# Delta RMP Special Study Proposal

# Intercalibration Study for Chlorophyll Fluorescence Sensors in the Bay-Delta, Phase II

Summary:
Chlorophyll is an important water quality parameter for assessing the effects of nutrients and for fisheries management in the Bay-Delta. This study is the second phase of a multi-year effort to improve the accuracy, precision, and comparability of chlorophyll data collected in the Bay-Delta. Phase I planning has shown that variability in the methods used for measurement chlorophyll across the Bay-Delta is significant and that reducing this variance is of interest to a wide variety of monitoring agencies. In FY18/19, we propose to tackle a portion of the problem with a series of tasks to help understand and reduce the variance in the measurements of chlorophyll by in-situ sensors and laboratory methods. The proposed tasks include: (1) assessing methods used by different monitoring programs; (2) performing field intercalibration exercises between programs; (3) organizing a laboratory intercalibration study; and (4) preparing a summary report through technical workgroup discussion. Funding is requested for SFEI-ASC and USGS to lead the study. The study leverages $105,000 of in-kind support from the Department of Water Resources and the US Bureau of Reclamation.

Estimated Cost: $84,800

Oversight Group: Delta RMP Nutrients Technical Subcommittee

Proposed by: SFEI-ASC, USGS, DWR, and USBR

## Background

Accurate, precise measurements of phytoplankton biomass are critical to inform important management questions about productivity, nutrient management, and fisheries. Chlorophyll concentration is a widely-accepted proxy for phytoplankton biomass. There are presently more than 50 moored chlorophyll sensors using in-situ fluorescence in the Bay-Delta, belonging to networks maintained by the U.S. Geological Survey (USGS), Department of Water Resources (DWR), and others (Figures 1, 2, and 3). Prior to now there has been no effort to ensure that the groups making these measurements are using calibrations, sampling methods, and data processing techniques that ensure comparable results. Ensuring data comparability will save money and time, and will provide managers with better, high-resolution data for the entire estuary.

Therefore, to increase the utility and improve our return on the considerable effort to produce these data, the Delta Regional Monitoring Program and the San Francisco Bay Nutrient Management Strategy Science Program are jointly funding a project with the

goal of improving the comparability of the chlorophyll data collected by different programs across the region. While a seemingly simple task, achieving this goal requires overcoming several technical barriers to apply common approaches for sensor acceptance and performance criteria, sensor calibration, performance validation, data collection, data quality assurance, data management, and data access.

In FY17/18, the Delta RMP and the Nutrient Management Strategy each contributed $15,000 for SFEI-ASC to organize the stakeholders, conduct some initial analyses, and to develop a detailed workplan for FY18/19.

The stakeholder outreach process revealed a broad interest from many agencies in:

- Standardizing, improving processes
- Having data from different programs be interoperable
- Improving relationship between in-situ and lab chlorophyll-a
- Coordination
- Improving data accessibility

The survey of 13 monitoring programs found that a variety of methods are being used by the different programs especially in the areas of sensor settings, calibration procedures, sensor cleaning, and QA/post-processing. The method differences were significant enough to make comparing data from different programs difficult. For example, some of the programs conduct 2-point calibrations, others perform a single point test at zero, and others do no calibration check. The laboratories performing extracted chlorophyll-a analyses use two fundamentally different methods (spectrophotometry and fluorometry).

Finally, analysis of measurements from the different programs data showed a large amount of variability in chlorophyll fluorescence response (differences as much as a factor of two) between regions of the Bay-Delta and between programs (Figure 4). Variability of this magnitude impedes synthesis of data from across the Bay-Delta without using site-specific calibrations.

Overall, the effort in FY17/18 has shown that variability in the methods used for measurement chlorophyll across the Bay-Delta is significant and that reducing this variance is of interest to a wide variety of monitoring agencies. A conceptual model for variability in the chlorophyll fluorescence (Figure 5) provides a way to break this challenging problem into smaller tasks. In FY18/19, we propose to tackle a portion of the problem with a series of tasks to help understand and reduce the variance in the measurements of chlorophyll by in-situ sensors and laboratory methods.

This proposal was developed and reviewed by a workgroup with representatives from SFEI-ASC, USGS, DWR, US Bureau of Reclamation (USBR), and the Central Valley Regional Water Quality Control Board.

