

# Interpretive Report on Delta RMP Mercury Monitoring: 2016 – 2022

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## **EXECUTIVE SUMMARY**

Concentrations of methylmercury (MeHg) in fish from the Sacramento–San Joaquin Delta (the Delta) exceed thresholds for protection of human and wildlife health. From 2016-2022 the Delta Regional Monitoring Program (Delta RMP) designed and implemented a program of mercury monitoring with the goals of answering priority management questions and supporting management of MeHg under the Methylmercury TMDL for the Delta. The design was cost-effective and succeeded in meeting these goals by generating a high-quality dataset on mercury in fish and water, along with a suite of ancillary parameters. The results of the monitoring significantly solidified and advanced understanding of mercury impairment in the Delta.

The mercury monitoring was conducted to address this core management question and related subquestions:

- Is there a problem or are there signs of a problem?
  - a) Is water quality currently, or trending towards, adversely affecting beneficial uses of the Delta?
  - b) Which constituents may be impairing beneficial uses in subregions of the Delta?
  - c) Are trends similar or different across different subregions of the Delta?

A particular emphasis was placed on question c, which was addressed through a program of annual sampling at stations within most of the Delta subareas defined by the Methylmercury TMDL. Another point of emphasis was establishing regional and sub-regional baselines to track the potential influence of large-scale habitat restoration projects.

The most notable conclusions drawn from the Delta RMP mercury monitoring and the overall long-term dataset are as follows.

- Length-adjusted mercury concentrations in black bass are an excellent performance measure of progress in addressing MeHg impairment in the Delta. Concentrations in black bass are the ultimate indicator of impairment identified in the TMDL. The black bass element of the Delta RMP mercury monitoring was the most consistent, robust, and spatially extensive effort over the seven years of monitoring, in part because this monitoring is cost-effective.
- Unfiltered aqueous MeHg is another important performance measure of progress in addressing MeHg impairment in the Delta. These data are important for managing MeHg inputs, and are a key part of the TMDL with their own implementation goal. Water monitoring, however, is less integrative and more variable, and relatively expensive because it requires multiple cruises per year to obtain a representative assessment. A minimal, but still informative, water design was implemented at the beginning and end of the Delta RMP effort, with a two-year intensive phase in 2018 and 2019 that provided valuable data for the TMDL. Filtered MeHg, filtered and unfiltered total mercury, and other ancillary parameters

- were also measured and the data were summarized in the interpretive report on the first three years of DRMP mercury monitoring (Davis et al. 2021).
- Mean concentrations of mercury in bass and unfiltered aqueous mercury in water at almost all stations monitored (and therefore in each subarea) exceeded the water quality objective for fish tissue and the TMDL implementation goal for aqueous MeHg. Mean concentrations in bass were extremely high in the Mokelumne River subarea (1.25 ppm), over 5 times the bass tissue water quality objective for the Delta (0.24 ppm) and comparable to the 98<sup>th</sup> percentile of an extensive dataset for length-adjusted black bass in California. The lowest mean concentration for bass was 0.29 parts per million (ppm) at Middle River, with a 95% confidence interval that overlapped the 0.24 ppm water quality objective. All of the other confidence intervals of the bass means exceeded 0.24 ppm. For water, one of the stations had a mean (0.058 ng/L) below the unfiltered aqueous implementation goal of 0.060 ng/L.
- The regional spatial patterns of mercury in black bass and water in the Delta that have been documented in previous studies and the TMDL continue to persist. Concentrations continued to be higher on the northern, eastern, and southern periphery of the Delta, and lower in the Central Delta and West Delta.
- The addition of bass monitoring stations near restoration projects in 2019 helped to establish better baseline information to track the impact of recent and future restoration projects. The addition of these stations also provided for spatial replication within subareas. The general consistency observed across the stations within subareas provided support for the subarea delineations established by the TMDL. The replication also provided further confirmation of the strong patterns of spatial and temporal variation observed in the Delta.
- Annual monitoring of bass and water was enlightening, and provided a much clearer understanding of temporal trends. The answer to the key assessment question that guided the monitoring is that trends over time are very different among Delta subareas.
- High interannual variation was observed in two subareas (Lower Mokelumne River and San Joaquin River). At both of these stations bass mercury concentrations increased from 0.5 ppm to the extremely high level of 1.5 ppm in a one-year period. Significant decreases in consecutive years were also observed. This information has important implications for monitoring and managing MeHg impairment in the Delta areas with higher concentrations may be a higher priority for management, and areas with higher variance require more intensive sampling to discern trends.
- Inter- and intra-annual variation was much lower at the other stations, without a suggestion of long-term trend. The two exceptions were the Sacramento River at Freeport station, which exhibited a significant decline in MeHg concentrations in both bass and water, and the Sherman Island station, which exhibited a significant increase in bass MeHg.
- A possible driver of the high interannual variation in the Mokelumne River and San Joaquin Rivers subareas, supported by prior work with prey fish by Slotton et al. (2007), is

interannual variation in streamflow and flooding of upstream wetlands and floodplains in the Mokelumne River and San Joaquin River watersheds. The timing of the Delta RMP mercury sampling effort was fortuitous for evaluating this hypothesis, as it coincided with extreme variation in water year indices. The responses to high flows in the two subareas were different. In the Mokelumne River subarea, bass mercury responded within a year to the increased flow and then concentrations remained high for two years after the flows were reduced. The San Joaquin River at Vernalis station had a one-year lag between the high-flow water year and the increase in bass mercury, and the elevated level of bass mercury did not persist for more than one year - the correlation between water year index and bass mercury (with a one-year lag) was significant. Sustained annual monitoring, along with better information on hydrology and restoration activity, in these areas would be critical to understanding the causes of the extreme variation.

Based on the findings from this seven-year dataset, the following recommendations are presented.

- With the progress that has been made and the evolution of the regulatory process (i.e., the revised TMDL), a reevaluation of the Delta RMP's mercury management and assessment questions and their relative priority is in order. The assessment question framework that was established before the mercury monitoring began indicated that the status and trends questions for MeHg in fish and MeHg in water were to be *initial* priorities.
- Sustained annual monitoring of bass mercury would be the most effective and economical way to continue to determine long-term trends, to track interannual variation and develop an understanding of its drivers, and to assess the influence of the major habitat restoration projects that are being implemented in the Delta. One caveat is that fish collection via electroshocking is restricted in areas that provide habitat for Delta smelt (e.g., the Yolo Bypass South and West Delta subareas), which makes bass collection impractical.
- A better understanding of the details of hydrology and inundation of floodplains and wetlands, including the effects of intentional and unintentional levee breaches, would be a fundamental component of a conceptual model to explain mercury bioaccumulation in the Mokelumne River, San Joaquin River, and Yolo Bypass South subareas.
- The seven-year dataset for black bass can be used to conduct power analysis and design cost-effective longer-term monitoring.
- Ambient water monitoring is valuable given that water monitoring is required for permitted sources. Water monitoring would also be valuable if the Delta RMP prioritizes management questions regarding loading (including control measure effectiveness) or MeHg mass balance. Water data can also support models for forecasting, or mechanistic studies of sources and loadings. Due to seasonal and interannual variability in aqueous MeHg, a robust design for water monitoring, such as the design implemented in 2018 and

2019, would be needed to meaningfully track long-term trends in aqueous MeHg concentrations.

## INTRODUCTION

#### **BACKGROUND**

In 1990, the Central Valley Regional Water Quality Control Board (Water Board) identified the Sacramento–San Joaquin Delta (the Delta) (Figure 1) as impaired by mercury. Concentrations of methylmercury (MeHg) in fish from the Delta exceed thresholds for protection of human and wildlife fish consumers established by the Delta Methylmercury TMDL (Central Valley Water Board 2010). The TMDL, approved by USEPA and effective in 2011, established a phased Delta Mercury Control Program (Control Program) designed to achieve the MeHg goals, objectives, and allocations. The Control Program, in part, directs various discharger groups to conduct monitoring and evaluate management practices to control MeHg. The TMDL recognized the value of regional monitoring and allowed dischargers to comply with their receiving water monitoring requirements by participating in a regional monitoring program.

The Delta Regional Monitoring Program (Delta RMP) Steering Committee identified mercury as one of four initial priorities for the program. In August 2016, consistent with the FY 16/17 Delta RMP Detailed Workplan and Budget, the Delta RMP began monitoring MeHg and related conditions. The goal of this monitoring was to begin to characterize ambient concentrations of total mercury and MeHg in fish and water, particularly in subareas likely to be affected by major existing or new sources (e.g., large-scale restoration projects). An important element of this work was also the co-location of fish and water sampling stations to better understand the uptake of MeHg into the food web. The monitoring was established to answer specific management and assessment questions as summarized below and in Table 1. In addition, as an ancillary benefit, the monitoring would also assist in providing information to support reevaluation of the TMDL.

## **DELTA RMP MANAGEMENT QUESTIONS**

The Delta RMP established management and assessment questions for the MeHg monitoring program (Table 1). Assessment questions regarding status and trends in concentrations of MeHg in sport fish and water were designated as the highest priority for initial monitoring. The assessment question regarding MeHg loads from tributaries to the Delta was identified as a high priority in 2017 when the Water Board decided that the reevaluation of the TMDL would begin in late 2019 and would need an updated MeHg mass budget. Other assessment questions established by the RMP have been addressed to some extent by the monitoring, but were not drivers of the monitoring design.

Figure 1. Map showing the boundary of the Delta, the eight subareas delineated in the TMDL, and the sampling stations for fish and water in Delta RMP mercury monitoring.

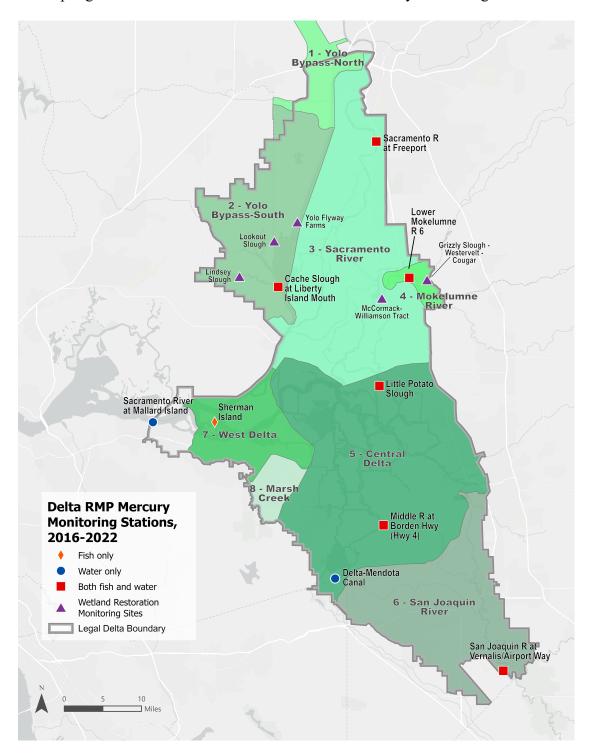


Table 1. Delta RMP mercury management and assessment questions addressed by each mercury monitoring element.

Questions highlighted in yellow were identified by the Steering Committee as the highest priority for initial studies.

Туре	Core Management Questions	Assessment Questions	Sub-Questions	Subregional Trends in Bass	Subregional Trends in Water	Restoration Monitoring
Status and Trends	Is there a problem or are there signs of a problem?  a. Is water quality currently, or trending towards, adversely affecting beneficial	ST1. What are the status and trends in ambient concentrations of total mercury and methylmercury	ST1A. Are trends over time in MeHg in sport fish similar or different among Delta subareas?	Х		
	uses of the Delta?  b. Which constituents may be impairing beneficial uses in subregions of the Delta?  c. Are trends similar or different across different subregions of the Delta?	(MeHg) in fish, water, and sediment, particularly in subareas likely to be affected by major sources or new sources (e.g., large-scale restoration projects)?	ST1B. Are trends over time in MeHg in water similar or different among Delta subareas?		х	
Sources, Pathways, Loadings, and Processes	Which sources and processes are most important to understand and quantify?  a. Which sources, pathways, loadings, and processes (e.g.,	SPLP1. Which sources, pathways, and processes contribute most to observed levels of MeHg in fish?	SPLP1A. What are the loads from tributaries to the Delta (measured at the point where tributaries cross the boundary of the legal Delta)?		х	
	transformations, bioaccumulation) contribute most to identified problems? b. What is the magnitude of each source and/or pathway (e.g., municipal wastewater, atmospheric deposition)? c. What are the magnitudes of internal sources (e.g., benthic flux) and sinks in the Delta?		SPLP1B. How do internal sources and processes influence MeHg levels in fish in the Delta?  SPLP1C. How do currently uncontrollable sources (e.g., atmospheric deposition, both as direct deposition to Delta surface waters and as a contribution to nonpoint runoff) influence MeHg levels in fish in the Delta?	X	X	X
Forecasting Scenarios	a. How do ambient water quality conditions respond to different management scenarios?     b. What constituent loads can the Delta assimilate without impairment of beneficial uses?     c. What is the likelihood that the Delta will be water quality-impaired in the future?	FS1. What will be the effects of in-progress and planned source controls, restoration projects, and water management changes on ambient methylmercury concentrations in fish in the Delta?		х	х	х
Effectiveness Tracking	a. Are water quality conditions improving as a result of management actions such that beneficial uses will be met?     b. Are loadings changing as a result of management actions?	[none]		х	х	х

The Delta RMP addressed the following management and assessment questions for MeHg in monitoring from 2016-2022.

- Status and Trends Is there a problem or are there signs of a problem? Specifically, are trends similar or different across different subregions of the Delta?
  - O ST1 What are the status and trends in ambient concentrations of total mercury and MeHg in fish, water, and sediment, particularly in subareas likely to be affected by major sources or new sources?
    - ST1A Are trends over time in MeHg in sport fish similar or different among Delta subareas?
    - ST1B Are trends over time in MeHg in water similar or different among Delta subareas?
- Sources, Pathways, Loadings, and Processes Which sources and processes are most important to understand and quantify?
  - SPLP1 Which sources, pathways, and processes contribute most to observed levels of MeHg in fish?
    - SPLP1A What are the loads from tributaries to the Delta (measured at the point where tributaries cross the boundary of the legal Delta)?
    - SPLP1B How do internal sources and processes influence MeHg levels in fish in the Delta?
- Forecasting Scenarios
  - FS1 What will be the effects of in-progress and planned source controls, restoration projects, and water management changes on ambient MeHg concentrations in fish in the Delta?
- Effectiveness Tracking
  - No specific assessment questions have been articulated for this topic.

The Delta RMP has monitored total mercury concentrations in black bass<sup>1</sup> as the most important performance measure of progress in addressing MeHg impairment in the Delta. Delta RMP bass monitoring has addressed all of the categories of mercury management questions articulated by the Delta RMP (Table 1). The Methylmercury TMDL provides important context

<sup>&</sup>lt;sup>1</sup> Total mercury in fish is measured as an index of MeHg. Nearly all of the mercury present in edible fish muscle is MeHg, and analysis of fish tissue for total mercury provides a valid, cost-effective estimate of MeHg concentration (Wiener et al. 2007). "Black bass" refers collectively to largemouth bass (*Micropterus salmoides*), smallmouth bass (*Micropterus dolomieu*), and spotted bass (*Micropterus punctulatus*).

for addressing the RMP management and assessment questions. The TMDL established three water quality objectives for MeHg in fish tissue:

- 0.24  $\mu$ g/g, or ppm, on a wet-weight basis in muscle of large, trophic level four (TL4) fish such as black bass;
- 0.08 ppm in muscle of large TL3 fish such as common carp (Cyprinus carpio); and
- 0.03 ppm in whole TL2 and TL3 fish less than 50 mm in length such as Mississippi silverside (*Menidia beryllina*).

