OCRL		2	2,400	Nonvascular plants - Acute
Chlorothalonil	Suspended Sediment	Fungicide	4.1	4.1	ng/L	OCRL		2	2,400	Nonvascular plants - Acute
Chlorpyrifos	Water	Insecticide	2.1	2.1	ng/L	OCRL		2	800,000	Invertebrates - Chronic
Chlorpyrifos	Suspended Sediment	Insecticide	2.1	2.1	ng/L	OCRL		2	800,000	Invertebrates - Chronic
Chlorpyrifos oxon	Water	Insecticide	5.0	5.0	ng/L	OCRL		2	--	--
Chlorpyrifos oxon	Suspended Sediment	Insecticide	5.0	5.0	ng/L	OCRL		2	--	--
Clomazone	Water	Herbicide	2.5	2.5	ng/L	OCRL		2	167,000	Nonvascular plants - Acute
Clomazone	Suspended Sediment	Herbicide	2.5	2.5	ng/L	OCRL		3	167,000	Nonvascular plants - Acute
Clothianidin	Water	Insecticide	3.9	3.9	ng/L	OCRL		2	1,100	Invertebrates - Chronic
Coumaphos	Water	Insecticide	3.1	3.1	ng/L	OCRL		3	33.7	Invertebrates - Chronic
Coumaphos	Suspended Sediment	Insecticide	3.1	3.1	ng/L	OCRL		2	33.7	Invertebrates - Chronic
Cyantraniliprole	Water	Insecticide	4.2	4.2	ng/L	OCRL		1	6,560	Invertebrates - Chronic
Cyazofamid	Water	Fungicide	4.1	4.1	ng/L	OCRL		3	8,700	Invertebrates - Chronic
Cycloate	Water	Herbicide	1.1	1.1	ng/L	OCRL		2	1,200,000	Invertebrates - Acute
Cycloate	Suspended Sediment	Herbicide	1.1	1.1	ng/L	OCRL		2	1,200,000	Invertebrates - Acute
Cyfluthrin	Water	Insecticide	1.0	1.0	ng/L	OCRL		2	7.4	Invertebrates - Chronic
Cyfluthrin	Suspended Sediment	Insecticide	1.0	1.0	ng/L	OCRL		2	7.4	Invertebrates - Chronic
Cyhalofop-butyl	Water	Herbicide	1.9	1.9	ng/L	OCRL		2	47,400	Invertebrates - Chronic
Cyhalofop-butyl	Suspended Sediment	Herbicide	1.9	1.9	ng/L	OCRL		2	47,400	Invertebrates - Chronic
Cyhalothrin (all isomers)	Water	Insecticide	0.5	0.5	ng/L	OCRL		2	101,000	Fish - Chronic
Cyhalothrin (all isomers)	Suspended Sediment	Insecticide	0.5	0.5	ng/L	OCRL		2	101,000	Fish - Chronic
Cymoxanil	Water	Fungicide	3.9	3.9	ng/L	OCRL		1	--	--
Cypermethrin	Water	Insecticide	1.0	1.0	ng/L	OCRL		2	69.0	Invertebrates - Chronic
Cypermethrin	Suspended Sediment	Insecticide	1.0	1.0	ng/L	OCRL		2	69.0	Invertebrates - Chronic
Cyproconazole	Water	Fungicide	4.7	4.7	ng/L	OCRL		2	--	--
Cyproconazole	Suspended Sediment	Fungicide	4.7	4.7	ng/L	OCRL		2	--	--
Cyprodinil	Water	Fungicide	7.4	7.4	ng/L	OCRL		2	11.0	Invertebrates - Chronic
Cyprodinil	Suspended Sediment	Fungicide	7.4	7.4	ng/L	OCRL		3	11.0	Invertebrates - Chronic

Constituent	Matrix	Reporting group	RL	MDL	Unit	Lab	Note	Method	Min. OPP Aquatic Life Benchmark (ng/L)	Benchmark Category
DCPA	Water	Herbicide	2.0	2.0	ng/L	OCRL		2	110	Invertebrates - Chronic
DCPA	Suspended Sediment	Herbicide	2.0	2.0	ng/L	OCRL		2	110	Invertebrates - Chronic
DCPMU	Water	Herbicide	3.5	3.5	ng/L	OCRL		2	37.0	Invertebrates - Chronic
DCPU	Water	Herbicide	3.4	3.4	ng/L	OCRL		2	3,000,000	Invertebrates - Chronic
Deltamethrin	Water	Insecticide	0.6	0.6	ng/L	OCRL		2	4.1	Invertebrates - Chronic
Deltamethrin	Suspended Sediment	Insecticide	0.6	0.6	ng/L	OCRL		2	4.1	Invertebrates - Chronic
Desthio-prothioconazole	Water	Fungicide	3.0	3.0	ng/L	OCRL		2	--	--
Desulfinylfipronil	Water	Insecticide	1.6	1.6	ng/L	OCRL		2	590	Fish - Chronic
Desulfinylfipronil	Suspended Sediment	Insecticide	1.6	1.6	ng/L	OCRL		3	590	Fish - Chronic
Desulfinylfipronil amide	Water	Insecticide	3.2	3.2	ng/L	OCRL		3	--	--
Desulfinylfipronil amide	Suspended Sediment	Insecticide	3.2	3.2	ng/L	OCRL		2	--	--
Diazinon	Water	Insecticide	0.9	0.9	ng/L	OCRL		2	105	Invertebrates - Acute
Diazinon	Suspended Sediment	Insecticide	0.9	0.9	ng/L	OCRL		2	105	Invertebrates - Acute
Diazoxon	Water	Insecticide	5.0	5.0	ng/L	OCRL		2	--	--
Diazoxon	Suspended Sediment	Insecticide	5.0	5.0	ng/L	OCRL		2	--	--
Dichlorvos	Water	Insecticide	5.1	5.1	ng/L	OCRL	New in 2018	2	5.8	Invertebrates - Chronic
Dichlorvos	Suspended Sediment	Insecticide	5.1	5.1	ng/L	OCRL	New in 2018	3	5.8	Invertebrates - Chronic
Difenoconazole	Water	Fungicide	10.5	10.5	ng/L	OCRL		3	860	Fish - Chronic
Difenoconazole	Suspended Sediment	Fungicide	10.5	10.5	ng/L	OCRL		2	860	Fish - Chronic
Dimethomorph	Water	Fungicide	6.0	6.0	ng/L	OCRL		2	110,000	Invertebrates - Chronic
Dimethomorph	Suspended Sediment	Fungicide	6.0	6.0	ng/L	OCRL		2	110,000	Invertebrates - Chronic
Dinotefuran	Water	Insecticide	4.5	4.5	ng/L	OCRL		2	480,000	Fish - Chronic
Dithiopyr	Water	Herbicide	1.6	1.6	ng/L	OCRL		2	--	--
Dithiopyr	Suspended Sediment	Herbicide	1.6	1.6	ng/L	OCRL		2	--	--
Diuron	Water	Herbicide	3.2	3.2	ng/L	OCRL		2	2,400	Nonvascular plants - Acute
EPTC	Water	Herbicide	1.5	1.5	ng/L	OCRL		3	800,000	Invertebrates - Chronic
EPTC	Suspended Sediment	Herbicide	1.5	1.5	ng/L	OCRL		2	800,000	Invertebrates - Chronic
Esfenvalerate	Water	Insecticide	0.5	0.5	ng/L	OCRL		2	--	--
Esfenvalerate	Suspended Sediment	Insecticide	0.5	0.5	ng/L	OCRL		2	--	--
Ethaboxam	Water	Fungicide	3.8	3.8	ng/L	OCRL		2	7,000	Nonvascular plants - Acute
Ethalfuralin	Water	Herbicide	3.0	3.0	ng/L	OCRL		3	--	--
Ethalfuralin	Suspended Sediment	Herbicide	3.0	3.0	ng/L	OCRL		2	--	--