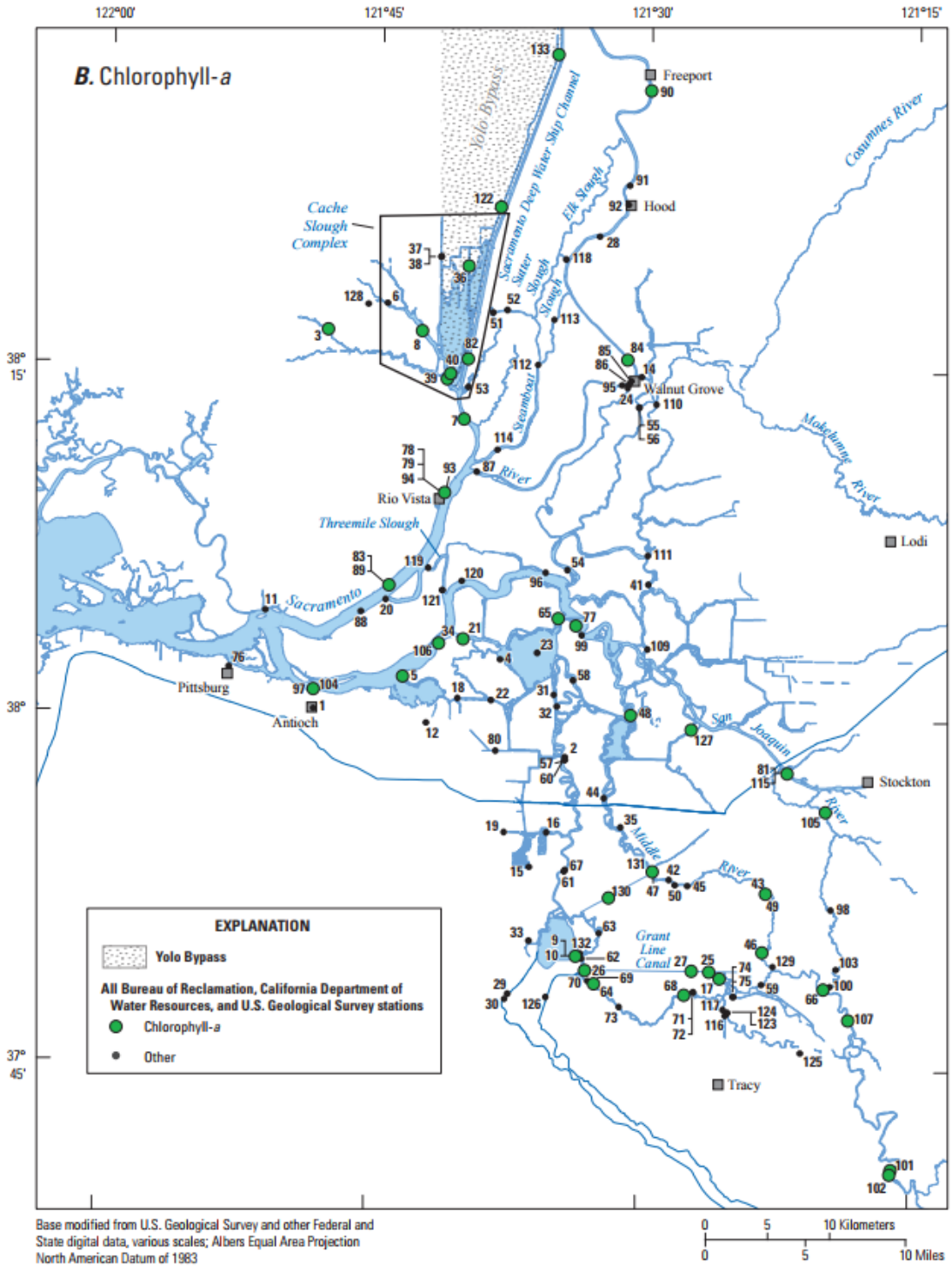


Figure 1: Chlorophyll fluorescence sensors in the Delta (from Bergamaschi et al., 2017)