Furthermore, the TMDL established a water quality objective of 0.24 ppm in largemouth bass muscle at a standard size of 350 mm as a means of ensuring that all of the fish tissue objectives are met. Black bass are widely distributed throughout the Delta and are excellent indicators of spatial variation due to their small home ranges. Past data from 1998–2007 for largemouth bass were a foundation for the development of the TMDL, including the division of the Delta into eight subareas (Figure 1).

The Delta RMP has also monitored MeHg concentrations in water as another important performance measure of progress in addressing MeHg impairment in the Delta. Delta RMP aqueous MeHg monitoring is addressing all of the categories of mercury management questions articulated by the Delta RMP (Table 1). The Methylmercury TMDL provides important context for addressing the RMP management and assessment questions. The analysis conducted for the TMDL established that there is a statistically significant relationship between the annual mean concentration of MeHg in unfiltered water and mean MeHg in 350 mm largemouth bass when the data are organized by subarea. This linkage provides a connection, essential for management, between MeHg inputs and impairment of beneficial uses. Because of this linkage, the TMDL established an implementation goal of 0.06 ng/L of unfiltered aqueous MeHg. This implementation goal provides an important benchmark for assessing the status of MeHg contamination in the Delta (ST1A and ST1B). Aqueous MeHg monitoring is also valuable in evaluating loads to the Delta (SPLP1A), processes within the Delta that affect net MeHg production and availability to the food web (SPLP1B), and in development of models to forecast the response to different management scenarios (FS1). In addition, coordinated collection of bass and water data has allowed for further analysis of the linkage between these two matrices, which has been done as part of the reevaluation of the MeHg TMDL that is currently in progress (Robbins et al. 2024).

#### **HYPOTHESES**

Given the focus of the mercury monitoring design on management question ST1 relating to trends by subarea, the primary hypothesis being evaluated was whether each subarea had a trend or not.

A preliminary power analysis for the bass monitoring was presented in the proposal for Year 2 mercury monitoring, using variance estimates based on historic data. The power analysis

was based on assessment of interannual trend using linear regression. The null hypothesis for this type of assessment is that there is no trend in the time series for annual mean concentrations in each subarea. With a seven-year dataset for bass now in hand, it is evident that a simple linear regression analysis is not appropriate for all stations. The original vision for the monitoring was to develop a 10-year dataset, which might provide a sufficient basis for a linear regression analysis of trend. However, the data obtained so far have brought to light two obstacles to a linear regression-based trend analysis: 1) a lack of trend at most stations, and 2) high interannual variation with pronounced step-changes at some stations. For the latter stations, a more elaborate model that includes water year type as a variable will be needed, along with a larger dataset.

Due to these obstacles, statistical evaluation of the data in this report is primarily based on simple comparisons of annual mean concentrations and the 95% confidence intervals of the means. This approach was used to evaluate interannual differences in concentration at each station, and also to compare mean concentrations to the fish tissue water quality objective or the TMDL implementation goal for aqueous MeHg. The linear regression approach was applied to a limited extent.

## SAMPLING STRATEGY

## LOCATIONS, FREQUENCY, AND TIMING

Sampling locations for Delta RMP mercury monitoring are shown in Figure 1. The design varied substantially over the years, as shown in Table 2.

Six core stations were sampled for fish tissue in the first and second year of Delta RMP mercury monitoring; a seventh (Sherman Island) in the West Delta was added in the third year. Five bass stations were added in 2019 to establish baselines and track trends near habitat restoration projects in the Yolo Bypass South subarea and in and near the Mokelumne River subarea. Restrictions on collection methods to protect Delta smelt were enacted in 2021, and caused reductions in the number of both core and restoration bass stations that could be successfully sampled. In addition, drought conditions interfered with collection of bass at the San Joaquin River at Vernalis core station in 2022.

Water monitoring began with a phase of low-intensity quarterly sampling at five to six stations from August 2016 through October 2017. Water monitoring at the Lower Mokelumne River station was not included in year 1 due to budget limitations. In January 2018 a high-intensity phase of water monitoring was initiated, with the goal of providing data to support an updated linkage analysis for the reevaluation of the TMDL. In this phase, monthly monitoring was conducted at eight stations for January through October for two years. The window for generating data to include in the TMDL reevaluation closed in October of 2019. After that the Program reverted back to a low-intensity design with sampling in the high-flow months of March and April, and one month (August) to represent the low-flow season.

Table 2. Sampling schedule for Delta RMP mercury monitoring, July 2016 – August 2022.

The March-October period used for the linkage analysis in the TMDL is indicated with gray shading.

Year →	2016 2017 2018												2019													2020																									
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Monitoring element (#																																							Г												
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Bass - Restoration						$\perp$		$\perp$			$\perp$								$\perp$		$\perp$		$\perp$	_	$\Box$	_													L	$\perp$	5	<u> </u>		$\perp$		$\perp$		$\perp$			
Prey Fish - Restoration						$\perp$		$\perp$			_								$\perp$		$\perp$		$\perp$			_													L	$\perp$	┸	$\perp$		$\perp$		$\perp$				8	
Water		5			5	$\perp$		5	5		5						6	_	$\perp$	8	3   8	3	8	8	8	8	8	8	8	8			8	8	8	8	8	8	8	8 8	8	1 8	3	$\perp$		$\perp$		7	7		
Sediment																	6			(	<u> </u>			6		6													上												
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Year →	202	0					20	021								_				2	022												202	23											12	2024	1				
Fiscal Yr →				F	Y 2	20/2	1 (Y	EAF	₹ 5)	)								FY 2	1/2	2 (Y	ΈΑΕ	₹6)	)							F	Y22	2/23	(YE	AR 7	7)				Γ				FY23/24 (YEAR 8)					٦			
Month →	7	8	9	10	11	1 12	2 1	2	2	3	4	5	6	7	8	9	10	11	1	2 1	2	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	<sup>'</sup> 8	9	1	0 1	11	12	1	2	3	4	5	6
Monitoring element (#	of s	ites	san	nple	d)																																		Г												
Bass - Core			7												5				Ι									4											L												
Bass - Restoration			5												4				$\perp$									3											L												
Prey Fish - Restoration												8													8																										
Water			7							7	7				7						$\perp$		7	7				7											L							$\Box$					
gray shading = Marc	h-O	ctol	oer	peri	od ı	use	d fo	r the	lin	kag	je ai	naly	sis	in th	ne T	MD	L																																		
red shading = misse	d ev	ent	s																																																
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Additional details on locations and timing are provided in data reports on years one through three of the monitoring (Davis et al. 2018, 2019, 2021). Data reports were not prepared for the later years of monitoring.

#### ANALYTES, METHODS, AND COLLECTION

For fish monitoring, in addition to total mercury in muscle fillets, parameters measured included: total length, fork length, weight, sex, moisture, and estimated age based on scale analysis.

For water monitoring, in addition to measurements of unfiltered and filtered water total mercury and MeHg, ancillary parameters measured included dissolved organic carbon (DOC), chlorophyll a (Chl a), total suspended solids (TSS), and volatile suspended solids (VSS).

Additional details on collection and analytical methods are provided in the data reports for years one through three (Davis et al. 2018, 2019, 2021). Cruise reports on sample collection are provided as appendices to these reports. The same methods were employed in later years.

## COMPLETENESS, PRECISION, AND ACCURACY

Quality assurance (QA) results for the six years of monitoring are summarized in separate documents. In general, the analyses met measurement quality objectives, and only minor deviations occurred, as noted below.

Year 1 - All data were reportable. There was one minor hold-time violation for a water sample (exceeded by one day). Full QA summary in Appendix 2 of Davis et al. (2018).

Year 2 - Ninety-seven percent of the lab results met the requirements of the Delta RMP Quality Assurance Program Plan (QAPrP). For MeHg and total Hg measurements in fish and water, 100% met the requirements of the QAPP. The primary issues found were blank contamination in some of the ancillary measurements for sediment (total organic carbon) and water (DOC, VSS), where blank samples had concentrations similar to or greater than some of the lower concentration field samples (i.e., >30% of the concentration in those samples). Those results were flagged as rejected. January 2018 water samples subcontracted to Delta Environmental had non-detects for DOC well below historical averages for four stations (according to Moss Landing), and results were censored based on best professional judgement. Full QA summary in Appendix 2 of Davis et al. (2019).

Year 3 - Of the 993 total lab results, 947 (95%) met the requirements of the QAPP. For MeHg and total Hg measurements in fish and water, 100% met the requirements of the QAPP. For ancillary water parameters, 88% of the measurements met the requirements of the QAPP. For dissolved organic carbon, 46 of 94 results did not meet the requirements of the QAPP due to hold-time exceedances stemming from a problem with analytical instrumentation and a decision

to send the samples to a subcontract lab. The hold-time limit was 30 days; the maximum hold-time was 115 days. In spite of this hold-time exceedance, the investigators have high confidence in the data – the values for the samples in question are typical of values for the Delta areas sampled. Total suspended solids and volatile suspended solids results had only one field blank, less than the four required to achieve the one per 20 frequency in the QAPP. Full QA summary in Appendix 5 of Davis et al. (2021).

Year 4 - All 847 lab results were reportable, with none censored. In addition to field samples not collected due to pandemic closures, one set of chlorophyll-a samples exceeded hold-time due to lab closure during the pandemic. TSS and VSS results had only one field blank, less than the four required to achieve the one per 20 frequency in the QAPP. Full QA summary in a report available on the Delta RMP website:

https://deltarmp.org/Water%20Quality%20Monitoring/Mercury/Delta%20RMP%20FY19-20%20Mercury%20QA%20Report%20Narrative%20Summary.pdf

Years 5 and 6 - QA results for years 5 and 6 were reviewed together. A total of 1,415 tissue and water environmental and QC sample results for chlorophyll a, DOC, TSS, VSS, mercury, and MeHg were verified as a part of the Year 5 and 6 mercury monitoring dataset. Of those, 1,386 (98%) met the requirements of SWAMP QAPrP MQOs. All of the tissue and all of the water MeHg results met all MQOs. Small numbers of results did not meet MQOs for field blanks (n=5), equipment blanks (n=5), lab blanks (n=5), lab duplicates (n=5), matrix spikes (n=3), and laboratory control spikes (n=4). The parameters affected included DOC, dissolved mercury, TSS, VSS, and total Hg. A full QA summary is provided in Appendix 1.

This report focuses exclusively on data for mercury in tissue and unfiltered MeHg in water - results for these analytes met QAPP requirements in all samples.

## **DATA ANALYSIS**

The measurement of mercury in individual black bass samples provided a foundation for statistical procedures to adjust for the relationship with fish length. A length of 350 mm has been used for length-adjustment of black bass in the Methylmercury TMDL and in past studies (e.g., Davis et al. 2008, Melwani et al. 2009, Wood et al. 2010), and represents the middle of the distribution of legal-sized (>305 mm, or 12 inches) fish that are commonly caught. Estimates of mean length-adjusted concentrations at each station presented in this report are based on simple linear regressions of the data for each station. This approach provides an independently-derived estimate of the station mean that can be compared to any other station mean of interest: other station means from the same sampling period; means from the same station in past sampling; or any other station mean.

## FISH MERCURY TRENDS

#### **DELTA SUBAREA SPATIAL TRENDS**

## Average Fish MeHg Trends by Subarea

#### Sacramento River

The Sacramento River subarea (all subarea boundaries are shown in Figure 1) included a core station (Sacramento River at Freeport) monitored all seven years and a restoration station (McCormack-Williamson Tract) monitored in four years from 2019-2022. The mean concentration at Sacramento River at Freeport (0.60 ppm) was in the middle of the range of station means, while the mean at McCormack-Williamson Tract (0.87) was the third highest among the 12 stations monitored. The McCormack-Williamson Tract station is very close to the Mokelumne River subarea, and is likely influenced by the high concentrations in that region.

## Yolo Bypass South

Restrictions on fish collections in this subarea to protect Delta smelt took effect in 2021 and significantly limited sampling in 2021 and 2022. The Yolo Bypass South area included a core station (Cache Slough at Liberty Island Mouth) that was monitored for five years (2016-2020) before the restrictions. Monitoring of three restoration stations in this subarea was initiated in 2019 but was successfully implemented for a full four years at Lindsey Slough, but only three years at Yolo Flyway Farms, and two years at Lookout Slough.

Mean concentrations at these stations were in the middle of the overall distribution of the 12 stations, ranging from 0.47 ppm at Cache Slough to 0.71 ppm at Lookout Slough. The relative consistency of concentrations within this subarea (and other subareas) provides support for the subarea delineations established by the TMDL.

#### Mokelumne River

Very high mean bass mercury concentrations were observed in the Mokelumne River subarea. This subarea included a core station (Lower Mokelumne River 6) monitored all seven years and a restoration station (Grizzly-Westervelt) monitored in four years from 2019-2022. The Grizzly-Westervelt station had the highest mean concentration (1.58 ppm) among the 12 stations monitored, and Lower Mokelumne River 6 had the second highest (1.25 ppm). California's Surface Water Ambient Monitoring Program has generated length-adjusted average concentrations for black bass from 205 lakes across the state (Davis et al. 2022). The two means from this subarea are both comparable to the 98th percentile of the bass lake distribution. As observed in other subareas, the similar magnitude and temporal variation of the concentrations at these two stations provides support for the subarea delineations established by the TMDL.

Concentrations at the McCormack-Williamson Tract station (third highest among the 12 DRMP stations), which is in the Sacramento River subarea but in close proximity to the Mokelumne River subarea, provide further evidence of elevated concentrations in this region. In addition, there appears to be a gradient from upstream (Grizzly-Westervelt) to downstream (Lower Mokelumne River and then McCormack-Williamson). Water flows at the McCormack-Williamson Tract station were likely dominated by Mokelumne River water, especially during the fall and spring when the Delta Cross Channel was closed.

#### West Delta

Sherman Island was the only station in the West Delta subarea. Sherman Island was a core station where sampling was initiated in 2018. The Delta smelt sampling restrictions caused monitoring at this station to end after only three years. The Sherman Island mean concentration (0.45 ppm) was at the lower end of the range for the 12 stations (third lowest). While this was low relative to the other stations, this mean was still significantly higher than the 0.24 ppm water quality objective for black bass, with a 95% confidence interval of the mean of 0.41-0.49 ppm.

#### Central Delta

The Central Delta subarea included two core stations (Little Potato Slough and Middle River) that were both sampled for all seven years. These stations had the two lowest means among the 12 stations: 0.34 ppm for Little Potato Slough and 0.29 ppm for Middle River. Middle River was the only station with a 95% confidence interval of the mean (0.23-0.35 ppm) that was not entirely above the 0.24 ppm water quality objective. As observed in some other subareas, the consistency of the concentrations at these two stations provides support for the Central Delta subarea delineation established by the TMDL.