Constituent	Matrix	Reporting group	RL	MDL	Unit	Lab	Note	Method	Min. OPP Aquatic Life Benchmark (ng/L)	Benchmark Category
Etofenprox	Water	Insecticide	2.2	2.2	ng/L	OCRL		2	10.0	Invertebrates - Chronic
Etofenprox	Suspended Sediment	Insecticide	2.2	2.2	ng/L	OCRL		2	10.0	Invertebrates - Chronic
Etoxazole	Water	Insecticide	4.2	4.2	ng/L	OCRL	New in 2018	2	130	Invertebrates - Chronic
Etoxazole	Suspended Sediment	Insecticide	4.2	4.2	ng/L	OCRL	New in 2018	2	130	Invertebrates - Chronic
Famoxadone	Water	Fungicide	2.5	2.5	ng/L	OCRL		2	75,000	Invertebrates - Chronic
Famoxadone	Suspended Sediment	Fungicide	2.5	2.5	ng/L	OCRL		3	75,000	Invertebrates - Chronic
Fenamidone	Water	Fungicide	5.1	5.1	ng/L	OCRL		2	4,700	Fish - Chronic
Fenamidone	Suspended Sediment	Fungicide	5.1	5.1	ng/L	OCRL		3	4,700	Fish - Chronic
Fenarimol	Water	Fungicide	6.5	6.5	ng/L	OCRL		2	120,000	Invertebrates - Acute
Fenarimol	Suspended Sediment	Fungicide	6.5	6.5	ng/L	OCRL		2	120,000	Invertebrates - Acute
Fenbuconazole	Water	Fungicide	5.2	5.2	ng/L	OCRL		2	--	--
Fenbuconazole	Suspended Sediment	Fungicide	5.2	5.2	ng/L	OCRL		2	--	--
Fenhexamid	Water	Fungicide	7.6	7.6	ng/L	OCRL		2	101,000	Fish - Chronic
Fenhexamid	Suspended Sediment	Fungicide	7.6	7.6	ng/L	OCRL		2	101,000	Fish - Chronic
Fenpropathrin	Water	Insecticide	0.6	0.6	ng/L	OCRL		2	60.0	Fish - Chronic
Fenpropathrin	Suspended Sediment	Insecticide	0.6	0.6	ng/L	OCRL		3	60.0	Fish - Chronic
Fenpyroximate	Water	Insecticide	5.2	5.2	ng/L	OCRL		2	16.0	Fish - Chronic
Fenpyroximate	Suspended Sediment	Insecticide	5.2	5.2	ng/L	OCRL		2	16.0	Fish - Chronic
Fenthion	Water	Insecticide	5.5	5.5	ng/L	OCRL		3	13.0	Invertebrates - Chronic
Fenthion	Suspended Sediment	Insecticide	5.5	5.5	ng/L	OCRL		1	13.0	Invertebrates - Chronic
Fipronil	Water	Insecticide	2.9	2.9	ng/L	OCRL		1	100,000	Invertebrates - Chronic
Fipronil	Suspended Sediment	Insecticide	2.9	2.9	ng/L	OCRL		2	100,000	Invertebrates - Chronic
Fipronil sulfide	Water	Insecticide	1.8	1.8	ng/L	OCRL		2	110	Invertebrates - Chronic
Fipronil sulfide	Suspended Sediment	Insecticide	1.8	1.8	ng/L	OCRL		2	110	Invertebrates - Chronic
Fipronil sulfone	Water	Insecticide	3.5	3.5	ng/L	OCRL		2	37.0	Invertebrates - Chronic
Fipronil sulfone	Suspended Sediment	Insecticide	3.5	3.5	ng/L	OCRL		2	37.0	Invertebrates - Chronic
Flonicamid	Water	Insecticide	3.4	3.4	ng/L	OCRL		2	3,000,000	Invertebrates - Chronic
Fluazinam	Water	Fungicide	4.4	4.4	ng/L	OCRL		2	6,300	Invertebrates - Chronic
Fluazinam	Suspended Sediment	Fungicide	4.4	4.4	ng/L	OCRL		2	6,300	Invertebrates - Chronic
Flubendiamide	Water	Insecticide	6.2	6.2	ng/L	OCRL	New in 2018	2	140	Invertebrates - Acute
Flubendiamide	Suspended Sediment	Insecticide	6.2	6.2	ng/L	OCRL	New in 2018	2	140	Invertebrates - Acute
Fludioxonil	Water	Fungicide	7.3	7.3	ng/L	OCRL		2	1,000	Invertebrates - Chronic

Constituent	Matrix	Reporting group	RL	MDL	Unit	Lab	Note	Method	Min. OPP Aquatic Life Benchmark (ng/L)	Benchmark Category
Fludioxonil	Suspended Sediment	Fungicide	7.3	7.3	ng/L	OCRL		2	1,000	Invertebrates - Chronic
Flufenacet	Water	Herbicide	4.7	4.7	ng/L	OCRL		2	--	--
Flufenacet	Suspended Sediment	Herbicide	4.7	4.7	ng/L	OCRL		2	--	--
Flumetralin	Water	Other	5.8	5.8	ng/L	OCRL		2	830,000	Nonvascular plants - Acute
Flumetralin	Suspended Sediment	Other	5.8	5.8	ng/L	OCRL		1	830,000	Nonvascular plants - Acute
Fluopicolide	Water	Fungicide	3.9	3.9	ng/L	OCRL		2	1,100,000	Fish - Chronic
Fluopicolide	Suspended Sediment	Fungicide	3.9	3.9	ng/L	OCRL		2	1,100,000	Fish - Chronic
Fluopyram	Water	Fungicide	3.8	3.8	ng/L	OCRL	New in 2018	3	--	--
Fluopyram	Suspended Sediment	Fungicide	3.8	3.8	ng/L	OCRL	New in 2018	1	--	--
Fluoxastrobin	Water	Fungicide	9.5	9.5	ng/L	OCRL		2	13,000	Vascular plants - Acute
Fluoxastrobin	Suspended Sediment	Fungicide	9.5	9.5	ng/L	OCRL		3	13,000	Vascular plants - Acute
Flupyradifurone	Water	Insecticide	3.0	3.0	ng/L	OCRL	New in 2018	2	5,200	Nonvascular plants - Acute
Fluridone	Water	Herbicide	3.7	3.7	ng/L	OCRL		2	480,000	Fish - Chronic
Flusilazole	Water	Fungicide	4.5	4.5	ng/L	OCRL		1	290	Nonvascular plants - Acute
Flusilazole	Suspended Sediment	Fungicide	4.5	4.5	ng/L	OCRL		2	290	Nonvascular plants - Acute
Flutolanil	Water	Fungicide	4.4	4.4	ng/L	OCRL		2	220,000	Fish - Chronic
Flutolanil	Suspended Sediment	Fungicide	4.4	4.4	ng/L	OCRL		1	220,000	Fish - Chronic
Flutriafol	Water	Fungicide	4.2	4.2	ng/L	OCRL		3	310,000	Invertebrates - Chronic
Flutriafol	Suspended Sediment	Fungicide	4.2	4.2	ng/L	OCRL		3	310,000	Invertebrates - Chronic
Fluxapyroxad	Water	Fungicide	4.8	4.8	ng/L	OCRL		3	--	--
Fluxapyroxad	Suspended Sediment	Fungicide	4.8	4.8	ng/L	OCRL		3	--	--
Hexazinone	Water	Herbicide	8.4	8.4	ng/L	OCRL		3	7,000	Nonvascular plants - Acute
Hexazinone	Suspended Sediment	Herbicide	8.4	8.4	ng/L	OCRL		2	7,000	Nonvascular plants - Acute
Imazalil	Water	Fungicide	10.5	10.5	ng/L	OCRL		2	--	--
Imazalil	Suspended Sediment	Fungicide	10.5	10.5	ng/L	OCRL		3	--	--
Imidacloprid	Water	Insecticide	3.8	3.8	ng/L	OCRL		2	5,200	Nonvascular plants - Acute
Imidacloprid urea	Water	Insecticide	4.0	4.0	ng/L	OCRL	New in 2018	2	3,000	Vascular plants - Acute
Indoxacarb	Water	Insecticide	4.9	4.9	ng/L	OCRL		2	75,000	Invertebrates - Chronic
Indoxacarb	Suspended Sediment	Insecticide	4.9	4.9	ng/L	OCRL		2	75,000	Invertebrates - Chronic
Iproconazole	Water	Fungicide	7.8	7.8	ng/L	OCRL		3	180,000	Fish - Chronic
Iproconazole	Suspended Sediment	Fungicide	7.8	7.8	ng/L	OCRL		2	180,000	Fish - Chronic
Iprodione	Water	Fungicide	4.4	4.4	ng/L	OCRL		2	120,000	Invertebrates - Acute
Iprodione	Suspended Sediment	Fungicide	4.4	4.4	ng/L	OCRL		2	120,000	Invertebrates - Acute

Constituent	Matrix	Reporting group	RL	MDL	Unit	Lab	Note	Method	Min. OPP Aquatic Life Benchmark (ng/L)	Benchmark Category
Isofetamid	Water	Fungicide	2.0	2.0	ng/L	OCRL	New in 2018	2	86,000	Fish - Chronic
Isofetamid	Suspended Sediment	Fungicide	2.0	2.0	ng/L	OCRL	New in 2018	2	86,000	Fish - Chronic
Kresoxim-methyl	Water	Fungicide	4.0	4.0	ng/L	OCRL		3	299,200	Vascular plants - Acute
Kresoxim-methyl	Suspended Sediment	Fungicide	4.0	4.0	ng/L	OCRL		2	299,200	Vascular plants - Acute
Malaoxon	Water	Insecticide	5.0	5.0	ng/L	OCRL		3	--	--
Malaoxon	Suspended Sediment	Insecticide	5.0	5.0	ng/L	OCRL		2	--	--
Malathion	Water	Insecticide	3.7	3.7	ng/L	OCRL		2	49.0	Invertebrates - Acute
Malathion	Suspended Sediment	Insecticide	3.7	3.7	ng/L	OCRL		2	49.0	Invertebrates - Acute
Mandipropamid	Water	Fungicide	3.3	3.3	ng/L	OCRL		1	30,000	Invertebrates - Chronic
Metalaxyl	Water	Fungicide	5.1	5.1	ng/L	OCRL		2	1,500	Invertebrates - Chronic
Metalaxyl	Suspended Sediment	Fungicide	5.1	5.1	ng/L	OCRL		2	1,500	Invertebrates - Chronic
Metconazole	Water	Fungicide	5.2	5.2	ng/L	OCRL		2	--	--
Metconazole	Suspended Sediment	Fungicide	5.2	5.2	ng/L	OCRL		2	--	--
Methidathion	Water	Insecticide	7.2	7.2	ng/L	OCRL		2	1,040	Nonvascular plants - Acute
Methidathion	Suspended Sediment	Insecticide	7.2	7.2	ng/L	OCRL		2	1,040	Nonvascular plants - Acute
Methoprene	Water	Insecticide	6.4	6.4	ng/L	OCRL		1	9,100	Fish - Chronic
Methoprene	Suspended Sediment	Insecticide	6.4	6.4	ng/L	OCRL		2	9,100	Fish - Chronic
Methoxyfenozide	Water	Insecticide	2.7	2.7	ng/L	OCRL		2	299,200	Vascular plants - Acute
Methyl parathion	Water	Insecticide	3.4	3.4	ng/L	OCRL		2	21,000	Nonvascular plants - Acute
Methyl parathion	Suspended Sediment	Insecticide	3.4	3.4	ng/L	OCRL		2	21,000	Nonvascular plants - Acute
Metolachlor	Water	Herbicide	1.5	1.5	ng/L	OCRL		2	1,000	Invertebrates - Chronic
Metolachlor	Suspended Sediment	Herbicide	1.5	1.5	ng/L	OCRL		2	1,000	Invertebrates - Chronic
Molinate	Water	Herbicide	3.2	3.2	ng/L	OCRL		3	105,000	Fish - Acute
Molinate	Suspended Sediment	Herbicide	3.2	3.2	ng/L	OCRL		2	105,000	Fish - Acute
Myclobutanil	Water	Fungicide	6.0	6.0	ng/L	OCRL		3	830,000	Nonvascular plants - Acute
Myclobutanil	Suspended Sediment	Fungicide	6.0	6.0	ng/L	OCRL		3	830,000	Nonvascular plants - Acute
Napropamide	Water	Herbicide	8.2	8.2	ng/L	OCRL		2	20,000	Fish - Chronic
Napropamide	Suspended Sediment	Herbicide	8.2	8.2	ng/L	OCRL		2	20,000	Fish - Chronic
Novaluron	Water	Insecticide	2.9	2.9	ng/L	OCRL		2	30.0	Invertebrates - Chronic
Novaluron	Suspended Sediment	Insecticide	2.9	2.9	ng/L	OCRL		2	30.0	Invertebrates - Chronic
Oryzalin	Water	Herbicide	5.0	5.0	ng/L	OCRL		2	13,000	Fish - Chronic
Oxadiazon	Water	Herbicide	2.1	2.1	ng/L	OCRL		3	5,200	Nonvascular plants - Acute