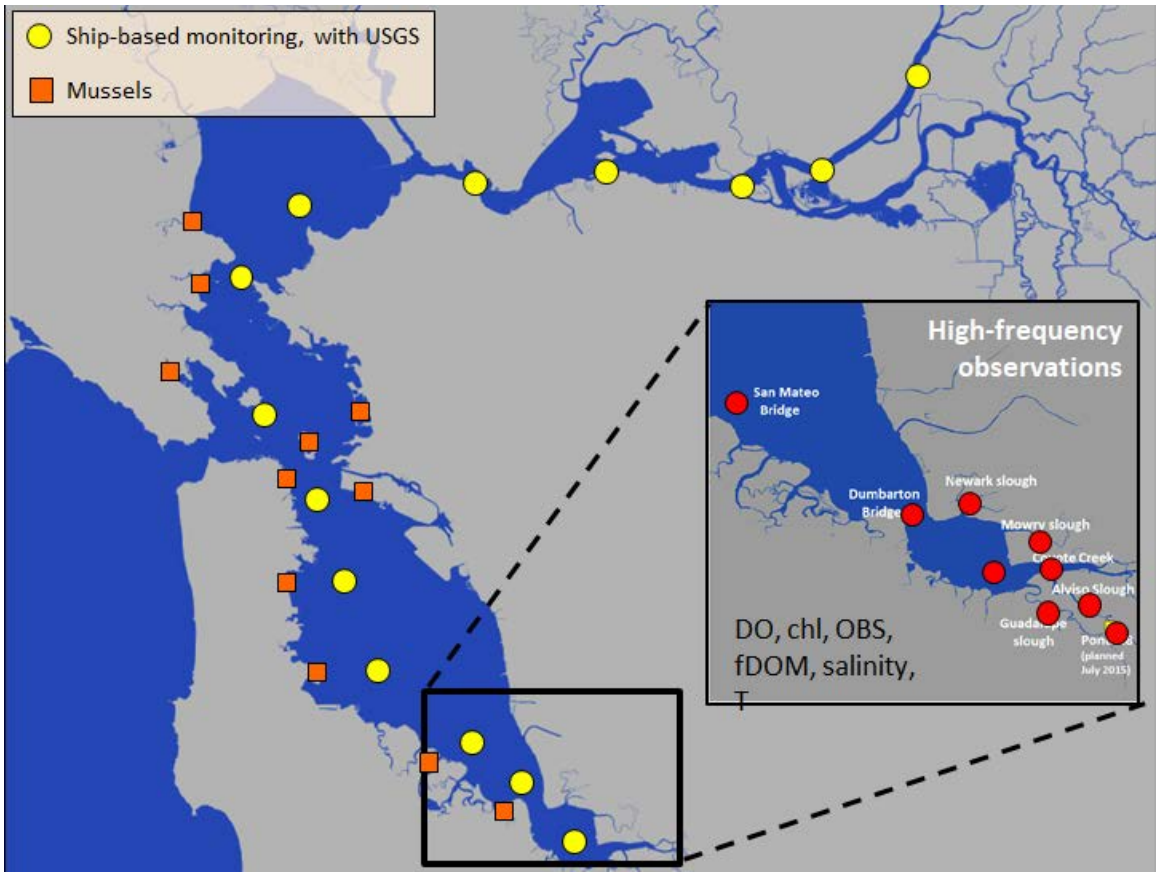


Figure 2: Chlorophyll fluorescence monitoring stations in the Bay. Continuous monitoring with moored sensors is performed at the red stations. Discrete measurements with sensors are made at ship-based monitoring sites (yellow) and mussel sites (orange). The graphic does not show all stations where chlorophyll fluorescence is monitored in the Delta, the Bay, and the coastal ocean.