## San Joaquin River

San Joaquin River at Vernalis was the only station in the San Joaquin subarea. This station was sampled successfully in the first six years, but could not be sampled in 2022 due to low water levels resulting from drought that prevented access with the electrofishing boat. This station had a relatively high mean concentration (0.82 ppm) - fourth highest of the 12 stations. The mean concentration for this subarea was the second highest among the six subareas sampled (Mokelumne River was the highest).

## **Comparative Analysis of Subarea Fish Mercury Concentrations**

The regional spatial pattern of mercury in black bass in the Delta that has been documented in previous studies and the TMDL (Davis et al. 2000, 2003, 2008; Grenier et al. 2007; Melwani et al. 2008) continues to persist. Concentrations in 2016-2022 continued to be higher on the northern, eastern, and southern periphery of the Delta, and lower in the Central Delta and West Delta (Table 3, Figure 2). This pattern appears to be driven by lower suspended sediment concentrations and higher MeHg photodegradation in the Central Delta (Byington et al.

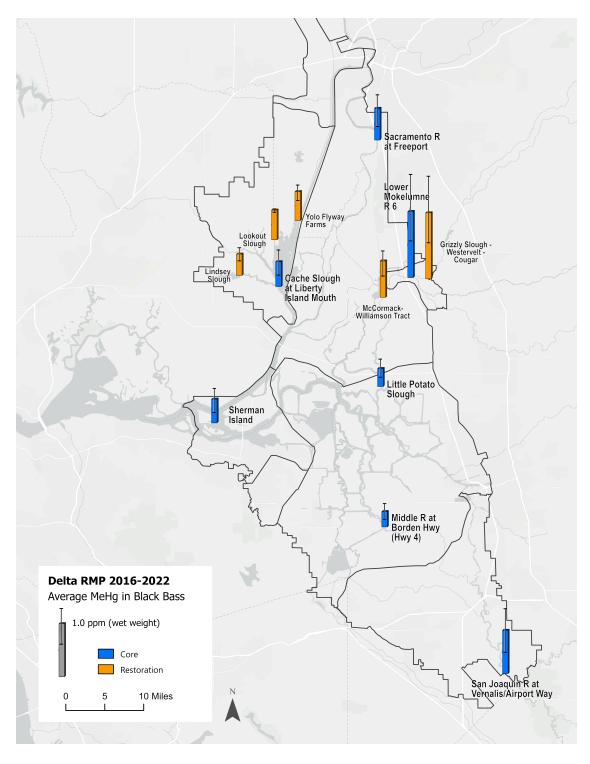
Table 3. Summary statistics for the bass monitoring stations.

Units are ppm wet weight.

			Mean				
	Station		Bass		95% CI of		
Station	Type	Delta Subarea	MeHg	SE	the Mean	N	Years
Sacramento River at Freeport	С	Sacramento River	0.60	0.03	0.54-0.66	7	2016-2022
McCormack Williamson	R	Sacramento River	0.87	0.18	0.51-1.23	4	2019-2022
Yolo Flyway Farms	R	Yolo Bypass-South	0.69	0.11	0.47-0.91	3	2019-2021
Lookout Slough	R	Yolo Bypass-South	0.71	0.02	0.67-0.75	2	2019-2020
Lindsey Slough	R	Yolo Bypass-South	0.51	0.09	0.33-0.69	4	2019-2022
Cache Slough	С	Yolo Bypass-South	0.47	0.03	0.41-0.53	5	2016-2020
Grizzly Westervelt	R	Mokelumne River	1.58	0.47	0.64-2.52	4	2019-2022
Lower Mokelumne River 6	С	Mokelumne River	1.25	0.14	0.97-1.53	7	2016-2022
Little Potato Slough	С	Central Delta	0.34	0.03	0.28-0.40	7	2016-2022
Middle River	С	Central Delta	0.29	0.03	0.23-0.35	7	2016-2022
Sherman Island	С	West Delta	0.45	0.02	0.41-0.49	3	2018-2020
San Joaquin River at Vernalis	С	San Joaquin River	0.82	0.18	0.46-1.18	6	2016-2021

Figure 2. Length-adjusted (350 mm) mean MeHg concentration (ppm wet weight) in black bass at each station.

Mean of all years of sampling from 2016-2022. Error bars show +/- 2SE.



2017, Robbins et al. 2024). Other explanations that have been suggested include proximity to legacy mining-related mercury sources, greater mercury methylation in seasonal wetlands at the periphery, and more tidal dispersion and rapid flushing in the Central Delta (Delta Independent Science Board 2018).

All of the station mean bass mercury concentrations were higher than the 0.24 ppm water quality objective (Table 3, Figure 3). The lowest mean at Middle River (0.29 ppm) had a 95% confidence interval of the mean (0.23-0.35 ppm) that overlapped the water quality objective. All of the other station means were significantly higher than the water quality objective.

Subarea mean concentrations in 2016-2022 were also all higher than the water quality objective (Table 3). The subarea means were also higher than the 2000 length-adjusted subarea mean concentrations that were used to summarize impairment status in the TMDL report. The 2016-2022 Mokelumne River subarea mean (1.40 ppm) was considerably higher than the Mokelumne River subarea mean in the TMDL (1.04 ppm). The degree of elevation for the other stations was less pronounced. One notable difference was that the mean concentration in the TMDL for the Central Delta (0.19 ppm) was below the water quality objective, but the mean for 2016-2022 (0.31 ppm) was above the objective.

The addition of restoration monitoring stations in 2019 provided for replication within subareas. The consistency observed across the stations within most subareas provided some support for the subarea delineations established by the TMDL. The replication also provided further confirmation of the strong patterns of spatial and temporal variation observed in the Delta.

#### WATER YEAR TRENDS

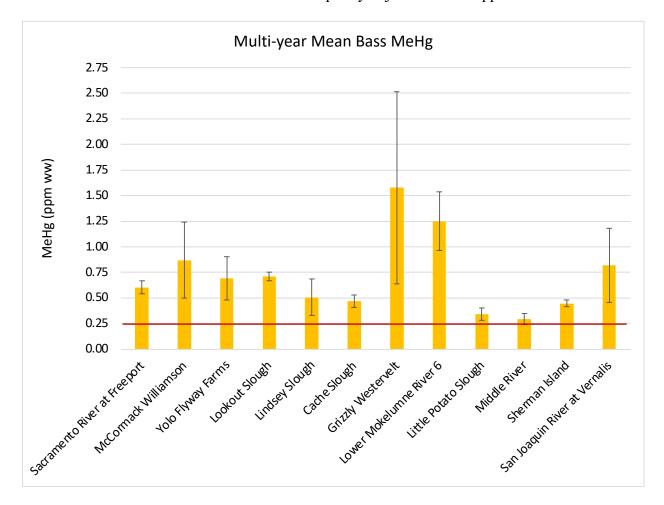
## **Average Fish Mercury Trends by Water Year**

Management Question ST1A (Are trends over time in MeHg in sport fish similar or different among Delta subareas?) was a primary focus of the sampling design for both the fish and water mercury monitoring from 2016-2022. To address Question ST1A, the Delta RMP conducted annual monitoring of mercury in fish tissue to 1) firmly establish a baseline for each Delta subarea and 2) to characterize the degree of interannual variation, which is essential to designing an efficient monitoring program for detection of long-term trends. The seven-year dataset generated by the Delta RMP greatly enhanced the long-term time series in the Delta subareas, answered question ST1A, and yielded crucial insights about interannual variability in the region. The answer to question ST1A is clear: trends over time are very different among Delta subareas, with two subareas showing marked interannual variation and reaching unusually high concentrations, stations in two subareas exhibiting significant trends based on linear

regression, and stations in the other subareas showing lower variance and no trends. This information has important implications for monitoring and managing MeHg impairment in the

Figure 3. Mean bass mercury concentrations at each Delta RMP fish monitoring station, 2016-2022.

Bars show the mean, error bars indicate +/- 2SE to show the 95% confidence interval of the mean. Red line indicates the bass tissue water quality objective of 0.24 ppm.



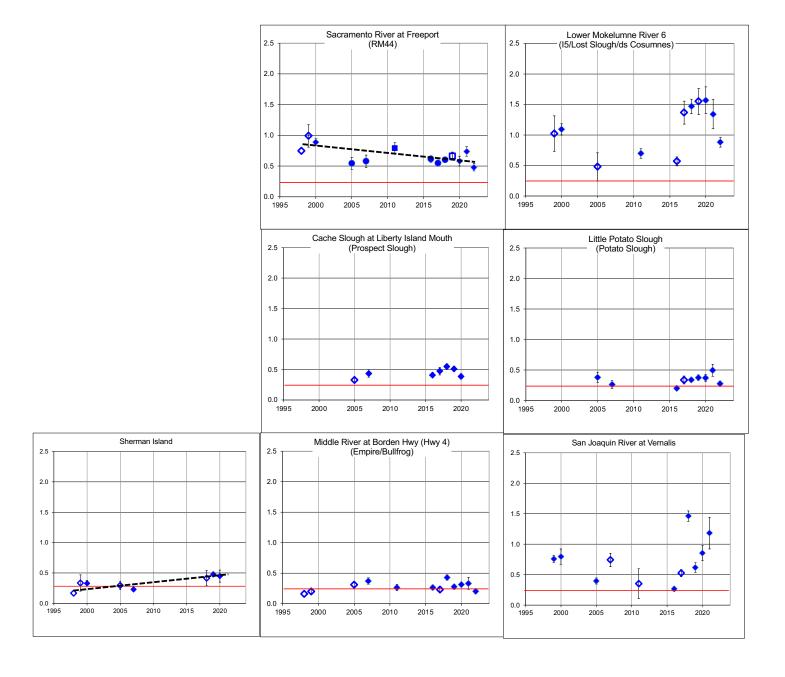
Delta – areas with higher concentrations may be a higher priority for management, and areas with higher variance require more intensive sampling to discern trends.

Long-term time series of estimated annual mean concentrations in black bass are presented in Figure 4. Each of the points on these graphs represents a mean of 12-16 fish. Most of these annual means are for length-adjusted concentrations estimated for a length of 350 mm. The estimated annual means have varying levels of uncertainty, which, as used here, refers to a combination of the estimated variance around the mean and the robustness of the method used to generate the mean. The uncertainty is generally lowest for station-year combinations where the

linear regression of length:mercury was significant and a 350 mm length-adjusted mean concentration could be calculated (solid symbols in Figure 4). Most of the station means in the four years of Delta RMP sampling could be calculated this way. The level of uncertainty is

Figure 4. Long-term time series of mean MeHg (ppm wet weight) in black bass for Delta RMP stations and nearby stations sampled historically.

Red line shows the 0.24 ppm bass tissue water quality objective. Details provided on page following the graphs. Dashed lines indicate significant linear regressions (discussed in text). Figure on next page.



#### Figure 4 Details

Points generally show 350 mm length-adjusted means (exceptions to this noted in plot details below) and error bars indicate two times the standard error. Delta RMP means are generally based on analyses of 16 individual fish; the numbers of fish represented by each mean varied in prior studies. Filled symbols indicate 350 mm length-adjusted means, hollow symbols indicate individual composite samples or arithmetic means when the station did not have a significant length:MeHg regression. Diamonds indicate largemouth bass; squares are spotted bass; circles are smallmouth bass. Data sources: Delta RMP – 2016-2018; the Surface Water Ambient Monitoring Program (Davis et al. 2013) - 2011; the Fish Mercury Project (Melwani et al. 2009) - 2005-2007; the CALFED Mercury Project (Davis et al. 2003) - 1999-2000; the Delta Fish Study (Davis et al. 2000) - 1998; and the Sacramento River Watershed Program (2002) - 1998.

#### **Sacramento River at Freeport**

Stations - Freeport: 2016-2018; RM44: All other years

Statistics - Individual composite results: 1998; mean of fish >305 mm: 1999; 350 mm length-

adjusted mean: all other years

#### **Lower Mokelumne River 6**

Stations - Lower Mokelumne River 6: 2016-2017; Mokelumne River near I-5: 2011; Lost Slough: 2005; Mokelumne River downstream of the Cosumnes River: 1999, 2000 Statistics - Mean of fish >305 mm: 1999, 2005, 2016, 2017; 350 mm length-adjusted mean: all other years

#### **Cache Slough at Liberty Island Mouth**

Stations - Cache Slough at Liberty Island Mouth: 2016-2017; Prospect Slough: 2005, 2007 Statistics - Mean of fish >305 mm: 2005; 350 mm length-adjusted mean: all other years

#### Little Potato Slough

Stations - Little Potato Slough: 2016-2017; Potato Slough (aka San Joaquin River at Potato Slough): 2005, 2007

Statistics - Mean of fish >305 mm: 2017; 350 mm length-adjusted mean: all other years

#### Middle River at Borden Hwy (Hwy 4)

Stations - Middle River at Borden Hwy (Hwy 4): 2016-2017; Middle River near Empire Cut: 2011; Middle River at Bullfrog: 1998, 1999, 2007; Middle River at HWY 4: 2005 Statistics - Individual composite result: 1998; mean of fish >305 mm: 1999, 2005, 2017; 350 mm length-adjusted mean: all other years

#### San Joaquin River at Vernalis

Stations - Same station all years

Statistics - Mean of fish >305 mm: 2007, 2011, 2017; 350 mm length-adjusted mean: all other years

### **Sherman Island**

Stations - San Joaquin River off Point Antioch near fishing pier: 1998, 1999; Sherman Lake: 2000; Big Break: 2005, 2007; Sherman Island: 2018

Statistics - Individual composite result: 1998; mean of fish >305 mm: 1999, 2005, 2018; 350 mm length-adjusted mean: all other years

generally higher for station-year combinations where the length:mercury regression was not significant. These non-significant regressions were often the result of high variance and outliers across the size range, but in some cases resulted from a low (close to zero) slope for the regression line. For these station-year combinations a simple mean of legal-sized bass (>305 mm) was calculated. The error bars in Figure 4 indicate two times the standard error of the mean and provide an approximation of the 95% confidence interval of the mean and a good index of the degree of uncertainty around each mean.

#### Sacramento River

The Sacramento River subarea included a core station (Sacramento River at Freeport) monitored all seven years and a restoration station (McCormack-Williamson Tract) monitored in four years from 2019-2022. The Sacramento River at Freeport has been a key station for multiple programs and projects, and has one of the most extensive long-term time series in the region.

The Sacramento River at Freeport station time series is suggestive of a long-term decline. A linear regression of this time series indicates a significant decline (p=0.02, R²=0.39). This is driven to a large degree by relatively high annual means in 1998, 1999, and 2000, which were based on less robust designs (composite samples in 1998, and a simple mean of legal-sized fish in 1999). Since 2005 the trend line has been flat, with the annual means ranging between 0.5-0.6 ppm. This station has had the greatest variation in black bass species over the years, with largemouth, smallmouth, and spotted bass all represented. The concentrations have been consistent in spite of this species variation, suggesting that differences among black bass species are not a major driver of variation. A significant negative regression in the long-term time series for aqueous MeHg at this station (discussed below) provides further support for a decline.

Substantial interannual variation was observed in the four-year dataset for the McCormack-Williamson Tract station. The mean at this station in 2019 was higher than the means in the following three years. The 2019 mean was based on spotted bass, while the later years were for largemouth, raising the question of whether there might be species-related variation. However, similar significant interannual variation was observed at two nearby stations in the Mokelumne River subarea, suggesting that the variation may have been a regional phenomenon.

