Mercury and Methylmercury in Fish and Water from the Sacramento-San Joaquin Delta:

Interpretive Report on the First Three Years of Monitoring

(August 2016 – October 2019)

by the

Delta Regional Monitoring Program

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Appendices

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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. In August 2016 the Delta Regional Monitoring Program (Delta RMP) began monitoring MeHg and related parameters at stations within most of the Delta subareas defined by the Methylmercury TMDL for the Delta. This monitoring was conducted to provide information needed to support the reevaluation of the implementation of the TMDL, as well as support future implementation of the TMDL and a process to reevaluate the TMDL. The Delta RMP established management questions and assessment questions for the MeHg monitoring program. This report presents the findings from the first three years of Delta RMP MeHg monitoring in the form of answers to those assessment questions. Recommendations for future monitoring based on the findings from this initial period are also presented.

Are trends over time in MeHg in sport fish similar or different among Delta subareas?

The first three years of Delta RMP monitoring of MeHg in black bass, combined with historic data from nearby stations, provide clear evidence that trends over time do vary among Delta subareas. Delta subareas fall into two sets with regard to temporal variation and trends. One set of subareas exhibited relatively low interannual and intra-annual variance from 2016-2019 and throughout the long-term time series, and no indication of a long-term trend. This set includes Sacramento River, Yolo Bypass-South, Central Delta, and West Delta. The other set of subareas (Mokelumne River and San Joaquin River) exhibited high interannual and intra-annual variance in 2016-2019 and throughout the long-term time series. Extremely high concentrations that are of high concern to both humans and wildlife were observed in these subareas, apparently in response to high flows in their watersheds (although levee breaches as part of wetland restoration in the Mokelumne River watershed may also play a role).

Are trends over time in MeHg in water similar or different among Delta subareas?

Delta subareas show different patterns of seasonal and interannual variation in aqueous MeHg concentrations, but are similar in exhibiting a lack of long-term trend over the past 20 years. Unfiltered MeHg concentrations were generally higher in the wet season across all of the stations, and the highest concentrations occurred during high flow events. Seasonal variation was relatively lower in the Sacramento River and Central Delta subareas, and relatively higher in the Mokelumne River, Yolo Bypass South, and San Joaquin River subareas.

What are the loads from tributaries to the Delta?

The aqueous MeHg concentration data obtained from the first three years of Delta RMP monitoring, along with concurrent flow rate estimates, will make it possible to construct an updated MeHg mass budget for the Delta. The monitoring period included both wet and dry years. However, at the time of this report an updated water budget for the Delta is not yet available and therefore an updated mass budget is not presented.

What is the relationship between MeHg in black bass and MeHg in water?

The linkage analysis in the TMDL established a clear relationship between MeHg in largemouth bass and unfiltered aqueous MeHg, but was based on limited datasets for bass and water. Although not addressing an explicit RMP assessment question, one of the objectives of the Delta RMP mercury monitoring has been to develop an expanded and current dataset on the linkage of MeHg concentrations in bass and water. A robust dataset on concentrations in bass and water from 2018 and 2019 exhibited a very similar relationship to that observed in 2000, supporting the implementation goal for aqueous MeHg of 0.06 ng/L presented in the TMDL. A narrower window of water data (May-August instead of the March-October window used in the TMDL) resulted in an even stronger overall regression for the linkage analysis.

Recommendations for Future Mercury Monitoring

With the progress made in answering the assessment questions, a reevaluation and refinement of the assessment questions and their relative priority is in order. The original assessment question framework indicated that the status and trends questions for MeHg in fish and MeHg in water were to be *initial* priorities. The Delta RMP committees have already decided to prioritize questions related to the impact of wetland restoration projects, approving the addition of a prey fish and additional black bass MeHg monitoring element in year 4 while reducing the collection of water samples and the overall mercury monitoring budget.

At the outset of Delta RMP mercury monitoring, an initial period of 10 years of annual Delta RMP black bass monitoring was envisioned, and this still appears to be an appropriate plan. The monitoring conducted to date has provided further evidence of the value of this indicator: it has confirmed spatial patterns observed in prior studies, documented extremely high concentrations and interannual variation in two subareas, and generated preliminary hypotheses regarding drivers of temporal variation. The cost of the annual black bass monitoring is relatively low for a high yield of information. A 10-year dataset would firmly establish baseline conditions for this critical impairment indicator and provide robust estimates of intra-annual and interannual variance that can be used to conduct power analyses and design cost-effective longer-term monitoring.

Acquiring data for the TMDL reevaluation was a key driver for aqueous monitoring. Now having met that goal, the need for continued monitoring of aqueous mercury is under consideration. Continued aqueous mercury monitoring will strengthen the dataset available for answering all four major categories of Delta RMP assessment questions: status and trends; sources, pathways, loadings, and processes; forecasting scenarios; and effectiveness tracking. One impetus for continued water monitoring is to generate data to support the mercury models for the Delta that are in development by the California Department of Water Resources. An additional impetus is evaluation of how large-scale wetland restoration in the Delta and climatic variation may affect the MeHg linkage between water and biota. The three-year dataset provides evidence that water sampling at many of the sites can be substantially reduced without sacrificing the ability to obtain good estimates of annual mean MeHg concentrations. Ancillary data were evaluated for value in predicting MeHg concentrations. Although significant positive correlations were found between some ancillary measurements and MeHg, predictive power was weak.

I. Introduction

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 (Wood et al. 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 2. In addition, as an ancillary benefit, the monitoring would also assist in providing information to support reevaluation of the TMDL.

The Delta RMP established management and assessment questions for the MeHg monitoring program (Table 2). 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.

The Delta RMP addressed the following management and assessment questions for MeHg in the first three years of monitoring.

- 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?
    - ST1 - What are the status and trends in ambient concentrations of total mercury and methylmercury 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 methylmercury concentrations in fish in the Delta?
- Effectiveness Tracking
    - No specific assessment questions have been articulated for this topic.

The Delta RMP has been monitoring MeHg concentrations in black bass[1] (Table 1) as the most important performance measure of progress in addressing MeHg impairment in the Delta. Delta RMP bass monitoring is addressing all of the categories of mercury management questions articulated by the Delta RMP (Table 2). The Methylmercury TMDL provides important context for addressing the RMP management and assessment questions. The TMDL established three water quality objectives for MeHg in fish tissue:

- 0.24 µg/g, or parts per million (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 an implementation goal 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. Largemouth 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

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[1] Total mercury in fish is actually 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*).

foundation for the development of the TMDL, including the division of the Delta into eight subareas (Figure 1).

The Delta RMP has also been monitoring MeHg concentrations in water (Table 1) as another important performance measure of progress in addressing MeHg impairment in the Delta. Delta RMP aqueous MeHg and THg monitoring is addressing all of the categories of mercury management questions articulated by the Delta RMP (Table 2). 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 development of models to forecast the response to different management scenarios (FS1). In addition, coordinated collection of bass and water data allows for further assessment of the linkage between these two matrices, which was identified in Mercury Subcommittee discussions as a priority information need.

Sediment monitoring was also conducted in year 2 only, but not continued after that due to funding limitations and the lower relative priority of this monitoring element (Table 1).

To date, the Delta RMP has completed three years of MeHg monitoring and documented the results in three annual data reports (Davis et al. 2018, 2021a,b). In 2019, the Water Board began to reevaluate the TMDL. This report is intended to provide an interpretive summary of the first three years of Delta RMP MeHg monitoring to, as a primary objective, address the management and assessment questions and, as a secondary objective, inform the reevaluation of the TMDL. This report presents the findings from the first three years of Delta RMP MeHg monitoring in the form of answers to the management and assessment questions addressed. Answers to the questions identified by the Delta RMP as high priorities for initial monitoring (ST1A and ST1B) are provided to the extent possible. The progress toward answering question SPLP1A is also described, as this is a priority for TMDL reevaluation. An updated assessment of the correlation (linkage) between fish and water concentrations, which was identified by the Water Board in Mercury Subcommittee discussions as another priority element of TMDL reevaluation, is also provided. Progress and plans for addressing the questions that were not high priorities for this first three years of Delta RMP mercury monitoring are also provided in the Section 6.

II. Are trends over time in MeHg in sport fish similar or different among Delta subareas?

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

- ST1.A. Are trends over time in MeHg in sport fish similar or different among Delta subareas?

Question ST1A is a high priority for managers and the Delta RMP (Table 2) that relates to the TMDL and has been a primary focus of the sampling design for fish monitoring. To address Question ST1A, the Delta RMP is conducting annual monitoring of MeHg 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.

Six 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. In addition to total mercury in muscle fillets, parameters measured include: total length, fork length, weight, sex, moisture, and estimated age based on scale analysis.

The first three years of Delta RMP monitoring of MeHg in black bass, combined with historic data from nearby stations (Figure 2 – Figure caption provides details on the historic data included), have provided a clear answer to this assessment question: trends over time do vary among Delta subareas. 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.

The black bass monitoring stations are spread across the subareas, with one station per subarea (Figure 1). The exceptions are the Central Delta, which has two stations (Little Potato Slough and Middle River at Borden Highway), and the Marsh Creek and Yolo Bypass North subareas, which have no stations. The Marsh Creek and Yolo Bypass North subareas are not covered by Delta RMP mercury monitoring and consequently are also not covered by this report. The stations are intended to represent each monitored subarea. More intensive monitoring in the past that has shown a consistent spatial pattern across the Delta supports this approach (Grenier et al. 2007, Davis et al. 2008, Melwani et al. 2008). Sampling one black bass station per subarea was also considered the best use of limited monitoring funds.

Long-term time series of estimated annual mean concentrations in black bass are presented in Figure 2. 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 data for each station in each year, the regression results, and details of the length-adjustment method are provided in the annual data reports for the Delta RMP mercury monitoring (Davis et al. 2018, 2021a,b). 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*years where the linear regression of length:MeHg was significant and a 350 mm length-adjusted mean concentration could be calculated (solid symbols in Figure 2). Most of the station means in the four years of Delta RMP sampling could be calculated this way. The level of uncertainty is generally higher for station*years where the length:MeHg 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*years a simple mean of legal-sized bass (>305 mm) was calculated. The error bars in Figure 2 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. The Sherman Island station only has two recent data points because it was added in 2018.

As background prior to the discussion of interannual trends in the following paragraphs, it is worth noting that the regional spatial pattern of MeHg 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 2016-2019 were higher on the northern, eastern, and southern periphery, and lower in the Central Delta and West Delta (Table 3, Figure 3). Concentrations in 2016-2019 were generally similar to the 2000 length-adjusted concentrations that were used to summarize subarea impairment status in the TMDL report (Table 3, last column), however, the mean concentrations for 2016-2019 were higher than the 2000 values in the Central Delta and the West Delta. In 2000, the Central Delta had a mean concentration (0.19 ppm) that was below the implementation goal for 350 mm bass of 0.24 ppm, but the mean for 2016-2019 (0.31 ppm) was above the goal. In 2016 the mean concentration for the Central Delta (0.23 ppm) was below the goal, but the means were above the goal in the following three years (Figure 2).

The Delta RMP data for 2016-2019, 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 and intra-annual variance from 2016-2019 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 2016-2019, mean concentrations at each of these stations fluctuated within a 0.2 ppm range. Two of the stations (Little Potato Slough and Middle River at Borden Highway) did show low magnitude but significant interannual variation in 2016-2019, as indicated by the non-overlapping error bars in Figure 2. Over the longer term, none of these time series is indicative of a distinct trend.

The other set of stations (Lower Mokelumne River 6 and San Joaquin River at Vernalis) exhibited high interannual and intra-annual variance in 2016-2019 and throughout the long-term time series. Mean bass MeHg at Lower Mokelumne River 6 in 2016 (0.57 ppm) was at the low end of the historic range for this station. The mean concentration was much higher in 2017 (1.37 ppm), and remained above this level in 2018 (1.47 ppm) and 2019 (1.55 ppm). The 2017-2019 concentrations are comparable to some of the highest station means observed in extensive statewide monitoring of black bass by the Surface Water Ambient Monitoring Program (Davis et al. 2019): only two of 194 lakes sampled have had mean concentrations above 1.2 ppm. Mean bass MeHg at San Joaquin River at Vernalis in 2016 (0.27 ppm) was the lowest observed in the long-term time series for this station. The estimated mean concentration was higher in 2017 (0.53 ppm), then sharply higher in 2018 (1.46 ppm), then back down to 0.62 ppm in 2019.

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 (Figures 4-6). During this same time period, no increases were observed at stations in the Yolo Bypass-North, Yolo Bypass-South, and Central Delta subareas (Figure 4). Concentrations in Mississippi silverside, one of the primary indicator species in the Slotton et al. study, fell back to pre-July levels by the next round of sampling in November 2006. On the other hand, concentrations in other species, including young-of-the-year largemouth bass and bluegill, remained elevated through November 2006. Monitoring of Mississippi silverside continued into 2007, a dry water year, and found concentrations at Cosumnes River that were lower than all of the results for 2006, while concentrations at San Joaquin River at Vernalis were similar to the non-July values for 2006 (Figure 7). Overall, Slotton et al. documented the time-course 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 prey fish MeHg. Water and fish datasets for the San Joaquin River at Vernalis in 2005 and 2006 provided a specific example of this (Figure 8; Janis Cooke, Central Valley Regional Water Board, personal communication).

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 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.

Like water year 2006, water year 2017 was classified as a wet year, ending a five-year drought. The previous findings and interpretation of data from the Mokelumne by Slotton et al. (2007) suggest the strong possibility that the marked increase in mean MeHg concentration at Lower Mokelumne River 6 in the summer of 2017 was related to the high flows in the preceding wet winter. However, water year 2018 had below normal flows (WY Index = 7.2; the Sacramento Valley Index was used in the absence of an index for the Mokelumne/Cosumnes River watershed), yet concentrations in bass at Lower Mokelumne River 6 remained very high (1.47 ppm) in that year, suggesting a lack of correlation. Flows were again high in 2019 (WY Index = 10.2), and bass MeHg was once again very high (1.55 ppm). 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 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 clear relationship between bass MeHg and flow in the preceding winter (Figure 9a). 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). The possibility of a one-year lag between the high flows and the increase in bass MeHg was also explored (Figure 9b). The regression line had a higher R^2 and lower p-value (p=0.10), but was not significant at alpha=0.05.

The relationship between bass MeHg and water year was also examined for San Joaquin River at Vernalis, and a significant relationship was observed between bass MeHg and the water year index from the previous water year. The regression between bass MeHg and current water year index was nowhere close to significance, but the relationship between bass MeHg and previous year water year index was strong ($R^2 = 0.67$, $p = 0.01$) (Figure 10a,b).

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 water year type as a driver of temporal variation in fish MeHg in these subareas. The relationship appears to be weaker at Lower Mokelumne River 6 (but might be improved by using a specific water year index for the Cosumnes, if one were available), and significant at San Joaquin River at Vernalis. 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).

III. Are trends over time in MeHg in water similar or different among Delta subareas?

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

ST1.B. Are trends over time in MeHg in water similar or different among Delta subareas?

Water was collected from the Delta, at a regional scale, to support questions ST1 (section II above), ST1.B., and SPLP1 (section IV below).

The number of stations and timing of water sample collections both increased significantly in the second and third year of monitoring (Table 1) resulting in an expanded spatial and temporal water dataset better suited to answer management questions as well as aiding outside efforts (e.g. re-opening of the TMDL). Water monitoring at the Lower Mokelumne River station was not included in year 1 due budget limitations. 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). A YSI multimeter was used to measure temperature, pH, dissolved oxygen, specific conductivity, and turbidity. In addition, oxygen percent saturation and salinity values were calculated by the multimeter and recorded in the field.