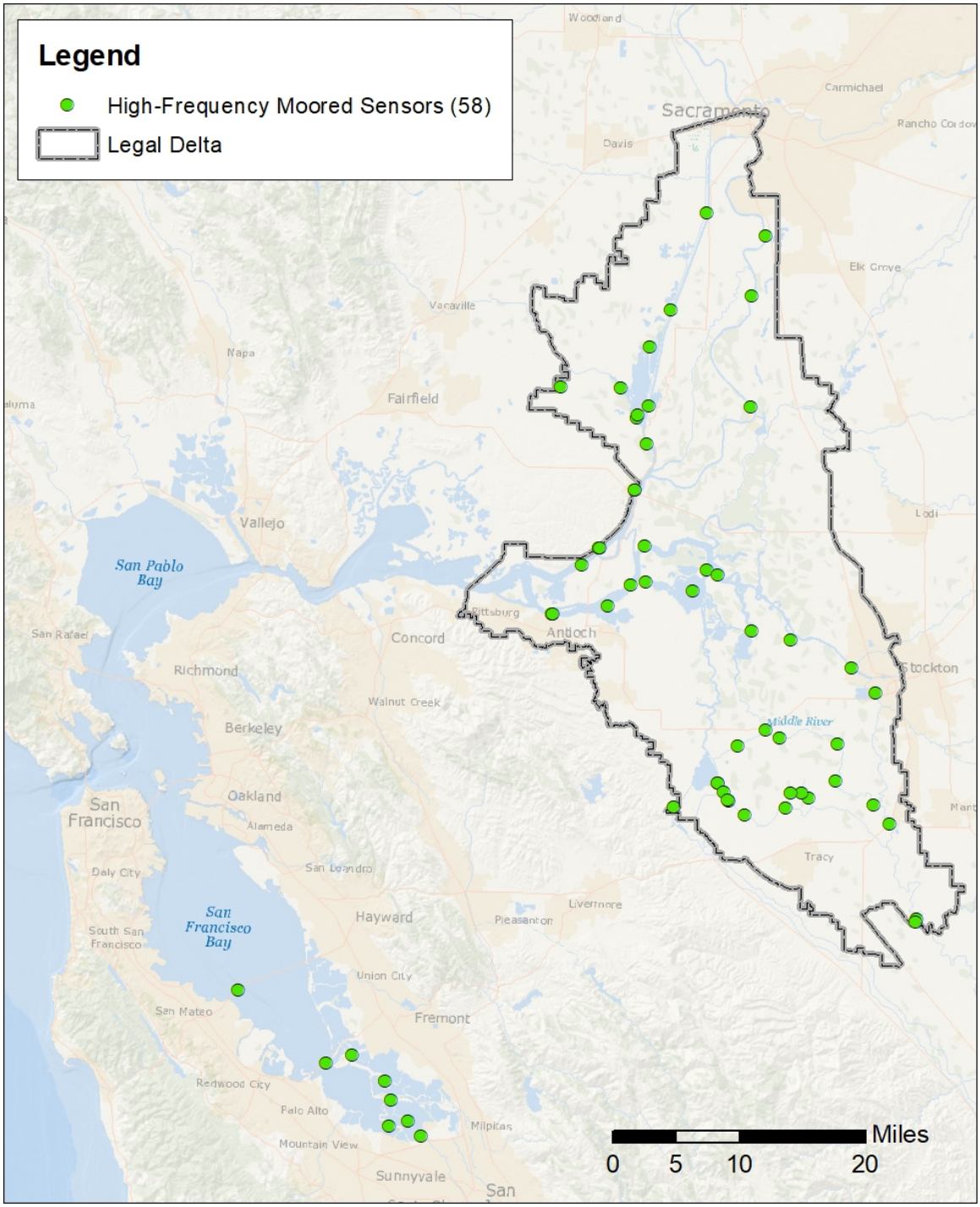


Figure 3: Stations with high-frequency moored sensors for chlorophyll that are managed by organizations that have agreed to participate in this study. Additional organizations will be invited to join the study.

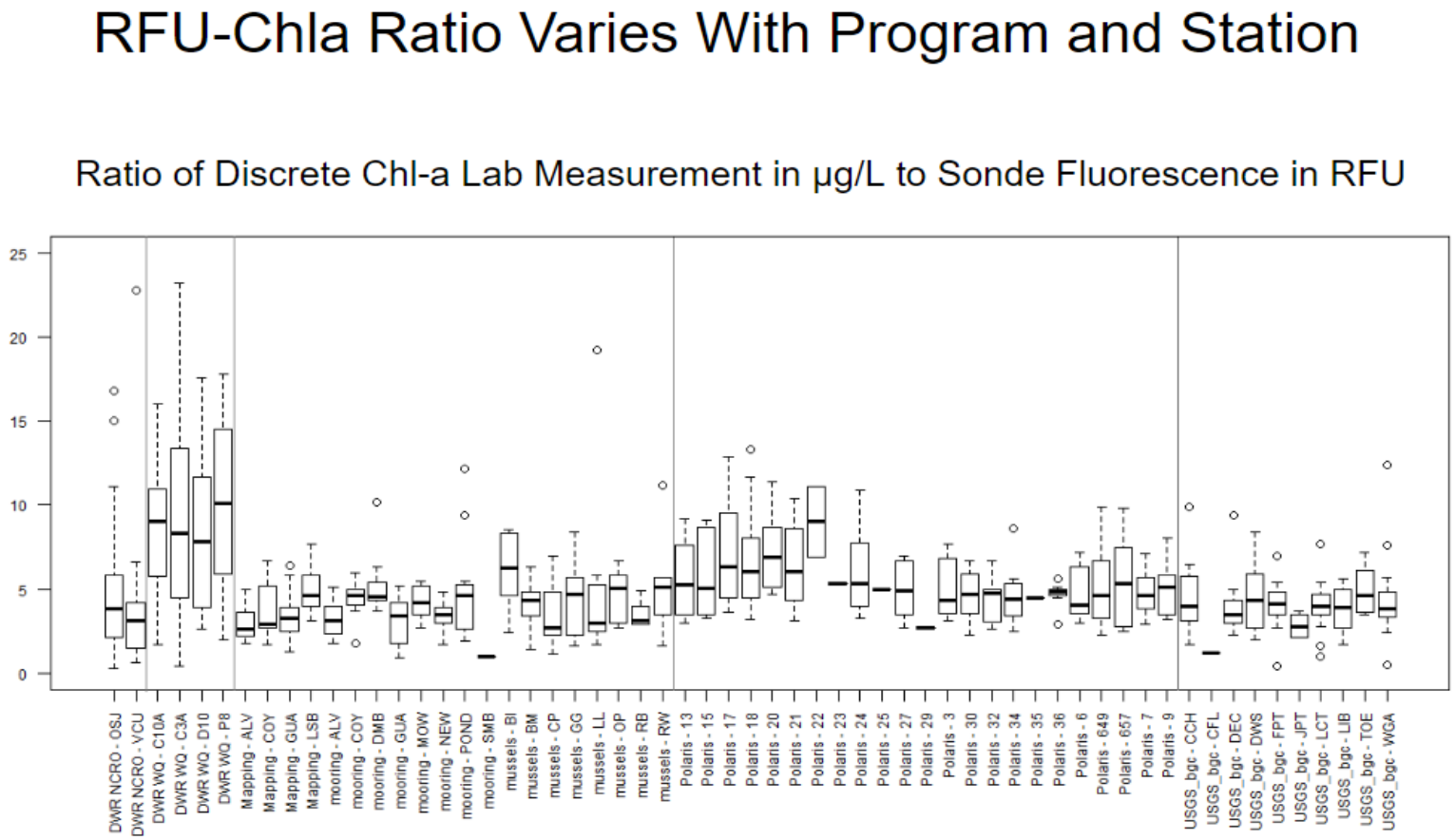


Figure 4: Ratio of sonde relative fluorescence units (RFU) from YSI EXO sondes to extracted chlorophyll measured in the laboratory across multiple programs and multiple locations in the Bay-Delta. The variance shown on this figure is from a combination of factors (see Figure 4). Natural variability among sites is evident when comparing different sites monitored by the same program. There can be natural differences between stations due to differences in salinity, tidal influence, and phytoplankton community. However, this graphic illustrates that some of the variance observed could be due to different protocols used by different programs.