Constituent	Matrix	Reporting group	RL	MDL	Unit	Lab	Note	Method	Min. OPP Aquatic Life Benchmark (ng/L)	Benchmark Category
Oxadiazon	Suspended Sediment	Herbicide	2.1	2.1	ng/L	OCRL		2	5,200	Nonvascular plants - Acute
Oxathiapiprolin	Water	Fungicide	3.2	3.2	ng/L	OCRL	New in 2018	3	140,000	Nonvascular plants - Acute
Oxyfluorfen	Water	Herbicide	3.1	3.1	ng/L	OCRL		3	2,240	Nonvascular plants - Acute
Oxyfluorfen	Suspended Sediment	Herbicide	3.1	3.1	ng/L	OCRL		2	2,240	Nonvascular plants - Acute
p,p'-DDD	Water	Insecticide	4.1	4.1	ng/L	OCRL		1	--	--
p,p'-DDD	Suspended Sediment	Insecticide	4.1	4.1	ng/L	OCRL		2	--	--
p,p'-DDE	Water	Insecticide	3.6	3.6	ng/L	OCRL		1	--	--
p,p'-DDE	Suspended Sediment	Insecticide	3.6	3.6	ng/L	OCRL		3	--	--
p,p'-DDT	Water	Insecticide	4.0	4.0	ng/L	OCRL		1	--	--
p,p'-DDT	Suspended Sediment	Insecticide	4.0	4.0	ng/L	OCRL		2	--	--
Paclobutrazol	Water	Fungicide	6.2	6.2	ng/L	OCRL		2	8,000	Vascular plants - Acute
Paclobutrazol	Suspended Sediment	Fungicide	6.2	6.2	ng/L	OCRL		2	8,000	Vascular plants - Acute
Pebulate	Water	Herbicide	2.3	2.3	ng/L	OCRL		3	230,000	Nonvascular plants - Acute
Pebulate	Suspended Sediment	Herbicide	2.3	2.3	ng/L	OCRL		3	230,000	Nonvascular plants - Acute
Pendimethalin	Water	Herbicide	2.3	2.3	ng/L	OCRL		1	5,200	Nonvascular plants - Acute
Pendimethalin	Suspended Sediment	Herbicide	2.3	2.3	ng/L	OCRL		3	5,200	Nonvascular plants - Acute
Penoxsulam	Water	Herbicide	3.5	3.5	ng/L	OCRL		2	3,000	Vascular plants - Acute
Pentachloroanisole	Water	Insecticide	4.7	4.7	ng/L	OCRL		2	190,000	Invertebrates - Chronic
Pentachloroanisole	Suspended Sediment	Insecticide	4.7	4.7	ng/L	OCRL		2	190,000	Invertebrates - Chronic
Pentachloronitrobenzene	Water	Fungicide	3.1	3.1	ng/L	OCRL		2	13,000	Fish - Chronic
Pentachloronitrobenzene	Suspended Sediment	Fungicide	3.1	3.1	ng/L	OCRL		2	13,000	Fish - Chronic
Penthiopyrad	Water	Fungicide	3.2	3.2	ng/L	OCRL	New in 2018	2	100,000	Fish - Chronic
Permethrin	Water	Insecticide	0.6	0.6	ng/L	OCRL		2	42,000	Invertebrates - Chronic
Permethrin	Suspended Sediment	Insecticide	0.6	0.6	ng/L	OCRL		3	42,000	Invertebrates - Chronic
Phenothrin	Water	Insecticide	1.0	1.0	ng/L	OCRL		2	470	Invertebrates - Chronic
Phenothrin	Suspended Sediment	Insecticide	1.0	1.0	ng/L	OCRL		3	470	Invertebrates - Chronic
Phosmet	Water	Insecticide	4.4	4.4	ng/L	OCRL		2	17,500	Invertebrates - Acute
Phosmet	Suspended Sediment	Insecticide	4.4	4.4	ng/L	OCRL		1	17,500	Invertebrates - Acute
Picoxystrobin	Water	Fungicide	4.2	4.2	ng/L	OCRL		3	1,000	Invertebrates - Chronic
Picoxystrobin	Suspended Sediment	Fungicide	4.2	4.2	ng/L	OCRL		2	1,000	Invertebrates - Chronic
Piperonyl butoxide	Water	Other	2.3	2.3	ng/L	OCRL		2	30,000	Invertebrates - Chronic
Piperonyl butoxide	Suspended Sediment	Other	2.3	2.3	ng/L	OCRL		2	30,000	Invertebrates - Chronic

Constituent	Matrix	Reporting group	RL	MDL	Unit	Lab	Note	Method	Min. OPP Aquatic Life Benchmark (ng/L)	Benchmark Category
Prodiamine	Water	Herbicide	5.2	5.2	ng/L	OCRL		2	1,500	Invertebrates - Chronic
Prodiamine	Suspended Sediment	Herbicide	5.2	5.2	ng/L	OCRL		2	1,500	Invertebrates - Chronic
Prometon	Water	Herbicide	2.5	2.5	ng/L	OCRL		2	1,000	Invertebrates - Chronic
Prometon	Suspended Sediment	Herbicide	2.5	2.5	ng/L	OCRL		2	1,000	Invertebrates - Chronic
Prometryn	Water	Herbicide	1.8	1.8	ng/L	OCRL		2	1,040	Nonvascular plants - Acute
Prometryn	Suspended Sediment	Herbicide	1.8	1.8	ng/L	OCRL		1	1,040	Nonvascular plants - Acute
Propanil	Water	Herbicide	10.1	10.1	ng/L	OCRL		2	9,100	Fish - Chronic
Propanil	Suspended Sediment	Herbicide	10.1	10.1	ng/L	OCRL		2	9,100	Fish - Chronic
Propargite	Water	Insecticide	6.1	6.1	ng/L	OCRL		2	7,000	Invertebrates - Acute
Propargite	Suspended Sediment	Insecticide	6.1	6.1	ng/L	OCRL		2	7,000	Invertebrates - Acute
Propiconazole	Water	Fungicide	5.0	5.0	ng/L	OCRL		2	21,000	Nonvascular plants - Acute
Propiconazole	Suspended Sediment	Fungicide	5.0	5.0	ng/L	OCRL		3	21,000	Nonvascular plants - Acute
Propyzamide	Water	Herbicide	5.0	5.0	ng/L	OCRL		2	224,000	Fish - Chronic
Propyzamide	Suspended Sediment	Herbicide	5.0	5.0	ng/L	OCRL		2	224,000	Fish - Chronic
Pyraclostrobin	Water	Fungicide	2.9	2.9	ng/L	OCRL		2	1,500	Nonvascular plants - Acute
Pyraclostrobin	Suspended Sediment	Fungicide	2.9	2.9	ng/L	OCRL		2	1,500	Nonvascular plants - Acute
Pyridaben	Water	Insecticide	5.4	5.4	ng/L	OCRL		2	2,760	Invertebrates - Chronic
Pyridaben	Suspended Sediment	Insecticide	5.4	5.4	ng/L	OCRL		2	2,760	Invertebrates - Chronic
Pyrimethanil	Water	Fungicide	4.1	4.1	ng/L	OCRL		2	20,000	Fish - Chronic
Pyrimethanil	Suspended Sediment	Fungicide	4.1	4.1	ng/L	OCRL		2	20,000	Fish - Chronic
Pyriproxyfen	Water	Other	5.2	5.2	ng/L	OCRL	New in 2018	3	15.0	Invertebrates - Chronic
Pyriproxyfen	Suspended Sediment	Other	5.2	5.2	ng/L	OCRL	New in 2018	3	15.0	Invertebrates - Chronic
Quinoxifen	Water	Fungicide	3.3	3.3	ng/L	OCRL		2	13,000	Fish - Chronic
Quinoxifen	Suspended Sediment	Fungicide	3.3	3.3	ng/L	OCRL		2	13,000	Fish - Chronic
Resmethrin	Water	Insecticide	1.0	1.0	ng/L	OCRL		2	140	Fish - Acute
Resmethrin	Suspended Sediment	Insecticide	1.0	1.0	ng/L	OCRL		2	140	Fish - Acute
Sedaxane	Water	Fungicide	5.2	5.2	ng/L	OCRL		2	--	--
Sedaxane	Suspended Sediment	Fungicide	5.2	5.2	ng/L	OCRL		2	--	--
Simazine	Water	Herbicide	5.0	5.0	ng/L	OCRL		3	2,240	Nonvascular plants - Acute
Simazine	Suspended Sediment	Herbicide	5.0	5.0	ng/L	OCRL		3	2,240	Nonvascular plants - Acute
Sulfoxaflor	Water	Insecticide	4.4	4.4	ng/L	OCRL	New in 2018	2	24,500	Invertebrates - Acute
tau-Fluvalinate	Water	Insecticide	0.7	0.7	ng/L	OCRL		2	64.0	Fish - Chronic
tau-Fluvalinate	Suspended Sediment	Insecticide	0.7	0.7	ng/L	OCRL		2	64.0	Fish - Chronic