## Yolo Bypass South

As described above, restrictions on fish collections in this subarea to protect Delta smelt took effect in 2021 and significantly limited sampling in 2021 and 2022. A core station (Cache Slough at Liberty Island Mouth) was monitored for five years (2016-2020) before the restrictions, and also had earlier data from 2005 and 2007. Annual means at this station are not suggestive of a trend, and have consistently been in the 0.4-0.5 ppm range over the period of record.

Monitoring of the three restoration stations in this subarea was initiated in 2019 but was successfully implemented for a full four years at Lindsey Slough, but only three years at Yolo

Flyway Farms, and two years at Lookout Slough (Figure 5). Concentrations at Lindsey Slough were progressively lower over the four years of monitoring, with the 2022 mean significantly lower than the 1999 mean. The time series is too limited, however, to conclude that this is a trend.

## Mokelumne River

The observation of high variation by water year in this subarea is one of the most important findings of the Delta RMP mercury monitoring. The core station in this subarea (Lower Mokelumne River 6) was monitored in all seven years of the DRMP and monitoring nearby in four years (1999, 2000, 2005, 2011) by other programs adds to the long-term time series. High variability was observed in the four pre-Delta RMP years, with annual means ranging from 0.48 ppm in 2005 to 1.09 ppm in 2000. The seven years of Delta RMP monitoring were very enlightening. The mean in 2016 (0.57 ppm) was not elevated relative to other observations in the Delta. In 2017 concentrations increased markedly and significantly to 1.37 ppm. Concentrations remained elevated at approximately 1.5 ppm for the next three years, and then were slightly lower (but not significantly) in 1.34 ppm in 2021. In 2022 the mean was significantly lower at 0.88 ppm. The mean concentrations observed from 2017-2021 were among the highest that have been observed in extensive black bass monitoring across the State.

A restoration station (Grizzly-Westervelt) upstream of the core station was monitored in four years from 2019-2022, and provided confirmation of the exceptionally high concentrations in this subarea and the high interannual variation (Figure 6). The temporal pattern at this station matched the pattern at the core station, with high values from 2019-2021 (ranging between 1.67 and 2.02 ppm), followed by a significantly lower mean in 2022 (0.92 ppm). The concentrations at Grizzly-Westervelt were even higher than the high values at Lower Mokelumne River 6. The maximum mean observed (2.02 ppm) has been exceeded by only three of the 205 lakes with length-adjusted black bass means in California.

#### West Delta

Sherman Island was the only station in the West Delta subarea. Sherman Island was a core station where Delta RMP sampling was initiated in 2018. The Delta smelt sampling restrictions caused monitoring at this station to end after only three years. This station was sampled in five previous years by other programs, giving it one of the stronger long-term time series in the Delta. This time series suggests that concentrations in this subarea have increased, with a significant linear regression (p=0.02, R<sup>2</sup>=0.64). Mean concentrations observed from 1998-2007 ranged from 0.17 (1998) ppm to 0.34 ppm (1999). The means observed by the Delta RMP ranged from 0.42 ppm (2018) to 0.48 ppm (2019).

Figure 5. Time series of mean mercury (ppm wet weight) in black bass for stations in the Yolo Bypass subarea.

Red line shows the 0.24 ppm bass tissue water quality objective. Filled symbols indicate 350 mm length-adjusted means, hollow symbols indicate individual composite samples or arithmetic means when the station did not have a significant length: MeHg regression.

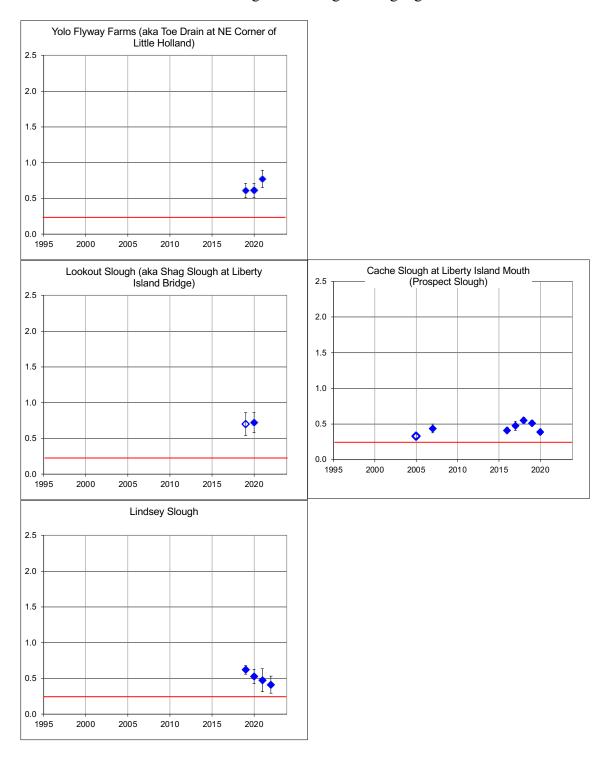
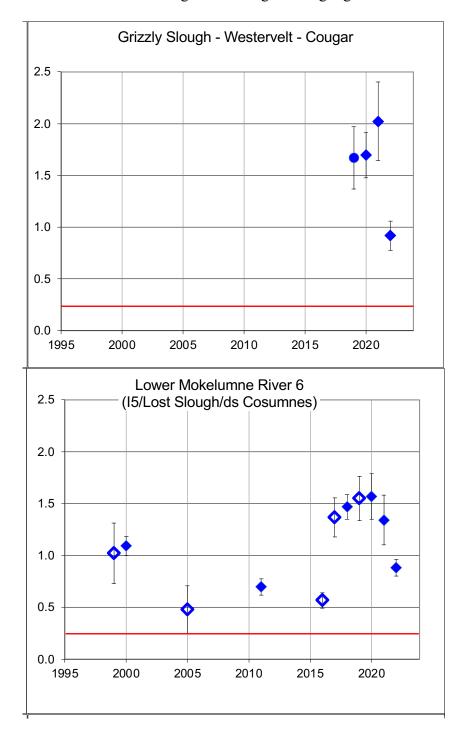


Figure 6. Time series of mean mercury (ppm wet weight) in black bass for stations in the Mokelumne River subarea.

Red line shows the 0.24 ppm bass tissue water quality objective. Filled symbols indicate 350 mm length-adjusted means, hollow symbols indicate individual composite samples or arithmetic means when the station did not have a significant length:MeHg regression.



#### Central Delta

The Central Delta subarea included two core stations (Little Potato Slough and Middle River) that were both sampled for all seven years of the Delta RMP. Middle River has a relatively good long-term time series, with five rounds of sampling in prior years. The long-term time series for Little Potato Slough is not as strong, with only two rounds prior to the Delta RMP. The time series for both of these stations indicate no trend and little interannual variation over the period of record.

## San Joaquin River

San Joaquin River at Vernalis, the only station in the San Joaquin subarea, was sampled successfully in the first six years, but could not be sampled in 2022. This has been one of the primary stations monitored by prior programs, with five rounds of sampling before the Delta RMP. Long-term interannual variation at this station has been high and generally very similar to that observed at Lower Mokelumne River. Concentrations prior to the Delta RMP were somewhat variable, ranging between 0.35 ppm (in 2011) and 0.80 ppm (in 2000). After the first year of Delta RMP monitoring, yielding a mean of 0.27 ppm for 2016, the time series appeared suggestive of a linear long-term decline. The mean in 2017 was significantly higher, however, at 0.53 ppm. Then in 2018 the mean was markedly and significantly higher, at 1.46 ppm. As discussed for the Mokelumne River subarea, concentrations in this range are exceptionally high, over 5 times the bass tissue objective for the Delta (0.24 ppm) and comparable to the 98<sup>th</sup> percentile of the extensive statewide dataset for length-adjusted black bass in reservoirs. In 2019, the mean was sharply lower again (0.62 ppm), followed by higher means in 2020 (0.86 ppm) and 2021 (1.18 ppm). As observed in the Mokelumne River subarea, annual sampling in the San Joaquin River subarea has revealed sporadically exceptionally high concentrations and substantial interannual variation. Awareness of this variation is fundamental to understanding MeHg impairment in the Delta and attempting to discern long-term trends.

## **Comparative Analysis of Water Year Fish MeHg Concentrations**

The Delta RMP core station data for 2016-2022, along with data from prior studies, indicate that Delta subareas fall into two categories with regard to interannual variation and trends. One set of stations exhibited relatively low interannual variance from 2016-2022 and throughout the long-term time series. This set includes Sacramento River at Freeport, Cache Slough at Liberty Island Mouth, Little Potato Slough, Middle River at Borden Highway, and Sherman Island. In general, mean concentrations at each of these stations fluctuated within approximately a 0.2 ppm range. Over the long-term, only two of these time series were indicative of a distinct trend.

The other two core stations (Lower Mokelumne River 6 and San Joaquin River at Vernalis) exhibited high interannual variance in 2016-2022 and throughout the long-term time series. A possible driver of the high interannual variation at these stations, based on prior work with prey fish by Slotton et al. (2007), is interannual variation in streamflow and flooding of upstream wetlands and floodplains in the Mokelumne River and San Joaquin River watersheds. Slotton et al. (2007) performed intensive seasonal sampling of prey fish at these two stations in 2005-2007. Water year 2006 (October 2005 – September 2006) was classified as a wet year by the California Department of Water Resources (DWR). In July 2006, Slotton et al. observed a sharp increase in MeHg in multiple species at their Cosumnes River station (in the same area as the Delta RMP Lower Mokelumne River 6 station) and at the San Joaquin River at Vernalis. During this same time period, no increases were observed at stations in the Yolo Bypass-North, Yolo Bypass-South, and Central Delta subareas. Overall, Slotton et al. documented the timecourse of a sharp, short-term increase in prey fish mercury after the high flows of water year 2006. Slotton et al. also noted that other studies of aqueous MeHg (Foe et al. 2007a,b; Marvin-DiPasquale et al. 2007) found corresponding increases on dates preceding the increases in prev fish MeHg. A more detailed review of the studies mentioned in this paragraph is included in Davis et al. (2021).

Slotton et al.'s hypothesis to explain this increase after high flows was that the Cosumnes River and San Joaquin River stations were strongly influenced by hydrology and upstream inundation of floodplains and wetlands, while the other Delta stations were not. More specifically, they attributed it to deep flooding of the Cosumnes River floodplain, and extensive areal flooding of land adjacent to the San Joaquin River in the Mud Slough region. Many studies in the mercury literature have documented increased net MeHg production and bioaccumulation in association with flooding, as submerged organic matter decomposes and creates the anaerobic conditions that favor the presence and activity of sulfate-reducers and other microbes that convert inorganic mercury to MeHg. While Slotton's hypothesis seems to have merit, other processes could also potentially explain the observed increases. Increased transport of mercury-contaminated sediment from upper watershed areas is another possible flow-related mechanism.

Delta RMP data for the Mokelumne River and San Joaquin River subareas prompted consideration of the floodplain and wetland inundation hypothesis as an explanation of the strong interannual variation that was observed. The timing of the Delta RMP mercury sampling effort was fortuitous for evaluating this hypothesis, as it coincided with extreme hydrologic variation.

The first year of sampling in 2016 was conducted after a dry year (using the California Department of Water Resources water year classification scheme) at the end of a five-year drought. Water year 2017 was a wet year, coming in at second place for statewide runoff over the period of record since 1895. This was followed by a below-normal year in 2018, a wet year in 2019, a dry year in 2020, and two critically dry years in 2021 and 2022 (Figure 7).

## Correlation with Water Year Type at the Lower Mokelumne River Station

The sharp increase in bass mercury at Lower Mokelumne River 6 in fall 2017 appears to support the floodplain inundation hypothesis, but bass mercury in the following five years did not correlate with flow in a simple manner. In spite of annual fluctuations between dry or below normal and wet conditions, bass mercury remained elevated for the next four years (in approximately the 1.4-1.6 ppm range) and then fell significantly to 0.88 ppm in 2022 (Figure 7).

Although water year 2018 was generally a below-normal flow year in the Central Valley, the level of the Cosumnes River reached monitoring stage (defined as a level that may produce overbank flows sufficient to cause minor flooding of low-lying lands and local roads) prior to the March and April water sampling, accompanied by high aqueous MeHg concentrations (discussed further in the next section). Although a water year index for the Cosumnes River would be more appropriate, the authors are not aware of one so a more general flow index from DWR for the Sacramento Valley was used to examine the correlation between water year and MeHg in bass.

The long-term time series for this station also does not suggest a within-water year correlation relationship between bass MeHg and flow in the preceding winter (Figure 8a). Studies using extensive datasets on selenium bioaccumulation in the Bay-Delta watershed have documented the existence of a lag between increases in aqueous selenium and selenium increases in biota, with greater lags for higher trophic level species, including lags of more than a year in piscivorous fish (Beckon 2016). Given Beckon's conceptual model, the possibility of a one-year lag between the high flows and the increase in bass MeHg was also explored (Figure 8b). The regression line was suggestive of a possible positive relationship, but was not significant (R<sup>2</sup>=0.17, p=0.21).

## Correlation with Water Year Type at the San Joaquin River at Vernalis Station

The relationship between bass MeHg and water year was also examined for San Joaquin River at Vernalis (Figure 9). The DWR water year index for the San Joaquin Valley paralleled the index for the Sacramento Valley. The bass mercury pattern at this station was similar to the Lower Mokelumne River station in that it included a sharp increase in concentration and significant interannual variation. However, the pattern was different in some important ways. In the very wet water year of 2017, concentrations at Vernalis rose significantly but modestly, from 0.27 ppm in 2016 to 0.53 ppm in 2017. A much bigger increase occurred in 2018 (to 1.46 ppm),

Figure 7. Length-adjusted mean bass mercury at the Lower Mokelumne 6 station compared to DWR water year index for the Sacramento Valley.

Water year types during the Delta RMP monitoring were as follows:

2016 Below normal 2017 Wet 2018 Below normal 2019 Wet 2020 Dry 2021 Critically dry 2022 Critically dry

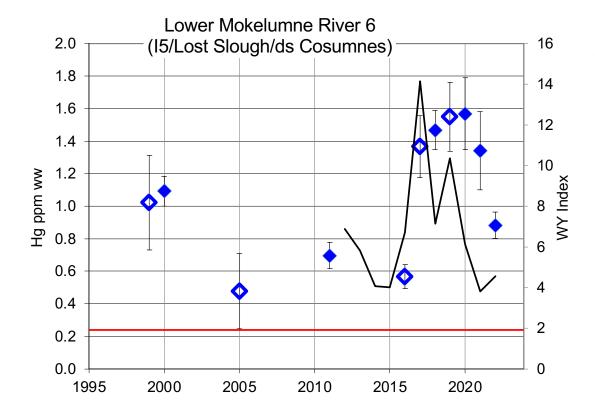
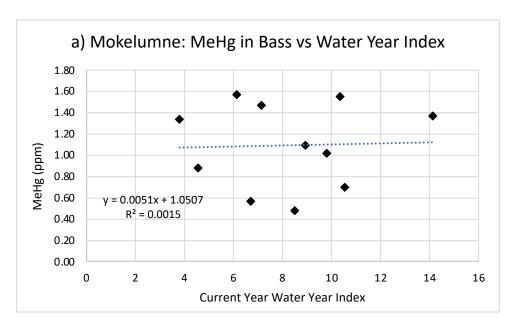


Figure 8. MeHg concentration in black bass (ppm) versus DWR water year index for the Sacramento Valley: a) current water year index; b) previous year water year index.