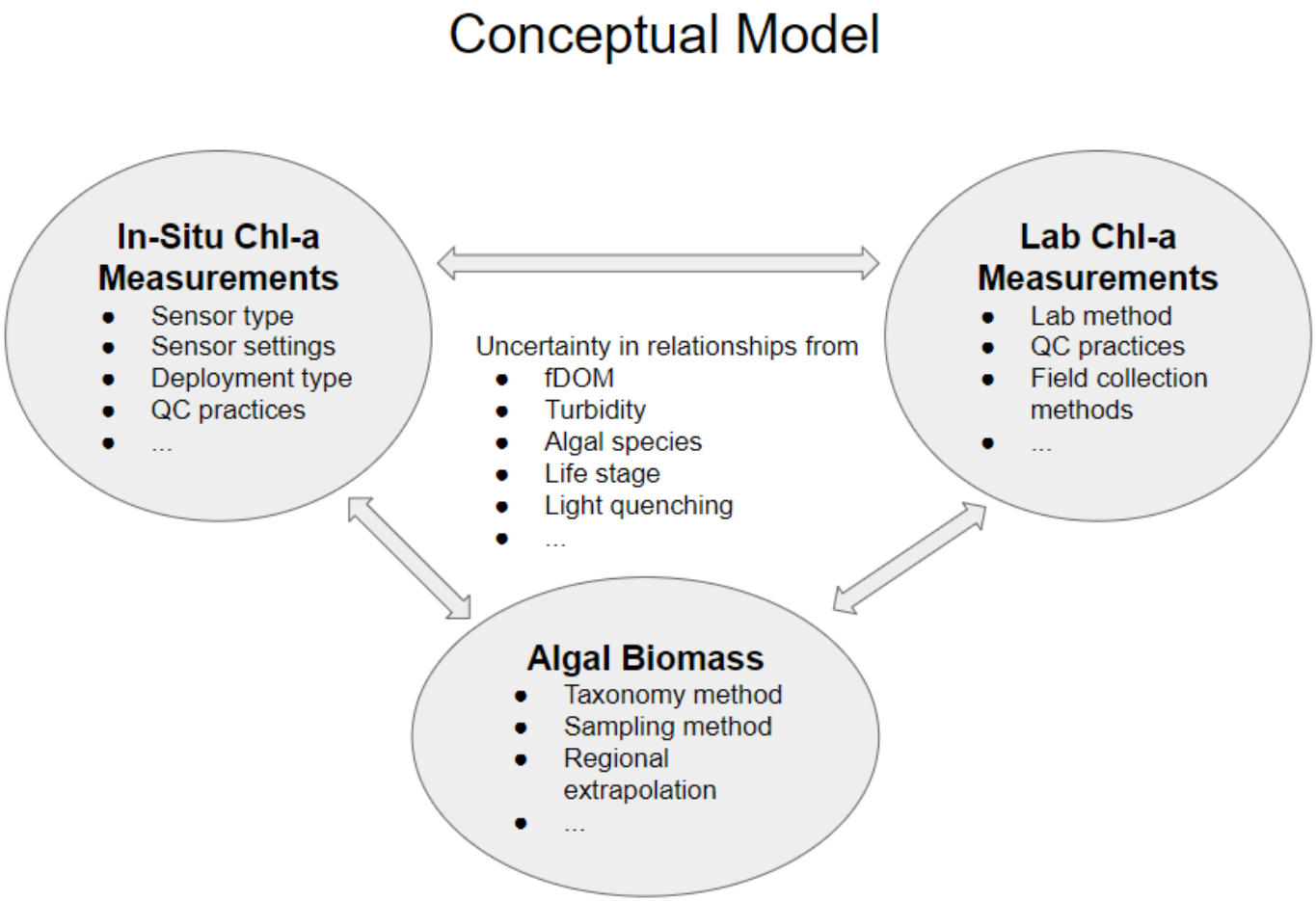


Figure 5: Conceptual model developed in FY17/18 for variance in extracted chlorophyll-a, in-situ chlorophyll fluorescence, algal biomass, and the relationships between these related parameters.

## Study Objectives and Applicable RMP Management Questions

The objectives of the project and how the information will be used relative to the Delta RMP's management and assessment questions are shown in Table 1.

