Mercury Imports and Exports of Four Tidal Wetlands in the Sacramento-San Joaquin Delta, Yolo Bypass, and Suisun Marsh for Delta Mercury Control Program Compliance

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Acronyms and Abbreviations

ADCP – Acoustic Doppler Current Profiler
Blacklock – Blacklock Tidal Wetland
BPA – Basin Plan Amendment
Delta – Sacramento-San Joaquin Delta
DMCP – Delta Mercury Control Plan as laid out by the Delta Mercury Total Maximum Daily Load and Basin Plan Amendment
DOC – Dissolved organic carbon
Dutch Slough – Dutch Slough Tidal Marsh Restoration Project
DWR – California Department of Water Resources
EIR – Environmental Impact Report
Lookout Slough – Lookout Slough Tidal Habitat Restoration and Flood Improvement Project
Lower Yolo Ranch – Lower Yolo Ranch Restoration Project
MDL – Method detection limit
MeHg – Monomethyl mercury
MQO – Measurement quality objective
MWT – McCormack-Williamson Tract
North Lindsey – North Lindsey Slough Tidal Wetland
POC – Particulate organic carbon
Regional Board – Central Valley Regional Water Quality Control Board
RL – Reporting limit
RPD – Relative percent difference
THg – Unfiltered total mercury, all mercury species
TMDL – Total Maximum Daily Load
TOC – Total organic carbon
TSS – Total suspended solids
Westervelt – Westervelt Cosumnes River Tidal Wetland
YWA – Yolo Wildlife Area
Yolo – Yolo Wildlife Area Tidal Wetland

Executive Summary

In 2010, the Central Valley Regional Water Quality Control Board (Regional Board) approved the Sacramento-San Joaquin Delta Methylmercury (MeHg) Total Maximum Daily Load (TMDL) and Basin Plan Amendment (BPA) which established a Delta Mercury Control Program (DMCP) for the Sacramento-San Joaquin Delta (Delta) and Yolo Bypass. The California Department of Water Resources (DWR) was named as a discharger and wetlands were given a discharge allocation.

To calculate discharge allocations for wetlands, the TMDL/BPA relied on a small amount of existing MeHg wetland data, and dischargers such as DWR were called upon to develop management practices to decrease the amount of MeHg being discharged by tidal wetlands. However, the data underlying the wetland allocations were not representative of tidal wetlands, partly because not enough characterization data existed; not enough tidal wetland restoration projects had been completed to characterize. Because of the lack of characterization data, any management practices built upon the existing data were unlikely to be effective. Consequently, DWR chose to characterize four tidal wetlands to determine whether tidal wetlands were importing or exporting MeHg and by what mechanisms.

To characterize MeHg, DWR studied imports and exports of MeHg, total mercury (THg), and organic carbon at four tidal wetlands: the Yolo Wildlife Area Tidal Wetland (Yolo) in the Yolo Bypass, Blacklock Tidal Wetland (Blacklock) in Suisun Marsh, North Lindsey Slough Tidal Wetland (North Lindsey) in the Cache Slough Complex, and the Westervelt Cosumnes River Tidal Wetland (Westervelt) east of the confluence of the Cosumnes and Mokelumne Rivers. DWR collected the concentration data from approximately monthly tidal events and combined that with flow data to calculate loads, which are masses of mercury; loads were calculated per 25-hour tide as well as estimated per month. DWR also compared mercury ebb and flood concentrations to determine if there was a significant difference.

Based on the collected data and analyses, none of the four wetlands appear to be a significant source of MeHg to their adjacent waterbodies, nor are concentrations of MeHg significantly higher leaving the wetland than entering the wetland. Generally, the waters entering the wetlands are not meeting the Regional Board's DMCP water quality criterion of 0.06ng/L, and there does not seem to be a measurable annual increase in MeHg loads in receiving waters due to the tidal wetlands.

While the four tidal wetlands do not appear to be a source of MeHg annually, Westervelt and North Lindsey appear to be a source of THg. Westervelt is a source of particulate THg, although because of how few times DWR was able to sample mercury, more data would be advantageous to determine any patterns. Blacklock and Yolo appear to be sinks of THg, predominantly in the particulate form.

DWR did not see any strong mercury seasonal patterns, possibly because of the small data sets. Additionally, the majority of mercury was in the particulate fraction for most of the wetlands,

except for North Lindsey which had a higher median percent of filtered MeHg than particulate MeHg.

Several future directions for studies present themselves: better resolution of the data to include more frequent sampling, a larger number of wetlands, and a longer period of time would be incredibly beneficial to see if estimates are representative. This study did not look at the toxicity of mercury in the biota, it only looked at water concentrations. Delving into the toxicity and measuring concentrations of MeHg in native organisms is necessary to determine any direct effects of mercury on those organisms, and organisms that prey on them. Lastly, this dataset provides a base for modeling tidal wetland mercury dynamics, which could help improve knowledge of mercury cycling.

Introduction and Background

The Sacramento-San Joaquin Delta Methylmercury (MeHg) Total Maximum Daily Load (TMDL) and Basin Plan Amendment (BPA) established a Delta Mercury Control Program (DMCP) for the Sacramento-San Joaquin Delta (Delta) and Yolo Bypass. The TMDL and BPA were approved by the Central Valley Regional Water Quality Control Board (Regional Board) in 2010. The DMCP established two phases for potential dischargers of MeHg, which included the California Department of Water Resources (DWR), to comply with the TMDL and BPA. Phase 1 directed DWR to develop management practices for named "discharges", including tidal wetlands, to reduce MeHg discharge as per wetland allocations outlined in the TMDL/BPA. This report of our Phase 1 study is for submission to the Regional Board for review. Based on our report from Phase 1 and other new information, the Regional Board may adjust MeHg wetland allocations prior to implementing Phase 2. Phase 2 directs dischargers to implement the management practices that were developed in Phase 1 to decrease MeHg discharge to meet allocations (Wood, Morris, Cooke, & Louie, 2010; Wood, Foe, Cooke, & Louie, 2010).

To develop the DMCP MeHg allocations for all wetlands, the Regional Board used existing data to characterize the area. The existing data was derived from managed permanent and seasonal wetlands, back end sloughs, and a hydrodynamically leaky tidal wetland that had a highly estimated flow measurement; none of these wetlands were representative of the tens of thousands of acres of tidal wetland restorations being planned by DWR and other organizations (Wood, Foe, Cooke, & Louie, 2010; CDWR, 2013). This meant that MeHg and unfiltered total mercury (THg) dynamics, imports, and exports of tidal wetlands were poorly understood at the time the TMDL and BPA allocations were developed.

The lack of adequate wetlands to study in the Delta and Yolo Bypass meant that very little information existed about when and how tidal wetlands may affect MeHg in the DMCP project area. Without some basic characterizations of imports and exports of tidal wetlands, potential management practices could not be developed nor could DWR or the Regional Board be assured that any management practices that were developed would be effective or necessary. Consequently, the Regional Board approved DWR's Phase 1 workplan to study and characterize MeHg and THg imports and exports of several tidal wetlands.

Since the collection of the data used to calculate allocations by the Regional Board, several tidal wetlands have been restored within the Delta, Yolo Bypass, and Suisun Marsh. Consequently, DWR had access to study more hydrodynamically contained tidal wetlands within the DMCP project area. In this study, DWR chose four tidal wetlands within the DMCP area and nearby Suisun Marsh to collect data. This report and the data from this study will be provided to the Regional Board so that any allocation adjustments and future management practices that are deemed necessary will be based upon a more robust and applicable data set for tidal wetlands. To date, this is the largest study of MeHg imports and exports of tidal wetlands within the Delta and Yolo Bypass, and future work will be important to build upon, verify, and refine these results.

In the original workplan, DWR presented five objectives and hypotheses that have remained unchanged; this report is centered around those (CDWR, 2013).

Objectives of the study were the following:

1. Determine whether these tidal wetlands are net sources or net sinks of MeHg and THg by measuring and calculating imports and exports;
2. Measure and calculate monthly and/or bimonthly MeHg imports and exports to determine if seasonal differences occur;
3. Measure and calculate net yearly organic carbon, chlorophyll-a, total suspended solids imports and exports;
4. Determine if organic carbon and MeHg concentrations are correlated; and
5. Provide data to the Regional Board for a revision of the MeHg allocations.

The following hypotheses were evaluated for each wetland:

1. Tidal wetlands are a net source of total MeHg on an annual basis;
2. Tidal wetlands are a net source of total THg on an annual basis;
3. Tidal wetlands have higher total and dissolved MeHg exports during the warmer, summer months;
4. Tidal wetlands are a net source of dissolved MeHg and a sink for particulate MeHg and THg on an annual basis; and
5. Organic carbon concentrations and MeHg concentrations are positively correlated.

Updates to the Workplan Hypotheses and Objectives

In the original workplan, DWR had outlined possible wetlands for characterization studies. After consideration and consultation with Regional Board staff, we chose four tidal wetlands. The four tidal wetlands include 1) the Yolo Wildlife Area Tidal Wetland (Yolo) in the Yolo Bypass, 2) the Blacklock Tidal Wetland (Blacklock) in Suisun Marsh, 3) the North Lindsey Slough Tidal Wetland (North Lindsey), and 4) the Westervelt Cosumnes River Tidal Wetland (Westervelt) near the confluence of the Mokelumne and Cosumnes Rivers.

As outlined in DWR's progress report (Lee, Bosworth, & Manning, 2015), few changes were made to the original workplan. We discussed changes and received approval from Regional Board staff. DWR has not made other changes to this study but did include supplemental information within this report beyond what was previously discussed. The changes mentioned in DWR's 2015 progress report included:

- DWR collected data from four wetlands.
- DWR studied the Yolo first, followed by Blacklock, then North Lindsey, and completed the study with Westervelt.
- DWR sampled monthly, or as close to monthly as possible throughout the year, except during times of equipment failures and large weather events.

DWR did not measure groundwater, evapotranspiration, or precipitation contributions to the water balance as it was too cost prohibitive, and ultimately, they were not direct contributors of mercury to the receiving waters as outlined in the TMDL and BPA.

Additionally, we have provided an analysis of particulate and filtered mercury fractions, imports and exports of MeHg and THg per acre for each wetland, and a brief summary of DWR's currently planned restoration projects and restoration projects under construction.

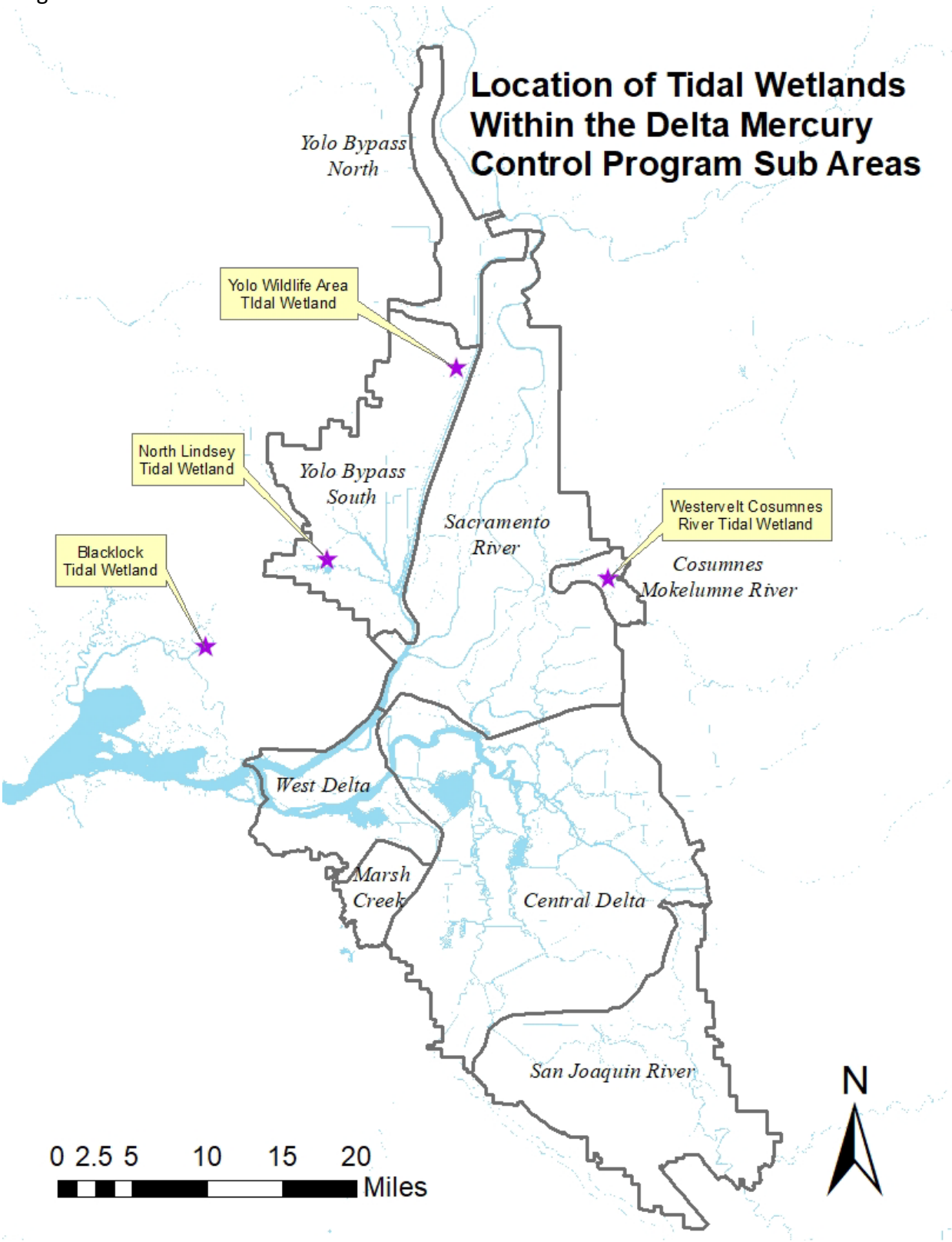
Lastly, the mercury nomenclature we have used in this report differs slightly from the previous DWR reports, the TMDL and BPA, and our monitoring plan. We have used the terms "unfiltered THg" and "unfiltered MeHg" to replace "total THg" and "total MeHg". We have also used the terms "filtered THg" and "filtered MeHg" rather than the terms "dissolved THg" and "dissolved MeHg".