Constituent	Matrix	Reporting group	RL	MDL	Unit	Lab	Note	Method	Min. OPP Aquatic Life Benchmark (ng/L)	Benchmark Category
Tebuconazole	Water	Fungicide	3.7	3.7	ng/L	OCRL		2	11,000	Fish - Chronic
Tebuconazole	Suspended Sediment	Fungicide	3.7	3.7	ng/L	OCRL		2	11,000	Fish - Chronic
Tebufenozide	Water	Insecticide	3.0	3.0	ng/L	OCRL	New in 2018	2	29,000	Invertebrates - Chronic
Tebupirimfos	Water	Insecticide	1.9	1.9	ng/L	OCRL		2	299,200	Vascular plants - Acute
Tebupirimfos	Suspended Sediment	Insecticide	1.9	1.9	ng/L	OCRL		3	299,200	Vascular plants - Acute
Tebupirimfos oxon	Water	Insecticide	2.8	2.8	ng/L	OCRL		2	--	--
Tebupirimfos oxon	Suspended Sediment	Insecticide	2.8	2.8	ng/L	OCRL		2	--	--
Tefluthrin	Water	Insecticide	0.6	0.6	ng/L	OCRL		2	4.0	Fish - Chronic
Tefluthrin	Suspended Sediment	Insecticide	0.6	0.6	ng/L	OCRL		2	4.0	Fish - Chronic
Tetraconazole	Water	Fungicide	5.6	5.6	ng/L	OCRL		3	190,000	Invertebrates - Chronic
Tetraconazole	Suspended Sediment	Fungicide	5.6	5.6	ng/L	OCRL		2	190,000	Invertebrates - Chronic
Tetradifon	Water	Insecticide	3.8	3.8	ng/L	OCRL		2	--	--
Tetradifon	Suspended Sediment	Insecticide	3.8	3.8	ng/L	OCRL		2	--	--
Tetramethrin	Water	Insecticide	0.5	0.5	ng/L	OCRL		2	1,850	Fish - Acute
Tetramethrin	Suspended Sediment	Insecticide	0.5	0.5	ng/L	OCRL		2	1,850	Fish - Acute
Thiabendazole	Water	Fungicide	3.6	3.6	ng/L	OCRL		2	42,000	Invertebrates - Chronic
Thiacloprid	Water	Insecticide	3.2	3.2	ng/L	OCRL		3	970	Invertebrates - Chronic
Thiamethoxam	Water	Insecticide	3.4	3.4	ng/L	OCRL		2	17,500	Invertebrates - Acute
Thiamethoxam Degradate (CGA-355190)	Water	Insecticide	3.5	3.5	ng/L	OCRL	New in 2018	3	--	--
Thiamethoxam Degradate (NOA-407475)	Water	Insecticide	3.4	3.4	ng/L	OCRL	New in 2018	2	--	--
Thiazopyr	Water	Herbicide	4.1	4.1	ng/L	OCRL		2	--	--
Thiazopyr	Suspended Sediment	Herbicide	4.1	4.1	ng/L	OCRL		2	--	--
Thiobencarb	Water	Herbicide	1.9	1.9	ng/L	OCRL		2	1,000	Invertebrates - Chronic
Thiobencarb	Suspended Sediment	Herbicide	1.9	1.9	ng/L	OCRL		2	1,000	Invertebrates - Chronic
Tolfenpyrad	Water	Insecticide	2.9	2.9	ng/L	OCRL		2	81.5	Fish - Acute
Triadimefon	Water	Fungicide	8.9	8.9	ng/L	OCRL		2	52,000	Invertebrates - Chronic
Triadimefon	Suspended Sediment	Fungicide	8.9	8.9	ng/L	OCRL		3	52,000	Invertebrates - Chronic
Triadimenol	Water	Fungicide	8.0	8.0	ng/L	OCRL		2	--	--
Triadimenol	Suspended Sediment	Fungicide	8.0	8.0	ng/L	OCRL		2	--	--
Triallate	Water	Herbicide	2.4	2.4	ng/L	OCRL		3	14,000	Invertebrates - Chronic
Triallate	Suspended Sediment	Herbicide	2.4	2.4	ng/L	OCRL		1	14,000	Invertebrates - Chronic
Tribufos	Water	Herbicide	3.1	3.1	ng/L	OCRL		1	1,560	Invertebrates - Chronic

Constituent	Matrix	Reporting group	RL	MDL	Unit	Lab	Note	Method	Min. OPP Aquatic Life Benchmark (ng/L)	Benchmark Category
Tribufos	Suspended Sediment	Herbicide	3.1	3.1	ng/L	OCRL		2	1,560	Invertebrates - Chronic
Tricyclazole	Water	Fungicide	4.1	4.1	ng/L	OCRL	New in 2018	2	--	--
Trifloxystrobin	Water	Fungicide	4.7	4.7	ng/L	OCRL		2	2,760	Invertebrates - Chronic
Trifloxystrobin	Suspended Sediment	Fungicide	4.7	4.7	ng/L	OCRL		2	2,760	Invertebrates - Chronic
Triflumizole	Water	Fungicide	6.1	6.1	ng/L	OCRL		2	33,000	Fish - Chronic
Triflumizole	Suspended Sediment	Fungicide	6.1	6.1	ng/L	OCRL		2	33,000	Fish - Chronic
Trifluralin	Water	Herbicide	2.1	2.1	ng/L	OCRL		2	1,900	Fish - Chronic
Trifluralin	Suspended Sediment	Herbicide	2.1	2.1	ng/L	OCRL		2	1,900	Fish - Chronic
Triticonazole	Water	Fungicide	6.9	6.9	ng/L	OCRL		2	--	--
Triticonazole	Suspended Sediment	Fungicide	6.9	6.9	ng/L	OCRL		2	--	--
Zoxamide	Water	Fungicide	3.5	3.5	ng/L	OCRL		2	3,480	Fish - Chronic
Zoxamide	Suspended Sediment	Fungicide	3.5	3.5	ng/L	OCRL		2	3,480	Fish - Chronic

## Appendix 2 USGS PFRG Data Review Process

This information applies to all analytical results generated by the Pesticide Fate Research Group (PFRG) Organic Chemistry Research Laboratory (OCRL).

Following sample analysis at the OCRL all analytical results are reviewed by the USGS Project Director (PD) responsible for submitting the samples for analysis. Results are reviewed as they become available from the laboratory. The PD reviews each sample for completeness to ensure that all requested analytes have been quantitated, and reviews each analytical result for unexpected presence/absence or unexpectedly high or low result values (based on previous results and/or known trends in pesticide use and occurrence). If quality control samples were analyzed the PD reviews these samples to ensure that project measurement quality objectives, as outlined in the project Quality Assurance Project Plan (QAPP), have been met. During these review processes the PD flags any suspect results which are then sent back to the OCRL Chief Chemist (CC) for review. The CC then reviews the quantitation for any flagged results to verify the initial result or make corrections as appropriate. If questions persist as to the quality of the data, sample extracts may be reanalyzed. Additionally, samples with high results which fall outside the instrument calibration curve, may be diluted and reanalyzed at this time. The CC then returns the final, verified results to the PD for review. If questions regarding the data persist, the USGS California Water Science Center (CAWSC) Water Quality Specialist will be consulted to review the data and make any suggestions for corrective actions and/or proper coding of the data. If the PD has no further questions or comments about the data they are entered in the project specific data reporting spreadsheet.

At the end of the project, or at an earlier date as specified in the project QAPP or data management plan, the finalized data reporting spreadsheet is provided to the PFRG database manager (DM). The DM then enters the laboratory analytical results in the OCRL Access database which also contains field sample collection and laboratory sample tracking information. The DM then performs a semi-automated process to format the analytical results and necessary field collection information for entry into the USGS National Water Information System (NWIS) database. Once formatted, the data are uploaded to NWIS using a batch process. All data are uploaded to NWIS with a "Data Quality Indicator" code of "Provisional". At this point the data are publicly viewable.

Prior to publication in any USGS series report the data undergo an additional, extensive review process. During this process the CAWSC Water Quality Specialist reviews the draft publication and data to ensure that they meet USGS accuracy and reporting standards. CAWSC data management staff (DMS) also review the data to verify that the data in the publication match the data stored in NWIS. Once the publication and data have been approved by the Water Quality Specialist and DMS the PFRG DM will switch the data quality indicator codes for all data results to "Reviewed and Accepted".

In rare instances where OCRL data are not reported in a USGS series report or scientific journal the data will be reviewed and approved by the CAWSC Water Quality Specialist prior to the PFRG DM switching the data quality indicator codes to “Reviewed and Accepted”.

The following information applies to results from the USGS National Water Quality Laboratory (NWQL), produced for projects managed by PFRG personnel.

Some research projects may require that samples be submitted to the NWQL for analysis. Analytical results produced by the NWQL are reviewed by the PD as they become available from the laboratory. The PD reviews each sample for completeness to ensure that all requested analytes have been reported, and reviews each analytical result for unexpected presence/absence or unexpectedly high or low result values (based on previous results and/or known trends in pesticide use and occurrence). If quality control samples were analyzed the PD reviews these samples to ensure that specific project measurement quality objectives as outlined in the project Quality Assurance Project Plan (QAPP) have been met. During these processes the PD flags any suspect results and may request a rerun of the sample if possible, or work with laboratory personnel to better understand/evaluate unexpected results. The PD also manually queries NWQL laboratory QC data for relevant analytical batches. These data are evaluated by the PD to determine if any environmental or field QC samples need to be coded in NWIS to reflect laboratory QC problems. All NWQL environmental, field QC, and laboratory QC data are entered in a project specific data reporting spreadsheet.