Background on Interannual Variation in Hydrology

MeHg cycling in the Delta is strongly influenced by seasonal and annual variation in hydrology (Foe et al., 2008). Water year is defined by the calendar year in which it ends and runs October 1st to September 30th. The data presented here span the tail end of water year 2016 to the first month of water year 2020. Table 4 lists water year hydrologic classification from 2015 to 2019 for the Sacramento and San Joaquin valleys.

According to DWR (2017a), water year 2015 marked the 4th year of drought in California and was characterized by record high temperatures, record low precipitation, and a record low snowpack. While water year 2016 was expected to be a strong wet El Niño year, many of the predicted characteristics of an El Niño year did not materialize. Air temperatures were above normal as was precipitation in the northern Sierra Nevada with the majority of the winter's rain falling in January and March (DWR 2017a). However, statewide snowpack was below average and impacted snowmelt and streamflow with the Sacramento and San Joaquin Rivers 32% and 22% below average respectively (DWR 2017a). Water year classification for the Sacramento River system was classified as "below normal" and "dry" for the San Joaquin River even as the overall 2016 water year was an improvement over previous drought years (DWR 2017a).

Water year 2017 ended California's five-year drought, coming in at second place for statewide runoff over the period of record, behind the wettest year (1983) on record since 1895. Most of the state experienced at least average precipitation and key Sierra Nevada watersheds were well above average (DWR 2017b). Water year 2017 continued the trend of warmer statewide temperatures which began in the 1980s (DWR 2017b). A large number of atmospheric rivers made landfall in water year 2017 with the west coast as a whole experiencing 53 events (DWR 2017b).

Water year 2018 marked a return to dry conditions for the state of California with most of the state experiencing below average precipitation (DWR, 2018). Record setting high temperatures continued and snowpack was 58% of normal as much of the precipitation fell as rain rather than snow (DWR 2018). Water year 2018 was classified as below normal for both the Sacramento and San Joaquin systems.

Water year 2019 was characterized by a continuation of climate change effects in the form of greater variability and more extremes (DWR 2019). A dry fall transitioned into wet winter with atmospheric rivers causing both flooding and heavy snow pack (DWR 2019). Water year 2019 was classified as wet for both Sacramento and San Joaquin valleys. The water year ended with 139% of average precipitation in the Northern Sierra and 168 % of average April-July streamflow in the Sacramento River and 171% of average for the San Joaquin River (DWR 2019). Snowpack was 175% of average marking the fifth largest snowpack with records dating back to 1950 (DWR 2019).

Aqueous MeHg Trends

Delta subareas show different patterns of seasonal and interannual variation in aqueous MeHg concentrations across Delta subareas. Although it appears Delta subareas lack a long-term trend in unfiltered MeHg water concentrations over the past 20 years the limited data set at Little Potato Slough and a 10-year data gap for all other sites leaves this question unanswered.

Figure 11 shows unfiltered and filtered MeHg concentrations for each station sampled. This provides a regional picture of seasonal MeHg trends and shows the complete Delta RMP aqueous MeHg dataset up to October 2019. 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 subregions as well as implications for bioaccumulation and movement through the food web.

Unfiltered MeHg concentrations were generally higher in the wet season across all of the stations. 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.

On a regional scale filtered MeHg accounted for approximately 57% of the total unfiltered MeHg concentration in Delta waters which similar to previously reported data (Choe and Gill, 2003) (Figure 12). At sub regional scale the dominant fraction (filtered or particulate) of MeHg varied. At Mallard particulate bound MeHg accounted for 60% of the total unfiltered MeHg ($n = 20$; $r^2 = 0.96$). Freeport, Cache Slough, and San Joaquin River particulate and filtered fraction were similar as filtered water fraction of MeHg accounted for 49% ($n = 25$; $r^2 = 0.93$), 50% ($n = 25$; $r^2 = 0.91$), and 52% of the total unfiltered water MeHg ($n = 25$; $r^2 = 0.97$) respectively. Mokelumne River, Potato Slough, Middle River, and DMC had filtered MeHg as the dominate water fraction with 60% ($n = 21$; $r^2 = 0.99$), 70% ($n = 25$; $r^2 = 0.98$), 70% ($n = 25$; $r^2 = 0.98$), and 72% ($n = 20$; $r^2 = 0.97$) of the unfiltered MeHg water respectively.

Relative to all other sites filtered MeHg water concentrations at Freeport were both low (~2x RL) and unvarying. In contrast, particulate MeHg concentrations were not uniform with elevated concentrations observed during wet season. This may be explained by a lack of local internal MeHg production at this site coupled with an increase in suspended sediment and associated bound MeHg during the wet season from upstream sources (Heim et al., 2007; Foe et al., 2008). The tributaries and upstream reach of the Sacramento River has previously been shown to be a source of MeHg (Foe et al). However, Foe et al, (2008) suggests the lower Sacramento River channel (including the Freeport site) with a deeper depth and sides armored with rock may be less conducive to in-stream MeHg production.

Ancillary data (DOC, TSS, VSS) were evaluated to determine if any predictive value or surrogates could be identified for MeHg on a regional scale. Filtered MeHg in water was significantly positively correlated with DOC ($r^2 = 0.11$, $n = 186$, $P < 0.05$). Particulate MeHg in water was significantly positively correlated with TSS ($r^2 = 0.31$, $n = 186$, $P < 0.05$) and to VSS ($r^2 = 0.10$, $n = 186$, $P < 0.05$). Ancillary measurements did not give predictive power suitable for replacement of direct measure of MeHg.

Figure 13 shows long-term time series of March-October period annual means of unfiltered MeHg concentrations for Delta RMP sites. These means, in some cases, are based on limited numbers of samples. No historic data are available for Little Potato Slough. These long-term series highlight the variable nature of MeHg cycling and transport in the Delta as it is influenced by California's complex and variable hydrology as well as sub regional site characteristics. For some sites, such as Sacramento River at Freeport, Cache Slough, Lower Mokelumne, and Sacramento River at Mallard, unfiltered MeHg concentrations averaged 0.1 ng/L at each site with relatively small interannual variation. Other sites such as Middle River and San Joaquin River at Vernalis have exhibited higher intra-annual and interannual variability. The recent measurements by the Delta RMP were generally consistent with prior data from the 2000-2006 period.

Binning unfiltered MeHg concentrations by month for each Delta RMP monitoring station (Figure 14) highlights differences in seasonal variation among subareas and is useful for planning future water monitoring. For many stations (Sacramento River at Freeport, Little Potato Slough, and Middle River) the low variance observed suggests limiting the number of sampling events is possible without increasing uncertainty in the estimated annual mean. For other sites with higher variance (Cache Slough, San Joaquin River, and Mokelumne River) sampling more frequently in the wet season and less often in the dry season would be an appropriate balance to capture variation while limiting program cost.

IV. What are the loads from tributaries to the Delta?

Sources, Pathways, Loadings and Processes

- SPLP1. Which sources, pathways and processes contribute most to observed levels of methylmercury in fish?
  - SPLP1.A. What are the loads from tributaries to the Delta (measured at the point where tributaries cross the boundary of the legal Delta)?

A mass budget for MeHg in the Delta is a critical element of the TMDL. The mass budget provides essential context for understanding the importance of inputs from discharges and internal sources and processes. Obtaining data to expand and update the dataset on MeHg inputs to the Delta is a high priority to support TMDL refinement and implementation. MeHg export from the Delta is similarly an important component of the mass budget and a high priority information need.

The aqueous MeHg concentration data obtained from the first three years of Delta RMP mercury monitoring will be essential in constructing an updated mercury mass budget for the Delta. The budget will be developed using both concentration data and water flow data for each station sampled. DWR and USGS gaging stations are the source of the flow data. The mass budget will be constructed following the approach used by Wood et al. (2010). At the time of this report Regional Board staff have not completed water budgets for the Delta RMP monitoring stations and therefore an updated mass budget is not presented.

V. What is the relationship between MeHg in black bass and MeHg in water?

Another priority question addressed by Delta RMP MeHg monitoring relates to the linkage analysis discussed in the Introduction, which is a key element of the technical basis for the TMDL: What is the relationship between MeHg in black bass and unfiltered MeHg in water? This question was not articulated in the core management questions and assessment questions established by the Delta RMP Steering Committee, but was nevertheless identified as a priority by the Mercury Subcommittee and explicitly included in the annual workplans for mercury monitoring.

The linkage of MeHg concentrations in fish to MeHg concentrations in water is a key element of the TMDL (Wood et al. 2010). The linkage analysis in the TMDL developed a Delta-specific mathematical relationship between aqueous and fish MeHg concentrations. The relationship was used to determine an aqueous MeHg goal of 0.06 ng/L that, if met, was predicted to produce safe fish tissue levels for both human and wildlife consumption. The aqueous MeHg goal was then used to allocate MeHg reductions for within-Delta and tributary sources under the TMDL implementation plan.

The linkage analysis in the TMDL (Wood et al. 2010) established a clear relationship between MeHg in largemouth bass and unfiltered aqueous MeHg, but was based on limited datasets for both terms. At the time the TMDL was developed, water and fish had not been sampled in the Delta for the specific purpose of developing a linkage analysis. As a result, there was an acceptable temporal overlap for only a portion of the available fish and water data. The linkage analysis focused on data from 2000, for which water collected from March-October could be compared to largemouth bass collected in September-October. A strong relationship was observed between average bass MeHg and average unfiltered aqueous MeHg across the five subareas (Figure 15A). This relationship was used to translate the 0.24 ppm implementation goal for 350 mm largemouth bass into the aqueous MeHg concentration of 0.066 ng/L that, with incorporation of a 10% margin of safety, became the 0.06 ng/L implementation goal for water.

From the beginning, Delta RMP mercury monitoring of bass and water has been conducted at the same stations. With a smaller budget in the first year (July 2016 – June 2017) quarterly water monitoring was conducted (Table 1). In the latter half of year 2 (July 2017 - June 2018), an increased budget was used to begin conducting monthly water monitoring, with coverage of the March–October period used for the TMDL linkage analysis (Table 1). Monthly sampling in March-October was then sustained through October 2019, providing two full years of monthly water data to compare to concurrent bass data (Figure 16).

The water (March-October subarea mean) and fish (subarea mean) data from 2018 and 2019 exhibited a very similar relationship to that observed in 2000 and presented in the TMDL (Figures 15A,B). One difference between the TMDL dataset and the recent dataset is the availability of data for the Yolo Bypass-South subarea in the latter. If only the five subareas included in the TMDL linkage analysis are considered (Sacramento River, San Joaquin River, Mokelumne River, Central Delta, and West Delta), the 2018-2019 results were remarkably consistent with the 2000 results. A linear regression for these five subareas yields an R^2 of 0.99 ($p < 0.001$), and a 350-mm bass concentration of 0.24 ppm that translates an aqueous MeHg concentration of 0.065 ng/L (Figure 17A). However, the point for Yolo Bypass-South was inconsistent with the points for the other five subareas. A regression for the subareas including this point was not significant at $\alpha=0.05$ ($p=0.10$). For this dataset and regression line, a 350-mm bass concentration of 0.24 ppm translates to an aqueous MeHg concentration of 0.057 ng/L (Figure 17B).

The apparent inconsistency of the bass:water relationship in Yolo Bypass-South raises the question of whether this area has distinct MeHg dynamics relative to the other subareas. One possible explanation is that high concentrations that occur in the Yolo Bypass during flooding may pass through this subarea with a short residence time (in other words, there may be brief exposure periods to high MeHg concentrations) in the wet season and not have much influence on late summer bass MeHg. The Cache Slough at Liberty Island Mouth station did exhibit high aqueous MeHg concentrations in March and April of 2019, with March being especially high (0.36 ng/L). Another possible explanation is that higher growth rates of fish in this productive area could lead to “biodilution”

To explore whether the March and April data were obscuring the bass:water relationship, additional regression analysis was conducted using a narrower window of water data. A four-month window (May-August) was used (Figure 15C). March and April were excluded to reduce the potential undue influence of high wet season aqueous concentrations (due to the potentially brief exposure periods mentioned above). September and October were excluded because the bass collections have occurred in August and September, so the October aqueous MeHg cannot influence the bass and the kinetics of MeHg transfer through the food chain make it unlikely that even the September aqueous MeHg could influence the bass.

The regressions based on May-August water data were significant with and without the inclusion of Yolo Basin-South (Figures 17C and 17D). The relationship between bass and water was very strong when Yolo Basin-South was excluded (Figure 15C), with an R^2 of 0.96 ($p < 0.01$), and a 350 mm bass concentration of 0.24 ppm that translates an aqueous MeHg concentration of 0.060 ng/L.
When Yolo Basin-South was included, this station again was furthest from the regression line, but not as far away as it was for the regression using the March-October water data (Figure 17D). The regression based on May-August water data and including Yolo Basin-South had an R^2 of 0.76 ($p = 0.02$), and a 350 mm bass concentration of 0.24 ppm that translates an aqueous MeHg concentration of 0.062

ng/L. The narrower window of water data therefore resulted in a stronger overall regression for the linkage analysis including all six Delta subareas that were monitored.

VI. Recommendations for Future Monitoring

Progress to Date

The first three years of mercury monitoring in the Delta RMP have answered the status and trends assessment questions to a significant degree. The sport fish monitoring, in combination with data from prior studies, has provided clear evidence that temporal trends vary considerably across Delta subareas, with three subareas exhibiting consistent MeHg concentrations over time, and two subareas (Mokelumne River and San Joaquin River) exhibiting highly variable concentrations that appear to be driven by interannual variation in hydrology. Extremely high concentrations observed in these latter two subareas indicate a higher degree of impairment than was previously known to occur. Temporal trends in aqueous MeHg concentrations have also been shown to vary significantly across the subareas, generally matching the variation in fish concentrations. The water monitoring has also documented differing degrees of seasonal variation across the subareas, providing information that will be useful in designing future water monitoring programs. The water monitoring has also provided data that will make it possible to update the MeHg mass budget for the Delta – an important element of the TMDL. Together, the fish and water monitoring have provided support for another key element of the TMDL: the linkage analysis.

Revisiting the Assessment Questions

With the progress that has been made, a reevaluation of the mercury assessment questions and their relative priority is in order. The assessment question framework that was established before the mercury monitoring began (Table 2) indicated that the status and trends questions for MeHg in fish and MeHg in water were to be *initial* priorities. The Delta RMP committees have already decided to shift toward placing a greater priority on questions related to the impact of wetland restoration projects (questions SPL1B and FS1 in Table 2), approving the addition of a prey fish and expanded black bass MeHg monitoring element in year 4 (July 2019 –June 2020). Furthermore, refinement of the existing assessment questions appears to be in order.

Specific considerations about each of the questions are as follows (numbering refers to the scheme in Table 2).

ST1A (Are trends over time in MeHg in sport fish similar or different among Delta subareas?) and ST1B (Are trends over time in MeHg in water similar or different among Delta subareas?): As noted above, the Status and Trends questions for fish and water have been answered – there are differences in trends over time among Delta subareas. A more refined status and trend question, especially appropriate for fish, to consider is: What is the long-term trend in MeHg in sport fish in each Delta subarea? A related question is: What is a cost-effective monitoring design to determine these trends?

SPL1A (What are the loads from tributaries to the Delta (measured at the point where tributaries cross the boundary of the legal Delta)?): Monitoring in years 2 and 3 have generated data to address this question. Considerations regarding this question relate to its priority relative to the other assessment questions in the near-term and the long-term. How extensive of a dataset is needed for mass budget updates? Is the information generated in 2018 and 2019 enough for now? How often should this dataset be updated (e.g., once every 10 years)?