Bass MeHg dataset is the same as shown by year in Figure 2. Water year data are from DWR (<a href="https://cdec.water.ca.gov/reportapp/javareports?name=WSIHIST">https://cdec.water.ca.gov/reportapp/javareports?name=WSIHIST</a>) and are the data used for "Official Year Classifications based on May 1 Runoff Forecasts."



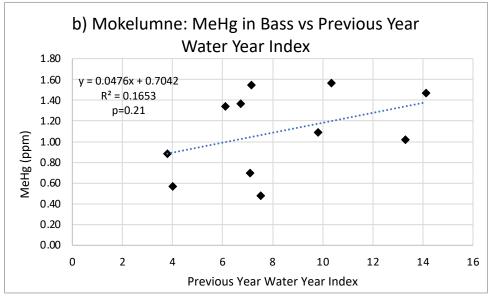
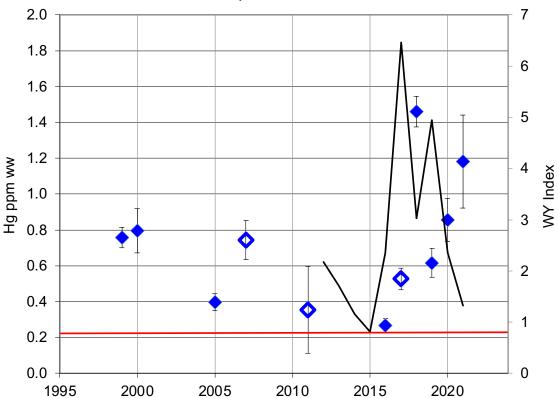


Figure 9. Length-adjusted mean bass mercury at the San Joaquin River at Vernalis station compared to DWR water year index for the San Joaquin Valley.

Water year types during the Delta RMP monitoring were as follows:

2016 Dry 2017 Wet 2018 Below normal 2019 Wet 2020 Dry 2021 Critically dry 2022 Critically dry

# San Joaquin River at Vernalis



even though WY 2018 was a below-normal flow year. Bass mercury dropped sharply in 2019 (to 0.62 ppm), and then increased again in 2020 (0.86 ppm) and 2021 (1.18 ppm).

Correlations between bass mercury and water year index were also examined for this station (Figures 10a and 10b). The data were suggestive of a negative correlation of bass mercury with current-year hydrology, but this was not significant (p=0.12) (Figure 10a). There was, however, a positive and significant (p=0.05) correlation between bass mercury and the water year index from the previous year (Figure 10b). The dataset for this station appears to support a conceptual model of a relationship of bass mercury to interannual variation in hydrology with a one-year lag time.

# General Discussion of Water Year Type as a Driver

Overall, the Delta RMP bass data for these two stations appear to add to the findings of Slotton et al. (2007) to indicate the general importance of hydrology as a driver of temporal variation in fish MeHg in the Mokelumne River and San Joaquin River subareas. The details of the relationship appear to be different in the two subareas.

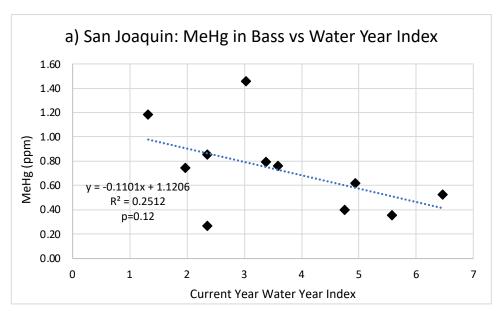
In the Mokelumne River subarea, bass concentrations rose sharply within the same water year as the high flows and then remained elevated for a total of five years, in spite of a belownormal flow year in 2018 (Figure 7). As mentioned above, there may still have been flooding on the Cosumnes River when it reached monitoring stage in the spring of 2018. Overall, there may have been three years of floodplain inundation in and upstream of this subarea, followed by dry conditions from 2020-2022. Bass remained high, however, in 2020 and 2021, before dropping significantly in 2022. In summary, bass mercury in this subarea responded quickly to the increased flow and then concentrations remained high for two years after the flows were reduced.

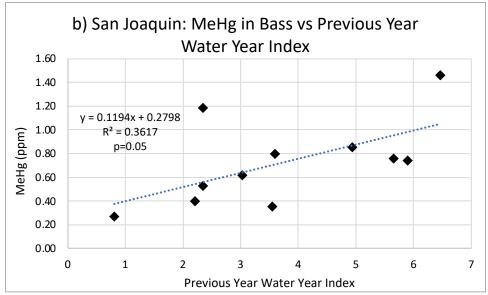
In contrast, bass in the San Joaquin subarea exhibited a slower and less persistent response to the high degree of inundation in 2017 (Figure 9). The San Joaquin River at Vernalis station had a one-year lag between the high-flow water year and the increase in bass mercury, and the elevated level of bass mercury did not persist for more than one year. In general, the fluctuations in bass mercury tended to match the annual fluctuations in hydrologic regime, with a one-year lag, leading to the significant regression result (Figure 10b).

A more thorough understanding of the details of floodplain and wetland inundation in these regions is needed as a basis for robust conceptual models to explain the extreme interannual variation at these stations. As noted for the Cosumnes River in 2018, floodplain inundation may occur and potentially drive net MeHg production even in a relatively dry water year if the precipitation is concentrated at a particular time. More precise indices of floodplain and wetland inundation upstream of these subareas would likely yield better correlations with bass mercury.

Figure 10. MeHg concentration in black bass (ppm) versus DWR water year index for the San Joaquin Valley: a) current water year index; b) previous year water year index.

Bass MeHg dataset is the same as shown by year in Figure 2. Water year data are from DWR (<a href="https://cdec.water.ca.gov/reportapp/javareports?name=WSIHIST">https://cdec.water.ca.gov/reportapp/javareports?name=WSIHIST</a>) and are the data used for "Official Year Classifications based on May 1 Runoff Forecasts."





#### Other Drivers

#### LEVEE BREACHING

In addition to general hydrologic conditions as indicated by water year type, intentional and unintentional breaching of levees could have a major influence on net MeHg production and bioaccumulation. The potential influence of intentional breaching as part of habitat restoration projects was a major motivation for the Delta RMP mercury monitoring element, as reflected in the wording of Assessment Question ST1 (Table 1). In addition, targeted monitoring of areas near restoration projects was incorporated into the design in 2019 to specifically assess this influence. Information on the restoration projects was gathered to guide selection of monitoring station locations (Table 4). Breaching of three major projects that were selected as priorities for monitoring was originally planned for 2021, but actually occurred or are occurring later. Lookout Slough was just breached in September 2024 (DWR 2024). Breaching of Grizzly Slough is planned for October 2025 (Otome Lindsey, DWR, personal communication). Breaching of the McCormack-Williamson Tract occurred, to a large extent, in 2023.

Breaching of the McCormack-Williamson Tract (MWT) provides an example of the complexity of restoration activity and the challenge of understanding its impact on food web mercury. MWT has a long history of over-topping and levee failures (Judah Grossman, DWR, personal communication). Records indicate that MWT levees failed in 1955, 1958, 1964, 1986, 1997, 2017, and most recently in 2023. GEI Consultants (2023) provides information on the 2023 levee failure and current plans for restoration. During the state and federally declared emergencies from winter 2023 storms, the Mokelumne River Levee along MWT overtopped and subsequently breached in January 2023. This resulted in the complete inundation of the MWT interior due to levee breaches in three locations – along the Mokelumne River, Dead Horse Cut, and Snodgrass Slough. DWR, in coordination with Reclamation District 2110, has decided not to drain the floodwaters and return the MWT interior to its pre-January 2023 condition. Restoration of substantial amounts of habitat will be achieved by leaving the tract inundated and following up with a Phase B of the project that includes further levee removal and was completed in summer of 2024 (Judah Grossman, DWR, personal communication). Longduration inundation is known to often lead to increased net MeHg production and bioacccumulation, in a phenomenon known as the "reservoir effect" because it has been wellcharacterized in newly flooded reservoirs.

#### FOOD WEB DYNAMICS

A solid understanding of food web dynamics in these subareas may also be essential to understanding their temporal patterns of bioaccumulation. The dataset of Slotton et al. (2007) showed that the temporal response patterns of different prey fish species can vary, with Mississippi silverside in the Mokelumne River subarea exhibiting a shorter duration of elevation after a high-flow period than other species like young-of-the-year largemouth bass and bluegill. The bioaccumulation lag-time concept of Beckon (2016) also needs to be considered as part of

Table 4. Restoration project information, including rationale for sampling site selection.

Name	Туре	Restoration Timing (Breach)	Acres (Tidal Wetland or Floodplain)	Site Details	Additional Details
Lindsey Slough	Comparison	2014	159	Restoration site on the natural edge of the Delta where it transitions to uplands.	Site farther up Lindsey Slough, near wetlands not associated with restoration project. Near Lindsey Slough wetland.
Lookout Slough	Restoration	2024	3400	Large restoration project. Site design includes channel network and raised peninsulas.	Near Lookout Slough, an opportunity to sample regional Hg pre-breach.
Liberty Island	Comparison	1997	5303	Large wetland resulting from unplanned breach	Wetlands established after unplanned breach in 1997. Treating this as comparison marsh because it was not a recent, planned restoration.
Yolo Flyway Farms	Restoration	2018	350	One large channel excavated to connect to toe drain	New restoration. Farther up the fluvial-tidal gradient than nearby sites. New (2020) restoration project nearby.
McCormack Williamson Tract	Restoration	2023	908	Large planned restoration in the northwest Delta; Elevation gradient across site.	Near McCormack Williamson Tract, an opportunity to sample regional Hg pre-breach.
Westerveldt Restoration	Restoration	2011	472	Established floodplain restoration	Older restoration site. Site recommended by DWR as an alternative restoration project since Grizzly Slough restoration is not yet complete.
Cougar Wetland	Restoration	2019	154	Recent floodplain restoration	Recent restoration site. Site recommended by DWR as an alternative restoration project since Grizzly Slough restoration is not yet complete.
Grizzly Slough	Restoration	2025 (planned)	400	Planned floodplain restoration	

conceptual models of bioaccumulation for these subareas. Habitat restoration projects can be expected to lead to food web alterations that could affect MeHg bioaccumulation.

#### **Summary**

Annual monitoring of bass has shown that MeHg concentrations are highly dynamic at these two stations, and the results seem to be pointing to an understanding of factors that drive the variation. In addition, the monitoring has documented extremely high concentrations at these stations that are of high concern to both humans and wildlife, and that seem to be more persistent in the Mokelumne River subarea. Continued annual monitoring is needed to evaluate the hypothesized relationship between elevated concentrations and high flows in comparison to other potential explanations (e.g., for the Mokelumne watershed, levee breaches as part of wetland restoration). Water year 2023 was, as indicated in the MWT discussion above, another wet year. If the monitoring in the Mokelumne River and San Joaquin River subareas had continued that would have provided another opportunity to gain an improved understanding of interannual variation and its drivers in the Delta's most highly impaired subareas. The monitoring that has been conducted has provided information on baseline conditions that will be useful in evaluating the impact of restoration projects.

# **AQUEOUS METHYLMERCURY TRENDS**

This section focuses on the dataset for unfiltered aqueous MeHg, which is the key aqueous parameter in the TMDL. The TMDL focused on this parameter based on its connection to concentrations in largemouth bass, and established an implementation goal of 0.06~ng/L of unfiltered aqueous MeHg that would translate to reaching the largemouth bass water quality objective of 0.24~ppm. The interpretive report on the first three years of monitoring (Davis et al. 2021) included discussion of other forms of mercury (filtered MeHg, filtered and unfiltered total Hg), and other ancillary water parameters. A relatively small number of data points were added to the water dataset in years four through six, so these analyses are not presented again in this report.

#### **DELTA SUBAREA TRENDS**

## Average Aqueous MeHg Trends by Subarea and Comparative Analysis

Figure 11 shows the full dataset for unfiltered MeHg concentration at each station sampled. Water monitoring began with a phase of low-intensity quarterly sampling at five to six stations from August 2016 through October 2017. In January 2018 a second phase of high intensity monitoring began and continued through October of 2019. After that a third phase began with a low-intensity design of sampling in the high-flow months of March and April, and one month (August) to represent the low-flow season. This discussion of long-term mean concentrations focuses on the March through October period which was the basis for the linkage analysis in the TMDL, and was targeted in the sampling design.

#### Sacramento River

The Sacramento River at Freeport was the water monitoring station in this subarea (all subarea boundaries are shown in Figure 1), and was sampled from 2017-2022. The grand mean of March-October annual means at this station was 0.083 (SE=0.002) ng/L (Figure 12). This was a moderate mean concentration relative to the other stations, but had a 95% confidence interval that exceeded the implementation goal. This station had relatively consistent annual mean concentrations, as reflected in the lowest standard error and narrowest 95% confidence interval of the mean. Only two of the 33 monthly measurements were below the implementation goal (Figure 11).

# Yolo Bypass South

Cache Slough at Liberty Island Mouth was the water monitoring station in this subarea, and was sampled from 2017-2022. The grand mean of March-October annual means at this station was 0.113 (SE=0.014) ng/L (Figure 12). This was a high mean concentration relative to the other stations (third highest of the eight stations) This station had moderately variable annual mean concentrations, but the 95% confidence interval of the mean was still well above the

Figure 11. Concentrations of unfiltered methylmercury over monthly timescale at Delta RMP stations.

Panels on left and right represent west and east locations, respectively. Figure on next page.

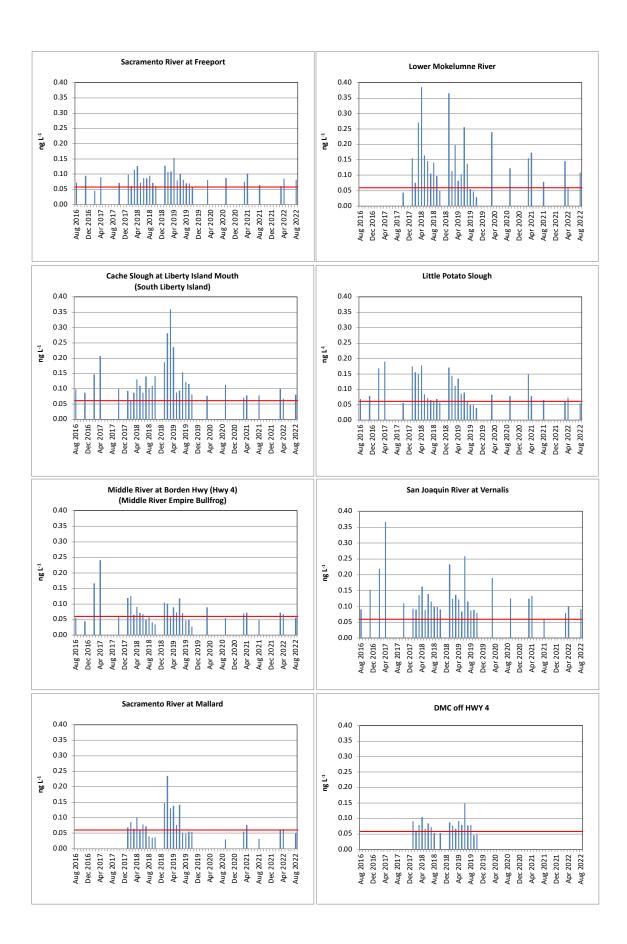
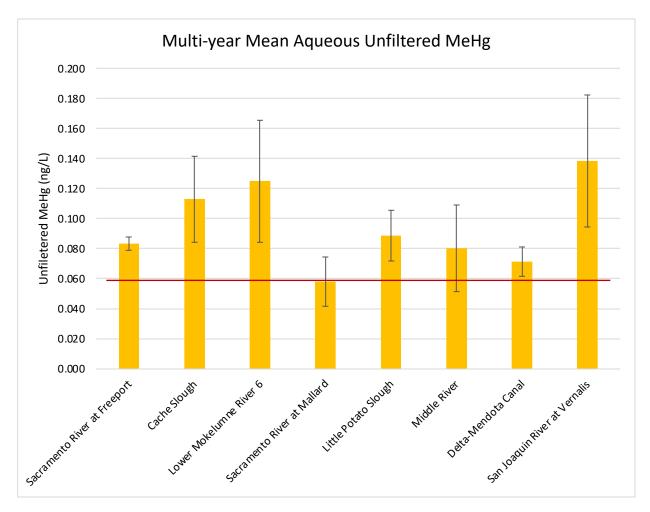


Figure 12. Mean unfiltered MeHg concentrations at each Delta RMP water monitoring station, 2017-2022.