Environmental and field QC data produced by the NWQL are automatically flagged for some laboratory quality control issues as described in the NWQL’s Quality Assurance and Quality Control Manual available at ([http://wwwnwql.cr.usgs.gov/qas/QCM\\_v1.0.pdf](http://wwwnwql.cr.usgs.gov/qas/QCM_v1.0.pdf)). Data are automatically uploaded to the USGS NWIS database with a “Data Quality Indicator” code of “Provisional” At this point the data are publicly viewable.

Prior to publication in any USGS series report the data undergo an additional, extensive review process. During this process the CAWSC Water Quality Specialist reviews the draft publication and data to ensure that they meet USGS accuracy and reporting standards. CAWSC data management staff (DMS) also review the data to verify that the data in the publication match the data stored in NWIS. Once the publication and data have been approved by the Water Quality Specialist and DMS the PFRG DM will switch the data quality indicator codes for all data points to “Reviewed and Accepted”.

In rare instances where PFRG project data produced by the NWQL are not reported in a USGS series report or scientific journal the data will be reviewed and approved by the CAWSC Water Quality Specialist prior to the PFRG DM switching the data quality indicator codes to “Reviewed and Accepted.”

The following information applies to analytical results produced by the OCRL or USGS National Water Quality Laboratory (NWQL), which are submitted to non-USGS environmental databases (for example CEDEN).

Some research projects may require that analytical results be submitted to non-USGS environmental databases, in addition to NWIS, for storage. In addition to the data quality review procedures described earlier in this document, data destined for non-USGS databases undergo additional data formatting and review prior to submittal. After the data have been entered into the PFRG Access database the PFRG DM performs a semi-automated process to format the analytical results and necessary field collection information for entry into the external database using that database's coding and required fields. The formatted upload files are then provided to two USGS PFRG personnel for review. Each reviewer performs an independent review comparing analytical results, field collection information and method detection limits to data contained in the PFRG Access and USGS NWIS databases. Any discrepancies are flagged by the reviewers and the DM is notified. The DM makes any necessary corrections to the upload files which are then resubmitted to the reviewers to verify the corrections. Once this internal review process is completed the data are submitted to the non-USGS database and undergo any review processes pertinent to that database.

# Appendix 3 Statistical Power Analysis

## Technical Memorandum

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**TO:** Matthew Heberger (Aquatic Science Center)  
**FROM:** Aroon Melwani (Applied Marine Sciences, Inc.)  
**DATE:** April 26, 2018  
**SUBJECT:** Statistical Analysis to Support the Delta Regional Monitoring (DRMP) Program FY 2018 Pesticide Monitoring Designs

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### Background

The Delta Regional Monitoring Program (DRMP) includes evaluation of current-use pesticides and the extent to which they contribute to observed aquatic toxicity in the Delta. Between July 2015 and June 2017 (FY 2015-2016 and FY 2016-17), the DRMP collected baseline monthly water samples at five integrator sites that were analyzed for pesticides and paired toxicity analysis of 4-5 different species/endpoints (Figure 1). The DRMP is now undertaking an evaluation of these data to optimize the sampling design for future pesticides monitoring, with the specific goal of detecting a significant relationship between aquatic concentrations and toxicity.

On behalf of the DRMP Pesticides Subcommittee, the Aquatic Science Center contracted with Dr. Aroon Melwani (Applied Marine Sciences, Inc.) to conduct a power analysis and provide technical guidance towards employing a targeted or probabilistic sampling design for pesticides monitoring. The scope of work consisted of three tasks: 1) a preliminary analysis of variability in pesticide concentrations to inform stratification of baseline data, 2) evaluation of power to detect statistical relationships between pesticide concentrations and toxicity across a range of sample sizes, and 3) guidance on sampling effort and bias associated with probabilistic monitoring designs. This memorandum summarizes the results from these evaluations. This information is being used by the DRMP Pesticide Subcommittee to facilitate further discussions about an appropriate monitoring study design to address DRMP priorities.

### Methods

A two-year dataset of 152 pesticides (including degradates) analyzed monthly between June 2015 – July 2017 at five integrator sites in the Delta were the basis for all statistical analyses discussed herein. Only dissolved pesticide concentrations were used.

Based on initial discussions with the Pesticides Subcommittee, these data were summarized for analysis using the Pesticide Toxicity Index (PTI) values, following the methods of Munn and Gilliom (2001) and Nowell et al. (2014). The PTI is an index that combines the measured concentrations of any number of pesticides into a single value, to assess the potential toxicity of pesticide mixtures to freshwater aquatic organisms. It is



based on the concept of additive toxic units, well known in the field of risk assessment. TUs were calculated for individual compounds that were measured above the method detection limits, and summed for each location and sampling event using a database query in MS Access. The spreadsheet and database are available upon request from Matthew Heberger (matth@sfei.org).

Application of the PTI calculation to the pesticide concentration data resulted in a single index value for each analyzed sample (n = 24 per site; N = 120 total). It should be noted that several calculation assumptions exist for summarizing pesticide concentration into the PTI. To provide the most relevant and conservative calculation methodology for integration with the DRMP toxicity data, the Fish Sensitive and Cladoceran Sensitive calculations were used. Methods to represent an invertebrate endpoint or less conservative assumptions also exist.

Two chronic toxicity tests were selected for statistical evaluations based on recommendations from the Pesticides Subcommittee. For comparison to the Cladoceran Sensitive PTI, the *Ceriodaphnia dubia* reproductive test was selected (Figure 2), while for the Fish Sensitive PTI, the *Pimephales promelas* survival test was used (Figure 3). All toxicity results (as % effect) were included, irrespective if the result was statistically significant or not.

### **Task 1. PTI Variability**

The PTI data were initially assessed for patterns in variability to generate appropriate simulated data for power analysis. Summary statistics of the PTI results for the five sites are provided for context (Tables 1 and 2).

An analysis of variance test was used to determine significant differences in the PTI data. Due to the lack of temporal resolution and replication (1 sample per site per month for two years; n = 2 per group), temporal effects could not be tested with this analysis. The analysis of variance thus focused on spatial variability.

Based on the ANOVA results, two variance groups were identified by pooling sites that were not statistically different ( $p < 0.05$ ). Significance of groups was established through the use of 'dummy' variables for each site in the ANOVA tests. Subsequently, the mean, standard deviation, and coefficient of variation were calculated by stratifying the data into the respective groups ("A" and "B").

### **Task 2. Power Analysis**

A power analysis simulation was designed to evaluate the necessary sample size to make statistical associations between PTI data and toxicity. The power analysis procedure simulated 2000 datasets, based on estimates of arithmetic mean and variability (standard deviation) in PTI for each variance group and sample size scenario. It assumed for each scenario that the modeled level of variation remains constant during the monitoring period. Sample size was varied from n = 12 to n = 240.

The statistical model for examining the PTI vs. toxicity relationship was:

$$y_i = y_o + r(\text{PTI}) + \varepsilon \quad (\text{Equation 1})$$

Where,  $y_i$  = a simulated toxic effect value,  $y_o$  = the initial toxic effect value (intercept),  $r$  = slope of toxic effect vs. PTI (the effect size), PTI = individual pesticide toxicity index value, and  $\varepsilon$  (model error) is a normally distributed error term. The error term estimate was calculated as the standard deviation of the regression model error (i.e., sigma,  $\delta$ ). In employing this methodology, it is acknowledged that the model error estimate ( $\varepsilon$ ) consists of the unexplained temporal variance as well as other potential driving factors.

Linear regression analysis was performed on each simulated dataset to determine statistical significance (p-value). The proportion of results that exhibited statistically significant slopes ( $p < 0.05$ ) estimated the statistical power. The results of the power analysis were summarized in power curves (sample size vs. power) at varying effect sizes. The effect sizes selected were approximately an order of magnitude higher than the current size of the slope in the PTI: toxicity endpoint relationships.

### ***Task 3. Probabilistic Monitoring***

To address the final task in the scope of work, a technical review of the main concepts and recommendations for designing an ambient monitoring design was presented to the DRMP Pesticides Subcommittee. A summary of the design concepts discussed with the group is provided below.

## **Results**

### ***Task 1. PTI Variability***

Two PTI datasets were assessed for spatial differences. Tables 1 and 2 summarize the mean PTI and variance for each site.<sup>1</sup> For either calculation model (Fish or Cladoceran), Ulatris Creek exhibited average PTI and standard deviation that was twice that of the other sites. As a result, two variance scenarios were developed (A and B) to represent the range in future pesticide distributions.

### ***Task 2. Power Analysis***

Summary statistics of the two groups (Table 3) indicate that the coefficient of variation in each group was similar, but Group B (only Ulatris Creek) exhibited higher pesticide concentrations (and thus higher PTI values) than Group A. No significant relationship was apparent in the baseline data for either scenario or toxicity endpoint (Figure 4).

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<sup>1</sup> In general, TU values approaching 1 are cause for concern. However, According to Nowell et al. (2004), PTIS is “not necessarily appropriate as a sensitive tool for predicting whether pesticide mixtures in water samples are likely to be toxic to aquatic organisms.” Rather, it was originally designed to be an indicator of relative toxicity. PTI values for samples, seasons, or sites have been used as explanatory variables in multivariate analyses designed to determine the environmental variables that best explain spatial patterns in the structure of a biological community.”

Power curves employing the Cladoceran PTI using the Group A scenario indicated that to detect an effect size = 0.03 with > 80% power would require ~ 60 samples (Figure 5). For an effect size = 0.02, the same variance scenario would require > 75 samples.

Due to higher concentrations under the Group B scenario, power indicated that smaller effect sizes could be detected with similar levels of effort to Group A (Figure 6). For example, where an effect size = 0.03 would require a minimum of 60 samples to achieve > 80% power in Group A, a similar level of effort could detect an effect size < 0.01.