SPL1B (How do internal sources and processes influence MeHg levels in fish in the Delta?): Based on spatial and temporal patterns in aqueous and fish tissue concentrations, the MeHg mass budget for the Delta appears to be dominated by external loading and internal processes (both MeHg production and demethylation) that result in a net depletion of MeHg as water flows toward the Central Delta. This depletion occurred even when the external loading from the San Joaquin River and Mokelumne/Cosumnes watershed increased sharply in wet years. Photodemethylation appears to be the internal process driving the reduction (Byington et al. 2017), although further study is needed to establish this more definitively. Sustained bass monitoring, and water monitoring depending on whether and how water monitoring is sustained, will continue to track the persistence of the pattern of lower MeHg concentrations in the Central Delta. However, continued monitoring will not test the theorized mechanism – process-oriented studies would be needed for that. Prey fish and expanded bass monitoring is being initiated in Year 4 (May 2020) to track the influence of wetland restoration projects as internal sources of net MeHg production on a localized scale. Clarifying the intent of the Delta RMP with regard to answering this question would be helpful in establishing a long-term plan for Delta RMP mercury studies.

SPL1C (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?): Uncontrollable sources of mercury or MeHg, such as atmospheric deposition, are not directly being assessed by past or planned monitoring. MeHg models being developed by DWR are anticipated to address the influence of atmospheric deposition of inorganic mercury (Harris et al. 2019). This question could potentially be addressed through special studies (for example, one possibility is a mercury isotope study). Clarifying the intent of the Delta RMP with regard to answering this question would be helpful in establishing a long-term plan for Delta RMP mercury studies.

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?): Delta RMP monitoring is supporting forecasting and management scenario evaluation for MeHg by providing data that has been and will be used in development and validation of MeHg models for the Delta and the Yolo Bypass

(Harris et al. 2019). Clarifying whether that is sufficient to addressing this question would be helpful in establishing a long-term plan for Delta RMP mercury studies.

Effectiveness Tracking
This category has core management questions, but assessment questions have not yet been articulated. The first core management question in this category (Are water quality conditions improving as a result of management actions such that beneficial uses will be met?) would be addressed by the more refined version of ST1A recommended above. This analysis would need to separate changes from management action from the background variation, which might be driven by flow or other factors.

Linkage
As discussed above, a question about the linkage of MeHg concentrations in fish and water was not articulated in the core management questions and assessment questions established by the Delta RMP Steering Committee, but was nevertheless identified as a priority by the Mercury Subcommittee. Years 1-3 of monitoring have supported the existence of a linear relationship observed in the early 2000s and incorporated into the TMDL. It is possible, however, that this relationship could change over time due to the influence of extensive wetland restoration, changes in food web structure, or other factors. There would be value in tracking this relationship over time or periodically checking to determine whether it has changed.

Fish Monitoring Recommendations

At the outset of Delta RMP mercury monitoring, an initial period of 10 years of annual Delta RMP black bass monitoring was envisioned, and this still appears to be an appropriate plan. In other words, continuing the core bass monitoring as indicated in Table 1 to complete a 10-year dataset appears to be an appropriate plan. Black bass monitoring was identified by the TMDL as a key indicator for evaluating status and trends in impairment. The monitoring conducted to date has provided further evidence of the value of this indicator: it has confirmed spatial patterns observed in prior studies, documented extremely high concentrations and interannual variation in two subareas, and generated a hypothesis regarding the driver of temporal variation (interannual variation in flow). This hypothesis is preliminary though and should continue to be evaluated with a larger dataset and possibly targeted mechanistic studies. Continued monitoring of the subarea index stations will also provide added value as a frame of reference for interpreting results of black bass and prey fish monitoring near wetland restoration projects. The cost of the annual black bass monitoring is relatively low for a high yield of information.

A 10-year dataset will firmly establish baseline conditions for this critical impairment indicator and provide robust estimates of intra-annual and interannual variance that can be used to conduct power analysis and design cost-effective longer-term monitoring. A preliminary power analysis 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 trend using linear regression. Observations from Years 1-3 indicate 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.

Water Monitoring Recommendations

The water dataset generated by the Delta RMP has contributed substantially to answering Delta RMP assessment questions and will inform revisions to the MeHg TMDL for the Delta. With two years of monthly sampling completed (January through October), the need for continued monitoring of aqueous mercury is under consideration. Continued aqueous mercury monitoring will strengthen the dataset available for answering all four major categories of Delta RMP assessment questions: status and trends; sources, pathways, loadings, and processes; forecasting scenarios; and effectiveness tracking. One impetus for continued aqueous MeHg monitoring is to generate a long-term dataset to support future mercury models for the Delta. A ten-year gap exists between the last large regional mercury sampling and the start of the DRMP. Current modeling efforts had to rely on data that was over 10 years old. Aqueous mercury data are an essential part of both model construction and validation. Available water mercury datasets are sparse relative to the complexity of the Delta ecosystem, making construction of accurate predictive models challenging. An additional impetus is evaluation of how large-scale wetland restoration in the Delta may affect the MeHg linkage between water and biota, but to evaluate this with confidence would likely require more intensive sampling than is being contemplated. Continuing a streamlined aqueous mercury Delta RMP program would provide a balance between reducing overall costs to the DRMP program while maintaining our ability to investigate how remediations influence linkages, if at all. It will also aid interpretation related to climate change as we will have the ability to analyze a longer time series presumably moving in and out of wet and dry years.

One of the objectives of this report was to make a recommendation for continued aqueous monitoring based on the first three years of data. The data collected have brought into focus patterns for Delta RMP sites with respect to seasonal variation in MeHg concentrations. The following recommendations are based on MeHg observations rather than the dataset as a whole (i.e., total Hg observations are not considered). The current monitoring program ended with monthly (March-October) collections at eight stations. The three-year dataset makes it clear that water sampling at many of the sites can be substantially reduced without sacrificing the ability to obtain good estimates of annual mean MeHg concentrations. Table 5 presents a proposed sampling plan for continue seasonal MeHg water sampling.

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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 year 3 of Delta RMP mercury monitoring. Lower Mokelumne River 6 station was not sampled for water until October 2017.

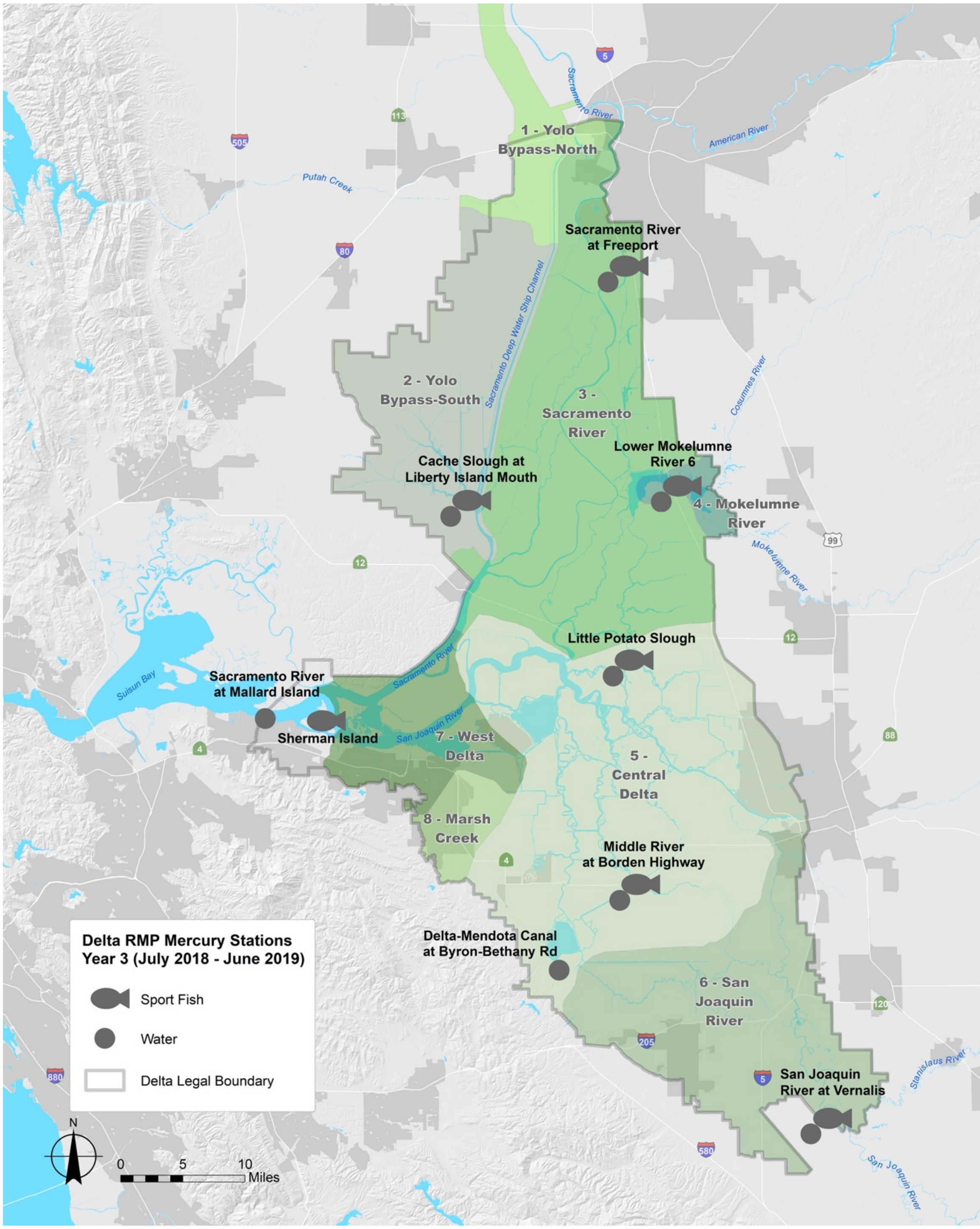


Figure 2. Long-term time series of mean MeHg (ppm wet weight) in black bass for Delta RMP stations and nearby stations sampled historically. Red line shows the 0.24 ppm TMDL implementation goal. Details provided on page following the graphs.

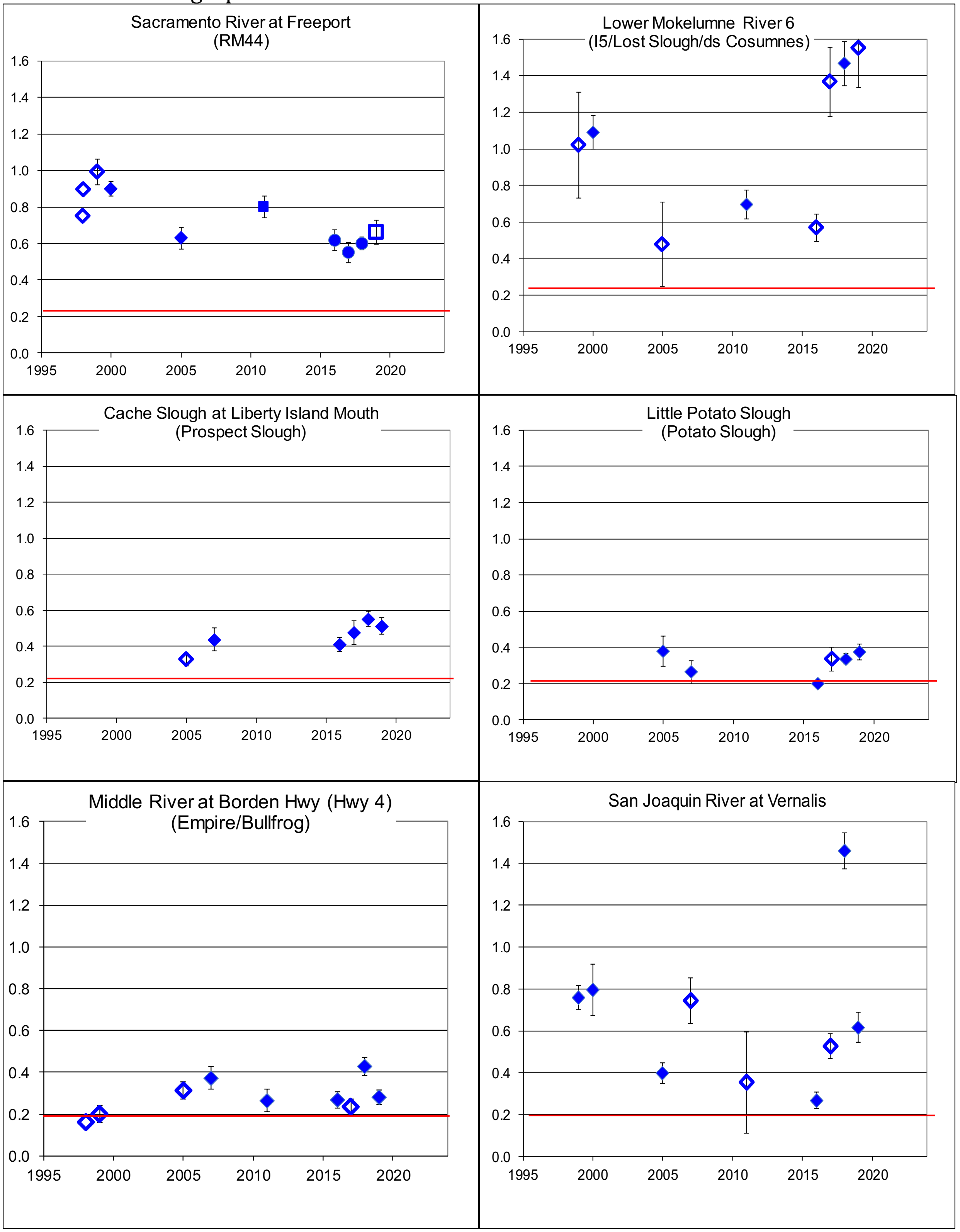


Figure 2. (continued)

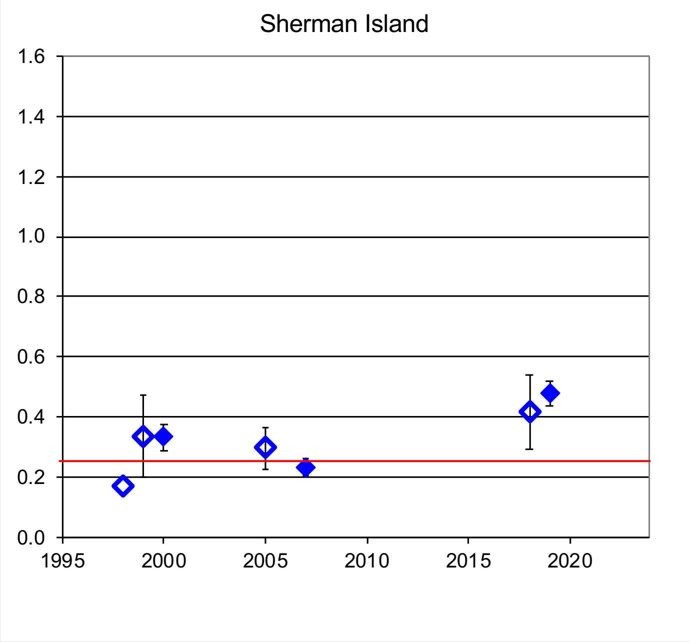


Figure 2 Details

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. 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

Figure 3. Length-adjusted (350 mm) mean MeHg concentration (ppm wet weight) in black bass at each station. Mean of four years of sampling from 2016-2019. Error bars show ± 2SE.