Study Area

The number of wetlands that DWR could feasibly and practically study was limited for several reasons. First, the study required an accurate water balance for tidal flow. In practice, measuring the imports and exports at each wetland required wetlands with one or two openings only. In addition, the wetland could not have connectivity to outside waterbodies other than at the one or two main opening(s). Second, porosity of the wetland compromised the water balance, so the wetland needed to be channelized or bounded by levees to measure an accurate water balance. Finally, we needed access to the land near the opening(s) to place flow and water quality equipment, which ruled out several wetlands as selected study sites, including the southern portion of Lindsey Slough Tidal Wetland and Wildlands, Inc. Liberty Island Conservation Bank Tidal Wetland. These requirements left only one privately owned tidal wetland, and a small number of State-owned tidal wetlands for us to study.

DWR chose to study four wetlands that met our requirements. The next section provides details for each of the wetlands studied, in order of date studied. Figure 1 shows an overview of wetland locations in and around the DMCP area.

Figure 1 – Location of Four Tidal Wetlands Studied by DWR in the Delta Mercury Control Program Area. Subareas are shown.

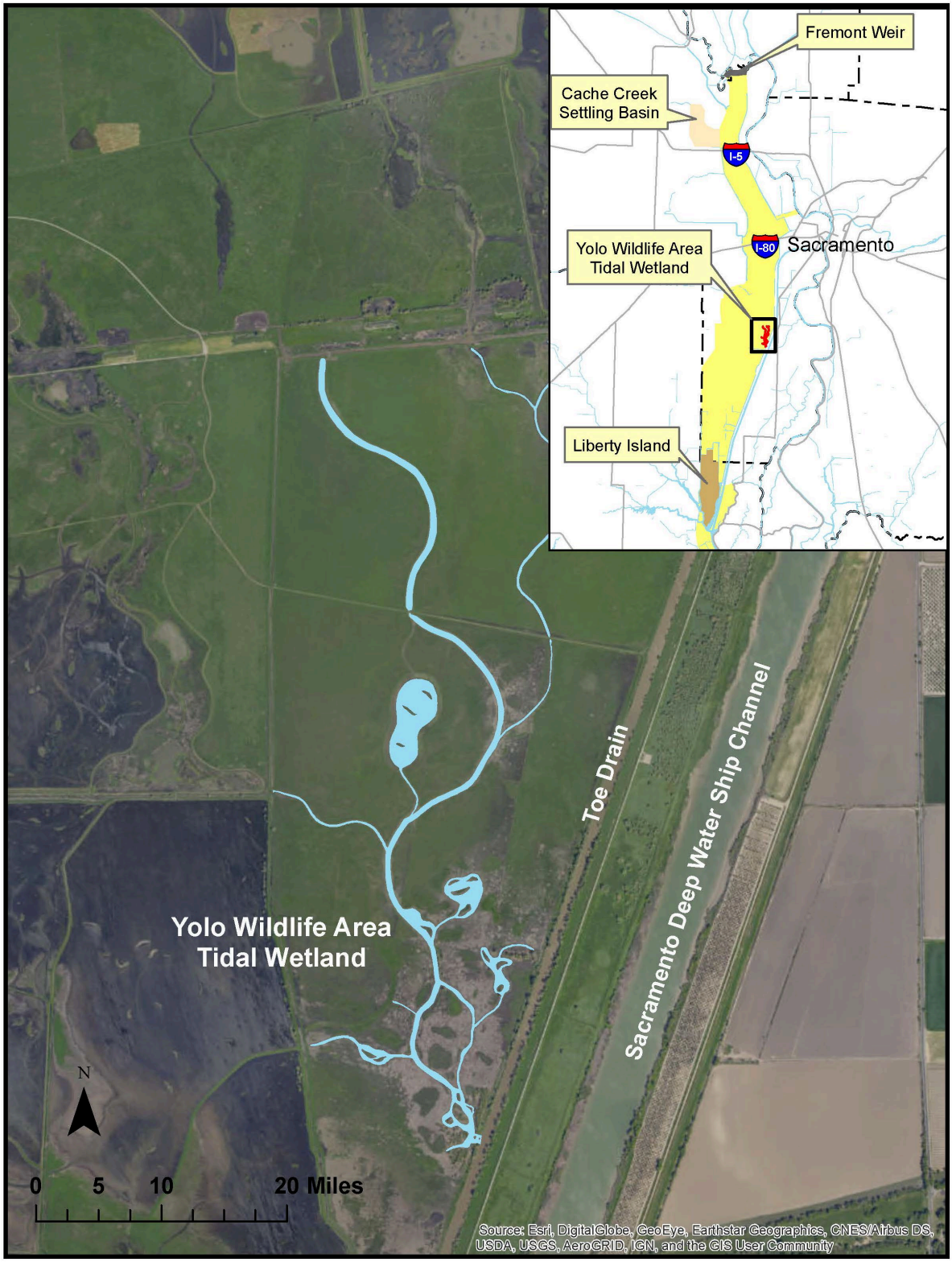


Yolo Wildlife Area Tidal Wetland

DWR studied the Yolo Wildlife Area Tidal Wetland (Yolo) from May 2014 through April 2015. The Yolo site is located in the Yolo Bypass – South Subarea; the Yolo Bypass is a 59,000-acre flood plain system designed to divert storm water from the Sacramento River around the City of Sacramento, so the wetland is inundated during flood flows. The opening of the Yolo is on the "Toe Drain", which is a channel along the eastern side of the Yolo Bypass that contains water throughout the year. The wetland is at the south-most edge of the Yolo Wildlife Area (see Figure 2).

The freshwater tidal wetland is managed by the California Department of Fish and Wildlife and contains approximately 31 acres of tidal channels; the wetland is very channelized, with fast moving water, and only rises out of bank during flood events. In 2010, the wetland was permanently breached after the existing channels had been deepened after several accidental breaches beginning in the 1990s. There is little to no vegetation within the channels besides water hyacinth, and tules and cattails grow sparsely along the channel edges. In December 2014, the eastern side of the Yolo Bypass flooded, and we had to remove our equipment temporarily.

Figure 2 – A map of the Yolo Wildlife Area Tidal Wetland located in the Yolo Bypass - South subarea.

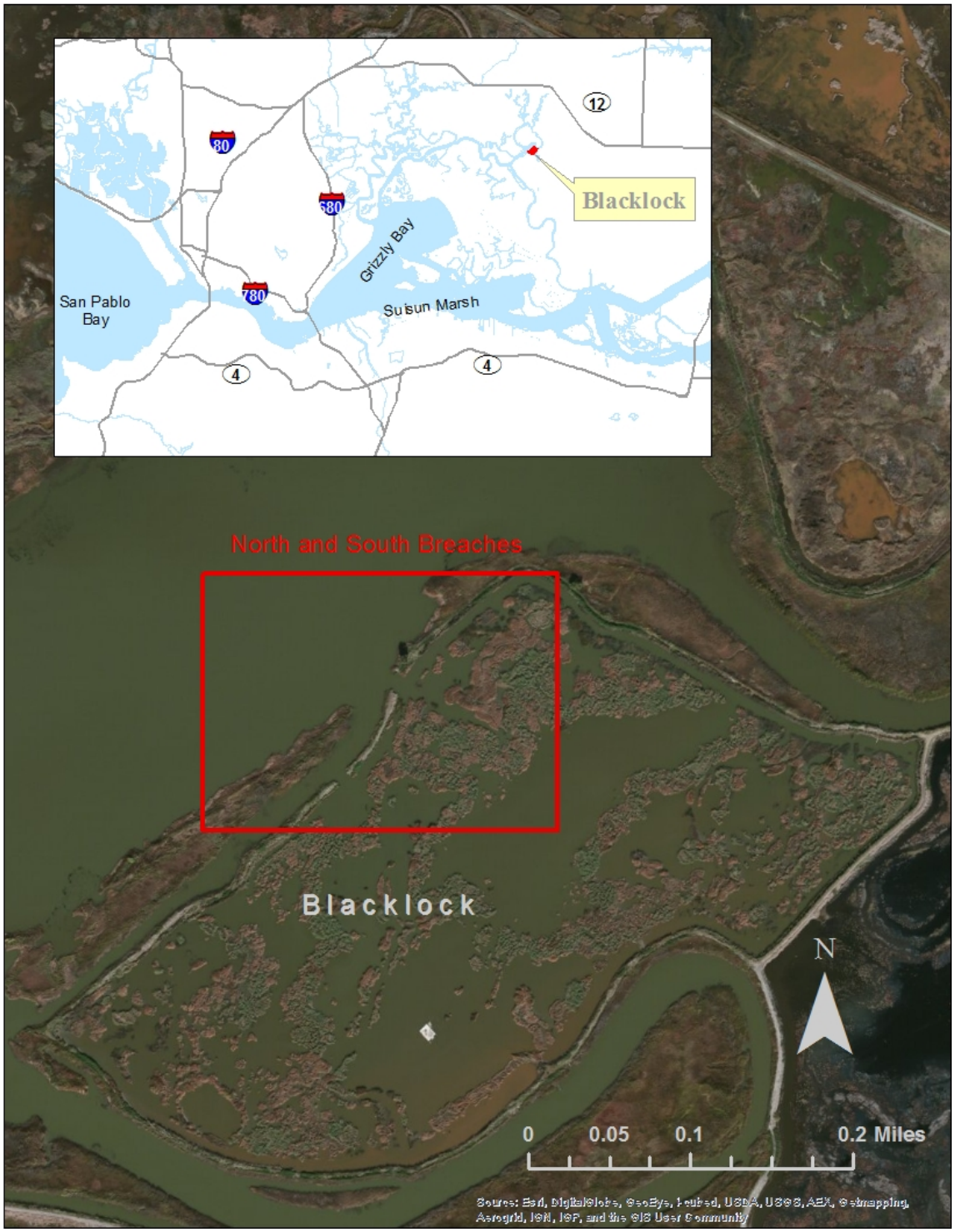


Blacklock Tidal Wetland

Beginning June 2015 through June 2016, we studied the second tidal wetland, the Blacklock Tidal Wetland (Blacklock). Blacklock is an approximately 70-acre brackish tidal wetland located west of the DMCP Area in Suisun Marsh and opens to Little Honker Bay (Figure 3). Suisun Marsh is regulated by the Suisun Marsh Mercury and Dissolved Oxygen TMDL (CRWQCB-SF, 2018). The wetland was chosen because 1) of its proximity to the DMCP Area, 2) the wetland is contained entirely within levees, 3) of the two wetland openings, 4) it was owned by DWR and therefore readily accessible, and 5) it is in an area where DWR is doing future tidal restorations.

Acquired by DWR in December 2003, an unplanned breach occurred on the property in July 2006, and this was followed by a second planned breach nearby in October 2006. The wetland is entirely flooded at high tide and at low tide has numerous shallow areas and exposed mud flats, but the soil never dries out. The wetland is inhabited by native tules, *Schoenoplectus sp*., and as the study progressed, the non-native *Phragmites australis* began to encroach the site and replace the *Schoenoplectus sp*.

Figure 3 – A map of the Blacklock Tidal Wetland located in Suisun Marsh, outside of the DMCP area.

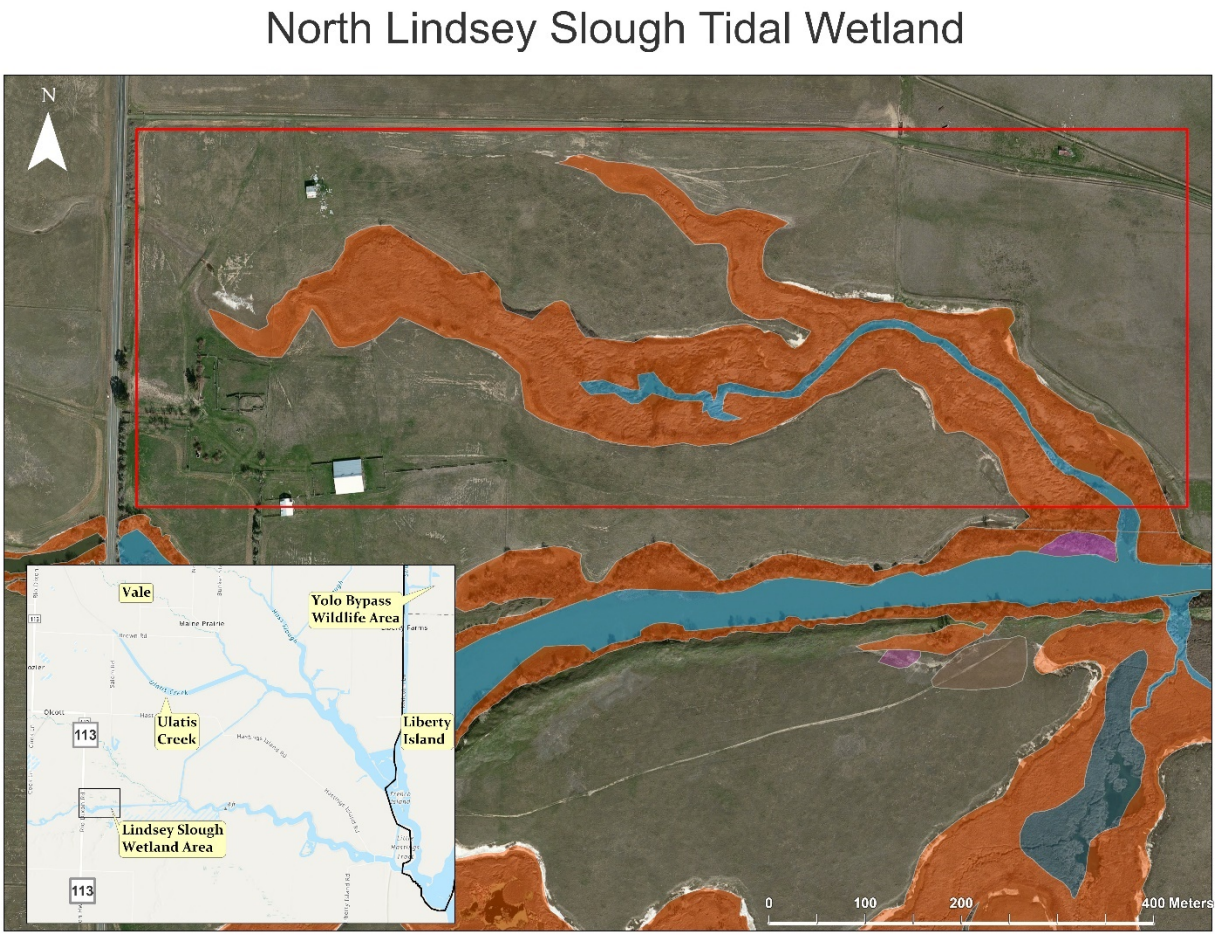


North Lindsey Slough Tidal Wetland

DWR studied the third wetland, North Lindsey Slough Tidal Wetland (North Lindsey), from December 2016 through June 2018. North Lindsey is located in the Cache Slough Complex, Yolo Bypass – South subarea, in what was historically back water sloughs and marsh. North Lindsey opens to Calhoun Cut to the south, and the wetland is the only historical wetland fragment that we studied. The wetland was muted tidal due to a broken flap gate and was officially breached in 2014 by the California Department of Fish and Wildlife (Carrothers, Email Communication, 2019).