In the scenarios to test the relationship between the Fish PTI and *Pimephales* toxicity, similar patterns were evident to the *Ceriodaphnia* results. Generally, the scenarios using Group B (Ulati Creek) indicated 80% power could be achieved with similar levels of effort of Group A and 50% smaller effect sizes. This is important observation given the current lack of significant relationships at any of the sites. For example, an effect size of 0.3 with 60 samples would have > 80% power in Group B, as would an effect size of 0.6 with 60 samples in Group A.

### **Task 3. Probabilistic Designs**

A probability sample is one where every element of the target population has a known likelihood of being selected. Two important features of a probability sample are that the site selection mechanism safeguards against selection bias, and is the basis for inference to characteristics of the entire target population. Good sampling designs tend to spread out the sample points more or less regularly.

U.S. EPA's Generalized Random Tessellation Stratified (GRTS) survey design methodology is a probabilistic sampling method for implementing a spatial survey (Stevens and Olsen, 2004), which has been adopted in many regional surveys in California and nationwide. GRTS incorporates several design concepts important for making inferences across a population with unbiased estimates of condition (Kincaid and Olsen, 2016), these include: 1) Stratified sampling; 2) Unequal probability sampling; 3) Panel sampling; 4) Over-sample selection.

No explicit guidance on the recommended sample size for GRTS survey designs exists. Budgetary and logistical constraints of individual study designs often dictate the level of effort employed. That said, probabilistic designs incorporating GRTS often aim to determine an estimate of a proportional extent, and thus refer to the binomial distribution to evaluate precision. Figure 7 depicts the binomial relationship between sample size and size of confidence interval for determining the likelihood that a sample estimate is within 80% of the population. In this scenario, a sample size of 30 would result in an estimated confidence interval of ~ 12%. Increasing the sample size would not significantly impact on the size of the confidence interval, while fewer than 30 samples would increase the confidence interval substantially. Consequently, a sample size of 30 can be considered an "industry standard", and has, in my experience, been selected as a default sample size in order to make statistical inferences about condition, with a relatively low degree of error. Ultimately, deciding upon an appropriate sample size for GRTS for the DRMP will require

consideration of the monitoring objectives, precision desired, and the expected variability in the resource being sampled.

## Conclusions

The take-home points from the power analysis simulations are:

- The Pesticide Toxicity Index does not exhibit a significant relationship with baseline DRMP toxicity results
- Ulatis Creek simulations indicate the highest probability of detecting small effect sizes in PTI-toxicity relationships in the future, due to the presence of some higher concentrations and toxic hits
- Using the Fish PTI, effect size would need to increase by 4-20x to detect significant relationship in the next 5-10 years (assuming  $n = 6-12/\text{yr}$ )

Overall, the baseline integrator site data set appears to only have captured a handful of high concentrations, which do not currently associate with toxicity results. The lack of extreme concentrations or frequently toxic samples in these short-term data sets does not necessarily mean that such events would not occur had a longer period been monitored. Though, it might just be as equally probable to spend continued effort to sample high concentrations / toxicity that are simply not present. Conversely, where high concentrations have been found (such as at Ulatis Creek), it is difficult to evaluate how common or rare such occurrences are, and what the underlying factors that are driving these variations. Therefore, the DRMP could benefit from implementing a probabilistic sampling approach, which incorporates spatial and temporal sampling to distinguish sites and seasons with sufficiently elevated concentrations to make associations with toxicity due to the presence of likely sources/runoff patterns. At a minimum, expanding upon the baseline resolution of pesticides sampling is a necessary next step for the Program.

## References

Kincaid, T. M. and Olsen, A. R. (2016). *spsurvey: Spatial Survey Design and Analysis*. R package version 3.3.

Stevens, D.L., Jr., and Olsen, A.R. (2004). Spatially-balanced sampling of natural resources. *Journal of the American Statistical Association* 99: 262-278.

## Figures

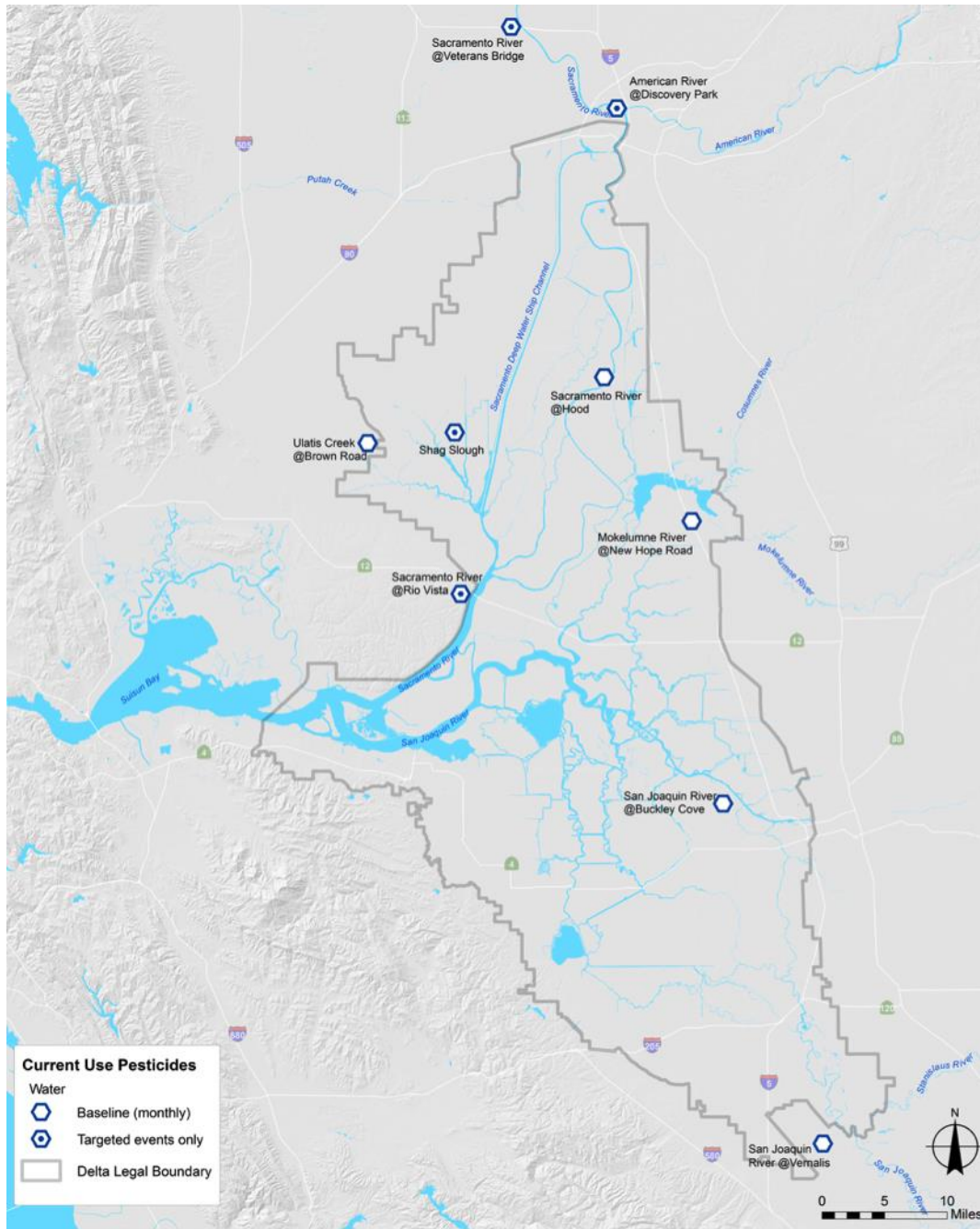
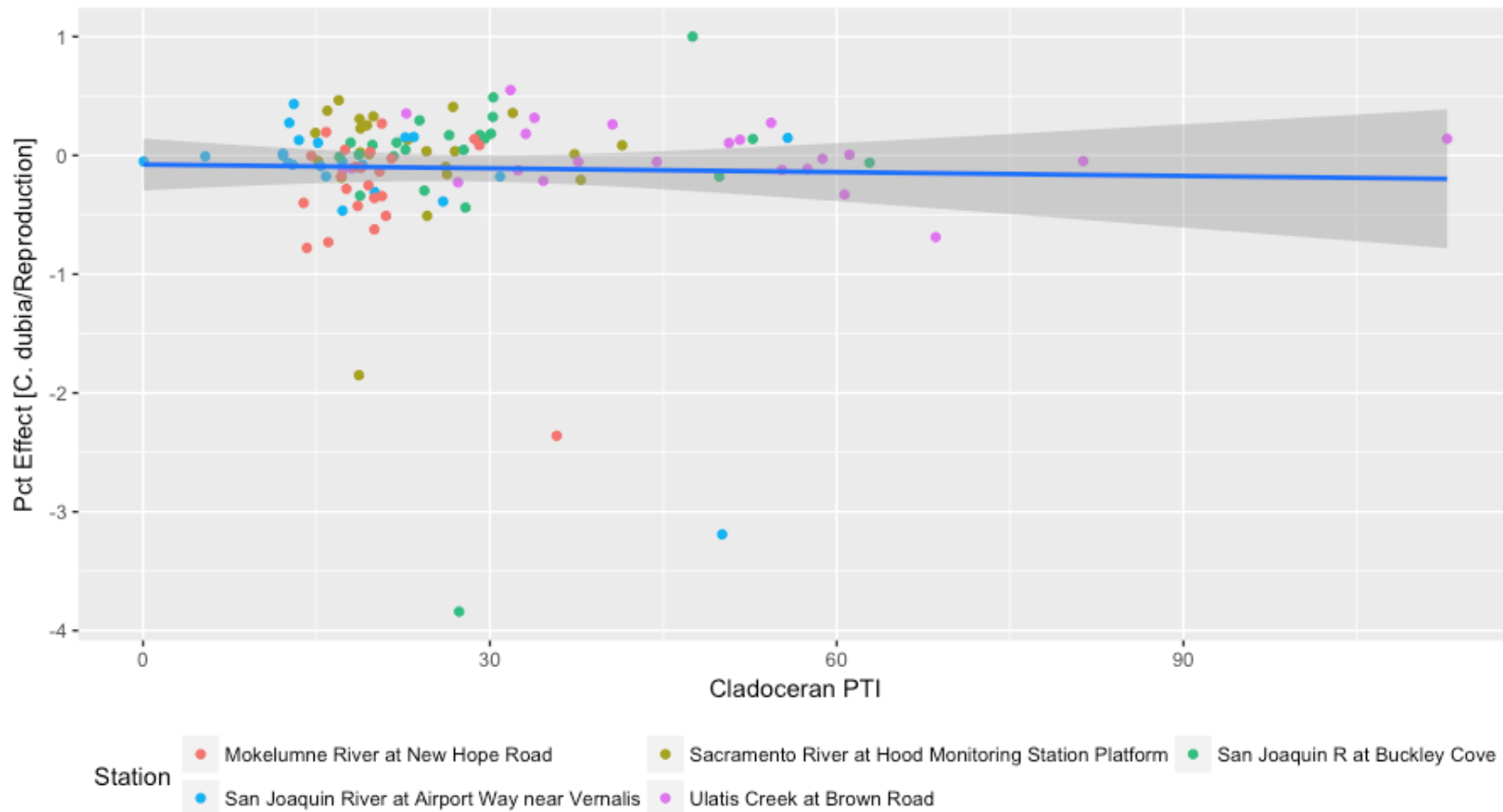
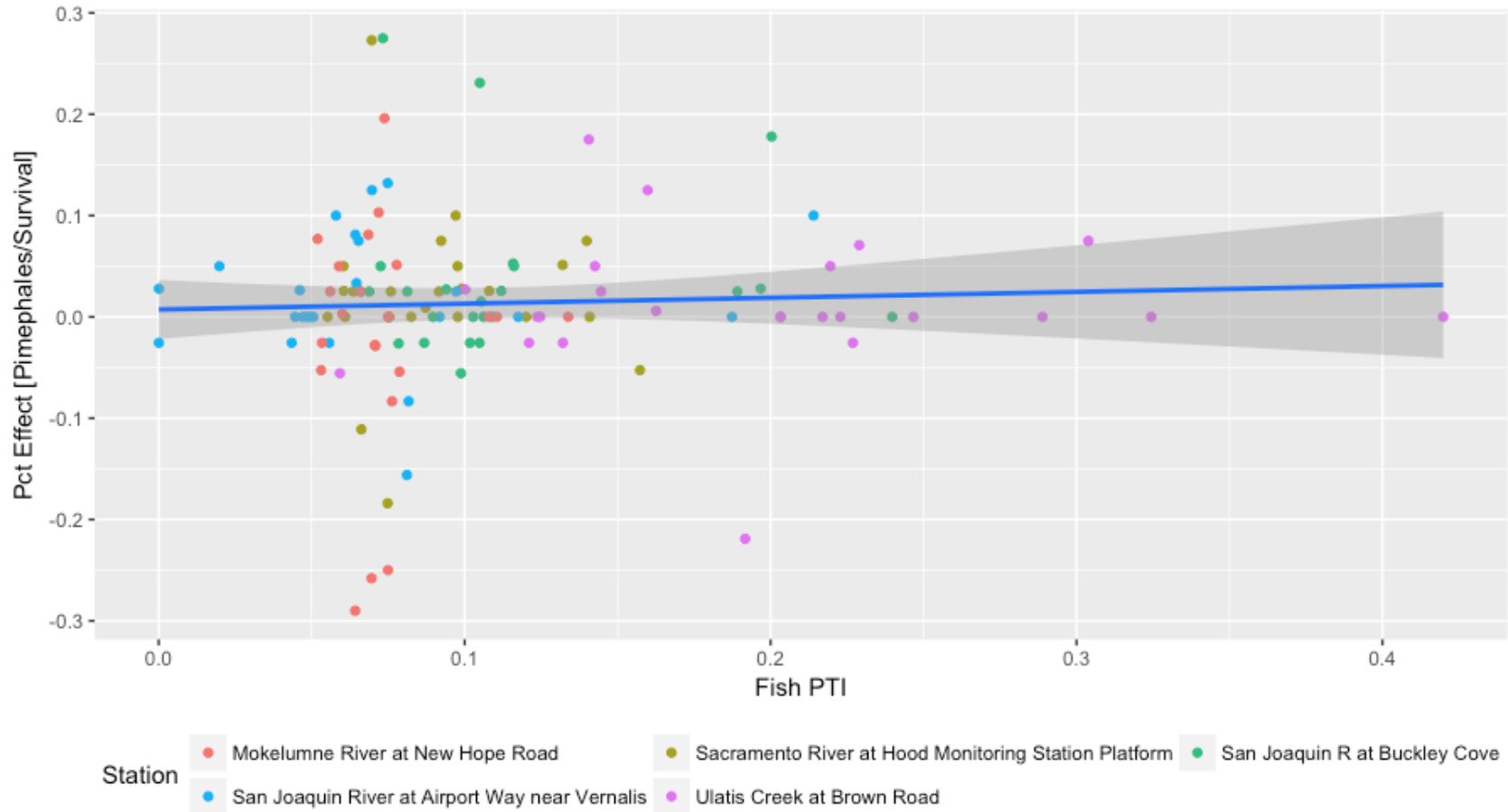