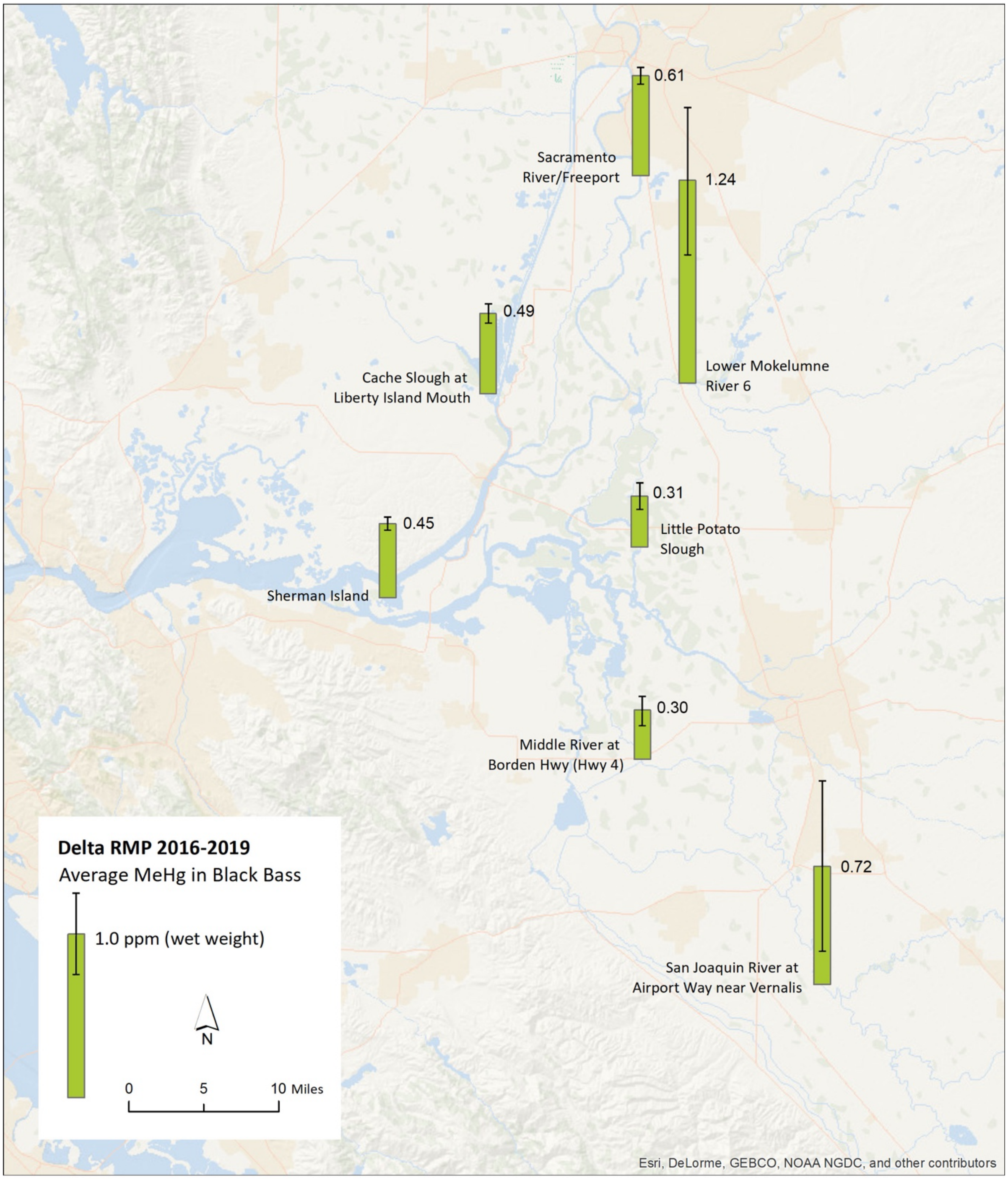


Figure 4. Spatial distribution of silverside seasonal mercury trends, Nov-05 – Nov-06. From Slotton et al. (2007). Condensed seasonal data, including Oct/Nov-05, Feb-06, Jul-06, and Nov-06

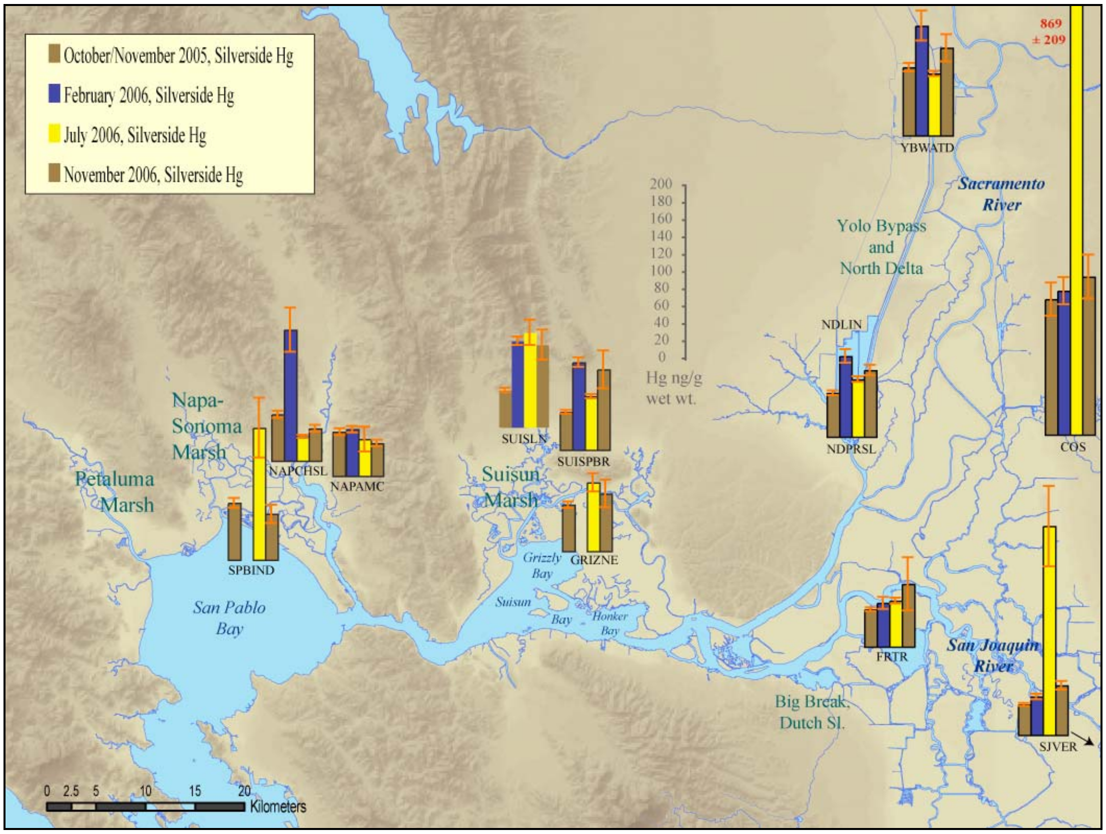
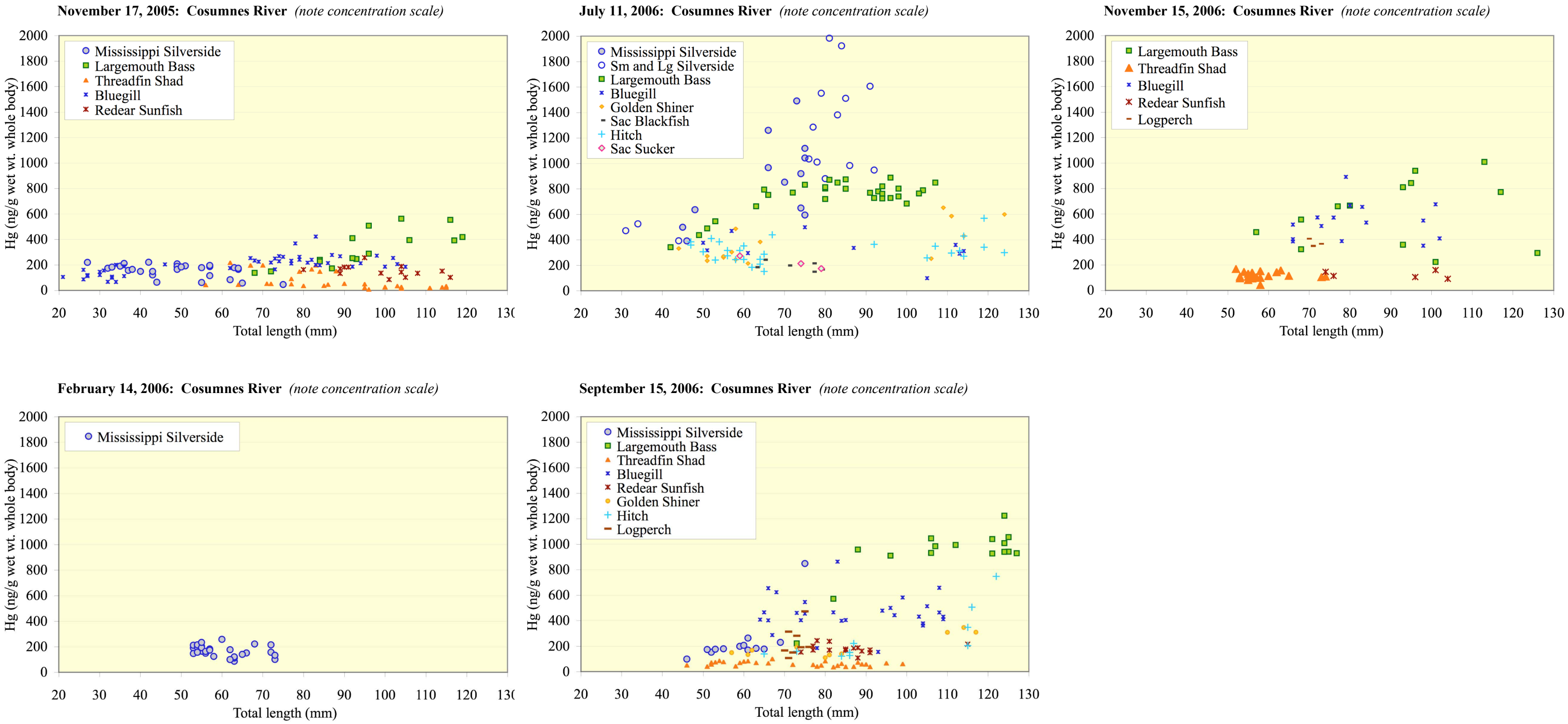


Figure 5. Multiple species, individual data from the Cosumnes River Intensive site, presented seasonally, Nov-2005 through Nov-2006. From the study by Slotton et al. (2007).



November 17, 2005: Cosumnes River *(note concentration scale)*

July 11, 2006: Cosumnes River *(note concentration scale)*

November 15, 2006: Cosumnes River *(note concentration scale)*

February 14, 2006: Cosumnes River *(note concentration scale)*

September 15, 2006: Cosumnes River *(note concentration scale)*

Figure 6. Multiple species, individual data from the San Joaquin River at Vernalis Intensive site, presented seasonally, Nov-2005 through Nov-2006. From the study by Slotton et al. (2007).

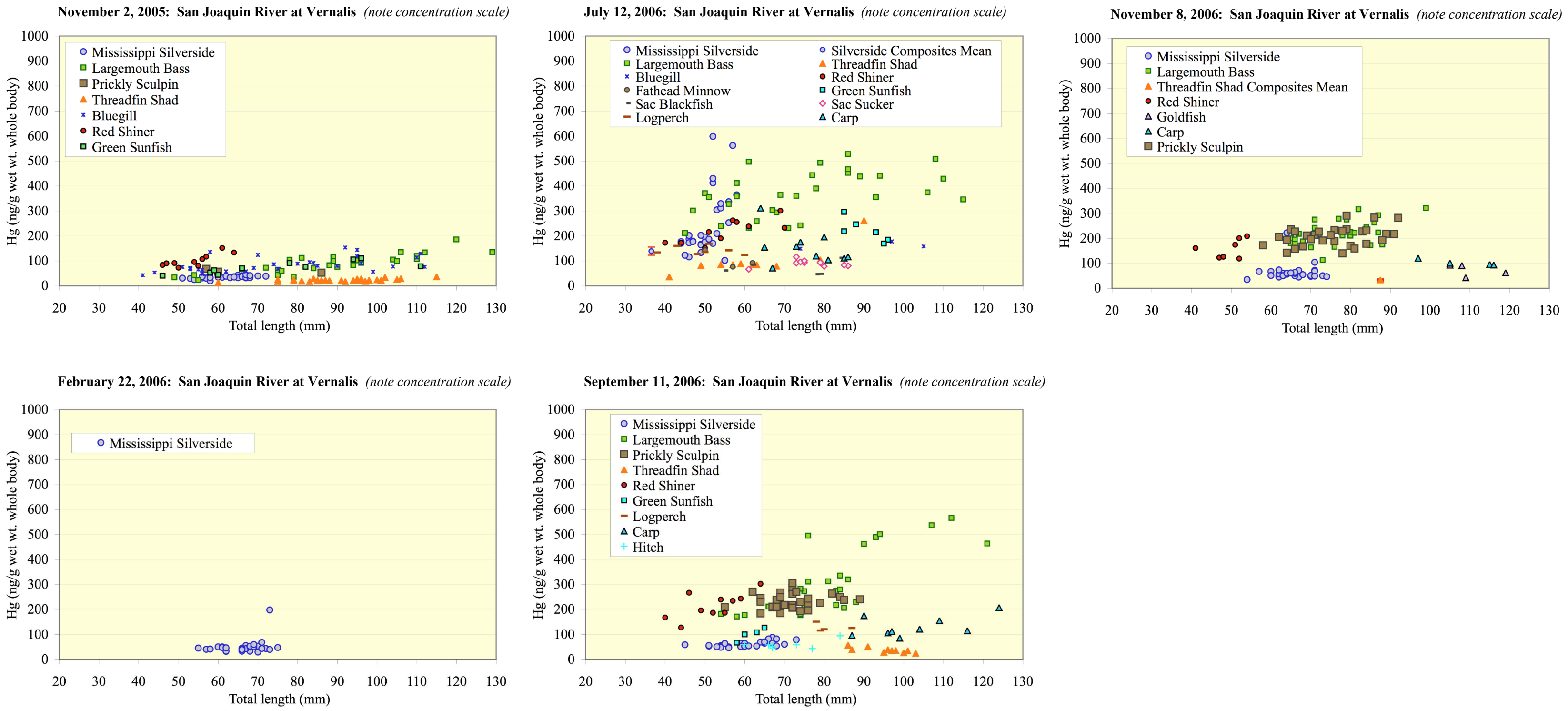


Figure 7. Mercury concentrations in silverside in seasonal sampling on the Cosumnes River and San Joaquin River at Vernalis. From Slotton (2008). Error bars show 95% confidence intervals of the mean.