North Lindsey is the smallest wetland we studied and is 22 acres, including a 1.8-acre channel; it also has the slowest negative and positive velocities. All work was done in the breached area about 100 meters from Calhoun Cut as the breach was relatively clear of tules compared to the rest of the wetland. See Figure 4 for maps of the tidal wetland.

Figure 4 – A map of the North Lindsey Slough Tidal Wetland located in the Cache Slough Complex, Yolo Bypass – South subarea. The blue area is the channelized water and the orange area is the full extent of the tidal wetland that stays wet and is submerged at higher tide.



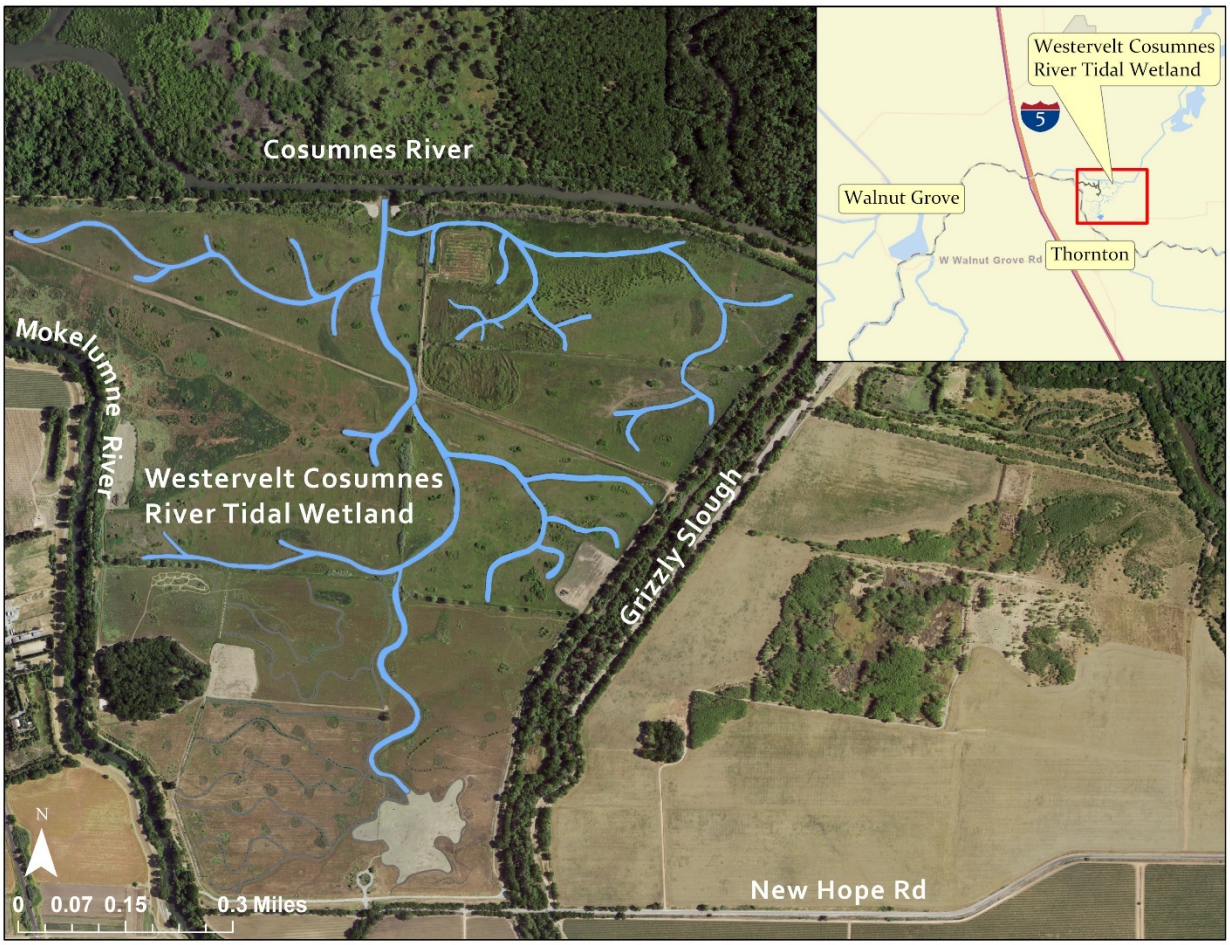
Westervelt Cosumnes River Tidal Wetland

The Westervelt Cosumnes River Tidal Wetland (Westervelt) was the fourth and final tidal wetland that DWR studied from August 2018 through July 2019. The wetland opening is at the Cosumnes River, east of the confluence of the Mokelumne River, and is located in the Cosumnes/Mokelumne River subarea (Figure 5).

While the wetland is tidally influenced, the area is also a flood plain during winter and spring months. When water levels are lower, the freshwater tidal wetland has approximately 22 acres of tidal channels and the water does not generally leave those channels. Once water levels rise, due to increased water from the Cosumnes River, the wetland's flood plain fills a nearly 500-acre area that is bounded by levees. During the heavy rains of 2017, the Westervelt wetland was flooded to its maximum of nearly 500 acres for several months and much of the existing cattail population was drowned and killed (Gause, 2020).

This wetland was unusual in that it was the only wetland we studied that was designed to include a flood plain portion along with channelized flows during non-flood flows. This design is common in the Cosumnes/Mokelumne River subarea as it is a flood plain. Yolo was also in a flood plain, the Yolo Bypass, but water flows over the Yolo, whereas Westervelt fills up and drains through its opening to the Cosumnes River.

Figure 5 – A map of the Westervelt Cosumnes River Tidal Wetland located in the Cosumnes/Mokelumne River subarea.



Methods

In this study, DWR followed selected methodologies of Mitchell and others (2012). We will summarize our methods in this section. Additional details about sampling, including our Standard Operating Procedures, are in the attached Monitoring Plan. DWR studied four wetlands for approximately one year each and collected four types of data, 1) continuous 15-minute flow data, 2) continuous 15-minute water quality sonde data, 3) discrete water quality grab sample data, and 4) 25-hour autosampler water quality event data. We established a monitoring station at the opening(s) of each tidal wetland and collected all four types of data within the opening, with one exception. At Blacklock, we were not able to deploy water quality sondes to collect the continuous 15-minute data because of deep channels and steep and unstable bank geometry in addition to high water velocities.

Ebb and Flood Tide Characterization

Continuous 15-Minute Flow Data

To measure the level and velocity used to calculate flows, we used a SonTek IQ Plus Acoustic Doppler Current Profiler (ADCP) that we placed on the bottom of the channel opening(s) of each wetland. The SonTek ADCPs use five up-looking beams to calculate level and velocity and data was reported at 15-minute minute intervals. DWR calculated flow using the methods of Levesque and Oberg (2012), and used cubic spline interpolation to estimate missing flow data up to six hours; gaps larger than six hours could not be estimated.

Continuous 15-Minute Water Quality Sonde Data and Discrete Water Quality Grab Sample Data

Basic water quality parameters were collected every 15-minutes using YSI EXO water quality sondes. The sondes were mounted within the opening to adjacent water body of each wetland, except Blacklock, to collect temperature, specific conductance, turbidity, dissolved oxygen, and total chlorophyll data. We followed the YSI EXO User Manual collection and calibration methods for the first three wetlands. As an agency, DWR began following a modification of the Wagner Method (Wagner, Boulger Jr., Oblinger, & Smith, 2006) for verifying sonde data, so we used that method to collect data at Westervelt beginning in 2018.

Sonde data was combined with discrete grab sample data to estimate continuous data for total suspended solids (TSS) and chlorophyll-a. To calculate estimated 15-minute TSS and chlorophyll-a values from continuous 15-minute turbidity and total chlorophyll sonde data, we collected the discrete TSS and chlorophyll-a water quality samples approximately weekly or as often as possible.

Using methods described in the YSI EXO User Manual, we used the continuous 15-minute turbidity sonde data and the discrete grab sample TSS data to estimate continuous 15-minute TSS data. The discrete TSS samples were matched to the continuous 15-minute turbidity sonde values by date and time and used to calculate a regression equation; the regression equation was used to calculate estimated continuous 15-minute TSS concentrations from the continuous 15-minute turbidity sonde values.

The discrete chlorophyll-a samples were used in a similar manner to estimate continuous 15-minute chlorophyll-a from the continuous 15-minute total chlorophyll sonde data. However, the chlorophyll data from the sonde was not as reliable, partly because of the low concentration of chlorophyll-a in two of the wetlands. Chlorophyll-a was calculated using a regression curve only at Westervelt. At the other two wetlands, Yolo and North Lindsey, DWR staff calculated a ratio of chlorophyll-a and total chlorophyll measurements, and used that to estimate continuous 15-minute chlorophyll-a values rather than using a poor regression equation (Proctor & Roesler, 2010; Earp, et al., 2011). Due to some methodological errors while filtering chlorophyll-a samples, we do not have high confidence in the chlorophyll-a estimations using total chlorophyll sonde data.

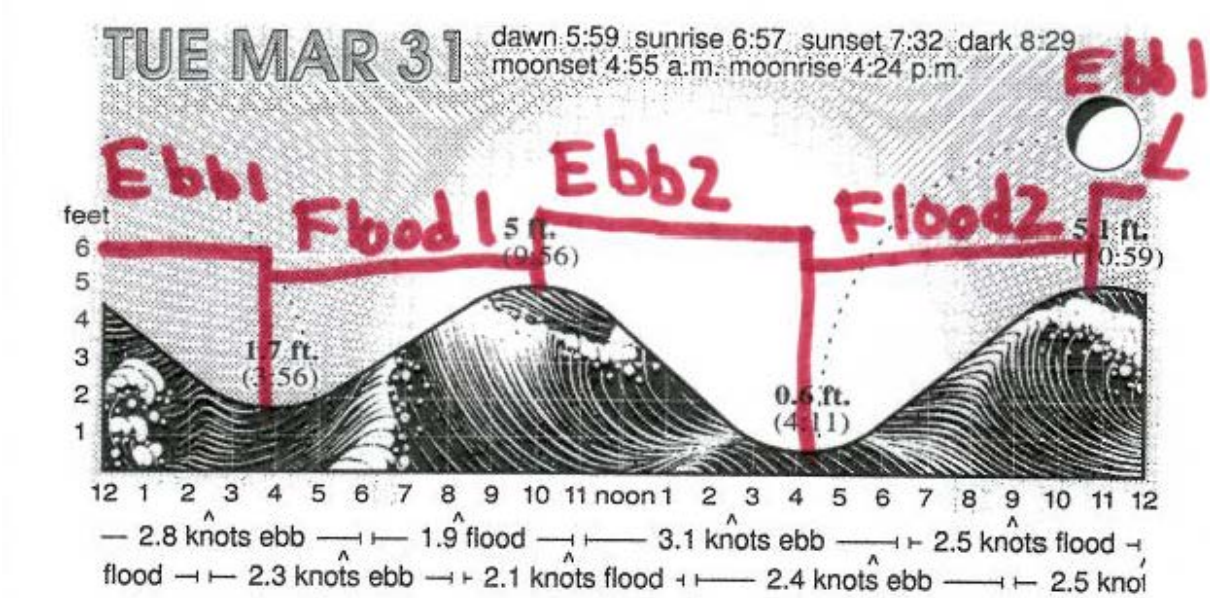
More information about sample collection methods and sonde parameters can be found in the Monitoring Plan attached to this report.

25-Hour Autosampler Water Quality Event Data

DWR used ISCO autosamplers deployed at the opening of each wetland to collect hourly water quality data over a 25-hour period, which is the length of time required to measure a full tidal cycle. The composited water samples discussed in this section were analyzed for unfiltered THg, filtered THg, unfiltered MeHg, filtered MeHg, total and dissolved organic carbon (TOC and DOC, respectively), and TSS. We will refer to this data as 25-hour event data throughout the rest of this report.

First, we used the flow data to calculate and composite four flow-weighted tides, two floods and two ebbs. Figure 6 is an example of how tides were divided into two floods and two ebbs using flow data. The methods of compositing the samples is explained in much more detail in the Monitoring Plan attached to this report.

Figure 6 – Example of flow-weighted compositing by tidal cycle.



Load Calculations Using Continuous and Event Data

We calculated loads using one of two methods. For analytes with 15-minute continuous data, we used the continuous data to estimate concentrations and calculate loads. For analytes without continuous 15-minute data, we relied on concentrations measured from our 25-hour event sampling to calculate loads. Based on this approach, TSS was the only analyte where loads were calculated using both methods.

Using the first method to calculate TSS and chlorophyll-a loads, we matched continuous 15-minute water quality data to the continuous 15-minute flow data. We calculated a load for each 15-minute interval and then summed each calendar day to get a total daily load. Both 15-minute water quality and flow data were missing at times, so days without a full set of data were omitted. Next, we averaged the daily loads in each calendar month, and then we multiplied each month's daily average by the total number of days in that month to get a monthly load.