**Table 1.** Study objectives and questions relevant to Delta RMP management questions

| Delta RMP Management Questions & Assessment Questions | Study Objectives | Example Information Application |
|---|---|---|
| Management Question:<br>Is there a problem or are there signs of a problem? | Assess the differences in methods used by each program to measure chlorophyll. | Water quality and resource managers will know the comparability of chlorophyll-a data from the major monitoring programs in the Bay-Delta. |
| Assessment Question:<br>How do concentrations of nutrients (and nutrient-associated parameters) vary spatially and temporally? (S&T1)<br><br>This study is relevant to these questions because it will improve our ability to discern spatial and temporal trends in chlorophyll using data from multiple programs operating in the Bay-Delta. | Determine whether differences in methods between programs result in significant variability in sensor and lab results for chlorophyll. | Data collection agencies will know which methods are important to address to improve the accuracy and precision of sensor and lab chlorophyll-a data in the Bay-Delta. |

## Approach

**Task 1: Assessment methods used to measure in-situ chlorophyll fluorescence by different monitoring programs in the Bay-Delta**

A small group of experts from the major programs (USGS, DWR, USBR, and SFEI-ASC) will summarize current practices for chlorophyll fluorescence measurements. At a minimum, the assessment will cover the following topic areas:

- Types of sensors and sonde equipment used
- Sensor settings
- Calibration
- Deployment and retrieval protocols
- Sensor servicing and cleaning
- Quality assurance
- Post-processing and data correction
- Reporting

The assessment will only cover current methods in use by programs; it will not survey past methods. Understanding the comparability of past methods to current methods is a priority for some agencies (e.g., DWR that has been monitoring since the 1980s) but it is beyond the scope of this effort.

A brief literature review will be conducted to ensure that this regional effort is informed by national and other relevant guidance. This review will not be exhaustive. It will focus on reports such as recent guidance/protocols for chlorophyll fluorescence sensors, previous intercalibration exercises with chlorophyll fluorescence sensors, and key foundational literature.

The deliverable for this task will be a short report on the results of the assessment, highlighting differences in methods for in-situ chlorophyll fluorescence between the major monitoring programs in the Bay-Delta, and the literature review. The report will become part of the final report for the overall project to be completed by the workgroup (Task 5)

For a schedule, the first step of this task will be prioritized to occur in July 2018. DWR has plans to deploy multiple new chlorophyll fluorescence sensors in the summer of 2018. Having initial information from the first step of this task will be helpful for setting up these sensors to be compatible with other major programs. The rest of the task will be completed during the first six months of the project.

**Task 2: Coordinate intercalibration exercises that can be used to show the effects of different methods on sensor results**

USGS will organize a series of field tests to measure chlorophyll fluorescence using different equipment and methods. Participants in these field tests will include at a minimum USGS, SFEI-ASC, DWR and USBR. The deliverable for this task will be a presentation to the workgroup.

Proposed Field Tests

- Side-by-side deployments by all programs that want to participate. Deployments would be in two locations that span a range of chlorophyll fluorescence and fDOM conditions (Mossdale and Montezuma Slough tentatively). Deployments would be during the summer and fall bloom period in 2018. A minimum of 4-6 weeks of side-by-side data will be collected. All sondes would be installed at the same depth in a common location and, at a minimum, will collect data on water temperature, specific conductance, dissolved oxygen, pH, turbidity, and chlorophyll fluorescence (and BGA and fDOM, if possible). The sondes will be serviced at whatever frequency each program normally uses. At the conclusion of the first side-by-side deployment, the organizers will decide if additional side-by-side deployments or a reproducibility study (described below) should be performed next.

Other Possible Field Studies

- Reproducibility study. This type of study tests for how much variance is due to operator, sonde type, or program protocols. Each program will send up to three technicians with their own calibrated sondes out on a boat together (USGS vessel). The boat will stop at a variety of sites. At each site, each technician will measure chlorophyll fluorescence (averaged over a duration of 10 minutes to reduce noise). Statistical analysis will be used to estimate the 95% confidence intervals (error bars) within and between technicians and programs.

**Task 3: Intercalibration study for laboratory chlorophyll-a measurements**

Laboratory measurements of extracted chlorophyll-a are used to calibrate and validate in-situ chlorophyll fluorescence measurements. Therefore, any effort to improve comparability in chlorophyll data needs to address variance in both in-situ and laboratory measurements. The proposed intercalibration study would show whether the laboratories in the region report similar results when given a split sample of the same water. Significant differences in the results between labs would trigger troubleshooting by chemists to find and fix the source of the variance.

A. <u>Inventory of the methods used by the major laboratories measuring chlorophyll-a in the Bay-Delta and secure their participation.</u>
    a. The known laboratories for major programs are DWR's Bryte Lab, USGS National Lab, SFSU Romberg Tiburon Center, and UC Davis. All laboratories will be allowed to be anonymous for the purposes of the study.
    b. A standardized survey instrument will be used to capture information on the field and analytical methods used and quality assurance procedures.