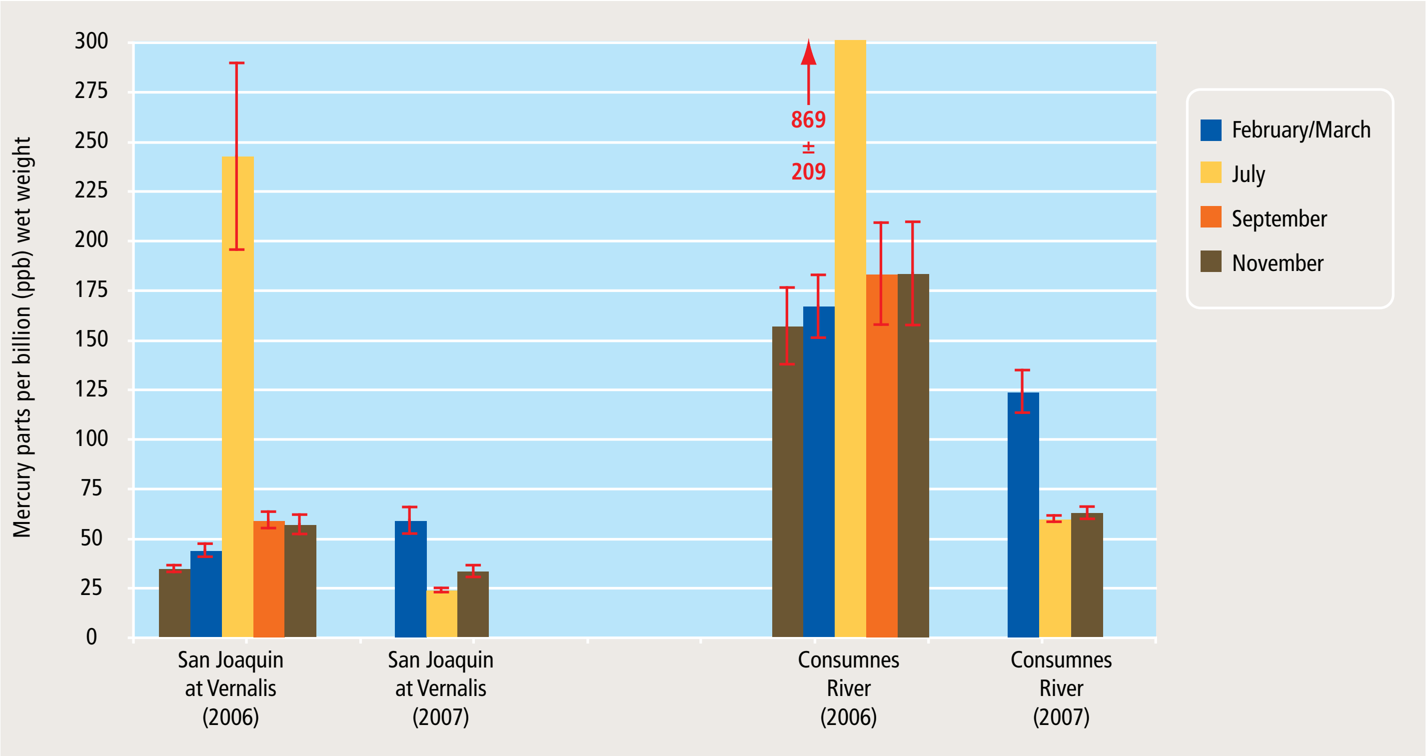


Figure 8. Water and fish MeHg concentrations for the San Joaquin River at Vernalis in 2005 and 2006 (Janis Cooke, Central Valley Regional Water Board, personal communication). Silverside data from Slotton et al. (2007); water data from Foe et al. (2008).

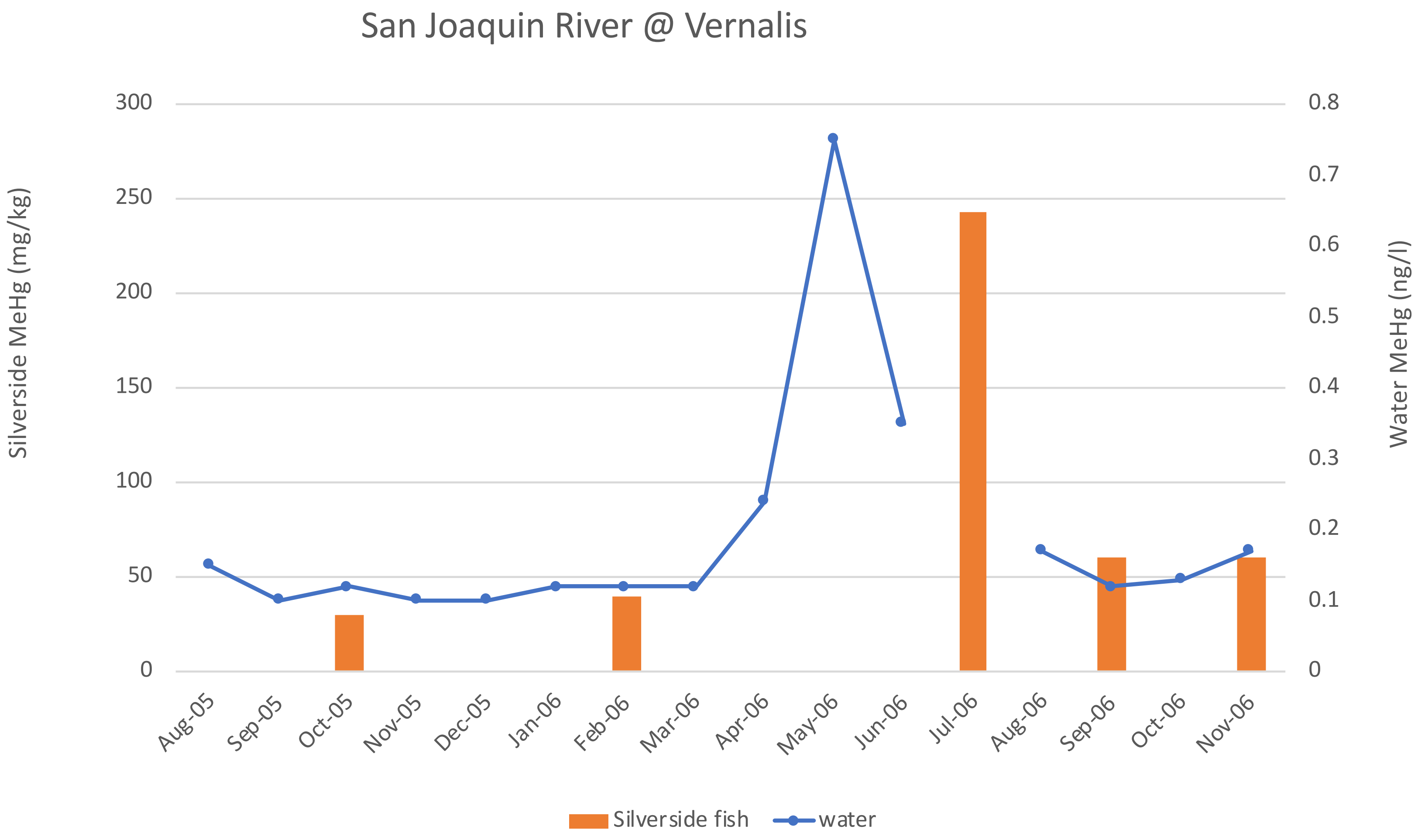


Figure 9. MeHg concentration in black bass (ppm) versus DWR water year index for the Sacramento Valley: a) current water year index; b) previous year water year index. Bass MeHg dataset is the same as shown by year in Figure 2. Water year data are from DWR (https://cdec.water.ca.gov/reportapp/javareports?name=WSIHIST) and are the data used for "Official Year Classifications based on May 1 Runoff Forecasts."

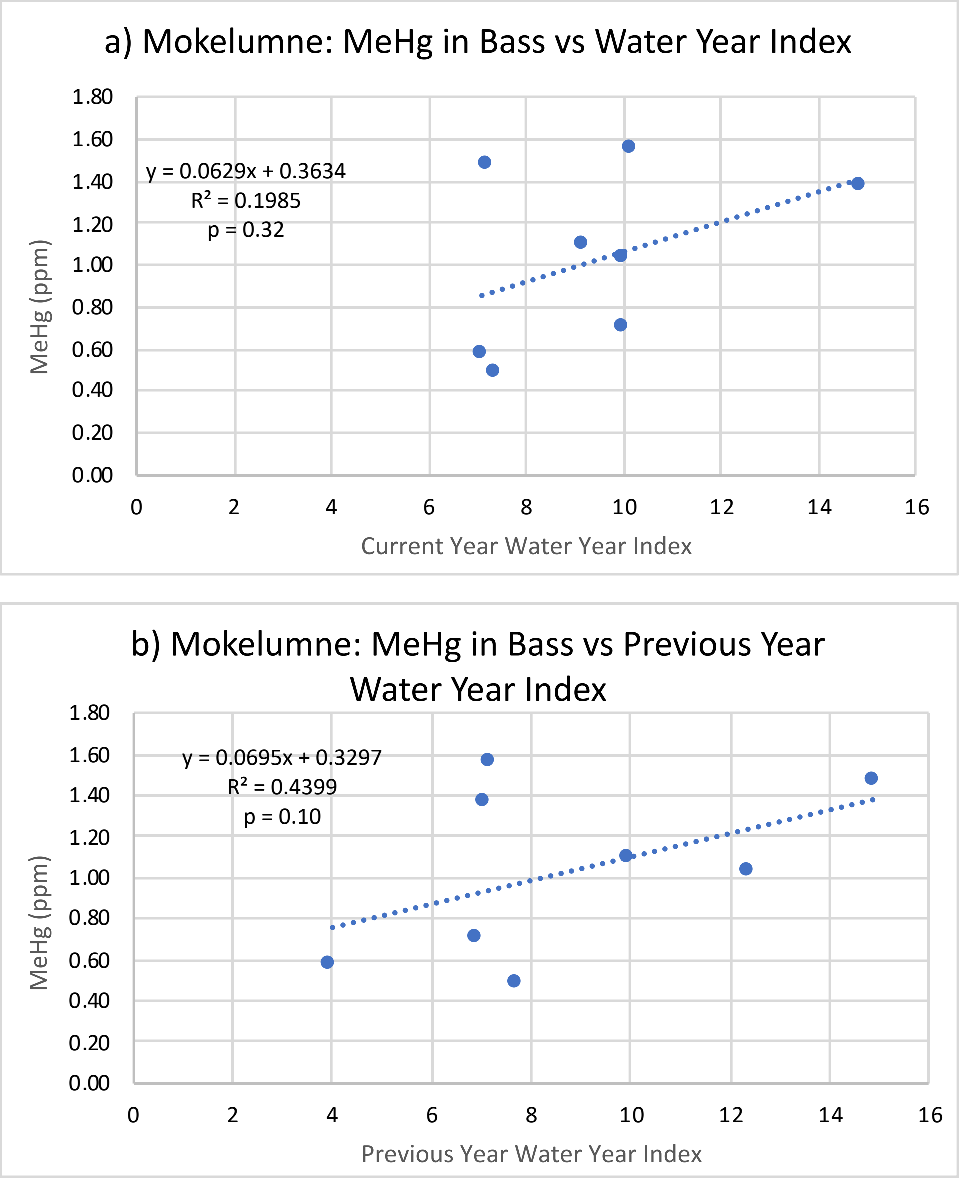


Figure 10. MeHg concentration in black bass (ppm) versus DWR water year index for the San Joaquin Valley: a) current water year index; b) previous year water year index. Bass MeHg dataset is the same as shown by year in Figure 2. Water year data are from DWR (https://cdec.water.ca.gov/reportapp/javareports?name=WSIHIST) and are the data used for "Official Year Classifications based on May 1 Runoff Forecasts."

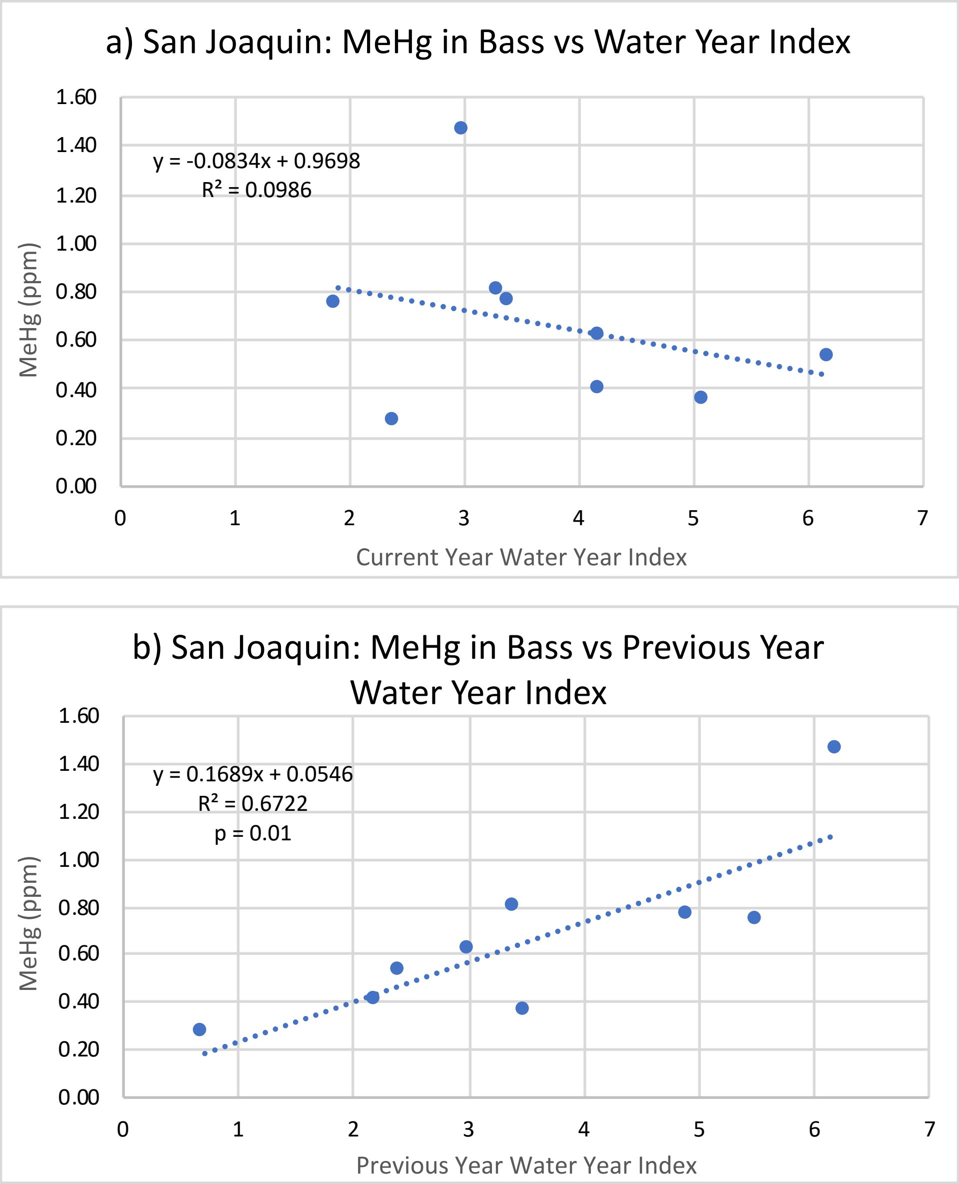


Figure 11. Concentrations of unfiltered and filtered methylmercury over monthly timescale at Delta RMP stations. The top six panels are input sites to the Delta and the bottom panels are export sites. Panels on left and right represent west and east locations, respectively.