We used the second method to calculate monthly mercury, organic carbon, and TSS loads; this method is more complicated and likely less accurate because we had fewer discrete concentration values when using the 25-hour event data. Because we had only collected 25-hour event data at monthly (or longer) intervals, this meant we had only 8-13 concentration data points to calculate loads, depending on the wetland. We calculated a flow-weighted ebb and flood concentration for each 25-hour event that we were able to use when populating concentration values; we used ebb concentrations for ebb flow values and flood concentrations for flood flow values.

When calculating monthly loads with 25-hour event concentration data, we began by calculating the date and time halfway between each 25-hour event and using that as a dividing line for assigning the concentration data to the flow data. Table 1 is an example of how we divided the time brackets used to assign 25-hour sampling event concentration data to the 15-minute flow data.

Next, we assigned the concentrations for the 25-hour events to the 15-minute flow data halfway before and after that 25-hour event date. We assigned the 25-hour event concentration data points to each 15-minute flow data point, then added up each day's load to calculate monthly loads. Figure 7 shows an example of the calculations.

Table 1 – An example of calculated time brackets around 25-hour events used to assign 25-hour water quality event data to continuous 15-minute flow data.

25-Hour Event Sample Dates and Times	Start Date and Time of Data Assigned to Flow Values Bracketing 25-Hour Sample Event	End Date and Time of Data Assigned to Flow Value Bracketing the 25-Hour Sample Event
6/27/2017 11:00 - 6/28/2017 11:00	6/1/2017 0:00	7/28/2017 22:45
8/28/2017 10:30 - 8/29/2017 10:30	7/28/2017 23:00	9/12/2017 10:45
9/26/2017 11:00 - 9/27/2017 11:00	9/12/2017 11:00	10/10/2017 23:15
10/24/2017 11:30 - 10/25/2017 11:30	10/10/2017 23:30	11/4/2017 11:45
11/14/2017 12:15 - 11/15/2017 12:15	11/4/2017 12:00	11/29/2017 0:00
12/12/2017 12:00 - 12/13/2017 12:00	11/29/2017 0:15	1/10/2018 0:30
2/6/2017 12:00 - 2/7/2017 12:00	1/10/2018 0:45	2/17/2018 12:00
2/27/2018 12:15 - 2/28/2018 12:15	2/17/2018 12:15	3/17/2018 11:45
4/3/2018 11:15 - 4/4/2018 11:15	3/17/2018 12:00	4/14/2018 11:15
4/24/2018 11:15 - 4/25/2018 11:15	4/14/2018 11:30	5/5/2018 11:30
5/15/2018 11:30 - 5/16/2018 11:30	5/5/2018 11:45	5/29/2018 23:15
6/12/2018 11:15 - 6/13/2018 11:15	5/29/2018 23:30	6/30/2018 23:45

Figure 7 – Example of THg monthly load calculations. Concentration data was derived from flow-weighted composited 15-minute event data.

Date and Time	Unfiltered THg (ng/	Filtered THg (ng/	Particulate THg (ng/l	Raw Flow (cfs)	Interpolated Flow (cfs)	Unfilt THg 15-min Load (	Filtered THg 15-min Load (g)	Particulate THg 15-min Load (	Tidal Cycle
07/29/2019 16:15	6.2	1.1	5.1	-59	-59	-0.009322472	-0.00165	-0.00767	Flood
07/29/2019 16:30	6.2	1.1	5.1	-60	-60	-0.00948048	-0.00168	-0.00780	Flood
07/29/2019 16:45	6.2	1.1	5.1	-58	-58	-0.009164464	-0.00163	-0.00754	Flood
07/29/2019 17:00	6.2	1.1	5.1	-56	-56	-0.008848448	-0.00157	-0.00728	Flood
07/29/2019 17:15	6.2	1.1	5.1	-49	-49	-0.007742392	-0.00137	-0.00637	Flood
07/29/2019 17:30	6.2	1.1	5.1	-39	-39	-0.006162312	-0.00109	-0.00507	Flood
07/29/2019 17:45	6.2	1.1	5.1	-25	-25	-0.0039502	-0.00070	-0.00325	Flood
07/29/2019 18:00	6.2	1.1	5.1	-10	-10	-0.00158008	-0.00028	-0.00130	Flood
07/29/2019 18:15	19.6	1.5	18.1	3	3	0.001498528	0.00011	0.00138	Ebb
07/29/2019 18:30	19.6	1.5	18.1	14	14	0.006993128	0.00054	0.00646	Ebb
07/29/2019 18:45	19.6	1.5	18.1	21	21	0.010489693	0.00080	0.00969	Ebb
07/29/2019 19:00	19.6	1.5	18.1	25	25	0.012487729	0.00096	0.01153	Ebb

For dates we lacked load data, we substituted an average daily load that we calculated from the daily loads from that month. If we had more than a month and a half gap between sampling dates, we used best professional judgment to apply concentrations to the flow data. This gave us a very rough estimate of mercury, organic carbon, and TSS loads for each month.

Missing Data in More Depth

Above we discussed how we dealt with missing data as part of our procedures, but this section discusses why there are data gaps and in a very general sense, when and where those data gaps occurred. Data is missing for several reasons which include, but are not limited to flood events, equipment failures, technical difficulties, wetland accessibility, and weather conditions.

At Yolo, we had missing data because of multiple equipment failures and a small flood event of the Yolo Bypass. Additionally, the tidal wetland was located within a hunting area, so staff was only able to collect 25-hour event data every other month from September 1, 2014 through the first full week of February 2015.

At Blacklock, the velocity and geometry of the breaches and nearby levees pre-empted placement of water quality sondes, meaning that Blacklock is the only wetland in which continuous water quality sondes were not used. Because we did not have sondes placed, we did not have continuous water quality data available to calculate continuous TSS and chlorophyll-a loads. Additionally, barnacles covered the ADCP because of the higher salinity of the brackish water, and the ADCPs were removed for cleaning and then replaced in the same area, in the openings to the adjacent water body of the wetland. We were not able to collect 25-hour event data during the winter of 2015-2016 until the ADCPs were replaced and new rating curves developed.

At North Lindsey, we deployed equipment in December 2016 and did one 25-hour sampling event before the wetland was inundated during massive flooding in early 2017; the flooding destroyed our equipment and we had to begin again in June 2017 when waters receded. Throughout the study, we had equipment failures multiple times and the slow velocities and large amount of detritus and debris at North Lindsey meant that the ADCP on the bottom of the channel was covered several times by depositional material that was cleaned off periodically; several flow data gaps can be attributed to depositional material. Eventually we repositioned the ADCP on a newly designed platform placed at the bottom of the channel.

We are missing the most data from Westervelt because of high water levels and wetland accessibility as water levels rose out of bank. When water levels rose out of bank at the opening, we could not calculate flow, and without flow data, we could not calculate loads. In 2019, we were only able to collect water quality data for three 25-hour events and those events were post flooding or when the wetland was still flooded slightly outside of the bounds of the channels (but in bank at the opening). Because of the variability of water coverage due to flooding, the water covered anywhere from 22 to 492 acres.

Quality Control Data

Most field and filter blank samples had concentrations below the method detection limit (MDL) or reporting limit (RL), with a few exceptions (Table 2). Unfiltered THg had the highest incident of detections at 8% for both equipment and field blanks; MeHg unfiltered equipment blanks had a 6% rate of detection, but all detections were under the reporting limit. We did larger numbers of equipment blanks because of cleaning our autosampler tubing and autosampler bottles and testing them, and we increased bottle rinsing after two blank detections of the autosampler bottles, which remedied the contamination. Sample concentrations were not corrected for blank values above the MDL or RL.

Most field duplicates met their Measurement Quality Objective (MQO) of a relatively percent difference (RPD) of 25%. This MQO criterion only applies to paired samples where one or both values are 10 times greater than the RL. One unfiltered MeHg pair, one filtered THg pair, and two unfiltered THg pairs exceeded the MQO. No data were removed from calculations or other analyses due to field duplicates that exceeded their MQOs.

Table 2 - Summary of field and filter blanks

Parameter	Units	RL	MDL	# of Blank Samples	# of Detected Blanks	% Detected Blanks	Minimum of Detected Blanks	Maximum of Detected Blanks	Median of Detected Blanks
Equipment Blank									
DOC	mg/L as C	0.5		41	3	7%	0.5	1	0.6
MeHg - filtered	ng/L	0.033	0.011	41	2	5%	0.012	0.018	0.015
MeHg - unfiltered	ng/L	0.033	0.011	86	5	6%	0.011	0.017	0.012
THg - filtered	ng/L	0.5		41	1	2%	1.3	1.3	1.3
THg - unfiltered	ng/L	0.5		86	7	8%	0.6	1.5	0.7
Field Blank									
MeHg - unfiltered	ng/L	0.033	0.011	41	1	2%	0.025	0.025	0.025
THg - unfiltered	ng/L	0.5		40	3	8%	0.7	1.5	1.0
TOC	mg/L as C	0.5		41	0	0%	0	0	0

Table 3 - Summary table of relative percent differences of field duplicates

Parameter	# of Field Duplicates Pairs	Minimum RPD	Maximum RPD	Median RPD	# of Duplicate pairs greater than MQO	% of Duplicate Pairs Greater Than MQO
DOC	40	0%	10%	2%	0	0%
MeHg - filtered	41	0%	50%	7%	0	0%
MeHg - unfiltered	42	1%	69%	6%	1	2%
THg - filtered	39	0%	106%	11%	1	3%
THg - unfiltered	42	0%	110%	4%	2	5%
TOC	42	0%	40%	3%	0	0%
TSS	35	0%	22%	1%	0	0%

Results and Discussion

In this section, DWR presents the results and discussion for each hypothesis and objective, except Objective 5, which is to "Provide data to the Regional Board for a revision of the MeHg allocation" (CDWR, 2013). To meet Objective 5, DWR will provide this report and the data to the Regional Board, and the data will be available through DWR's Water Data Library (http://wdl.water.ca.gov/waterdatalibrary/index.cfm). The hypotheses are presented below and the appropriate objective will be grouped with it.

Hypotheses and Objectives

Hypothesis 1 – Tidal wetlands are a net source of total (unfiltered) MeHg on an annual basis
Objectives 1 – Determine whether these tidal wetlands are net sources or net sinks of MeHg and THg by measuring and calculating imports and exports.

Based on the DMCP reports and allocations and other early findings that indicated that tidal wetlands may be MeHg sources, we tested the hypothesis that the tidal wetlands were net sources of unfiltered MeHg on an annual basis (Bergamaschi, et al., 2011; Hall, Aiken, Krabbenhoft, Marvin-DiPasquale, & Swarzenski, 2008; Langer, Fitzgerald, Visscher, & Vandal, 2001; Mitchell, Jordan, Heyes, & Gilmour, 2012; Wood, Morris, Cooke, & Louie, 2010; Wood, Foe, Cooke, & Louie, 2010; Foe, Louie, & Bosworth, 2008).

While those early findings indicated that MeHg is produced in tidal wetlands, whether that MeHg is exported is another question that this study looks into. Because of the frequency of our sampling for mercury, we were able to do a very rough estimate of yearly MeHg loads based on the measured mercury values during the 25-hour events. However, we were not able to estimate MeHg loads for all months as some sites had missing flow or concentration data. Because we were working with small data sets where we could not assume a distribution, we used non-parametric statistics using R and Minitab.

To determine if each tidal wetland was a net source of MeHg, we looked at the load and concentration data. We have two types of load data: 1) estimated 25-hour event load data from each individual event, and 2) the monthly estimated load data. Additionally, we have calculated concentration values for both the ebb and flood tides for each event from all four wetlands, which we used to determine if the difference between the ebb or flood concentrations were significantly different from zero. Negative values indicated an import, or sink of MeHg, and positive values indicated an export or source of MeHg. All three of these data sets were used to determine whether the wetlands were a net source of MeHg.

First, we used a 1-Sample Wilcoxon Signed Rank Test to determine if the net loads and flow for each 25-hour event was significantly positive or negative (compared to zero) ($\alpha = 0.05$). At Yolo only flow and the particulate MeHg and unfiltered MeHg, which was dominated by particulate, showed significance as sinks. See Table 4 for all results of Wilcoxon and Figure 8, Figure 9, Figure 10, and Figure 11 for loads per 25-hour event.

Second, we used a 1-Sample Wilcoxon Signed Rank Test to determine if the estimated monthly MeHg loads were significantly different from zero ($\alpha = 0.05$). Only Yolo and Blacklock were significant sinks of MeHg in the unfiltered, filtered, and particulate phases. All results for the calculated monthly load data are in Table 5 and Figure 12, Figure 13, Figure 14, and Figure 15 show loads for estimated monthly MeHg loads.

Third, we used a 1-Sample Wilcoxon Signed Rank Test to determine if calculated flow-weighted ebb and flood concentrations were significantly different ($\alpha = 0.05$). To use the Wilcoxon Test

on paired samples, a single flood and ebb concentration for each event were calculated, using flow-weighting. The flood concentrations were designated with a negative sign, and ebb concentrations were designated with a positive sign and these were tested against zero. Only North Lindsey was a significant sink of unfiltered and filtered MeHg using this calculation. All results are in Table 6 and Figure 16, Figure 17, Figure 18, and Figure 19 show calculated concentrations per event.

Based on the collected data and analyses, none of the four wetlands appear to be a significant source of MeHg to their adjacent waterbodies, nor are concentrations of MeHg significantly higher leaving the wetland than entering the wetland. Generally, the waters entering the wetlands are not meeting the Regional Board's DMCP annual water quality criterion of 0.06ng/L, and there does not seem to be a measurable annual increase in MeHg concentration due to tidal wetland exports measured in this study (Wood, Morris, Cooke, & Louie, 2010; Wood, Foe, Cooke, & Louie, 2010). As a note, Table 6 medians are derived from using positive and negative values for ebb and flood concentrations.

Table 4 – Results for 1-Sample Wilcoxon analysis of 25-hour event MeHg loads and flow. Bolded lines indicate significance (α = 0.05) and green and a negative median indicate a sink of MeHg and flow.