B. <u>Implement a "pre-coordination" round of analysis by participating laboratories</u>.
    a. For intercalibration study, the field samples will be collected by USGS during an opportunistic cruise.
    b. Samples will be collected during the summer growth period (July-Oct) at stations where chlorophyll-a concentrations are expected to exceed 5 ug/L.

c. A total three sampling rounds will be conducted. For each sampling round, one large sample will be collected by peristaltic pump from 1 meter below the surface. This large sample will be delivered to DWR to be split between the participating laboratories using a churn splitter. Each laboratory will receive triplicates of the sample in whatever format they usually require (e.g., a filter, a whole water sample, or something else). Each participating laboratory will receive three replicates of each sample.
d. For quality assurance, laboratories will also receive samples spiked with known concentrations of an algal culture. This process of "standard addition" will provide information on the accuracy of the methods used.

C. Analyze and report the results of the "pre-coordination" sampling round.
   a. Results of the study will be evaluated by comparing the mean and range of the triplicate samples from each laboratory. For a statistical evaluation of all the data across the three sampling days, the overall mean of all chlorophyll-a measurements from the same day will be subtracted from each individual result from the same day as a measure of deviation from the expected result. One-Way ANOVA will be used to determine whether there are any laboratories with statistically significant differences in the deviations.
   b. Quality Assurance. The measurement quality objectives for chlorophyll-a results by a single lab is presumed to be +/-30%. The goal of the study is to have the between-laboratory variance in this same range. A power analysis indicates that a sample size of 8 for each laboratory is needed to detect 50% differences between laboratories (e.g., for lab means of 10, 10, 10, and 5 ug/L with assumed error of 3 ug/L). Therefore, collecting 3 rounds of triplicate samples (9 samples total for each lab) will have sufficient sample size to detect between laboratory differences of management interest.

D. Organize coordination meeting with laboratories. Hold a meeting with representatives from the participating laboratories to discuss the results and coordinate regarding methods.

E. Prepare final report. The final report will summarize the results of the test, lessons learned, and recommendations.

**Task 4: Convene a workgroup to summarize findings and recommendations**

A workgroup of key practitioners will meet quarterly in FY18/19 to review the findings from the field and laboratory intercalibration studies. The workgroup meetings in FY17/18 have been highly productive and valued by the participants as a forum to learn from each other and to discuss important issues. The workgroup will review outcomes from the Tasks 1-3 and be responsible for developing a short report with conclusions and recommendations for next steps. Participants in the workgroup will include USGS-WSC, DWR, USBR, and SFEI/ASC at a minimum. At least one person who also sits on the Delta RMP Nutrients Subcommittee will be part of the workgroup. Participation will be open to any other interested parties.

The deliverable for this task will be a summary report with recommendations for next steps taking into account results from Tasks 1-4. The report will be submitted to the Delta RMP committees but is expected to be shared widely among Bay-Delta monitoring program once it is published.

## Proposed Deliverables and Timeline

**Table 2.** Deliverables

| **Deliverable** | **Due Date** |
|---|---|
| Task 1: Assessment of in-situ chlorophyll methods in use | Dec. 31, 2018 (final) |
| Task 2: Presentation to workgroup on field intercalibration exercises | Dec. 31, 2018 |
| Task 3: Report on laboratory intercalibration study | March. 31, 2019 |
| Task 4: Summary report with recommendations for next steps | April 30, 2019 (draft)<br>June 30, 2019 (final) |

**Table 3**. Timeline

| | 2018 | | | | | | 2019 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Task | J | A | S | O | N | D | J | F | M | A | M | J |
| Task 1 - Assessment of Methods | | | | | | X | | | | | | |
| Task 2 - Field IC Exercises | | | | | | X | | | | | | |
| Task 3 - Lab IC study | | | | | | | | | X | | | |
| Task 4 - Workgroup Meetings | | | X | | | X | | | X | | | X |
| Task 4 - Summary Report | | | | | | | | | | X | | X |

X = Deliverable due
= Activity

## Budget

Table 4 shows the estimated costs for this proposed special study.

**Table 4.** Proposed Budget

| Task | Funding Requested for USGS | Funding Requested for SFEI-ASC | Total Funding Requested | In-Kind Contributions (details in justification) |
|---|---|---|---|---|
| Task 1 - Assessment of Methods | $5,000 | $0 | $5,000 | DWR, USBR |
| Task 2 - Field IC Exercises | $6,750 | $5,250 | $12,000 | DWR, USBR |
| Task 3 - Lab IC Study | $4,300 | $13,500 | $17,800 | DWR, USBR |
| Task 4 - Workgroup Meetings | $10,000 | $20,000 | $30,000 | DWR, USBR |
| Task 4 – Summary Report | $10,000 | $10,000 | $20,000 | DWR, USBR |
| **Total Funding Requested** | **$36,050** | **$48,750** | **$84,800** | |
| **Leveraged In-Kind Contributions** | | | | **$104,927** |

Budget Justification

*Project Costs*

Task 1

- USGS will manage this task and prepare a summary report. The cost for this effort is $5,000 (60 hours, mostly project manager time).

Task 2

- USGS will manage the field data collection for this task. The cost for this effort is: $5,750 (56 hours, mostly technician time) + $1,000 for boat, vehicle, and fuel expenses.
- SFEI-ASC will analyze the data from the field exercises and prepare a presentation with the results. The cost for this effort is $5,250 (48 hours of effort, mostly technician time).