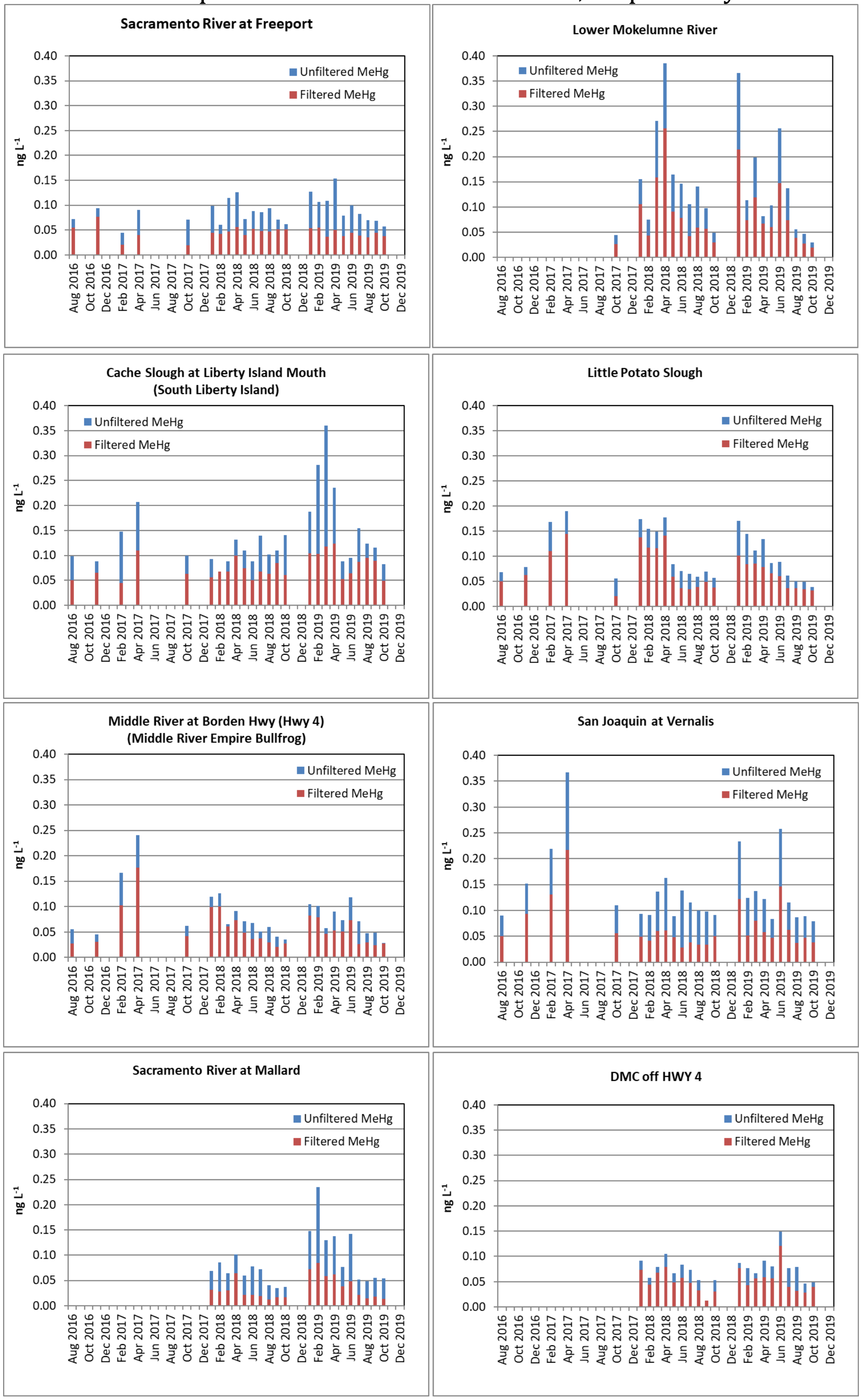


Figure 12. Relationship between unfiltered and filtered water MeHg concentrations measured from August 2016 - October 2019 (n = 186).

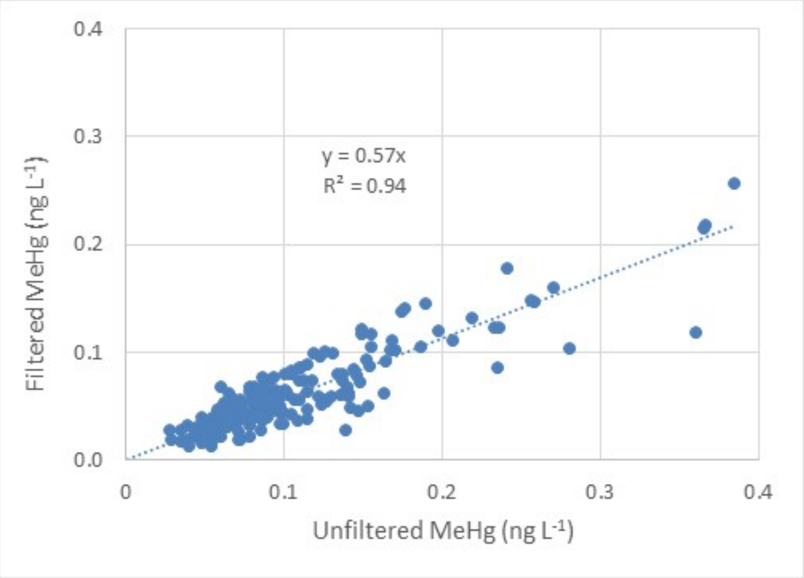
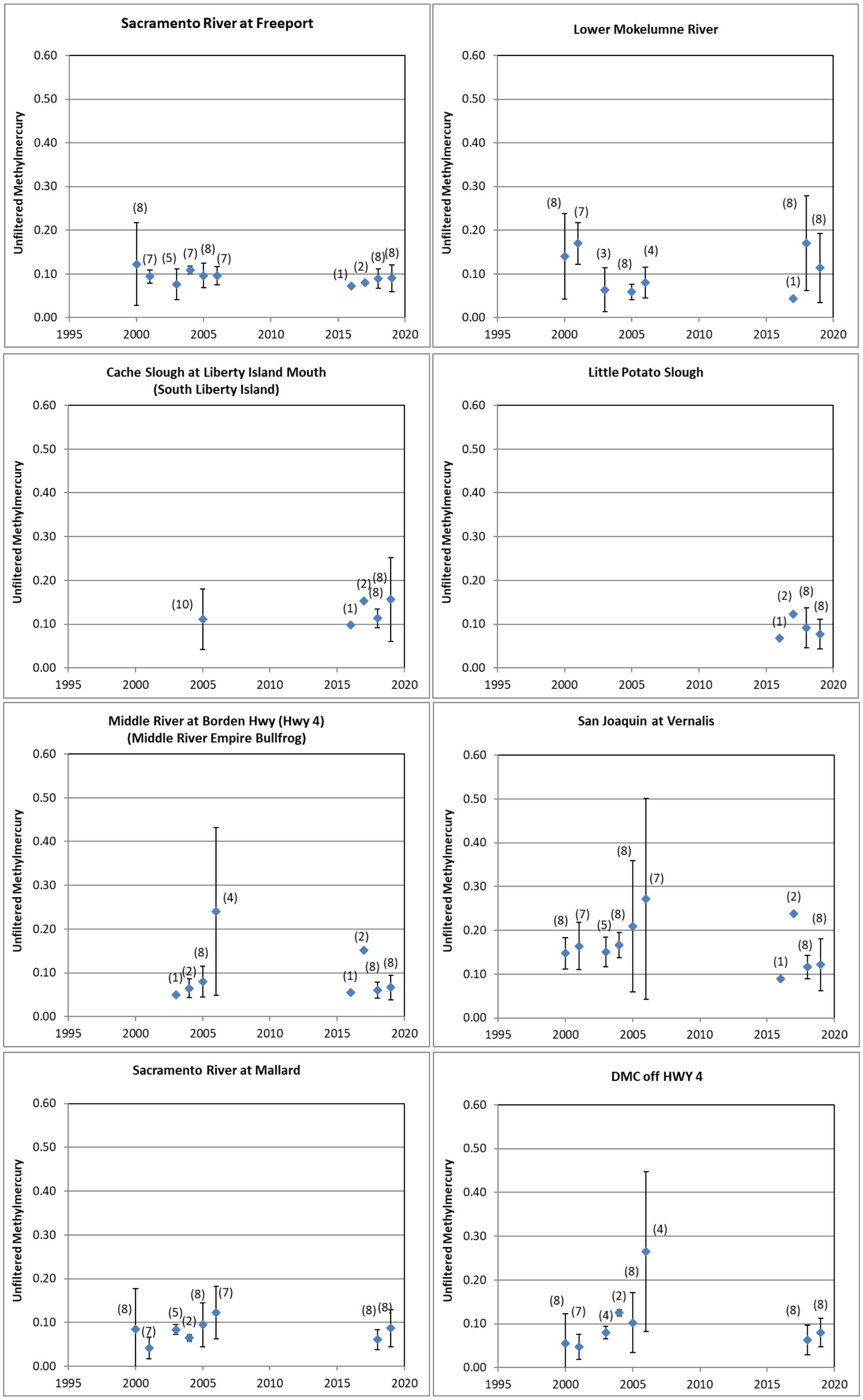


Figure 13. Annual mean aqueous unfiltered MeHg concentration (ng/L) at each Delta RMP monitoring station. Plots based on available March-October data for each calendar year. Number of samples shown in parentheses.



Sacramento River at Freeport

Lower Mokelumne River

Cache Slough at Liberty Island Mouth (South Liberty Island)

Little Potato Slough

Middle River at Borden Hwy (Hwy 4) (Middle River Empire Bullfrog)

San Joaquin at Vernalis

Sacramento River at Mallard

DMC off HWY 4

Figure 14. Unfiltered aqueous MeHg concentrations by month at each Delta RMP monitoring station. Plots show minimum and maximum, first and third quartile, median (line in boxplot) and average (X).

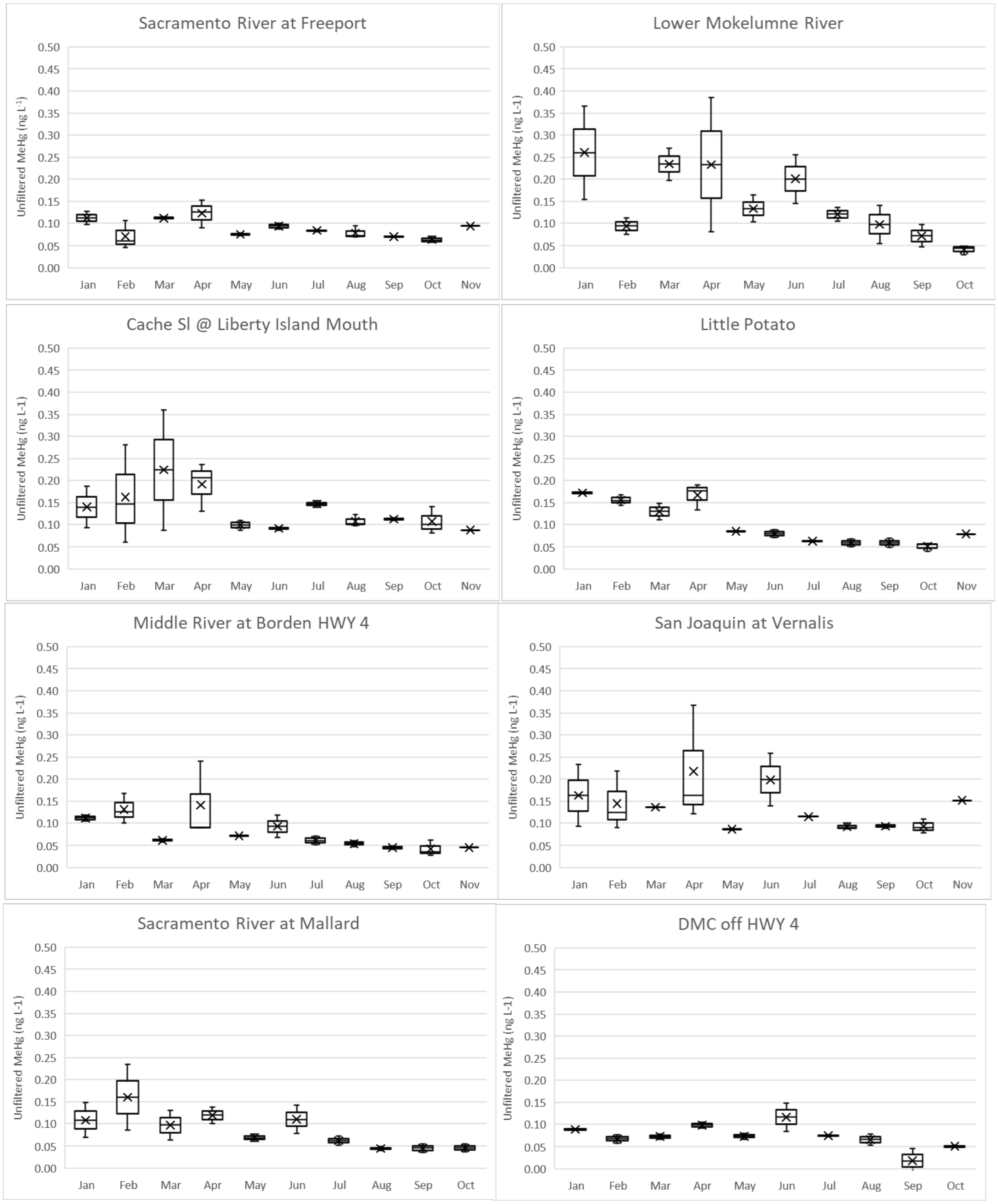


Figure 15. MeHg in black bass versus aqueous MeHg: A) the relationship used for the linkage analysis in the MeHg TMDL (Wood et al. 2010); B) Delta RMP using March-October water data; C) Delta RMP using May-August water data.

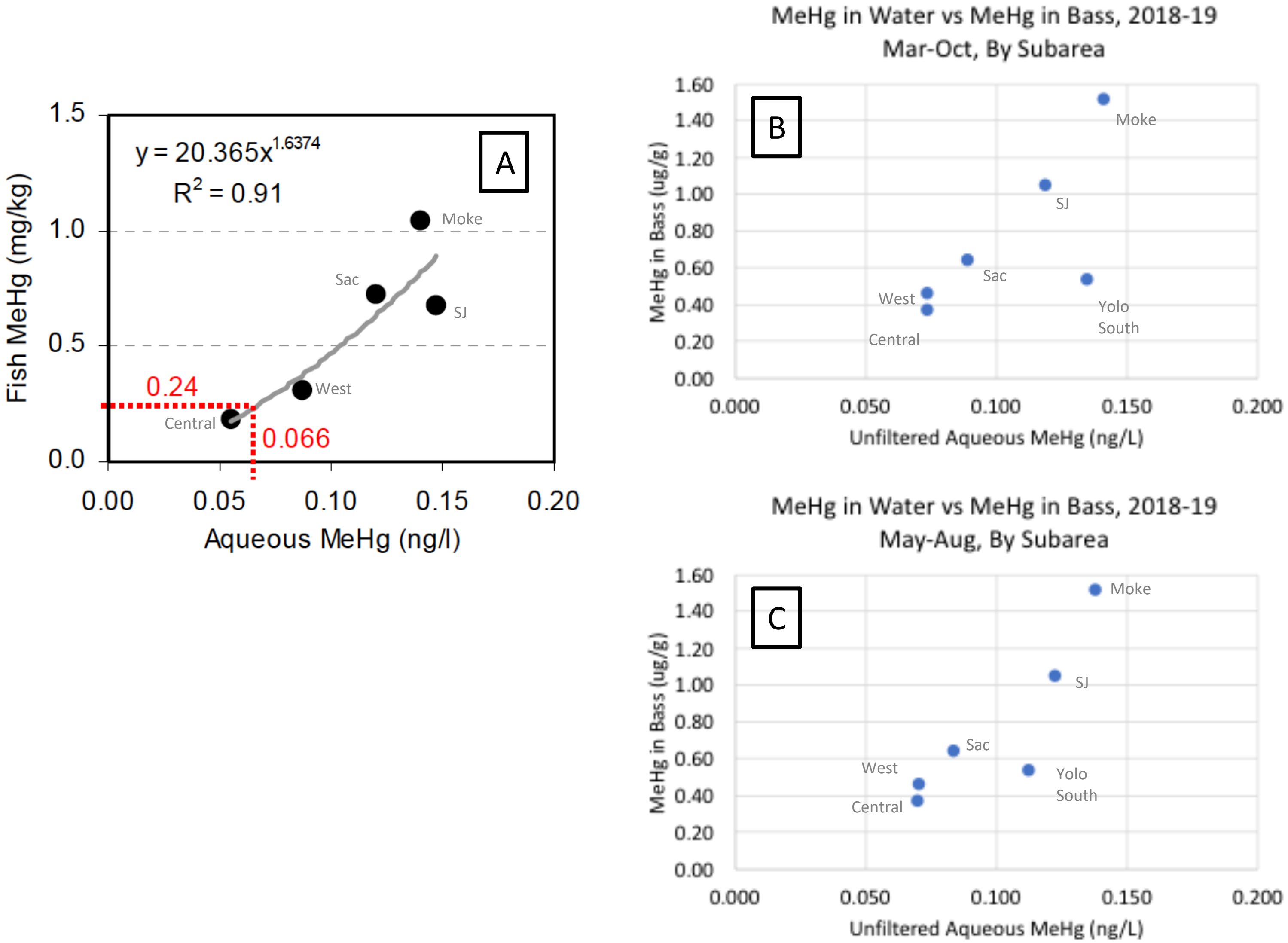


Figure 16. Concentrations of unfiltered and filtered methylmercury over monthly timescale at Delta RMP stations. Boxes indicate the March-October period.