Wetland	Sample	N for Test	Wilcoxon Statistic	P-Value	Median
Yolo	**Flow (L/tide)**	**10**	**0**	**0.01**	**-12095895**
Yolo	**Unfiltered MeHg (g/tide)**	**10**	**6**	**0.03**	**-0.0019**
Yolo	Filtered MeHg (g/tide)	10	11	0.10	-0.00063
Yolo	**Particulate MeHg (g/tide)**	**10**	**4**	**0.02**	**-0.0015**
Blacklock	Flow (L/tide)	10	11	0.10	-92155620
Blacklock	Unfiltered MeHg (g/tide)	10	16	0.26	-0.012
Blacklock	Filtered MeHg (g/tide)	10	18	0.36	-0.0046
Blacklock	Particulate MeHg (g/tide)	10	14	0.19	-0.0078
North Lindsey	Flow (L/tide)	13	54	0.58	1636918
North Lindsey	Unfiltered MeHg (g/tide)	13	31	0.33	-0.00021
North Lindsey	Filtered MeHg (g/tide)	13	37	0.58	-0.000070
North Lindsey	Particulate MeHg (g/tide)	13	35	0.49	-0.000083
Westervelt	Flow (L/tide)	8	9	0.23	-3987153
Westervelt	Unfiltered MeHg (g/tide)	8	29	0.14	0.0013
Westervelt	Filtered MeHg (g/tide)	8	26	0.29	0.00051
Westervelt	Particulate MeHg (g/tide)	8	27	0.23	0.00092

Table 5 – Results for 1-Sample Wilcoxon analysis of monthly estimated MeHg loads. Bolded lines indicate significance (α = 0.05) and green and a negative median indicate a sink of MeHg.

Wetland	Sample	N for Test	Wilcoxon Statistic	P-Value	Median
Yolo	**Unfiltered MeHg Load (g/month)**	**13**	**3**	**0.00**	**-0.067**
Yolo	**Filtered MeHg Load (g/month)**	**13**	**11**	**0.02**	**-0.024**
Yolo	**Particulate MeHg Load (g/month)**	**13**	**4**	**0.00**	**-0.046**
Blacklock	**Unfiltered MeHg Load (g/month)**	**13**	**13**	**0.03**	**-0.41**
Blacklock	**Filtered MeHg Load (g/month)**	**13**	**14**	**0.03**	**-0.15**
Blacklock	**Particulate MeHg Load (g/month)**	**13**	**17**	**0.05**	**-0.26**
North Lindsey	Unfiltered MeHg Load (g/month)	13	33	0.40	-0.0074
North Lindsey	Filtered MeHg Load (g/month)	13	37	0.58	-0.0054
North Lindsey	Particulate MeHg Load (g/month)	13	43	0.89	-0.00066
Westervelt	Unfiltered MeHg Load (g/month)	10	27	1.00	-0.0052
Westervelt	Filtered MeHg Load (g/month)	10	16	0.26	-0.049
Westervelt	Particulate MeHg Load (g/month)	10	29	0.92	0.0030

Table 6 – Results for Wilcoxon analysis of MeHg ebb and flood MeHg concentrations. Bolded lines indicate significance (α = 0.05) and green and a negative median indicate a possible sink of MeHg.

Wetland	Sample	N for Test	Wilcoxon Statistic	P-Value	Median
Yolo	Unfiltered MeHg Concentration (ng/L)	10	25	0.84	-0.0018
Yolo	Filtered MeHg Concentration (ng/L)	10	33	0.61	0.0015
Yolo	Particulate MeHg Concentration (ng/L)	10	23	0.68	-0.0024
Blacklock	Unfiltered MeHg Concentration (ng/L)	10	42	0.15	0.013
Blacklock	Filtered MeHg Concentration (ng/L)	10	38	0.31	0.0034
Blacklock	Particulate MeHg Concentration (ng/L)	10	40	0.22	0.0091
North Lindsey	**Unfiltered MeHg Concentration (ng/L)**	**13**	**3**	**0.00**	**-0.011**
North Lindsey	**Filtered MeHg Concentration (ng/L)**	**13**	**16**	**0.04**	**-0.0085**
North Lindsey	Particulate MeHg Concentration (ng/L)	13	28	0.24	-0.0037
Westervelt	Unfiltered MeHg Concentration (ng/L)	8	30	0.11	0.067
Westervelt	Filtered MeHg Concentration (ng/L)	8	28	0.18	0.021
Westervelt	Particulate MeHg Concentration (ng/L)	8	29	0.14	0.033

Figure 8 – MeHg loads per 25-hour event at Yolo Wildlife Area Tidal Wetland. Positive values indicate the wetland is a source of MeHg and negative values indicate the wetland is a sink of MeHg. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction.

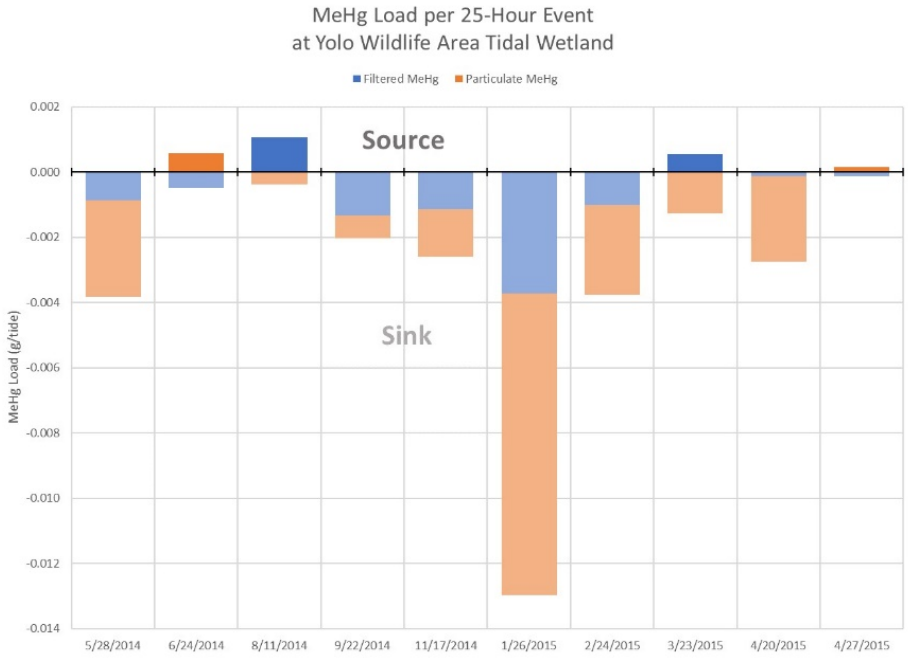


Figure 9 – MeHg loads per 25-hour event at Blacklock Tidal Wetland. Positive values indicate the wetland is a source of MeHg and negative values indicate the wetland is a sink of MeHg. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction.

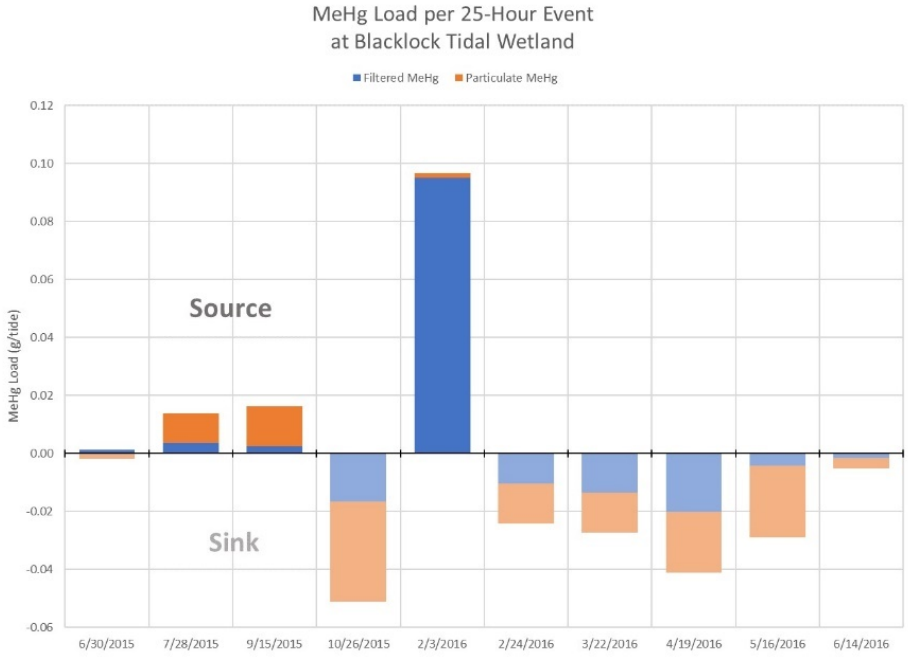


Figure 10 – MeHg loads per 25-hour event at North Lindsey Slough Tidal Wetland. Positive values indicate the wetland is a source of MeHg and negative values indicate the wetland is a sink of MeHg. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction.

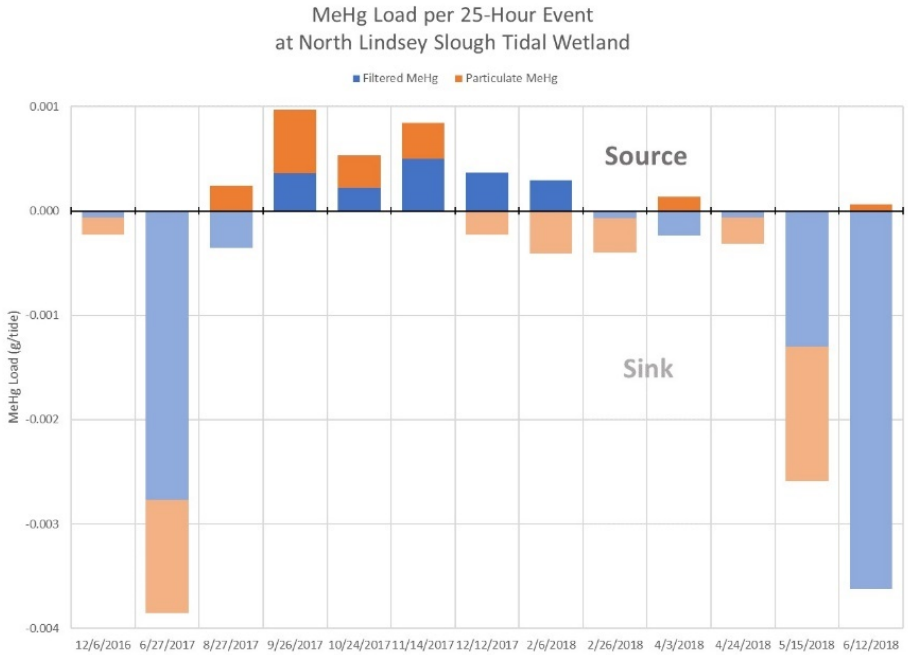


Figure 11 – MeHg loads per 25-hour event at Westervelt Cosumnes River Tidal Wetland. Positive values indicate the wetland is a source of MeHg and negative values indicate the wetland is a sink of MeHg. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction.

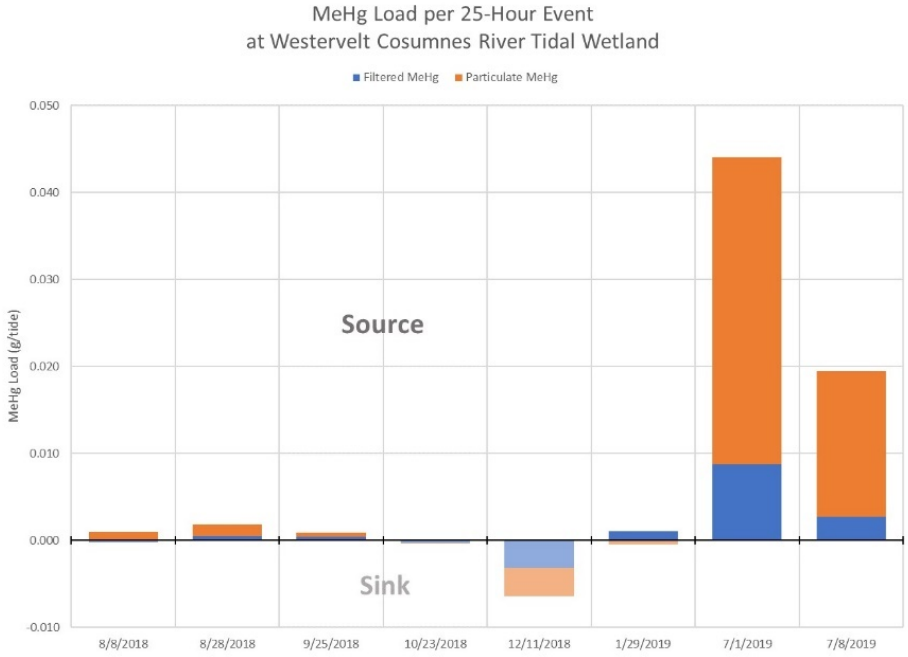


Figure 12 – Estimated monthly MeHg loads at Yolo Wildlife Area Tidal Wetland. Positive values indicate the wetland is a source of MeHg and negative values indicate the wetland is a sink of MeHg. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction.

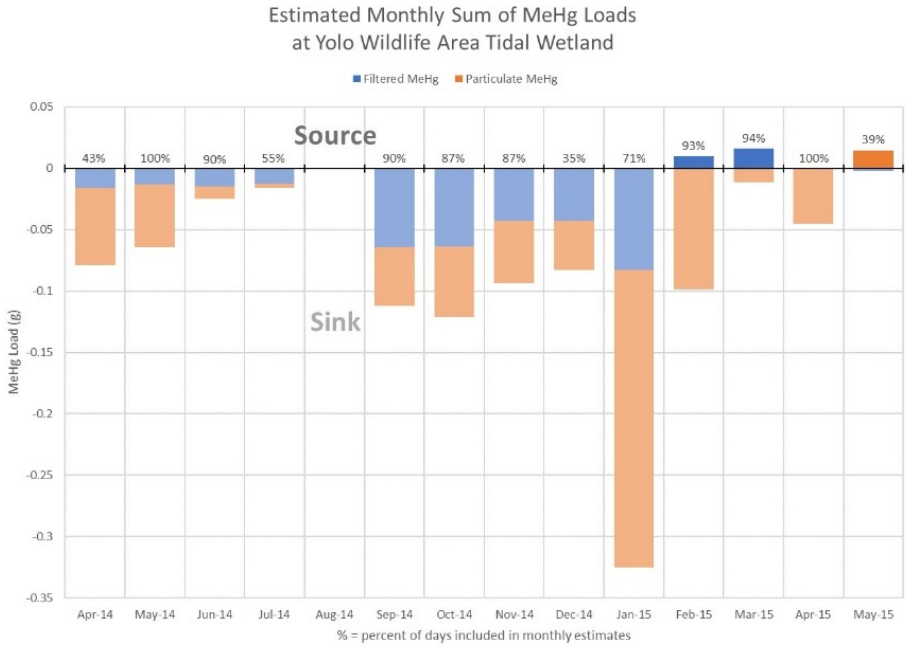


Figure 13 – Estimated monthly MeHg loads at Blacklock Tidal Wetland. Positive values indicate the wetland is a source of MeHg and negative values indicate the wetland is a sink of MeHg. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction.