Bars show the grand mean of available annual March-October means, error bars indicate  $\pm$  2SE to show the 95% confidence interval of the mean. Red line indicates the TMDL implementation goal of 0.06 ng/L. Only one sample in the March-October period was collected in 2016, so this year was excluded from this presentation.



implementation goal. Only one sample at this station was at or below the implementation goal (0.06 ng/L in February 2018).

#### Mokelumne River

Lower Mokelumne River 6 was the water monitoring station in this subarea, and was sampled from 2017-2022. The grand mean of March-October annual means at this station was 0.125 (SE=0.020) ng/L (Figure 12). This was the second highest concentration among the eight stations. Variance of the annual means was also relatively high at this station, but the 95% confidence interval of the mean was still well above the implementation goal. In spite of the high mean concentration, this station had five months with a concentration below the implementation goal, all occurring in the fall months (in 2017, 2018, and 2019) (Figure 11).

#### West Delta

The Sacramento River at Mallard Island was the water station in the West Delta subarea. Sampling at this station was initiated in 2018 and continued through 2022. This station had the lowest long-term mean concentration, just below the implementation goal at 0.058 ng/L (Figure 12). The variance of the annual means at this station was moderate. This station had a relatively high proportion of samples at or below the implementation goal (12 of 27, or 44%). Concentrations at this station were relatively high in January-June of 2019.

#### Central Delta

The Central Delta subarea included three water stations. Two of these (Little Potato Slough and Middle River at Borden Highway) were core stations that were co-located with fish monitoring, and one was a water-only station (Delta-Mendota Canal) that was monitored to provide information for updating the MeHg mass balance for the Delta. Little Potato Slough and Middle River had relatively moderate aqueous MeHg concentrations. The mean for Little Potato Slough (0.089 ng/L) was a little higher than Middle River (0.080 ng/L) (Figure 12). Variance was lower at Little Potato Slough, so the 95% confidence interval did not overlap the implementation goal. Middle River had higher variance along with the lower mean, so it did overlap the implementation goal. Little Potato Slough had seven of 33 months below the implementation goal, all of them in the late summer/fall period. Middle River had 13 of 33 months below the goal, all but one of them in the late summer/fall.

The Delta-Mendota Canal station had the second lowest multi-year mean (0.071 ng/L), but this was based on only two years of monitoring (Figure 12). The variance at this station was relatively low, so the 95% confidence interval did not overlap the implementation goal. This station had five of 19 months below the goal, all but one of them in the late summer/fall.

# San Joaquin River

The San Joaquin River at Vernalis station had the highest mean aqueous MeHg concentration (0.138 ppm). Variance was also high, but the 95% confidence interval was still

well above the implementation goal. None of the monthly samples were below the implementation goal (the minimum concentration 0.061 ng/L).

# **Comparative Analysis of Subarea Aqueous MeHg Concentrations**

The general pattern of spatial and temporal variation in unfiltered aqueous MeHg concentrations in Delta RMP monitoring matched the patterns observed for bass. Most notably, the Lower Mokelumne River and San Joaquin River at Vernalis stations had the highest concentrations (Figure 12), along with the highest inter- and intra-annual variation (Figure 11). The same primary driver of interannual variation discussed for the bass - interannual variation in floodplain and wetland inundation - probably also is a major driver of the aqueous concentrations.

There were some notable differences between the patterns for aqueous MeHg and bass mercury. For example, Cache Slough had the third-highest overall Delta RMP mean for aqueous MeHg, but only the fourth-highest among the core stations for fish (Figure 3). Sacramento River at Freeport was had the fifth-highest Delta RMP mean for water, but the third-highest for fish. A more thorough evaluation of the linkage between aqueous MeHg and bass mercury was beyond the scope of this report. A rigorous linkage analysis based on Delta RMP data through October 2019 and historic data was performed by Robbins et al. (2024).

#### WATER YEAR TRENDS

# Average Aqueous MeHg Trends by Water Year

Management Question ST1B (Are trends over time in MeHg in water similar or different among Delta subareas?) was a primary focus of the sampling design for water aqueous MeHg monitoring from 2016-2022. To address this question, as for fish, the Delta RMP conducted annual monitoring to 1) firmly establish a baseline for each Delta subarea and 2) to characterize the degree of interannual variation, which is essential to designing an efficient monitoring program for detection of long-term trends. The seven-year dataset generated by the Delta RMP greatly enhanced the long-term time series in the Delta subareas, answered question ST1B, and yielded valuable information on interannual variability in the region.

#### Sacramento River

The Sacramento River at Freeport has been a key station for multiple programs and projects, and has one of the most extensive long-term time series in the region. Data for seven years in the Delta RMP add to a long-term time series that included near-annual monitoring from 2000-2006. Both within-year and between-year variance has been low at this station, with the exception of high within-year variance in 2000. The annual means have consistently been in the 0.08-0.10 ng/L range. A linear regression of this time series indicates a significant decline

(p=0.02, R<sup>2</sup>=0.41). The annual means during the Delta RMP years were very consistent in spite of the extreme variation in water year index.

# **Yolo Bypass South**

Historic data for only one year are available for the Cache Slough station. Interannual variation in the Delta RMP means was moderate relative to the other stations, ranging from 0.076 - 0.157 ng/L. The one historic mean from 2005 (0.111 ng/L) had high variance and was similar to the overall mean for the Delta RMP years (0.113 ng/L). The highest means at this station in 2017 and 2019 corresponded to the years classified as wet years.

#### Mokelumne River

Lower Mokelumne River 6 has a relatively good historic time series to go with the Delta RMP data. Within-year and between-year variance have been high at this station. The Delta RMP means were generally higher than the historic means. A linear regression of the time series was not significant (p=0.61). The annual means during the Delta RMP years generally matched water year index (e.g., high means in the wet years of 2017 and 2019), but the historic means did not match water year index (above normal flows in 2000, 2003, and 2005, a dry year in 2000, and a wet year in 2006).

#### West Delta

The Sacramento River at Mallard Island had a more limited dataset under the Delta RMP than most of the other stations (five years) because monitoring began in 2018. The historic time series, however, is relatively strong. Interannual variance at this station was relatively low. Within-year variance was also generally low, but higher in the historic data. A linear regression of the time series was not significant (p=0.23). The Delta RMP data did not show a clear relationship to water year index.

#### Central Delta

The Central Delta subarea included three water stations. No historic data are available for Little Potato Slough. The Delta RMP annual means do not suggest a trend or a relationship to water year index.

Middle River had seven years of data under the Delta RMP and four years of historic data. Inter- and intra-annual variation were generally low, except for one year in the Delta RMP series (2017) and one year in the historic series (2006). Both of these years were classified as wet years. The long-term time series does not suggest a trend.

The Delta-Mendota Canal station only monitored for two years under the Delta RMP. These two annual means were similar to most of the six historic annual means, with an exception in 2006 which had a high mean and high intra-annual variance. The long-term time series does not suggest a trend.

# San Joaquin River

San Joaquin River at Vernalis had a relatively strong time series with seven years of data under the Delta RMP and six years of historic data. Inter- and intra-annual variation were generally high, with particularly high intra-annual variation in 2005 and 2006. The Delta RMP means did not match water year indices well (2018 and 2019 were below normal and wet, respectively). A linear regression on the long-term time series was not significant (p=0.13).

# **Comparative Analysis of Water Year Aqueous MeHg Concentrations**

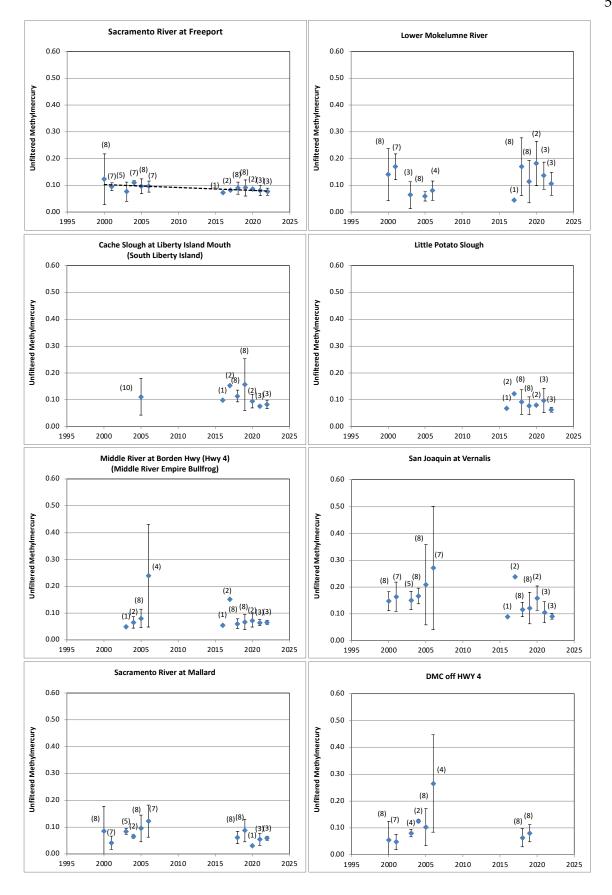
The answer to Delta RMP Management question ST1B is clear: trends over time are different among Delta subareas.

The Delta subareas showed different patterns of seasonal variation in aqueous MeHg concentrations. Unfiltered MeHg concentrations were generally higher in the wet season across all of the stations (Figure 11). The highest unfiltered MeHg concentrations (above 0.30 ng/L) were observed at Lower Mokelumne River, Cache Slough (receives water from Yolo Bypass), and San Joaquin River in the wet season. Increased unfiltered MeHg concentrations were observed during the 2017 high-flow events at San Joaquin River, Middle River, Cache Slough, and Little Potato Slough. Higher concentrations of unfiltered MeHg observed at Lower Mokelumne in March and April 2018 also appear to be related to runoff events as this site also receives water from the undammed Cosumnes River. Stage data for the Cosumnes in March and April 2018 indicate that the river was up to monitoring stage days prior to the water sampling event. These appear to be related to short-duration storms with snow levels of 8000 ft (so the precipitation was mostly rain). Elevated unfiltered MeHg concentrations in the wet season of 2019 at Lower Mokelumne and Cache Slough were also associated with the high flows of a wet winter.

The Delta subareas also showed different patterns of long-term temporal variation (Figure 13). As observed in the fish monitoring, the Lower Mokelumne River and San Joaquin River at Vernalis, in addition to having the highest concentrations, had the highest inter- and intra-annual variation (Figure 11). These stations did not show a long-term trend, but with the observed level of variation a larger dataset would be required to detect such a trend. The same primary driver of interannual variation discussed for the bass - interannual variation in floodplain and wetland inundation - probably also is a major driver of the aqueous concentrations.

Figure 13. Annual mean aqueous unfiltered MeHg concentration (ng/L) at each Delta RMP monitoring station.

Plots based on available March-October data for each calendar year. Error bars show one standard deviation. Number of samples shown in parentheses. Dashed line on Sacramento River at Freeport shows the significant regression line (p=0.02, R<sup>2</sup>=0.41). Figure on next page.



One station did exhibit a long-term trend: the time series for the Sacramento River at Freeport indicates a decline over the 22-year period of record. The bass long-term time series for this station also indicates a significant decline.

Trends were not apparent at the other stations, but this was largely due to the limited number of annual means in the long-term time series.

# **CONCLUSIONS**

From 2016-2022 the Delta RMP designed and implemented a program of mercury monitoring with the goals of answering priority management questions and supporting management of MeHg in the Delta under the TMDL. The design was cost-effective and succeeded in meeting these goals by generating a high-quality dataset on mercury in fish and water, along with a suite of ancillary parameters. The results of the monitoring significantly solidified and advanced understanding of mercury impairment in the Delta.

The mercury monitoring was conducted to address this core management question and related subquestions:

- Is there a problem or are there signs of a problem?
  - a) Is water quality currently, or trending towards, adversely affecting beneficial uses of the Delta?
  - b) Which constituents may be impairing beneficial uses in subregions of the Delta?
  - c) Are trends similar or different across different subregions of the Delta?

A particular emphasis was placed on question c, which was addressed through a program of annual sampling. Another point of emphasis was establishing regional and sub-regional baselines to track the potential influence of large-scale habitat restoration projects. The most notable conclusions of the Delta RMP mercury monitoring and the overall long-term dataset are as follows.

• Length-adjusted mercury concentrations in black bass are an excellent performance measure of progress in addressing MeHg impairment in the Delta. Concentrations in black bass are the ultimate indicator of impairment identified in the TMDL. The Delta RMP dataset adds to a large statewide dataset that demonstrates that length-adjusted mercury in black bass provides a reproducible and reliable indicator of spatial and temporal variation. The black bass element of the Delta RMP mercury monitoring was the most consistent, robust, and spatially extensive effort over the seven years of monitoring, in part because this monitoring is more economical because it requires only one visit per station per year to get the data, and the data are still integrative and representative of conditions at the stations. The black bass sampling was relatively easily expanded to provide more thorough coverage of restoration projects.