Task 3

- SFEI-ASC will coordinate the laboratory intercalibration study and prepare a short summary report with the results. The cost for this effort is $10,000 (70 hours of effort, mostly technician time).
- Up to $3,500 of direct costs are budgeted for sample shipping, supplies, and lab fees. If laboratories agree to participate for free, costs will be reduced.

- USGS will collect the field samples for the field study and be responsible for shipments to the laboratories. The cost for their participation is $3,300 (40 hours mostly project manager time) +$1,000 for boat, vehicle, and fuel expenses.

Task 4

- SFEI-ASC will organize and facilitate 4 quarterly meetings of the workgroup. Assuming 20 hours to prepare and run each meeting (80 hours) plus 40 hours for project management for a total cost of $20,000.
- SFEI-ASC will also contribute to, edit, and ensure completion of the final report (40 hours) for a total cost of $10,000.
- USGS will participate in 4 quarterly meetings and be the lead author in the final report. Total funding required for these tasks is $20,000 (combination of senior scientist and project manager time). This total cost has been split as $10,000 for the workgroup meetings and $10,000 for the report.

*Leveraged Funds and In-Kind Contributions*

Leveraged funds are cash contributions from another source that pay for a part of the scope of work. In-kind contributions are staff time or resources (e.g., boat time, lab analyses) that are contributed to the project to complete the scope of work.

- The DWR Office of Water Quality and Estuarine Ecology has authorized 6 staff to participate in the study, which is an in-kind contribution of $33,939.
- The DWR North Central Regional Office has authorized 2 staff to participate in the study, which is an in-kind contribution of $19,400.
- The DWR Bryte Lab will analyze 9 water samples for Task 4. Each analysis has a value of $150/sample. Therefore, this service is an in-kind contribution of $1,350.
- The USBR Bay Delta Office has authorized 2 staff to participate in this study and purchase of needed equipment/supplies. This is an in-kind contribution of $20,238.

USGS is also funding a laboratory study on “Developing corrections for observed biases on in situ chlorophyll fluorometers used in real time monitoring”. This study is directly related to the objectives of this study. Therefore, its value of $30,000 is also considered leveraged funds.

In FY17/18, the Nutrient Management Strategy for San Francisco Bay contributed $15,000 to Phase I of this effort. This program will likely be willing to contribute a similar amount in FY18/19 but the amount and the type of tasks it will choose to fund are not yet known. The Steering Committee will decide on budgets for FY18/19 in June.

## Reporting

The final deliverable from this project will be a technical report to the Delta RMP with the results from FY18/19 tasks and recommendations for future work. The lead author for

the study will be USGS but the report will be *published* by SFEI-ASC. Representatives from other participating organizations will be co-authors. The report will be prepared in the form of a manuscript to facilitate publication of some or all of the findings in the peer-reviewed literature.

## Optional Tasks for Future Funding

Achieving the high level goals of this study is expected to take several years. Accordingly, the proposed tasks for FY18/19 do not cover the full range of effort that is needed. The FY18/19 tasks will be useful to understand the scope of the problem, not necessarily to diagnose its causes. The project team anticipates the following tasks will be needed in FY19/20 plus recommendations that come out of the FY18/19 tasks. Furthermore, maintaining consistency and compatibility of water quality monitoring methods in the Delta must be an ongoing effort if it is to succeed. We envision an annual "Bay-Delta Monitoring Training Academy" where technicians can maintain proficiency in standard methods and share innovations.

Extension of Task 2: Coordinate intercalibration exercises that can be used to show the effects of different methods on sensor results

- Share equipment between programs, e.g., exchange of sensors and calibration check standards.
- Embed field crews from different programs to help identify where field methods differ and to share knowledge.
- Purchase 3 probes (sequential serial numbers) for all programs to check for variance in identical sensors and to remove variance from sensors of different ages.

Extension of Task 3: Intercalibration study for laboratory chlorophyll-a measurements

- Implement a "post-coordination" round of analysis by participating laboratories. The approach for this study would be the same as for the "pre-coordination" round. The samples will be collected in April and May 2019. The purpose of the post-coordination sampling round is to show improved correspondence between laboratories after coordination.

Analyze existing data to understand the magnitude of factors affecting chlorophyll fluorescence measurements

- For this task, existing data will be analyzed to understand the magnitude of the impact of other factors on chlorophyll fluorescence measurements. The effects that will be investigated are deployment depth, non-photochemical quenching, fDOM, and turbidity. The deliverable for this task will be a presentation to the workgroup.
- To understand if there is a large offset in chlorophyll fluorescence depending on the depth of the sensor, analyze profile data at sonde locations collected by USBR in the Deep Water Ship Channel (5 years of data). This dataset spans the range of vertical mixing conditions that are likely to be encountered in the Delta. The question to be addressed is: Do measurements of chlorophyll fluorescence at the surface or at the bottom need to be adjusted to be representative of the