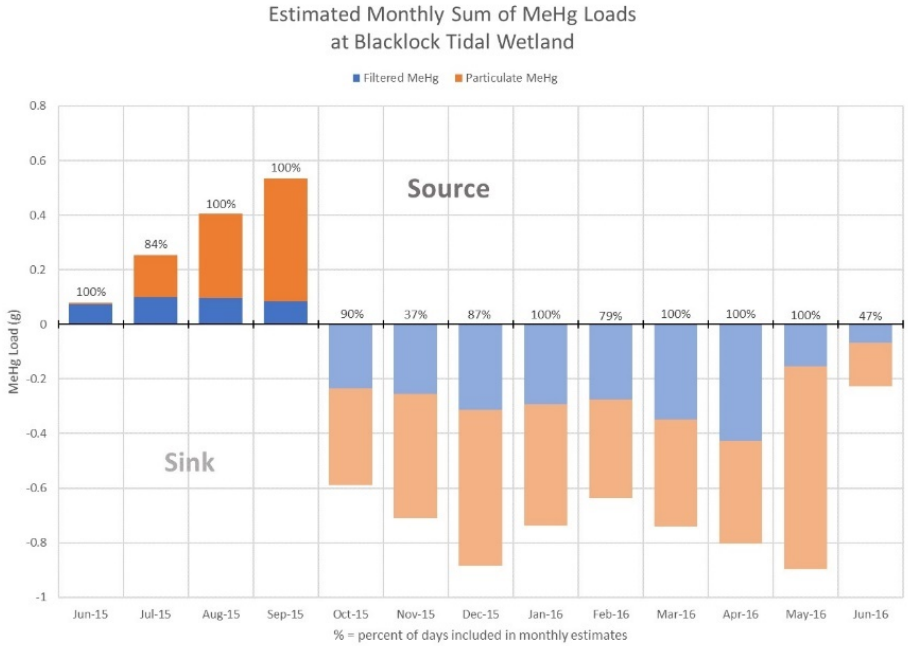


Figure 14 – Estimated monthly MeHg loads at North Lindsey Slough Tidal Wetland. Positive values indicate the wetland is a source of MeHg and negative values indicate the wetland is a sink of MeHg. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction.

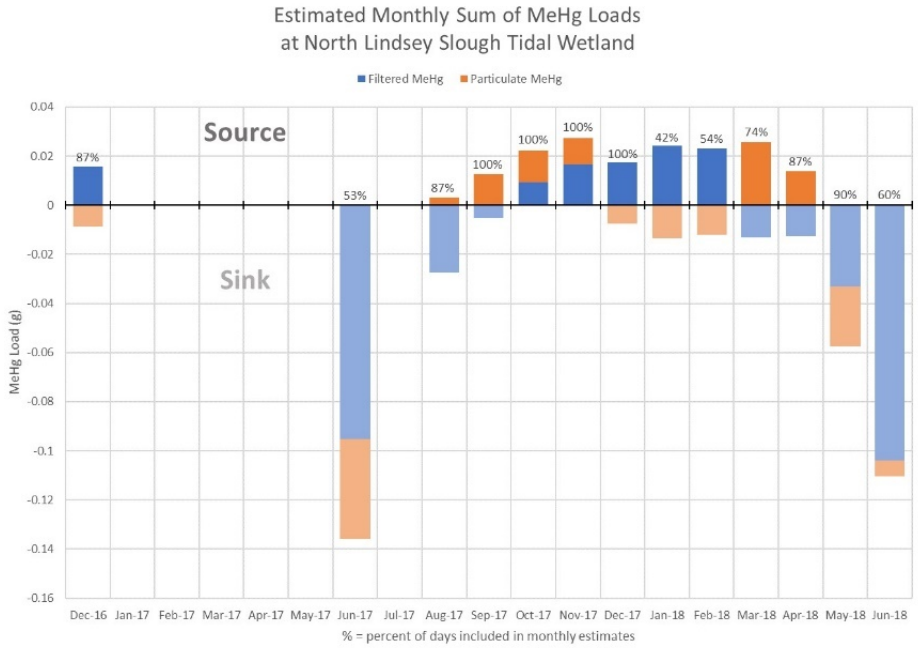


Figure 15 – Estimated monthly MeHg loads at Westervelt Cosumnes River Tidal Wetland. Positive values indicate the wetland is a source of MeHg and negative values indicate the wetland is a sink of MeHg. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction.

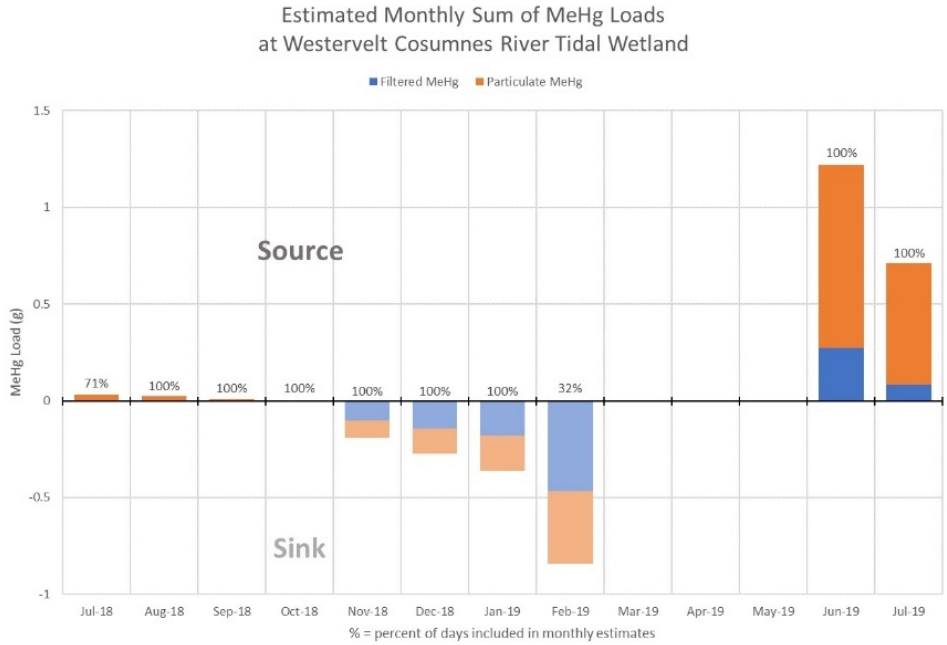


Figure 16 – MeHg flow-weighted average concentrations per 25-hour event at Yolo Wildlife Area Tidal Wetland. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction. The lighter shading indicates the flood tide concentration and the darker shading indicates the ebb tide concentrations.

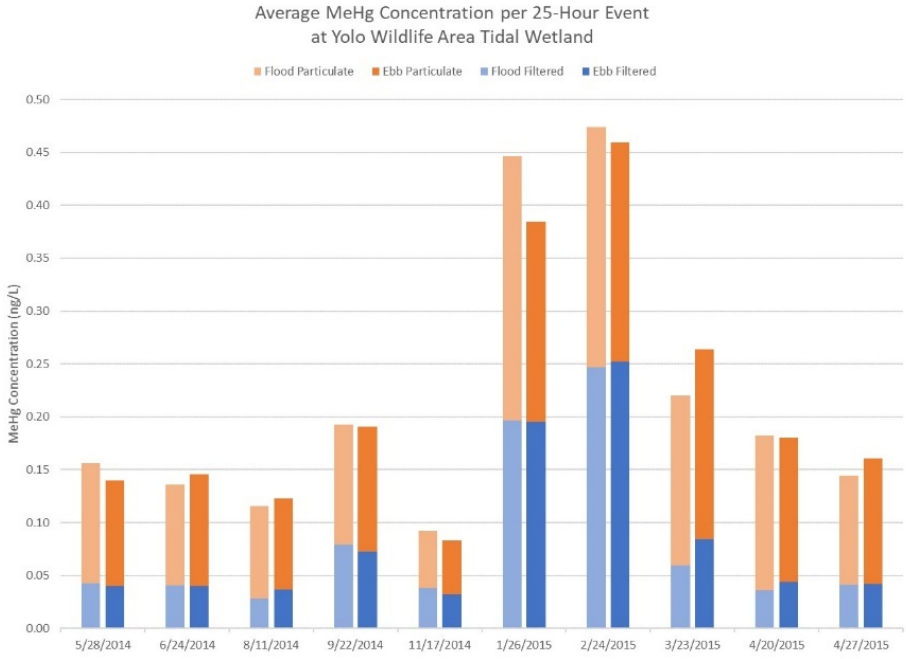


Figure 17 – MeHg flow-weighted average concentrations per 25-hour event at Blacklock Tidal Wetland. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction. The lighter shading indicates the flood tide concentration and the darker shading indicates the ebb tide concentrations.

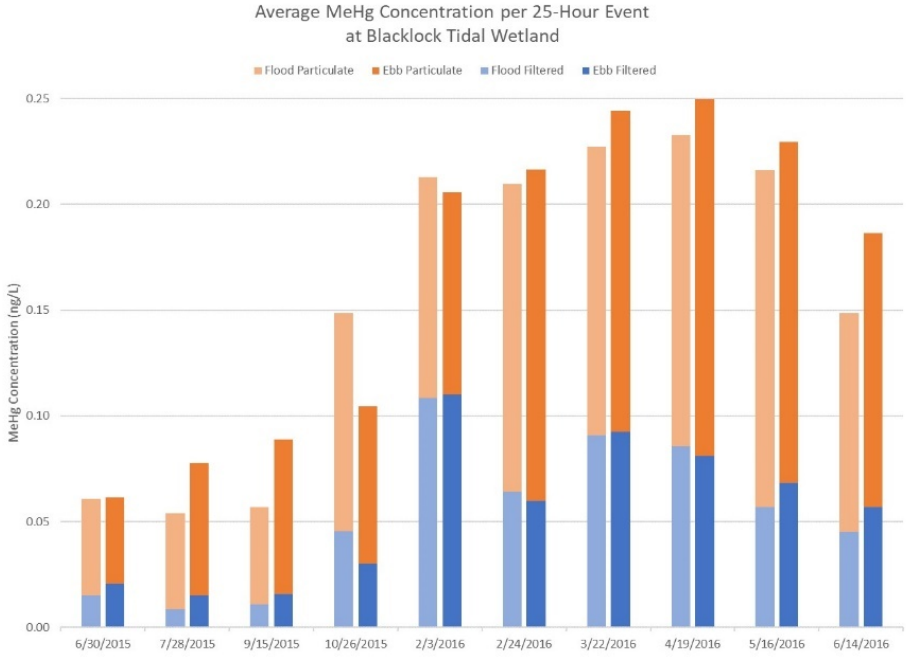


Figure 18 – MeHg flow-weighted average concentrations per 25-hour event at North Lindsey Slough Tidal Wetland. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction. The lighter shading indicates the flood tide concentration and the darker shading indicates the ebb tide concentrations.

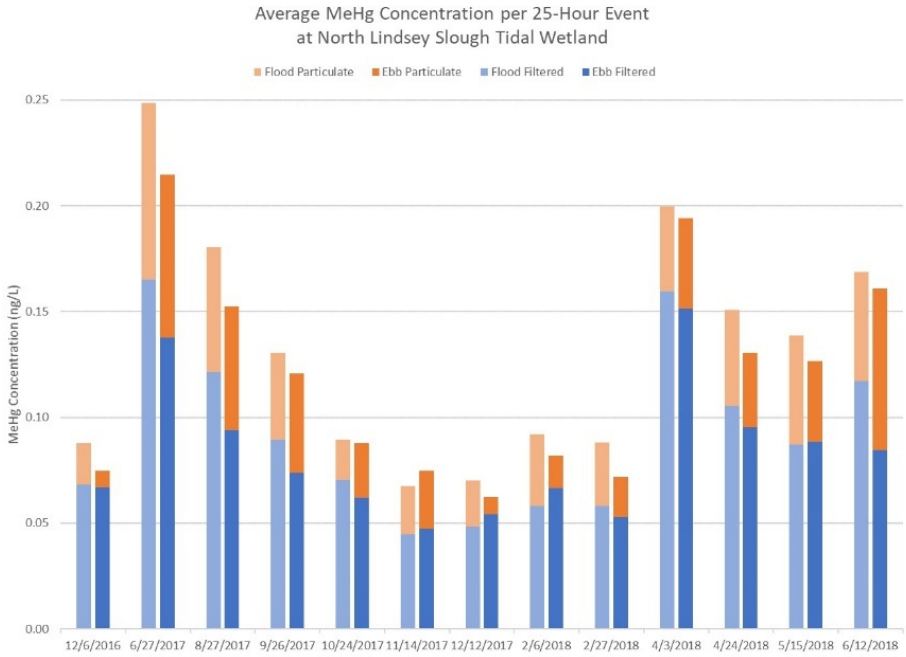
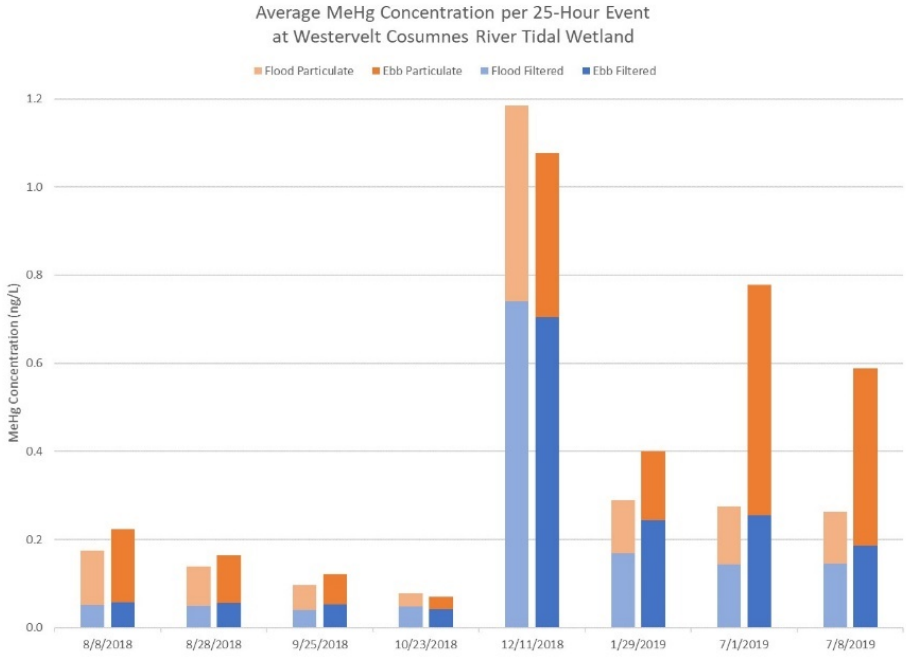


Figure 19 – MeHg flow-weighted average concentrations per 25-hour event at Westervelt Cosumnes River Tidal Wetland. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction. The lighter shading indicates the flood tide concentration and the darker shading indicates the ebb tide concentrations.