- Unfiltered aqueous MeHg is another important performance measure of progress in addressing MeHg impairment in the Delta. These data are important for managing MeHg inputs, and are a key part of the TMDL with their own implementation goal. Water monitoring, however, is less integrative and more variable, and relatively expensive because it requires multiple cruises per year to obtain a representative assessment. A minimal, but still informative, water design was implemented at the beginning and end of the Delta RMP effort, with a two-year intensive phase in 2018 and 2019 that provided valuable data for the TMDL. Filtered MeHg, filtered and unfiltered total mercury, and other ancillary parameters were also measured and the data were summarized in the interpretive report on the first three years of DRMP mercury monitoring (Davis et al. 2021). The monitoring of both unfiltered and filtered MeHg water is important as it allows for the particulate MeHg in water to be determined. The combination of suspended particulate and filtered MeHg water concentrations informs how MeHg is moving through the region and subareas and is useful in understanding bioaccumulation and movement through the food web.
- Mean concentrations of mercury in bass and unfiltered aqueous mercury in water at almost all stations monitored (and therefore in each subarea) exceeded the fish tissue water quality objective and the TMDL implementation goal for aqueous MeHg. Mean concentrations in bass were extremely high in the Mokelumne River subarea (1.25 ppm), over 5 times the bass tissue water quality objective for the Delta (0.24 ppm) and comparable to the 98th percentile of an extensive dataset for length-adjusted black bass in California. The lowest mean concentration for bass was 0.29 ppm at Middle River, with a 95% confidence interval that overlapped the 0.24 ppm water quality objective. All of the other confidence intervals of the bass means exceeded 0.24 ppm. For water, one of the stations had a mean (0.058 ng/L) below the unfiltered aqueous implementation goal of 0.060 ng/L.
- The regional spatial patterns of mercury in black bass and water in the Delta that have been documented in previous studies and the TMDL continue to persist. Concentrations continued to be higher on the northern, eastern, and southern periphery of the Delta, and lower in the Central Delta and West Delta.
- The addition of restoration monitoring stations in 2019 provided for spatial replication within subareas. The general consistency observed across the stations within subareas provided support for the subarea delineations established by the TMDL. The replication also provided further confirmation of the strong patterns of spatial and temporal variation observed in the Delta.
- Annual monitoring of bass and water was enlightening, and provided a much clearer understanding of temporal trends. The answer to the key assessment question that guided the monitoring is that trends over time are very different among Delta subareas.
- High interannual variation was observed in two subareas (Lower Mokelumne River and San Joaquin River). At both of these stations bass mercury concentrations increased from 0.5 ppm to the extremely high level of 1.5 ppm in a one-year period. Significant decreases in

consecutive years were also observed. This information has important implications for monitoring and managing MeHg impairment in the Delta – areas with higher concentrations may be a higher priority for management, and areas with higher variance require more intensive sampling to discern trends.

- Inter- and intra-annual variation was much lower at the other stations, without a suggestion of long-term trend. The two exceptions were the Sacramento River at Freeport station, which exhibited a significant decline in both bass and water, and the Sherman Island station, which had a significant increase in bass.
- A possible driver of the high interannual variation in the Mokelumne River and San Joaquin Rivers subareas, supported by prior work with prey fish by Slotton et al. (2007), is interannual variation in streamflow and flooding of upstream wetlands and floodplains in the Mokelumne River and San Joaquin River watersheds. The timing of the Delta RMP mercury sampling effort was fortuitous for evaluating this hypothesis, as it coincided with extreme hydrologic variation. The responses to high flows in the two areas were different. In the Mokelumne River subarea, bass mercury in this subarea responded within a year to the increased flow and then concentrations remained high for two years after the flows were reduced. The San Joaquin River at Vernalis station had a one-year lag between the high-flow water year and the increase in bass mercury, and the elevated level of bass mercury did not persist for more than one year the correlation between water year index and bass mercury (with a one-year lag) was significant. Sustained annual monitoring, along with better information on hydrology and restoration activity, in these areas would be critical to understanding the causes of the extreme variation.
- The addition of restoration monitoring stations in 2019 helped to establish better baseline information to track the impact of recent and future restoration projects.

# RECOMMENDATIONS

- With the progress that has been made and the evolution of the regulatory process (i.e., the revised TMDL), a reevaluation of the Delta RMP's mercury management and assessment questions and their relative priority is in order. The assessment question framework that was established before the mercury monitoring began indicated that the status and trends questions for MeHg in fish and MeHg in water were to be *initial* priorities.
- Sustained annual monitoring of bass mercury would be the most effective and economical way to continue to determine long-term trends, to track interannual variation and develop an understanding of its drivers, and to assess the influence of the major habitat restoration projects that are being implemented in the Delta.
- A better understanding of the details of hydrology and inundation of floodplains and wetlands, including the effects of intentional and unintentional levee breaches, would be a fundamental component of a conceptual model to explain mercury bioaccumulation in the Mokelumne River, San Joaquin River, and Yolo Bypass South subareas. Gathering this information was beyond the scope of this report.
- The seven-year dataset for black bass can be used to conduct power analysis and design cost-effective longer-term monitoring. This dataset indicates that a simple linear regression analysis may be appropriate for the subareas with low interannual variance, but not for the Mokelumne River and San Joaquin River where pronounced step-changes occur in the time series due to fluctuations in water year type. For these stations, a more elaborate model that includes water year type as a variable will be needed, and along with that a larger dataset will also be needed.
- Ambient water monitoring is valuable given that source monitoring is required for permitted sources. Water monitoring would also be valuable if the Delta RMP prioritizes management questions regarding loading (including control measure effectiveness) or MeHg mass balance. Water data can also support models for forecasting, or mechanistic studies of sources and loadings. Due to seasonal and interannual variability in aqueous MeHg, a robust design for water monitoring, such as the design implemented in 2018 and 2019, would be needed to meaningfully track long-term trends in aqueous MeHg concentrations.

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# Year 5 and 6 Quality Assurance Evaluation Summary

For the Mercury Project During Fiscal Years 2020-21, 2021-22, and 2022-23

March 5, 2025

Prepared By:





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# **ANALYTICAL OVERVIEW**

## **ANALYTICAL LABORATORY METHODS**

The preparation and analytical methods applied to Year 5 and 6 Delta Regional Monitoring Program (DRMP) mercury monitoring project samples are identified in **Table 1**.

Table 1. Analytical laboratory methods for Year 5 and 6 Delta RMP Mercury monitoring.

MATRIX	ANALYTE	LABORATORY	Preparation Method	ANALYTICAL METHOD
Water	Chlorophyll a	MPSL-DFW	EPA 445.0M	EPA 445.0M
Water	DOC	MBAS	None	SM 5310 C
Water	TSS	MPSL-DFW	None	SM 2540 D
Water	VSS	MPSL-DFW	None	SM 2540 E
Water	Mercury	MPSL-DFW	None	EPA 1631EM
Water	Methyl Mercury	MPSL-DFW	None	EPA 1630EM
Tissue - Fish	Mercury	MPSL-DFW	None	EPA 7473

# DATA VERIFICATION OVERVIEW

#### **VERIFICATION PROCESS**

The US Environmental Protection Agency (EPA) defines data verification as the process of evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual specifications. Verification of Delta RMP data was performed by the Surface Water Ambient Monitoring Program (SWAMP) based on the sample handling requirements and measurement quality objectives (MQOs) of Version 2.0 (January 2022) of the Surface Water Ambient Monitoring Program Quality Assurance Program Plan (QAPrP). Qualification of instrument tuning, calibration standards, calibration verifications, and internal standards were the responsibility of the submitting laboratory.

#### **VERIFIED DATASETS**

This report details the above verification process as applied to the analytical batches appearing in **Table 2**. The findings of the data verification process are outlined in the sections below. Percent moisture and age for tissue analyses were not verified since no SWAMP MQOs exist for these analytes.

Table 2. Verified datasets (analytical batches) for Year 5 and 6 Delta RMP Mercury

monitoring.

monito	monitoring.							
LAB	ANALYTICAL	Matrix	DATASETS DATASETS		Reviewed			
LAB	CATEGORY	IVIATRIX	PRODUCED	REVIEWED	DATASET (BATCH) IDS			
MPSL- DFW	Chlorophyll a	Water	7	7	MPSL- DFW_20200923_W_CHL,			
MBAS	DOC	Water	7	7	MBAS_20200924_W_DOC, MBAS_20210316_W_DOC, MBAS_20210427_W_DOC, MBAS_20210816_W_DOC, MBAS_20220322_W_DOC, MBAS_20220419_W_DOC, MBAS_20220825_W_DOC			
MPSL- DFW	TSS	Water	7	7	MPSL- DFW_20200910_W_TSS,			

LAB	ANALYTICAL	MATRIX	DATASETS		REVIEWED
	CATEGORY	1 17 11 117	PRODUCED	REVIEWED	DATASET (BATCH) IDS
MPSL- DFW	VSS	Water	7	7	MPSL- DFW_20200910_W_VSS,
MPSL- DFW	Mercury	Water	8	8	MPSL- DFW_20201102_W_Hg,

LAB	ANALYTICAL CATEGORY	MATRIX	DATASETS PRODUCED		
MPSL- DFW		Water	7	7	MPSL- DFW_20201022_W_MeHg

					MPSL-
					DFW_DMA020822a_T_Hg,
					MPSL-
					DFW_DMA020822b_T_Hg,
					MPSL-
					DFW_DMA021722a_T_Hg,
					MPSL-
					DFW_DMA022222a_T_Hg,
					MPSL-
					DFW_DMA022422a_T_Hg,
					MPSL-
					DFW_DMA022822a_T_Hg, MPSL-
					DFW_DMA030222a_T_Hg,
					MPSL-
					DFW_DMA101920a_T_Hg,
					MPSL-
					DFW_DMA102120a_T_Hg,
					MPSL-
					DFW_DMA102120b_T_Hg,
	Mercury	Tissue		25	MPSL-
MPSL-			25		DFW_DMA102720a_T_Hg,
DFW			25		MPSL-
					DFW_DMA102720b_T_Hg,
					MPSL-
					DFW_DMA110320a_T_Hg,
					MPSL-
					DFW_DMA110520a_T_Hg,
					MPSL-
					DFW_DMA110920a_T_Hg,
					MPSL-DFW_DMA111020a_T_Hg,
					MPSL-
					DFW_DMA111220a_T_Hg,
					MPSL-
					DFW_DMA111620a_T_Hg,
					MPSL-
					DFW_DMA111620b_T_Hg,
					MPSL-
					DFW_DMA121222a_T_Hg,
					MPSL-
					DFW_DMA121222b_T_Hg,
					MPSL-
					DFW_DMA121422a_T_Hg,

LAB	ANALYTICAL	MATDIX	DATASETS		
	CATEGORY		<b>PRODUCED</b>	REVIEWED	DATASET (BATCH) IDS
					MPSL-
					DFW_DMA121622a_T_Hg,
					MPSL-
					DFW_DMA121922a_T_Hg,
					MPSL-
					DFW_DMA121922b_T_Hg

# DATA VERIFICATION: SAMPLE HANDLING

During data verification, storage and holding times of Year 5 and 6 Delta RMP mercury monitoring samples were evaluated to ensure the integrity of the target analyte(s) in each matrix. For consistency with SWAMP and the Code of Federal Regulations, Title 40 *Protection of the Environment*, Section 136 *Guidelines Establishing Test Procedures for the Analysis of Pollutants*, DRMP holding times are defined as follows:

- *Pre-Preservation/Extraction*: Required holding times for sample preservation or extraction begin at the time of sample collection and conclude when the sample is preserved or extracted, respectively.
- *Pre-Analysis*: Required holding times for sample analysis begin either at the time of sample collection, filtration, or extraction and conclude when sample analysis is completed.

For the Year 5 and 6 Delta RMP mercury monitoring, 58 water samples and 463 tissue samples were verified against the sample handling requirements in **Table 3**. All verified samples met these SWAMP requirements.

Table 3. Sample handling requirements defined in the SWAMP QAPrP.

PARAMETER GROUP	Pre-Preser	RVATION/EXTRACTION	Pre-Analysis		
PARAMETER GROUP	Storage	Holding Time	Holding Time	Storage	
Chlorophyll a (Water)	0-6 °C in dark	Filter as soon as possible after collection and freeze with 4 hours of collection	28 days	0-6°C in dark	
DOC (Water)	0-6 °C in dark	Filter and acidify within 48 hours of collection	28 days	0-6 °C in dark	
TSS (Water)	TSS (Water) 0-6 °C in dark C		7 days	0-6 °C in dark	
VSS (Water)	0-6 °C in dark	Cool to 4 ±2°C	7 days	0-6 °C in dark	
Mercury, Dissolved (Water)	0-6 °C in dark	Filter and acidify within 48 hours of collection	90 days	Room Temperature	

PARAMETER GROUP	PRE-PRESER	RVATION/EXTRACTION	Pre-Analysis		
PARAMETER GROUP	Storage Holding Time		Holding Time	Storage	
Mercury, Total (Water)	0-6 °C in Acidify within 48 dark hours of collection		90 days	Room Temperature	
Methyl Mercury, Dissolved (Water)	ry, 0-6 °C in dark  Cool to 4 ±2 immediately collection, filte acidify within of collection		6 months	0-6 °C in dark	
Methyl Mercury, Total (Water) 0-6 °C in dark		Cool to 4 ±2 °C immediately after collection, filter and acidify within 48 hrs of collection	6 months	0-6 °C in dark	
Mercury (Tissue) ≤-20 °C Cool to ≤6 °C within freeze to ≤-20 °C		1 yr	Frozen ≤-20 °C		

# **DATA VERIFICATION: CHEMISTRY**

Delta RMP mercury monitoring chemistry data verification assesses QC samples associated with contamination, precision, and accuracy. For consistency with SWAMP, QC sample definitions in this section are based on the January 2022 QAPrP.

#### CONTAMINATION

For Marine Pollution Studies Laboratory – Department of Fish and Wildlife (MPSL-DFW) and Monterey Bay Analytical Services, Inc. (MBAS) water analyses, contamination is assessed with the analysis of field blanks, equipment blanks, and laboratory blanks. For MPSL-DFW tissue analyses, contamination is assessed with the analysis of laboratory blanks. Associated data verification results are detailed below.

#### Field Blanks

A field blank is a sample of analyte-free media that is transported to the sampling site, exposed to the sampling conditions, returned to the laboratory, and treated as a routine environmental sample. Preservatives, if any, are added to the sample container in the same manner as the environmental sample. The field blank matrix should be comparable to the sample of interest. This blank is used to provide information about contaminants that may be introduced during sample collection, storage, and transport.

For Year 5 and 6 Delta RMP mercury monitoring, one field blank was collected for chlorophyll a and dissolved organic carbon (DOC); seven field blanks were collected for total suspended solids (TSS), volatile suspended solids (VSS), and mercury; and eight field blanks were collected for methyl mercury analyses in water. Of these results, 83.8% (i.e., 26 of 31) met the SWAMP MQO by being below the reporting limit (RL). Field blanks failing the MQO appear in **Table 4**.

**Table 4. Field blank qualification for Year 5 and 6 Delta RMP Mercury monitoring.** Results appearing in this table were all flagged with the QA code: IP.

FIELD BLANK ID	SAMPLE DATE	MATRIX	ANALYTE	SAMPLE RESULT (mg/L)	RL (mg/L)
FieldQA_SWAMP	8/8/2022	Water	DOC	0.3	0.3
FieldQA_SWAMP	9/8/2020	Water	Mercury, Dissolved	0.686 ng/L	0.387 ng/L
FieldQA_SWAMP	3/8/2022	Water	TSS	0.145	-88
FieldQA_SWAMP	3/8/2022	Water	VSS	0.145	-88
FieldQA_SWAMP	4/4/2022	Water	TSS	0.068	-88

# **Equipment Blanks**

An equipment blank is a sample of analyte-free media that has been used to rinse the sampling equipment. It is collected after completion of decontamination and prior to sampling through clean equipment. This blank is useful in documenting adequate decontamination of sampling equipment and is used to provide information about contaminants/bias that may be introduced during sample collection when using filtration equipment or equipment that must be decontaminated between use.

For Year 5 and 6 Delta RMP mercury monitoring, five equipment blanks were collected for chlorophyll a and mercury in water, and six equipment blanks were collected for DOC and methyl mercury analyses in water. Of these results, 59% (i.e., 13 of 22) met the SWAMP MQO by being below the RL. Equipment blanks failing the MQO appear in **Table 5**.