Figure 1. Map of Delta RMP integrator sites for pesticides sampling

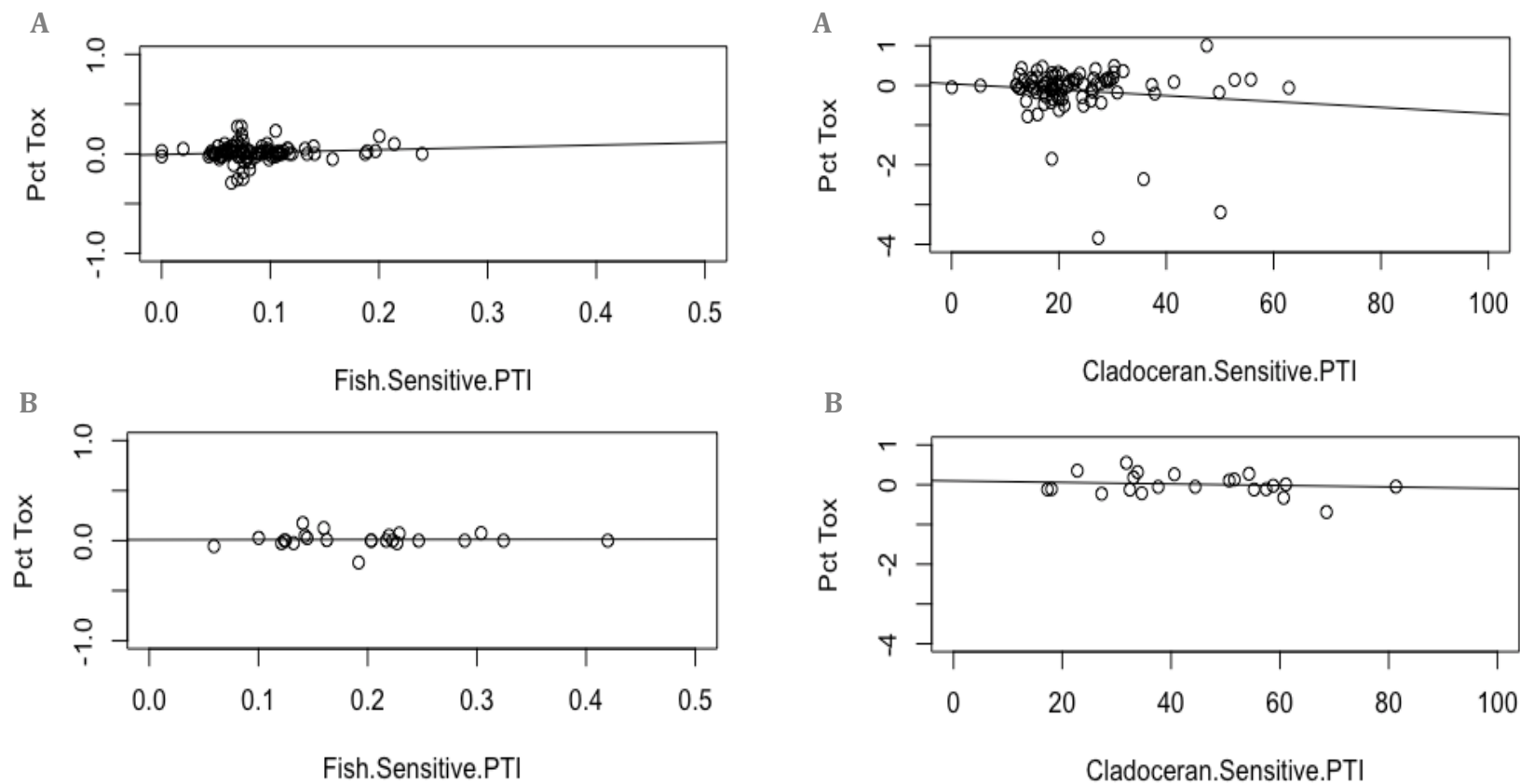
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**Figure 2.** Pesticide Toxicity Index (PTI, Cladoceran) plotted against Percent Toxic Effect in *Ceriodaphnia dubia* / Reproduction test. Colors designate each site. The trend line indicates there is no clear relationship between the two variables.