Hypothesis 2 – Tidal wetlands are a net source of total (unfiltered) THg on an annual basis. Objective 1 – Determine whether these tidal wetlands are net sources or net sinks of MeHg and THg by measuring and calculating imports and exports.

To be consistent with Hypothesis 1, we tested the hypothesis that the tidal wetlands were a net source of unfiltered THg as well. As with the MeHg data above, we have three types of data for THg: 1) calculated loads for each 25-hour event, 2) estimated monthly loads for data that we calculated the same way we did MeHg monthly, and 3) calculated flow-weighted concentration data for the flood and ebb tides. As with the MeHg data, some sites had missing flow or concentration data and we could not calculate loads.

First, as with MeHg, we used a 1-Sample Wilcoxon Signed Rank Test to determine if the net load for each 25-hour event was significantly positive or negative (compared to zero) ($\alpha = 0.05$); these observations only include statistically significant finds. The Yolo was a sink of filtered THg, and Blacklock was a sink of unfiltered and particulate THg. Westervelt was a source of THg in both the filtered and particulate form, and overall. See Table 7 for all results of Wilcoxon and Figure 20, Figure 21, Figure 22, and Figure 23 for loads per 25-hour event.

Second, we used a 1-Sample Wilcoxon Signed Rank Test to determine if the estimated monthly THg loads were significantly different from zero ($\alpha = 0.05$). Yolo was a sink of filtered THg, and Blacklock was a sink of THg in both the filtered and particulate fractions. Only North Lindsey was a source of particulate THg. All results for the calculated monthly load data are in Table 8 and Figure 24, Figure 25, Figure 26, and Figure 27 show loads for estimated monthly THg loads.

Third, we used a 1-Sample Wilcoxon Signed Rank Test to determine if flow-weighted ebb and flood concentrations were significantly different ($\alpha = 0.05$). The details of this calculation are explained in Hypothesis 1. Blacklock showed a significantly lower concentration of unfiltered and particulate THg leaving the wetland than entering it, whereas North Lindsey and Westervelt had significantly higher concentrations of unfiltered and all species of THg respectively, leaving each wetland. All results are in Table 9 and Figure 28, Figure 29, Figure 30, and Figure 31 show calculated concentrations per event.

Whereas the four tidal wetlands do not appear to be a source of MeHg annually, Westervelt and North Lindsey appear to be a source of THg. Westervelt is clearly a source of particulate THg, although because of how few 25-hour events we were able to collect, more data would be advantageous to determine any patterns. While Blacklock and Yolo appear to be sinks of THg, Blacklock is very clearly an annual sink of THg in the particulate form.

Table 7 – Results for 1-Sample Wilcoxon analysis of 25-hour event THg and flow loads. Bolded lines indicate significance (α = 0.05), green and a negative median indicate a sink of THg and flow, and pink and a positive median indicate a source of THg.

Wetland	Sample	N for Test	Wilcoxon Statistic	P-Value	Median
Yolo	**Flow (L/tide)**	**10**	**0**	**0.01**	**-12095895**
Yolo	Unfiltered THg (g/tide)	10	20	0.48	-0.036
Yolo	**Filtered THg (g/tide)**	**10**	**1**	**0.01**	**-0.011**
Yolo	Particulate THg (g/tide)	10	25	0.84	-0.018
Blacklock	Flow (L/tide)	10	11	0.10	-92155620
Blacklock	**Unfiltered THg (g/tide)**	**10**	**4**	**0.02**	**-3.1**
Blacklock	Filtered THg (g/tide)	10	11	0.10	-0.15
Blacklock	**Particulate THg (g/tide)**	**10**	**4**	**0.02**	**-2.9**
North Lindsey	Flow (L/tide)	13	54	0.58	1636918
North Lindsey	Unfiltered THg (g/tide)	13	64	0.21	0.0060
North Lindsey	Filtered THg (g/tide)	13	66	0.16	0.0025
North Lindsey	Particulate THg (g/tide)	13	68	0.12	0.0045
Westervelt	Flow (L/tide)	8	9	0.23	-3987153
Westervelt	**Unfiltered THg (g/tide)**	**8**	**35**	**0.02**	**0.13**
Westervelt	**Filtered THg (g/tide)**	**8**	**33**	**0.04**	**0.013**
Westervelt	**Particulate THg (g/tide)**	**8**	**36**	**0.01**	**0.12**

Table 8 – Results for 1-Sample Wilcoxon analysis of monthly estimated THg loads. Bolded lines indicate significance (α = 0.05), green and a negative median indicate a sink of THg, and pink indicates a source of THg.

Wetland	Sample	N for Test	Wilcoxon Statistic	P-Value	Median
Yolo	Unfiltered THg Load (g/month)	13	37	0.58	-2.2
Yolo	**Filtered THg Load (g/month)**	**13**	**0**	**0.00**	**-0.31**
Yolo	Particulate THg Load (g/month)	13	39	0.68	-1.6
Blacklock	**Unfiltered THg Load (g/month)**	**13**	**1**	**0.00**	**-70**
Blacklock	**Filtered THg Load (g/month)**	**13**	**7**	**0.01**	**-3.2**
Blacklock	**Particulate THg Load (g/month)**	**13**	**1**	**0.00**	**-65**
North Lindsey	Unfiltered THg Load (g/month)	13	71	0.08	0.28
North Lindsey	Filtered THg Load (g/month)	13	67	0.14	0.09
North Lindsey	**Particulate THg Load (g/month)**	**13**	**77**	**0.03**	**0.20**
Westervelt	Unfiltered THg Load (g/month)	10	39	0.26	2.2
Westervelt	Filtered THg Load (g/month)	10	26	0.92	-0.0057
Westervelt	Particulate THg Load (g/month)	10	40	0.22	2.1

Table 9 – Results for Wilcoxon analysis of THg ebb and flood THg concentrations. Bolded lines indicate significance (α = 0.05), green and a negative median indicate a sink of THg, and pink and a positive median indicate a possible source of THg.

Wetland	Sample	N for Test	Wilcoxon Statistic	P-Value	Median
Yolo	Unfiltered THg Concentration (ng/L)	10	37	0.36	1.4
Yolo	Filtered THg Concentration (ng/L)	10	27	1.00	-0.00078
Yolo	Particulate THg Concentration (ng/L)	10	38	0.31	1.5
Blacklock	**Unfiltered THg Concentration (ng/L)**	**10**	**3**	**0.01**	**-3.0**
Blacklock	Filtered THg Concentration (ng/L)	10	22	0.61	-0.04
Blacklock	**Particulate THg Concentration (ng/L)**	**10**	**1**	**0.01**	**-2.9**
North Lindsey	**Unfiltered THg Concentration (ng/L)**	**13**	**86**	**0.01**	**0.22**
North Lindsey	Filtered THg Concentration (ng/L)	12	58	0.15	0.049
North Lindsey	Particulate THg Concentration (ng/L)	13	71	0.08	0.14
Westervelt	**Unfiltered THg Concentration (ng/L)**	**8**	**36**	**0.01**	**3.3**
Westervelt	**Filtered THg Concentration (ng/L)**	**8**	**36**	**0.01**	**0.33**
Westervelt	**Particulate THg Concentration (ng/L)**	**8**	**36**	**0.01**	**3.0**

Figure 20 – THg loads per 25-hour event at Yolo Wildlife Area Tidal Wetland. Positive values indicate the wetland is a source of THg and negative values indicate the wetland is a sink of THg. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction.

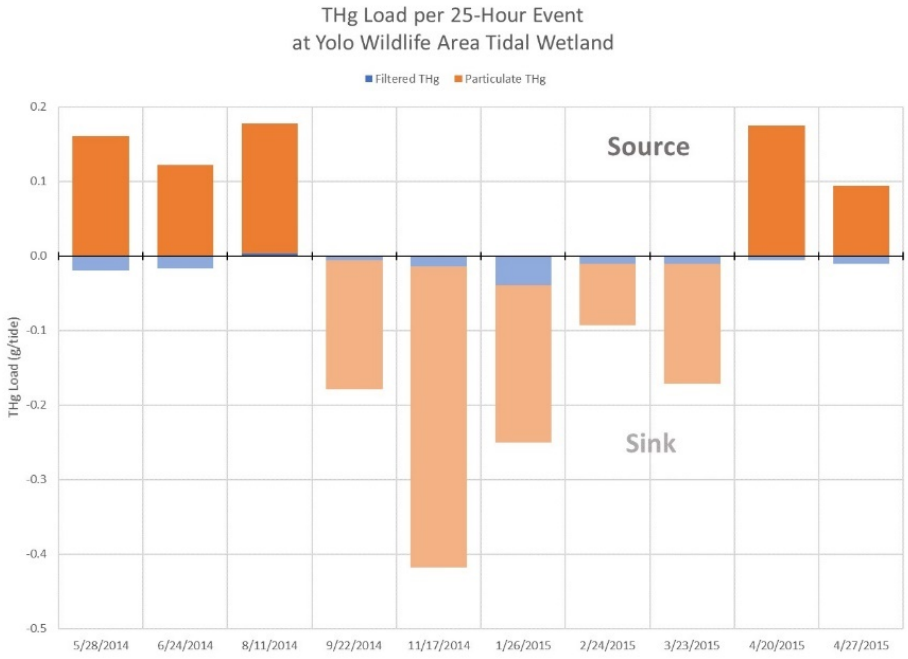


Figure 21 – THg loads per 25-hour event at Blacklock Tidal Wetland. Positive values indicate the wetland is a source of THg and negative values indicate the wetland is a sink of THg. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction.

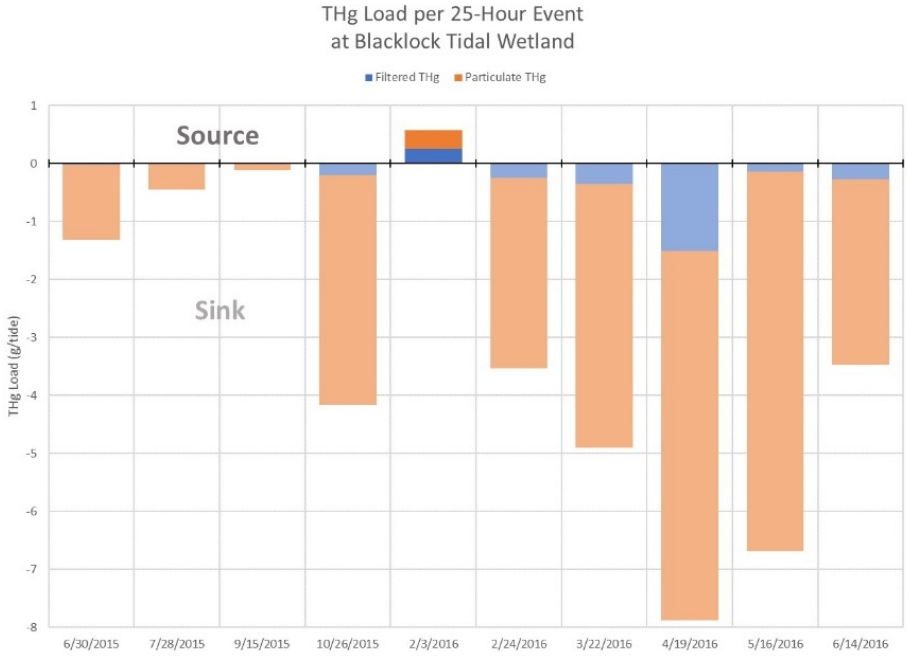


Figure 22 – THg loads per 25-hour event at North Lindsey Slough Tidal Wetland. Positive values indicate the wetland is a source of THg and negative values indicate the wetland is a sink of THg. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction.