Table 5. Equipment blank qualification for Year 5 and 6 Delta RMP Mercury monitoring. Results appearing in this table were all flagged with the QA code: IP.

1100 and 0 app out 110 and 110									
FIELD BLANK ID	SAMPLE DATE	MATRIX	ANALYTE	SAMPLE RESULT (mg/L)	RL (mg/L)				
FieldQA_SWAMP	3/10/2021	Water	DOC	0.3	0.3				
FieldQA_SWAMP	4/13/2021	Water	DOC	0.4	0.3				
510ST1317	8/9/2021	Water	DOC	0.6	0.3				
FieldQA_SWAMP	4/4/2022	Water	DOC	0.2	0.3				
FieldQA_SWAMP	3/10/2021	Water	Mercury, Dissolved	0.726 ng/L	0.606 mg/L				

# Laboratory Blanks

A laboratory blank is free from the target analyte(s) and is used to represent the environmental sample matrix as closely as possible. The laboratory blank is processed simultaneously with and under the same conditions and steps of the analytical procedures (e.g., including exposure to all glassware, equipment, solvents, reagents, labeled compounds, internal standards, and surrogates that are used with samples) as all samples in the analytical batch (including other QC samples). The laboratory blank is used to determine if target analytes or interferences are present in the laboratory environment, reagents, or instruments. Results of laboratory blanks provide a measurement of bias introduced by the analytical procedure.

For Year 5 and 6 Delta RMP mercury monitoring, laboratory blanks were prepared and analyzed for all DOC, TSS, VSS, mercury, and methyl mercury water batches. Laboratory blanks were analyzed at the required frequency of one per 20 samples or per batch (whichever is more frequent). Of these results, 95.2% (i.e., 99 of 104) met the SWAMP MQO by being below the RL. Laboratory blanks failing the MQO appear in **Table 6**.

Table 6. Laboratory blank qualification for Year 5 and 6 Delta RMP Mercury monitoring.

Results appearing in this table were all flagged with the QA code: IP.

DATASET ID	LAB BLANK ID MATRIX		ANALYTE	BLANK RESULT	I KI	
MPSL- DFW_20200910_W_VSS	MB1	Water	VSS	2.8	4.054	mg/L
MPSL- DFW_20200910_W_VSS	MB2	Water	VSS	2	4.054	mg/L
MPSL- DFW_20211001_W_Hg	MB2	Water	Mercury, Total	0.216	0.606	ng/L
MPSL- DFW_20220310_W_VSS	MB2	Water	VSS	0.2	-88	mg/L
MPSL- DFW_20220407_W_TSS	MB2	Water	VSS	0.205	-88	mg/L

For Year 5 and 6 Delta RMP mercury monitoring, laboratory blanks were prepared and analyzed for all mercury tissue batches. Laboratory blanks were analyzed at the required frequency of one per 20 samples or per batch (whichever is more frequent). All of these results (i.e., 75 of 75) met the SWAMP MQO by being below the RL.

#### **PRECISION**

For MPSL-DFW and MBAS water analyses, precision is studied with field duplicates, laboratory duplicates, matrix spike (MS) duplicates (MSDs), and/or laboratory control spike duplicates (LCSDs). For MPSL-DFW tissue analyses, precision is studied with laboratory duplicates, MSs, and MSDs. Associated data verification results are detailed below.

# Field Duplicates

A field duplicate is an independent sample that, as closely as possible, utilizes the same sampling location, time, and methodology as the field sample.

For Year 5 and 5 Delta RMP mercury monitoring, seven field duplicates collected and analyzed for chlorophyll a, DOC, TSS, VSS, mercury, and methyl mercury appear in **Table 7**.

Table 7. Field duplicates for Year 5 and 6 Delta RMP Mercury monitoring.

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DUPLICATE ID	SAMPLE DATE	MATRIX	ANALYTE					
544ADVLM6	9/8/2020	Water	Chlorophyll a, DOC, TSS, VSS, Mercury, Methyl Mercury					
541SJC501	3/11/2021	Water	Chlorophyll a, DOC, TSS, VSS, Mercury, Methyl Mercury					
510ST1317	4/12/2021	Water	Chlorophyll a, DOC, TSS, VSS, Mercury, Methyl Mercury					
544ADVLM6	8/10/2021	Water	Chlorophyll a, DOC, TSS, VSS, Mercury, Methyl Mercury					
544LILPSL	3/7/2022	Water	Chlorophyll a <sup>1</sup> , DOC, TSS <sup>1</sup> , VSS <sup>1</sup> , Mercury, Methyl Mercury					
541SJC501	4/5/2022	Water	Chlorophyll a <sup>1</sup> , DOC, TSS <sup>1</sup> , VSS <sup>1</sup> , Mercury, Methyl Mercury					
510ADVLIM	8/9/2022	Water	Chlorophyll a, DOC, TSS, VSS, Mercury <sup>1</sup> , Methyl Mercury <sup>1</sup>					
1 A I		: LIOA CIATAD:						

<sup>&</sup>lt;sup>1</sup> Analyses were reported under duplicate ID FieldQA\_SWAMP in the dataset

All field duplicate results met the SWAMP MQO by having a relative percent difference (RPD) <25% (n/a if concentration of either sample <RL).

# **Laboratory Duplicates**

A laboratory duplicate is an analysis or measurement of the target analyte(s) performed identically on two sub-samples of the same sample, usually taken from the same container. The results from laboratory duplicate analyses are used to evaluate analytical or measurement precision, and include variability associated with sub-sampling and the matrix (not the precision of field sampling, preservation, or storage internal to the laboratory).

For Year 5 and 6 Delta RMP mercury monitoring, chlorophyll a, DOC, TSS, VSS, mercury, and methyl mercury water laboratory duplicates were analyzed at the required frequency of one per 20 samples or per batch (whichever is more frequent).

For the laboratory duplicates, 84.8% (i.e., 28 of 33) of laboratory duplicate results met the SWAMP MQO by having an RPD <25% (n/a if concentration of either sample <RL). Laboratory duplicates failing the MQO appear in **Table 8**.

Table 8. Laboratory duplicate precision qualification for Year 5 and 6 Delta RMP Mercury monitoring.

Results appearing in this table were all flagged with the QA code: IL.

DATASET ID	DUPLICATE ID	Analyte	MATRI X	SAMPL E RESUL T (mg/L)	DUPLICAT E RESULT (mg/L)	RP D
MPSL- DFW_20200910_W_V SS	510ADVLI M	Volatile Suspended Solids	Water	2.236	ND	200
MPSL- DFW_20210415_W_V SS	207SRD10 A	Volatile Suspended Solids	Water	6.429	9.783	41. 4
MPSL- DFW_20210813_W_V SS	544ADVLM 6	Volatile Suspended Solids	Water	3.488	2.655	27. 1
MPSL- DFW_20220811_W_V SS	510ST1317	Volatile Suspended Solids	Water	1.06	0.665	45. 6
MPSL- DFW_20220407_W_V SS	207SRD10 A	Volatile Suspended Solids	Water	4.67	3.13	39. 7

For Year 5 and 6 Delta RMP mercury monitoring, mercury tissue laboratory duplicates were analyzed at the required frequency of one per 20 samples or per batch (whichever is more frequent). All of these results (i.e., 32 of 32) met the SWAMP MQO by having an RPD <25% (n/a if concentration of either sample <RL).

# Matrix Spike Duplicates

An MSD is prepared with an MS. Both the MS and MSD samples are analyzed exactly like an environmental sample within the laboratory batch. The purpose of analyzing the MS and MSD samples is to determine whether the sample matrix contributes bias to the analytical results, and to measure precision of the duplicate analysis.

For Year 5 and 6 Delta RMP mercury monitoring, eight DOC and 14 mercury and methyl mercury MSD pairs were prepared and analyzed in water at the required frequency of one per batch. All water MSD results (i.e., 36 of 36) met the SWAMP MQO by having an RPD <25%.

For Year 5 and 6 Delta RMP mercury monitoring, 29 mercury MSD pairs were prepared and analyzed in tissue at the required frequency of one per batch. All tissue MSD results (i.e., 58 of 58) met the SWAMP MQO by having an RPD <25%.

# Laboratory Control Spike Duplicates

An LCSD is prepared with an LCS. The LCS and LCSD are a sample matrix representative of the environmental sample (e.g., water, sand) that is prepared in the laboratory and is free from the analytes of interest. The LCSD is spiked with verified amounts of analytes or a material containing known and verified amounts of analytes. It is either used to establish intra-laboratory or analyst-specific precision and bias, or to assess the performance of a portion of the measurement system.

For Year 5 and 6 Delta RMP mercury monitoring, seven LCSD pairs were prepared and analyzed for DOC. All LCSD results (i.e., **14 of 14**) met the Delta RMP MQO by having an RPD <25%.

#### **ACCURACY**

For MPSL-DFW and MBAS water analyses, accuracy is studied with the analysis of MSs, LCSs, and certified reference materials (CRMs). For MPSL-DFW tissue analyses, accuracy is studied with the analysis of MSs and CRMs. Associated data verification results are detailed below.

# Matrix Spikes

An MS is a sample prepared by adding a known amount of the target analyte to an environmental sample in order to increase the concentration of the target analyte. The MS is used to determine the effect of the matrix on a method's recovery efficiency and is a measure of accuracy. The MS is analyzed exactly like an environmental sample within the laboratory batch. The purpose of analyzing the MS is to determine whether the sample matrix contributes bias to the analytical results.

For Year 5 and 6 Delta RMP mercury monitoring, eight DOC and 14 mercury and methyl mercury MSD pairs were prepared and analyzed in water at the required frequency of one per batch. Of these results, 93.0% (i.e., 67 of 72) met the 80-120% recovery MQO for chlorophyll a and DOC and the 75-125% recovery MQO for methyl mercury. MSs and MSDs failing the MQO appear in **Table 9**.

Table 9. Matrix spike qualification for Year 5 and 6 Delta RMP Mercury monitoring. Results appearing in this table were all flagged with the QA code: GB.

DATASET ID		ANALYTE			PK	MSD PR	RPD
MBAS_20200924_W_DOC	541SJC501	DOC	Water	mg/L	72	69	3.6
MBAS_20210316_W_DOC	207SRD10A	DOC	Water	mg/L	49	40	10.0
MBAS_20220825_W_DOC	000NONPJ	DOC	Water	mg/L	126	111	4.7

For Year 5 and 6 Delta RMP mercury monitoring, 29 mercury MSD pairs were prepared and analyzed in tissue at the required frequency of one per batch. All of these results (i.e., 58 of 58) met the 75-125% recovery MQO.

# **Laboratory Control Spikes**

An LCS is a sample matrix representative of the environmental sample (e.g., water, sand) that is prepared in the laboratory and is free from the analytes of interest. The LCS is spiked with verified amounts of analytes or a material containing known and verified

amounts of analytes. It is either used to establish intra-laboratory or analyst-specific precision and bias, or to assess the performance of a portion of the measurement system.

For Year 5 and 6 Delta RMP mercury monitoring, 23 LCSs and seven LCS/LCSDs were prepared and analyzed for chlorophyll a, DOC, and methyl mercury water batches at the required frequency of one per batch. Of these results, 89% (i.e., 33 of 37) met the 80-120% recovery MQO for chlorophyll a and DOC and the 75-125% recovery MQO for methyl mercury. LCSs failing the MQO appear in **Table 10**.

Table 10. Laboratory control spike qualification for Year 5 and 6 Delta RMP Mercury monitoring.

Results appearing in this table were all flagged with the QA code: EUM.

DATASET ID	LCS ID	MATRIX	ANALYTE	LCS PR
MBAS_20210316_W_DOC	LCSL	Water	DOC	198
MBAS_20210427_W_DOC	LCSL	Water	DOC	154
MBAS_20220322_W_DOC	LCSL	Water	DOC	127
MBAS_20200924_W_DOC	LCSL	Water	DOC	130

#### Certified Reference Materials

A CRM or substance has one or more properties that are characterized by a metrologically valid procedure, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability (typically from EPA or the National Institute of Science and Technology). CRMs are used for calibrating an apparatus, assessing a measurement method, or assigning values to materials (FEM Glossary, 2017). CRMs are used to measure the accuracy of analytical processes, either quantitatively to calibrate or determine concentration accuracy, or qualitatively to identify a substance or species

For Year 5 and 6 Delta RMP mercury monitoring, eight CRMs were prepared and analyzed for DOC, mercury, and TSS at the required frequency (i.e., of one per batch for DOC and mercury, per the method for TSS). All of these results (i.e., 24 of 24) met the 80-120% recovery MQO for DOC, the 75-125% recovery MQO for mercury, and the 75-125% method recovery MQO for TSS.

For Year 5 and 6 Delta RMP mercury monitoring, 25 CRMs were prepared and analyzed for mercury in tissue at the required frequency of one per batch. All of these results (i.e., 25 of 25) met the 75-125% recovery MQO.

# **SUMMARY**

#### **CHEMISTRY RESULTS**

As detailed in **Table 11**, a total of 521 environmental samples were collected and analyzed for Year 5 and 6 Delta RMP mercury monitoring. These samples consisted of 58 environmental water and 463 environmental tissue samples that were analyzed by MPSL-DFW for Chlorophyll a, TSS, VSS, mercury, and methyl mercury; and by MBAS for DOC. Depending on constituent group, each set of environmental samples was accompanied by up to seven water field duplicates, up to eight water field blanks, and up to six water equipment blanks. No field QC samples were required for fish tissues collections. A total of 542 samples were submitted to the laboratories for analysis.

Table 11. Summary of field sample collections for Year 5 and 6 Delta RMP Mercury

monitoring.

CONSTITUENT GROUP	LABORAT ORY	MATRIX	ENVIRONMENTAL SAMPLES	FIELD DUPLICATE	EQUIPM ENT BLANK	FIELD BLANK	TOTAL SAMPLES
Chlorophyl a	MPSL- DFW				5	1	
TSS	MPSL- DFW				0	7	
VSS	MPSL- DFW	Water	58	7	0	7	79
Mercury	MPSL- DFW			,	5	7	
Methyl Mercury	MPSL- DFW				6	8	
DOC	MBAS				6	1	
Mercury	MPSL- DFW	Fish Tissue	463	0	0	0	463
Total		521	7	6	8	542	

A total of 1,415 tissue and water environmental and QC sample results for chlorophyll a, DOC, TSS, VSS, mercury, and methyl mercury were verified as a part of the Year 5 and 6 mercury monitoring dataset (**Table 11**). Of those, 1,386 met SWAMP QAPrP MQOs.

# **DATA AVAILABILITY**

Mercury Year 5 and 6 data will be published to CEDEN for ambient locations and can be accessed through the Advance Query Tool

(https://ceden.waterboards.ca.gov/AdvancedQueryTool) under the project names (project code): 2020 Delta RMP Mercury (20DRMP5HG), 2021 Delta RMP Mercury (21DRMP5HG), 2022 Delta RMP Mercury (22DRMP5HG), 2020 Delta RMP Wetland Restoration Fish Mercury (20DRMP5REST), 2021 Delta RMP Wetland Restoration Fish Mercury (21DRMP5REST), 2022 Delta RMP Wetland Restoration Fish Mercury (22DRMP5REST).