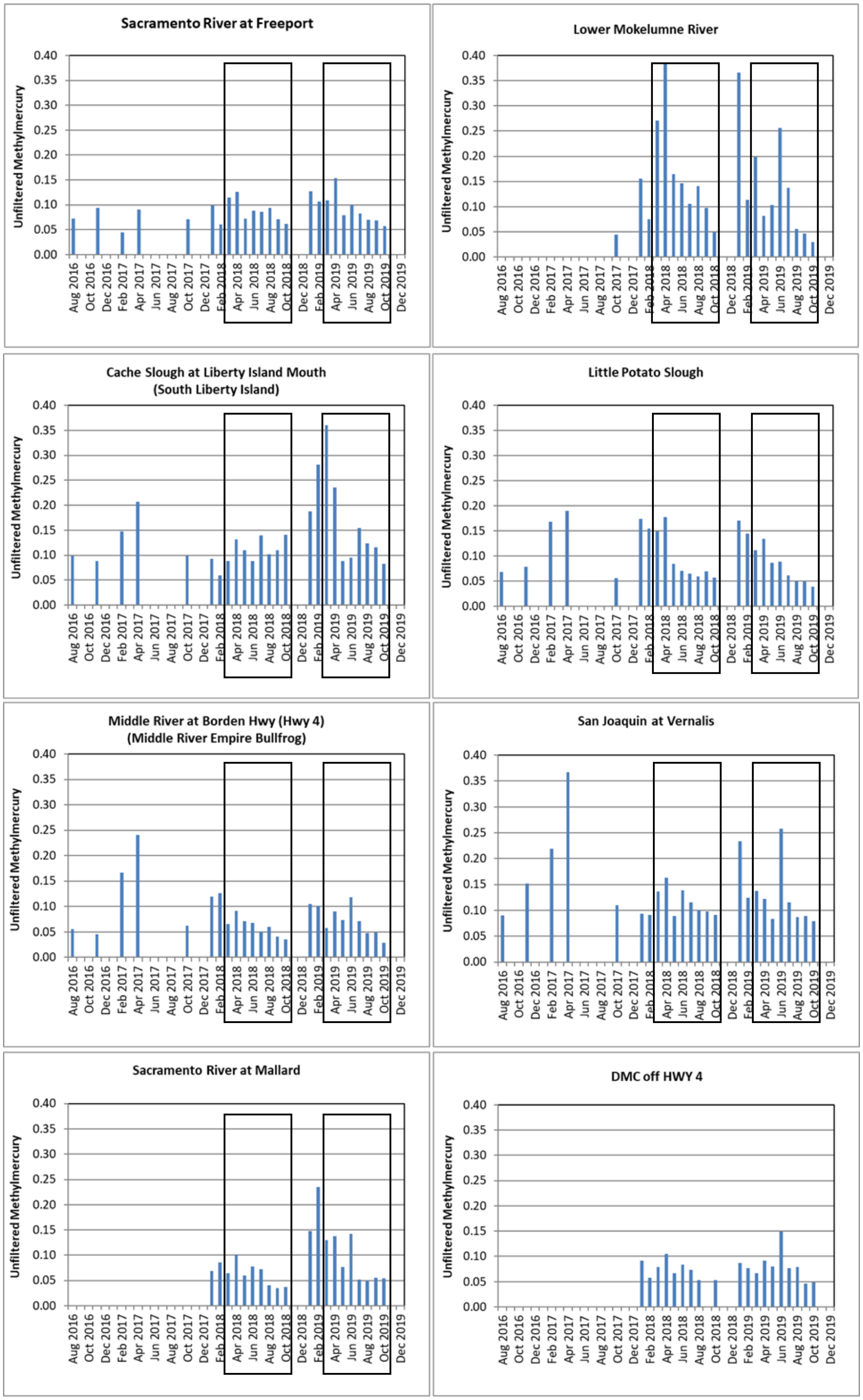
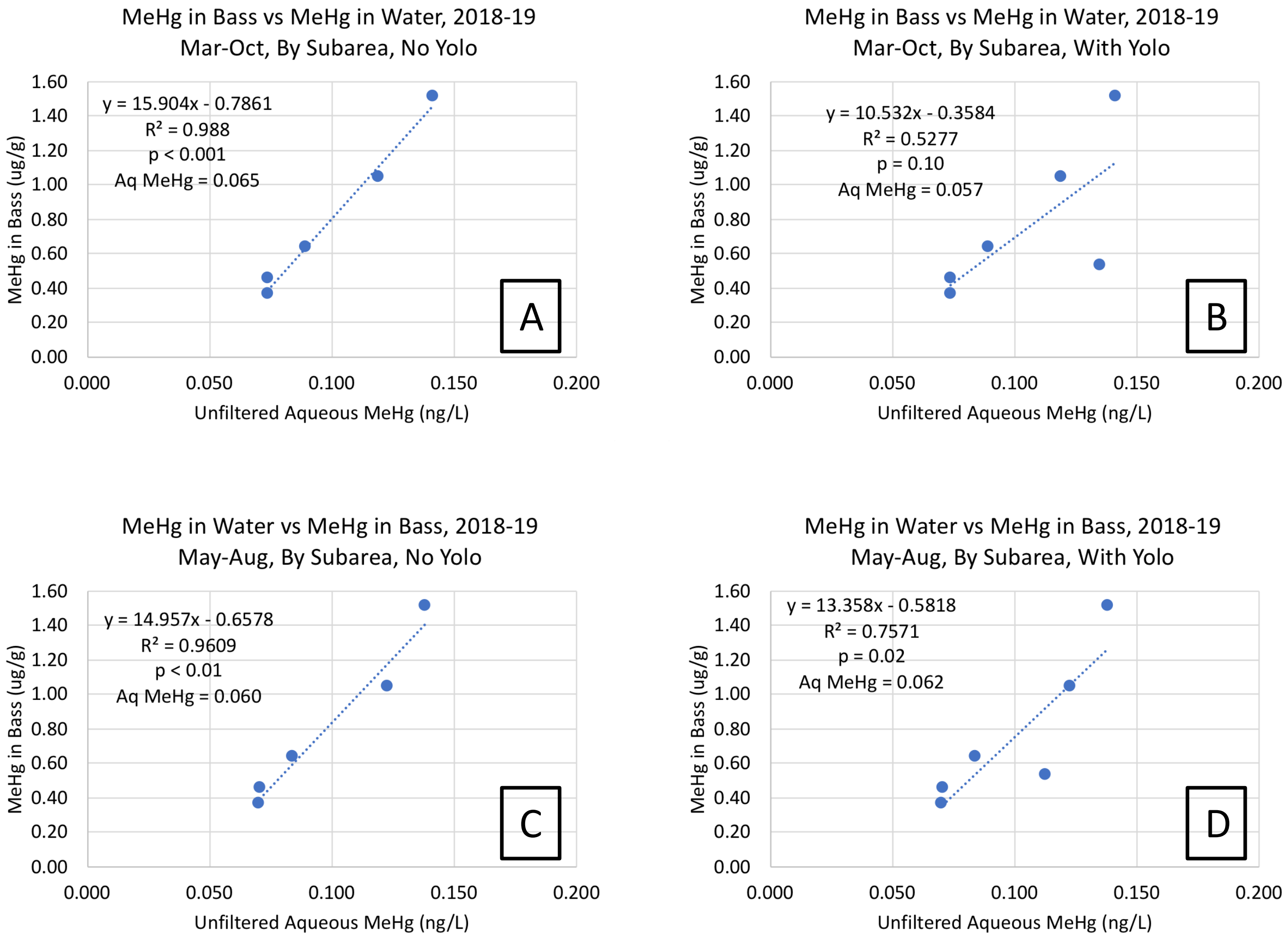


Figure 17. Linear regressions of MeHg in black bass versus aqueous MeHg.



MeHg in Bass vs MeHg in Water, 2018-19
Mar-Oct, By Subarea, No Yolo

MeHg in Bass vs MeHg in Water, 2018-19
Mar-Oct, By Subarea, With Yolo

MeHg in Water vs MeHg in Bass, 2018-19
May-Aug, By Subarea, No Yolo

MeHg in Water vs MeHg in Bass, 2018-19
May-Aug, By Subarea, With Yolo

Table 1. Sampling schedule for Delta RMP mercury monitoring, July 2016 – October 2019. The March-October period used for the linkage analysis in the TMDL is indicated with gray shading.

Year →	2016						2017												2018												2019											
Fiscal Yr →	FY 16/17												FY17/18												FY18/19												FY19/20					
Month →	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12
Monitoring element (# of sites sampled)																																										
Bass - Core		6												6												7													7			
Bass - Restoration																																							**5**			
Prey fish																																										
Water		5			5			5		5						6			8	8	8	8	8	8	8	8	8	8			8	8	8	8	8	8	8	8	8	8		
Sediment																6			6			6		6																		

gray shading = March-October period used for the linkage analysis in the TMDL

bold = proposed wetland restoration monitoring component

Table 2. 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.

Type	**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 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?	ST1. What are the status and trends in ambient concentrations of total mercury and methylmercury (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)?	ST1A. Are trends over time in MeHg in sport fish similar or different among Delta subareas?	X		
			ST1B. Are trends over time in MeHg in water similar or different among Delta subareas?		X	
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., 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?	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)?		X	
			SPLP1B. How do internal sources and processes influence MeHg levels in fish in the Delta?	X	X	X
			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?			
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?		X	X	X
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]		X	X	X

Table 3. Mean MeHg concentrations (ppm) in Delta RMP black bass monitoring, 2016-2019. Central Delta stations in italics because there are two stations that were combined to calculate a mean for the Central Delta subarea. Green shading indicates values below the TMDL implementation goal of 0.24 ppm.

Station	**Delta Subarea**	**2016 Mean**	**2017 Mean**	**2018 Mean**	**2019 Mean**	**4-Year Mean**	**SD**	**SE**	**2SE**	**Mean presented in TMDL**
Sacramento River at Freeport	Sacramento River	0.62	0.55	0.60	0.66	**0.61**	0.05	0.02	0.05	0.72
Lower Mokelumne River 6	Mokelumne River	0.57	1.37	1.47	1.55	**1.24**	0.45	0.23	0.45	1.04
Cache Slough at Liberty Island Mouth	Yolo Bypass-South	0.41	0.48	0.55	0.51	**0.49**	0.06	0.03	0.06	
Sherman Island	West Delta			0.42	0.48	**0.45**	0.04	0.02	0.04	0.31
Little Potato Slough	*Central Delta*	*0.20*	*0.34*	*0.34*	*0.38*	***0.31***	*0.08*	*0.04*	*0.08*	
Middle River at Borden Hwy (Hwy 4)	*Central Delta*	*0.27*	*0.23*	*0.43*	*0.28*	***0.30***	*0.09*	*0.04*	*0.09*	
	Central Delta	0.23	0.29	0.38	0.33	**0.31**	0.06	0.03	0.06	0.19
San Joaquin River at Vernalis	San Joaquin River	0.27	0.53	1.46	0.62	**0.72**	0.52	0.26	0.52	0.68

Overall Delta Mean (All Stations)	0.37	0.54	0.71	0.60

Table 4. Water year hydrologic classification from 2015 to 2019 for the Sacramento and San Joaquin valleys. Hydrologic classification index is shown in parentheses for a given year.
From https://cdec.water.ca.gov/reportapp/javareports?name=WSIHIST

Sacramento Valley Water Year Type	Sacramento Valley Water Year Hydrologic Classification	San Joaquin Valley Water Year Hydrologic Classification:	San Joaquin Valley Water Year Type
Wet (Equal to or greater than 9.2)	2017 (14.2) 2019 (10.3)	2017 (6.5) 2019 (4.9)	Wet (Equal to or greater than 3.8)
Above Normal (Greater than 7.8, and less than 9.2)			Above Normal (Greater than 3.1, and less than 3.8)
Below Normal (Greater than 6.5, and equal to or less than 7.8)	2018 (7.1) 2016 (6.7)	2018 (3.0)	Below Normal (Greater than 2.5, and equal to or less than 3.1)
Dry (Greater than 5.4, and equal to or less than 6.5)		2016 (2.4)	Dry (Greater than 2.1, and equal to or less than 2.5)
Critical (Equal to or less than 5.4)	2015 (4.0)	2015 (0.8)	Critical (Equal to or less than 2.1)

Table 5. Proposed aqueous mercury sampling design for Delta RMP for year 4 and beyond.