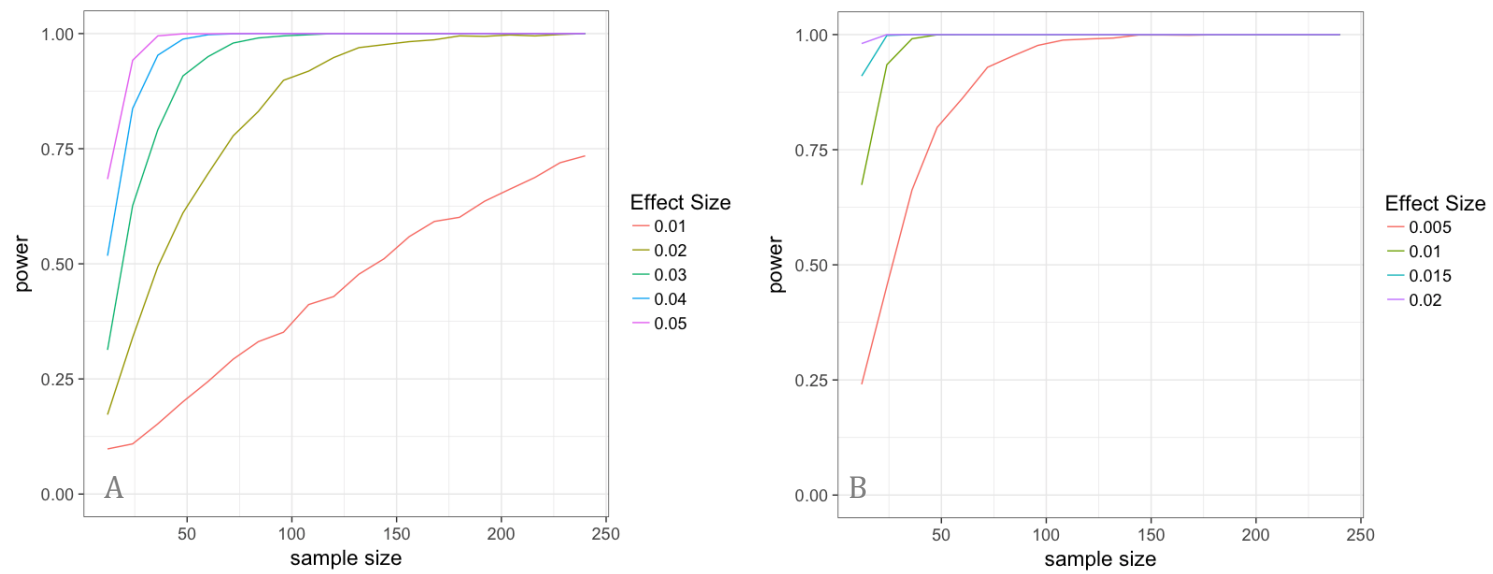


**Figure 3.** Pesticide Toxicity Index (PTI, Fish) plotted against Percent Toxic Effect in *Pimephales promelas* / Survival test. Colors designate each site. The trend line indicates there is no clear relationship between the two variables.

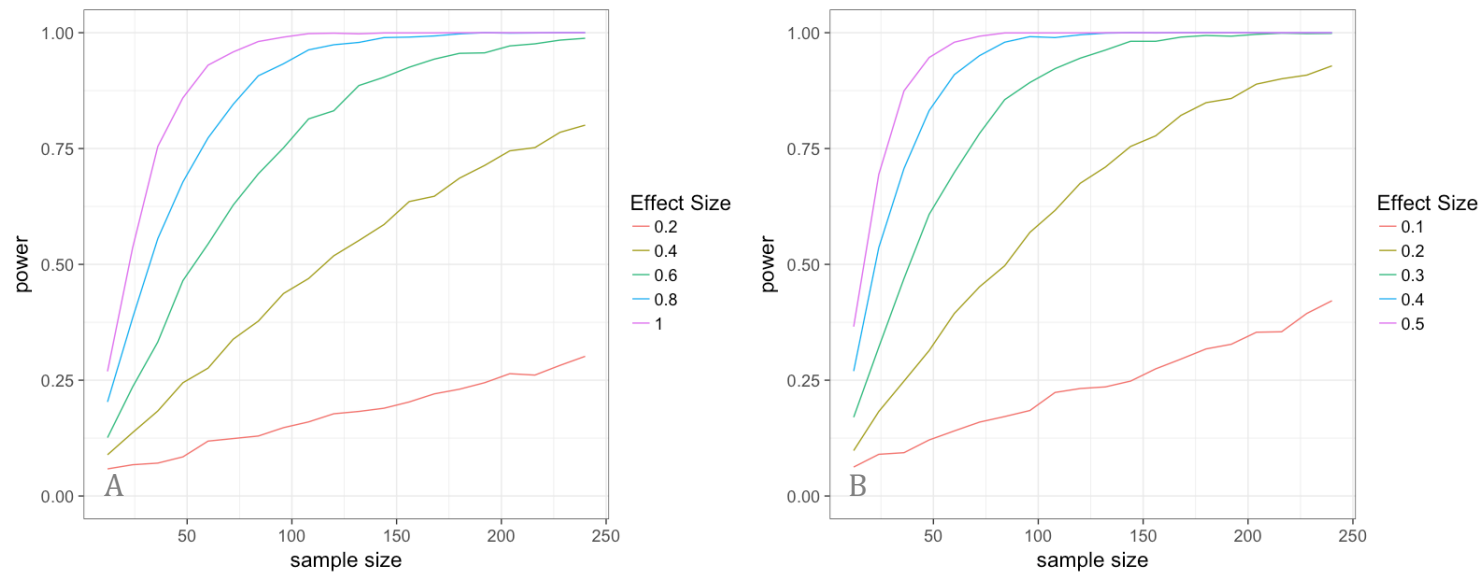


**Figure 4.** Pesticide Toxicity Index (PTI) plotted against Percent Toxic Effect for scenario A and B. Fish PTI data were plotted against *Pimephales promelas* / Survival test (left plots) and Cladoceran PTI were plotted against *Ceriodaphnia dubia* / Reproduction test (right plots). The trend line close to zero indicates there is no relationship between the two variables in any of the scenarios.

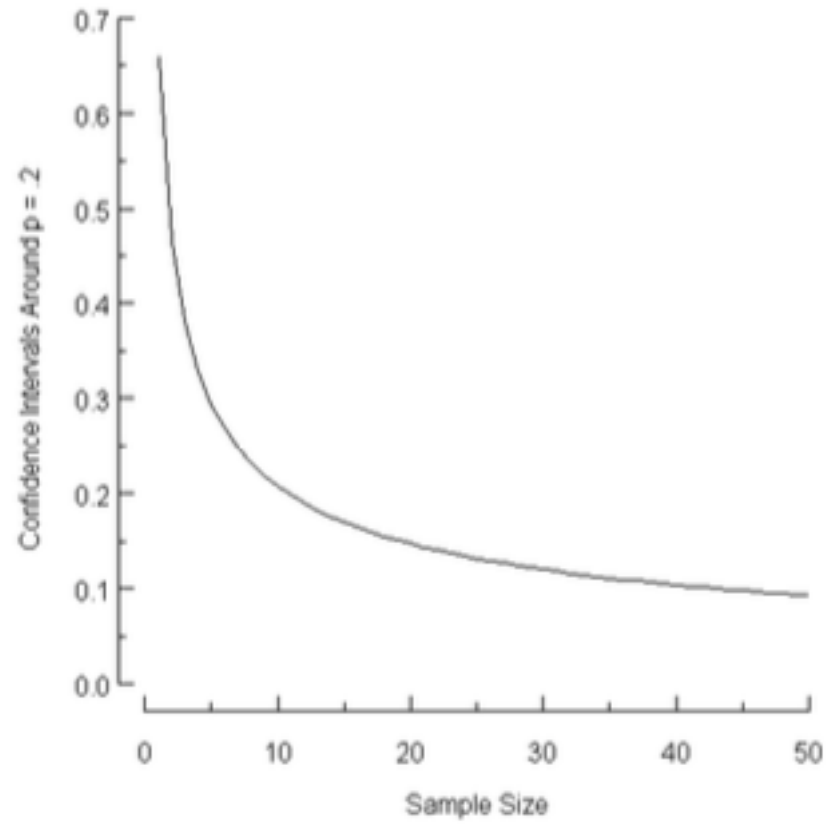




**Figure 5.** Power curve for scenarios A (left) and B (right) based on Cladoceran Sensitive PTI vs. *Ceriodaphnia* toxicity



**Figure 6.** Power curve for scenarios A (left) and B (right) based on Fish Sensitive PTI vs. *Pimephales* toxicity



**Figure 7.** Sample size and size of confidence interval for a binomial distribution ( $p = 0.2$ )

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**Table 1.** Mean, coefficient-of-variation, and result of ANOVA test on Pesticide Toxicity Index (Cladoceran-Sensitive)

<b>PTI - Cladoceran Sensitive</b>	<b>Mean +/- SD</b>	<b>Coefficient of Variation</b>	<b>Statistical Difference</b>
Mokelumne River at New Hope Road	20 +/- 5	26%	A
Sacramento River at Hood Monitoring	24 +/- 7	31%	A
San Joaquin R at Buckley Cove	29 +/- 12	40%	A
San Joaquin River at Airport Way near	18 +/- 13	69%	A
Ulatis Creek at Brown Road	47 +/- 22	46%	B

**Table 2.** Mean, coefficient-of-variation, and result of ANOVA test on Pesticide Toxicity Index (Fish-Sensitive)

<b>PTI - Fish Sensitive</b>	<b>Mean +/- SD</b>	<b>Coefficient of Variation</b>	<b>Statistical Difference</b>
Mokelumne River at New Hope Road	0.07 +/- 0.02	26%	A
Sacramento River at Hood Monitoring	0.09 +/- 0.03	31%	A
San Joaquin R at Buckley Cove	0.11 +/- 0.05	41%	A
San Joaquin River at Airport Way near	0.07 +/- 0.05	70%	A
Ulatis Creek at Brown Road	0.20 +/- 0.08	42%	B

**Table 3.** Variability estimates used for power analysis scenarios

<b>Variance Group</b>	<b>A</b>		<b>B</b>	
Station Composition	Hood, Buckley Cove, Mokelumne, Vernalis		Ulatis	
Predictor	Fish PTI	Cladoceran PTI	Fish PTI	Cladoceran PTI
N	96	96	24	24
Mean	0.09	23	0.20	47
SD	0.04	11	0.08	22
CV (%)	47%	46%	41%	46%