Station	High flow Season (March)	High flow Season (April)	Low flow Season (August)
Sacramento River at Freeport	X	X	X
Lower Mokelumne	X	X	X
Cache Slough	X	X	X
Mallard Island	X	X	X
Little Potato Slough	X	X	X
Middle River	X	X	X
San Joaquin River	X	X	X

APPENDIX 1

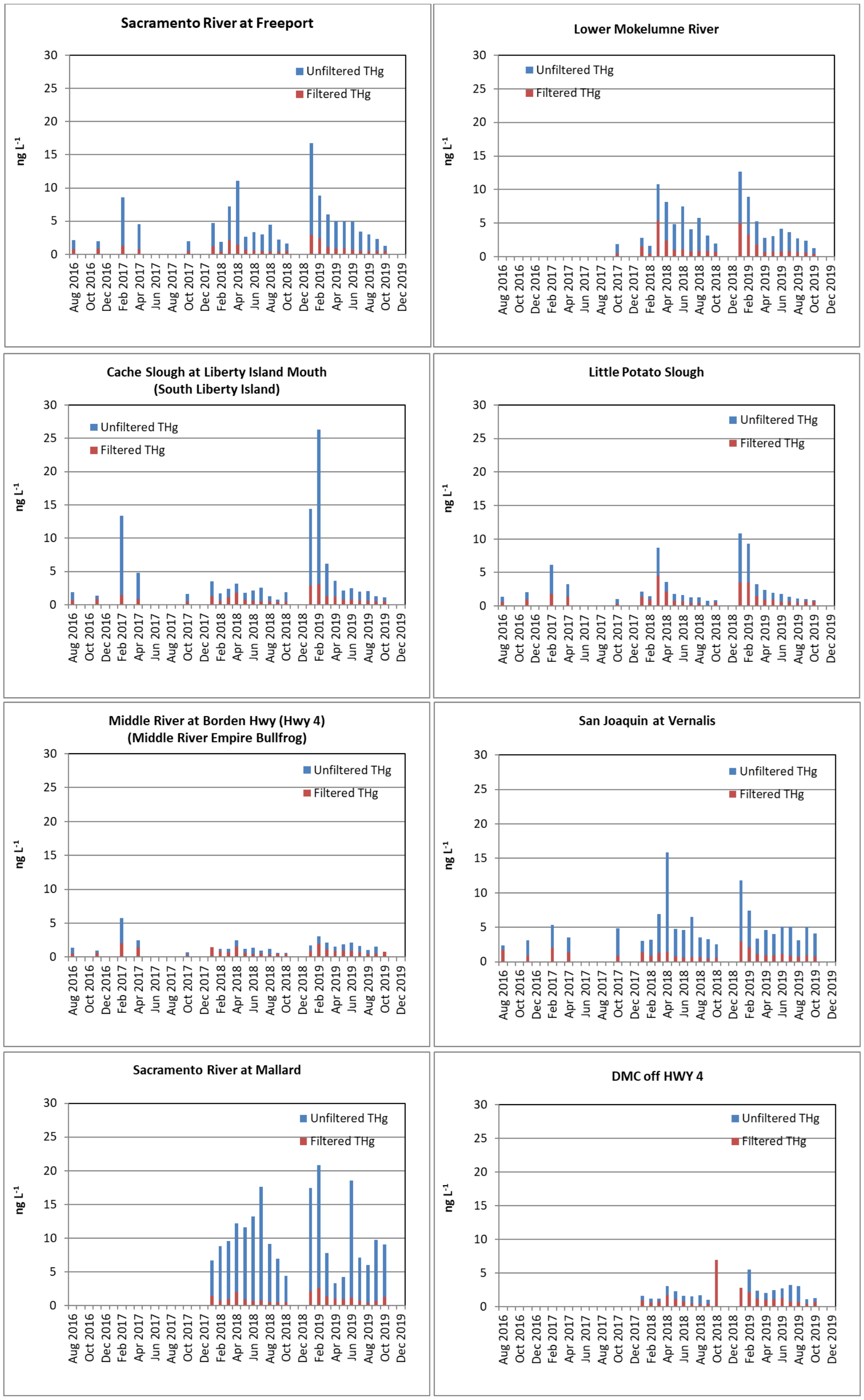
Aqueous Total Mercury

Aqueous total mercury (THg) concentrations were generally higher during the wet season and tapered off into the dry season (Figure 1). In contrast to MeHg, inorganic Hg (which predominates in THg) was preferentially bound to particles (average 90% of unfiltered THg was bound to suspended solids). The seasonal and spatial patterns in THg concentrations observed in the Delta are largely explained by the movement of suspended solids within and through the system mostly during higher flow events.

Excluding the export stations Sacramento River at Mallard and Delta Mendota Canal, total Hg concentrations were generally higher in the wet season and tapered off through the dry season (Figure 2). Sacramento River at Mallard total Hg concentrations were likely influenced by the location being at the boundary of San Francisco Bay and the estuarine turbidity maximum (an area at the interface of freshwater and saline water where suspended sediment concentrations are high) as reported by Cloern et al. (2017). This is due to the propensity of inorganic Hg to bind with particles. Unfiltered total Hg concentration was significantly positively correlated to TSS ($r^2 = 0.73$). Middle River and Delta Mendota both had uniformly low total Hg concentrations throughout the year due to a lack of suspended material in the water column at these stations.

References

Cloern, J.E., Jassby, A.D., Schraga, T.S., Nejad, E. and Martin, C. (2017), Ecosystem variability along the estuarine salinity gradient: Examples from long-term study of San Francisco Bay. Limnol. Oceanogr., 62: S272-S291. doi:10.1002/lno.10537


Sacramento River at Freeport

Lower Mokelumne River

Cache Slough at Liberty Island Mouth (South Liberty Island)

Little Potato Slough

Middle River at Borden Hwy (Hwy 4) (Middle River Empire Bullfrog)

San Joaquin at Vernalis

Sacramento River at Mallard

DMC off HWY 4

Figure A1-1. Concentrations of unfiltered and filtered total Hg over monthly timescale at sites representing a regional scale of the Delta. The top six panels are input sites to the Delta and the bottom panels are export sites. Panels on left and right represent relative west and east locations in the Delta, respectively.

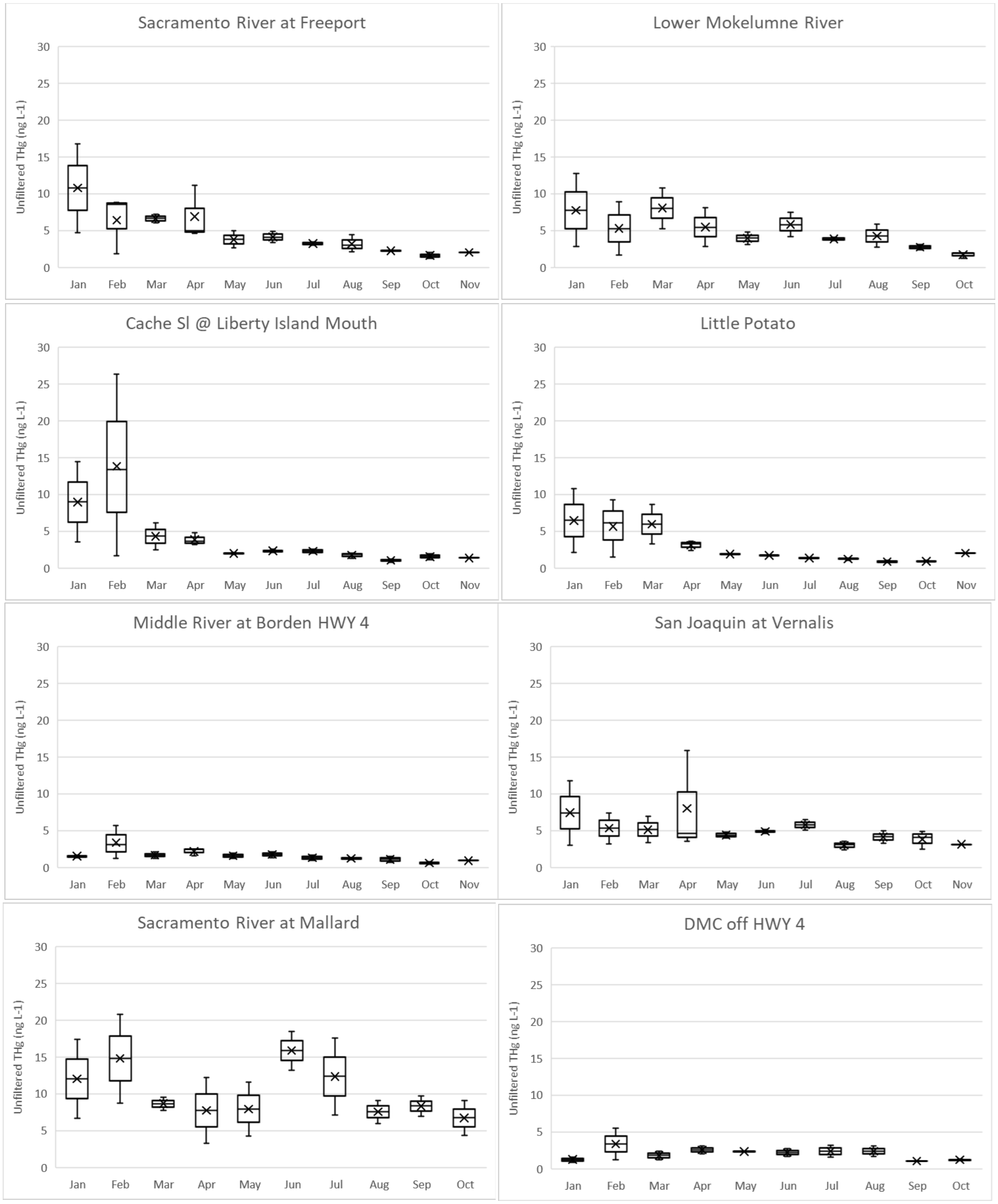


Figure A1-2. Unfiltered total Hg concentrations by month at each Delta RMP monitoring station. Plots show minimum and maximum, first and third quartile, median (line in boxplot) and average (X).

APPENDIX 2

Sediment

Sediment was collected from six Delta stations four times from October 2017 to June 2018. At each station sediment was collected from the bank as well as the thalweg. Sediment samples were measured as bulk sediment (not grain-size fractionated). Bank and thalweg THg and MeHg concentrations were not significantly different at these stations ($p = 0.23$ and 0.32 respectively). Therefore, bank and thalweg samples are used as replicates in the following discussion. Given bank and thalweg THg and MeHg concentrations were not significantly different, future sediment work at the stations need not make the distinction and it is unnecessary to target both locations for sampling for reasons other than replication.

Histograms of percent clay, silt, and sand for the top 2 cm of sediment indicate stations were dominated by sandy silt, and silt. Presence of clay in sediments was minimal at all stations. Cache Slough and Little Potato Slough were predominantly silty sediment with all other stations having a sandy silt surficial substrate.

Total organic carbon (TOC) ranged from 0.04 to 5.9% with a mean of 1.2% and a median of 0.4%. TOC was significantly positively correlated ($r^2 = 0.85$, $n = 35$, one outlier removed) with percent loss on ignition (LOI) in sediment. However, LOI under-predicted TOC by a factor of 3.6 at stations sampled and applying the correction would make it a useful proxy in the absence of TOC measurements.

Figure 1 (panel a) shows mean sediment total mercury (THg) concentrations. Sediment THg concentrations ranged from 0.01 to 0.13 $\mu g\ g^{-1}$. Four of the stations had mean THg concentrations less than 0.05 $\mu g\ g^{-1}$ indicating levels were at global background level of Hg contamination. Two stations, Cache Slough and Little Potato Slough had mean THg concentrations above background (0.12 ± 0.36 and 0.13 ± 0.46 $\mu g\ g^{-1}$ respectively). Mean THg concentrations did not have any obvious seasonal trend, remaining relatively constant over the year studied.

MeHg sediment concentrations varied from <RL to 3.09 $ng\ g^{-1}$ (Figure 1, panel b). The same four stations that had background levels of THg in sediment also had the lowest MeHg concentrations ranging from 0.065 ± 0.055 $ng\ g^{-1}$ to 0.214 ± 0.113 $ng\ g^{-1}$. The two stations with the highest THg concentrations, Little Potato Slough and Cache Slough, also had highest MeHg concentrations of 0.659 ± 0.440 $ng\ g^{-1}$ and 1.36 ± 0.99 $ng\ g^{-1}$ respectively.

Figure 1 (panel c) depicts the relative Hg methylation potential of each station as determined by the ratio of MeHg to THg. Most stations showed a lack of potential for mercury methylation with ratios of 0.5% or less. Cache Slough had the highest ratio (1.1 %) followed by Middle River. However, unlike Cache Slough which had relatively high concentration of MeHg, a high ratio at Middle River was driven by a lower THg concentration rather than by a higher MeHg concentration.

A multiple regression analysis was conducted to test if THg sediment concentration and percent total organic carbon (TOC) in sediment predicted sediment MeHg concentration. Results of the regression indicated the two predictors THg and TOC explained 43.7% of the variance in MeHg sediment concentration ($F(2, 45) = 17.49$, $p < .01$, $R^2 = .437$). THg sediment concentration significantly predicted MeHg sediment concentration ($\beta = 6.03$, $p < .01$), but TOC did not ($\beta = 0.074$, $p > .05$).

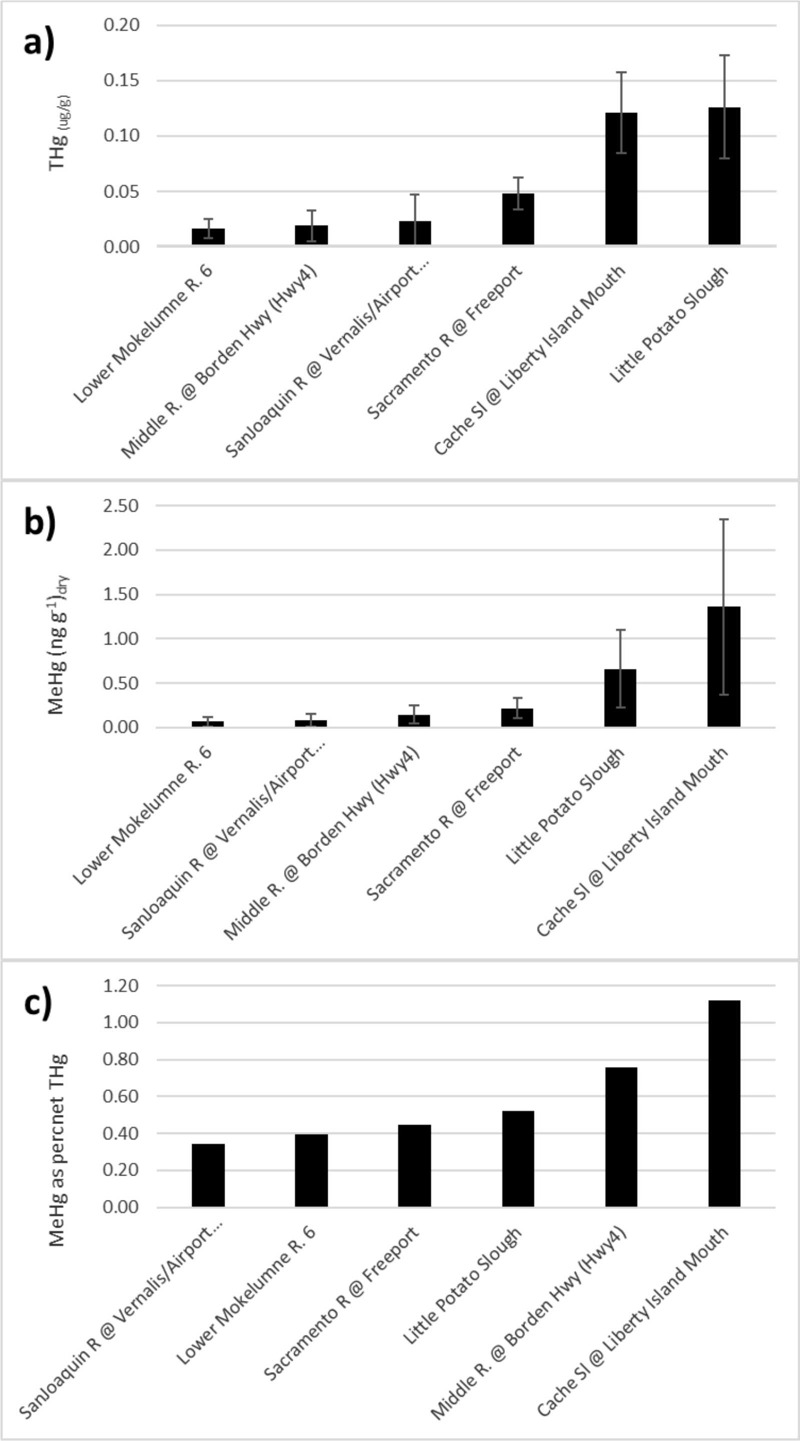


Figure A2-1. Sediment THg (a), MeHg (b), and MeHg as percent THg (c) at sampling sites. Results are presented as average of four sampling events with sediment grabs from bank and thalweg. Error bars indicate standard deviation.