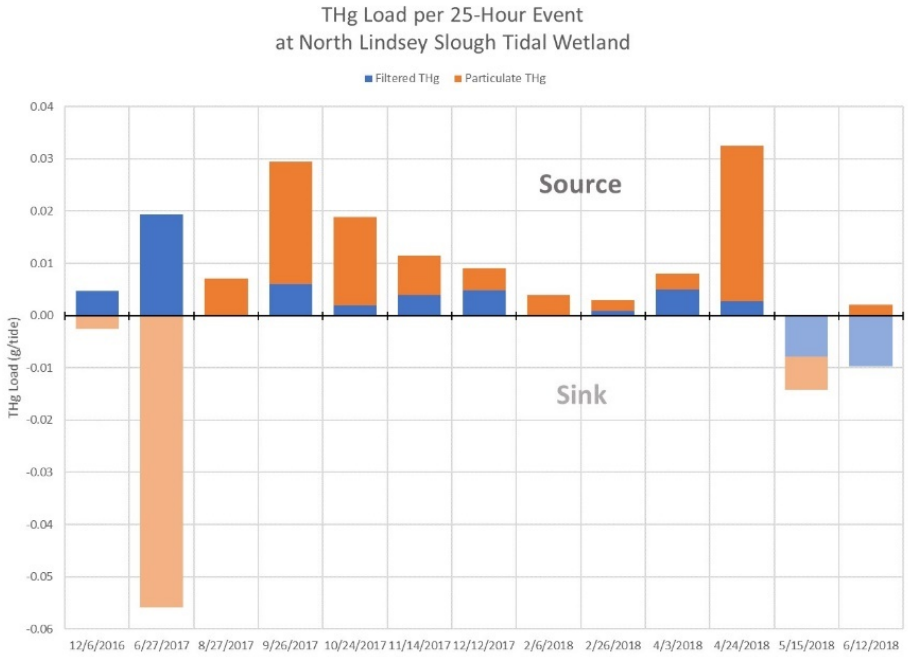


Figure 23 – THg loads per 25-hour event at Westervelt Cosumnes River Tidal Wetland. Positive values indicate the wetland is a source of THg and negative values indicate the wetland is a sink of THg. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction.

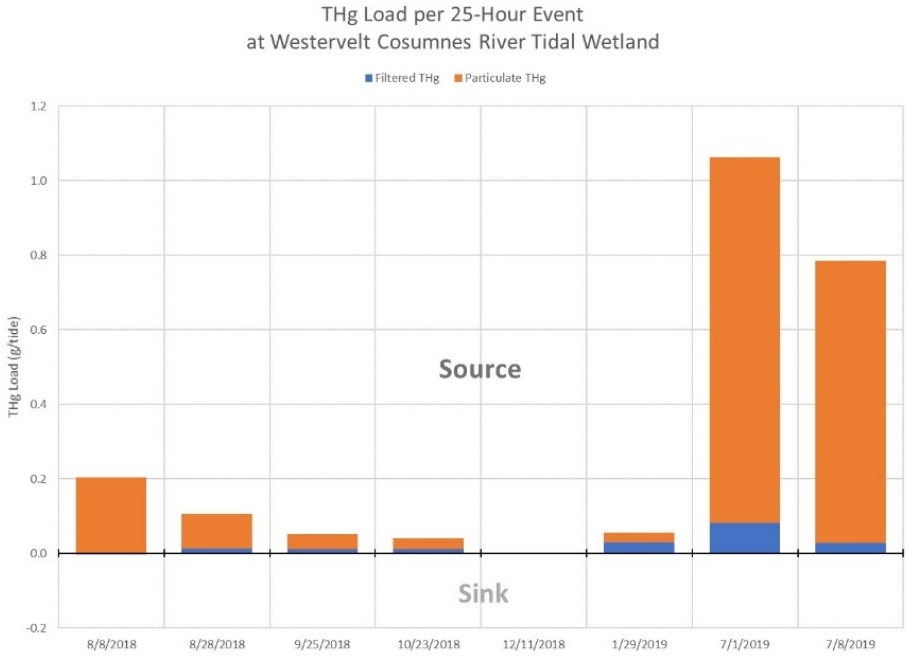


Figure 24 – Estimated monthly THg loads at Yolo Wildlife Area Tidal Wetland. Positive values indicate the wetland is a source of THg and negative values indicate the wetland is a sink of THg. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction.

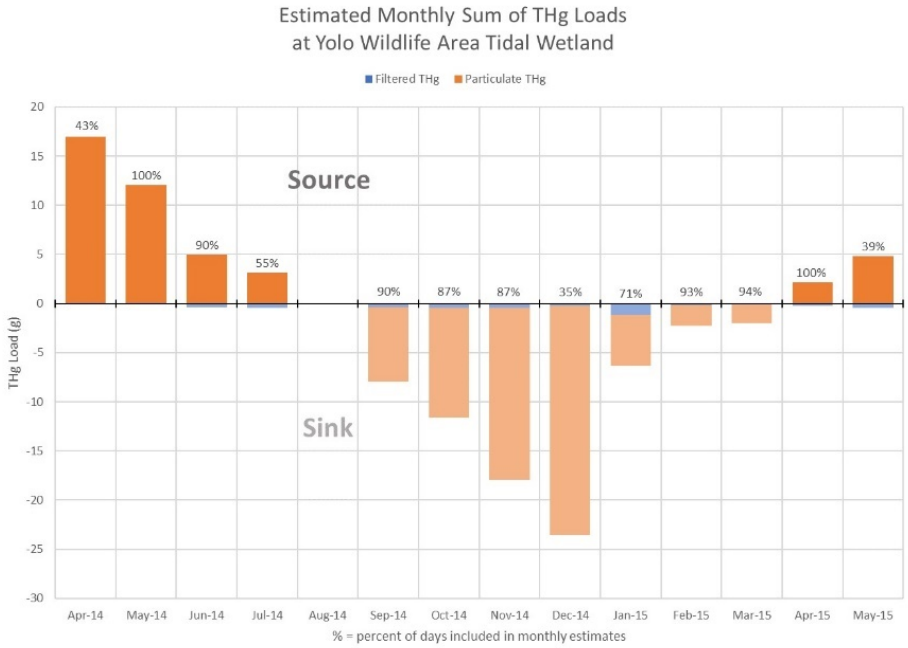


Figure 25 – Estimated monthly THg loads at Blacklock Tidal Wetland. Positive values indicate the wetland is a source of THg and negative values indicate the wetland is a sink of THg. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction.

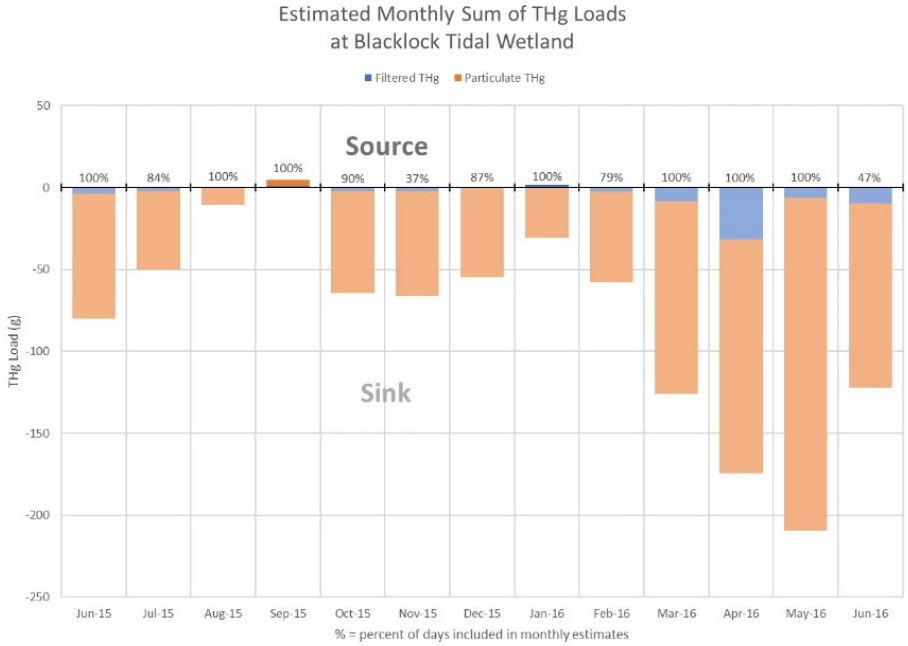


Figure 26 – Estimated monthly THg loads at North Lindsey Slough Tidal Wetland. Positive values indicate the wetland is a source of THg and negative values indicate the wetland is a sink of THg. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction.

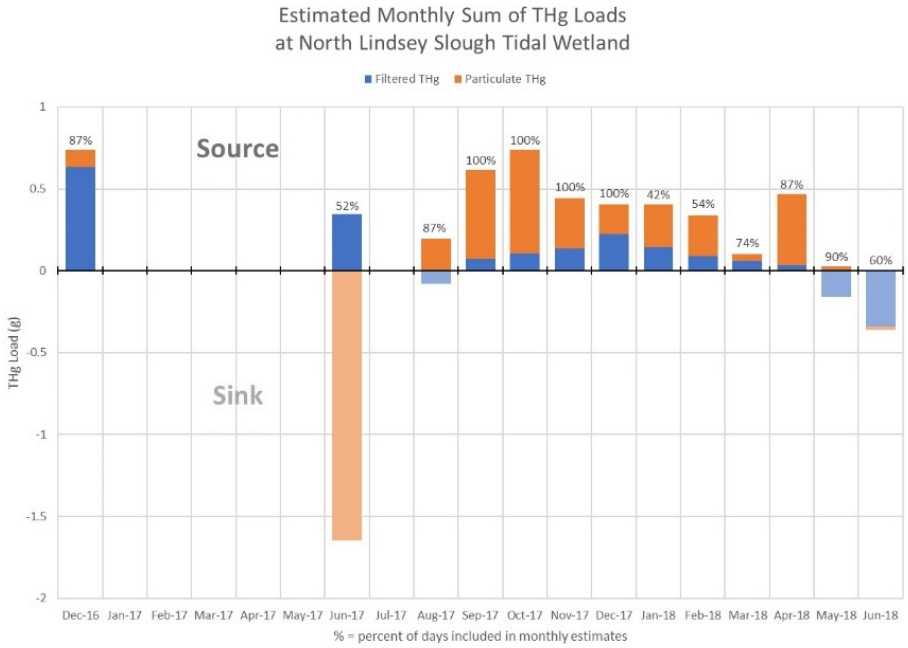


Figure 27 – Estimated monthly THg loads at Westervelt Cosumnes River Tidal Wetland. Positive values indicate the wetland is a source of THg and negative values indicate the wetland is a sink of THg. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction.

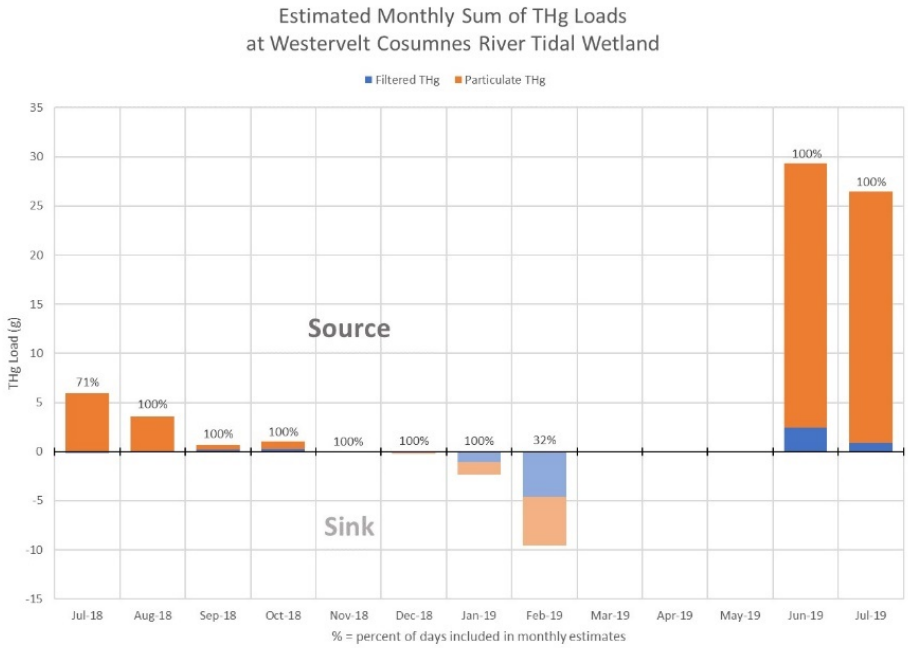


Figure 28 – THg flow-weighted average concentrations per 25-hour event at Yolo Wildlife Area Tidal Wetland. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction. The lighter shading indicates the flood tide concentration and the darker shading indicates the ebb tide concentrations.

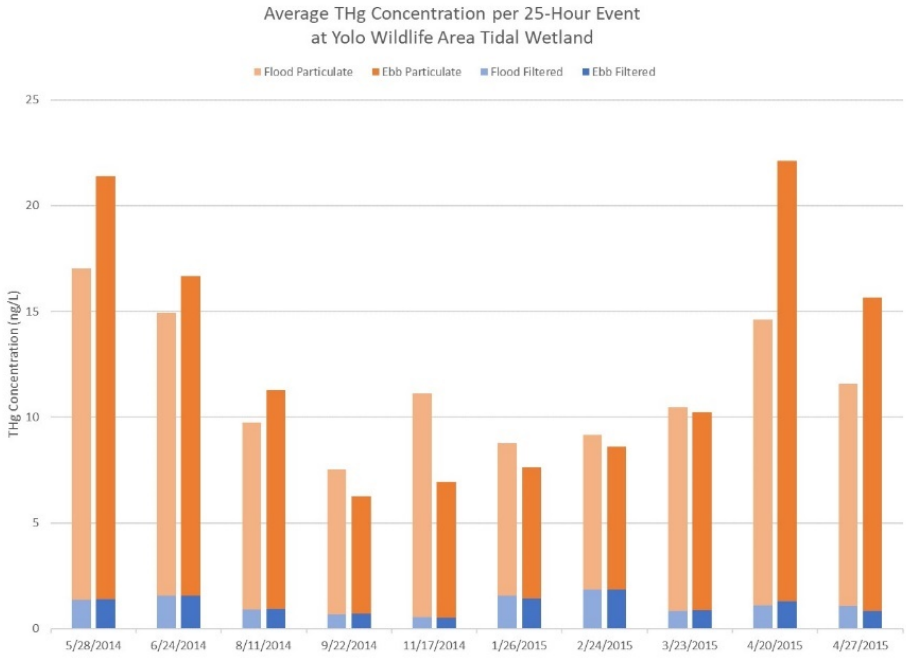


Figure 29 – THg flow-weighted average concentrations per 25-hour event at Blacklock Tidal Wetland. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction. The lighter shading indicates the flood tide concentration and the darker shading indicates the ebb tide concentrations.

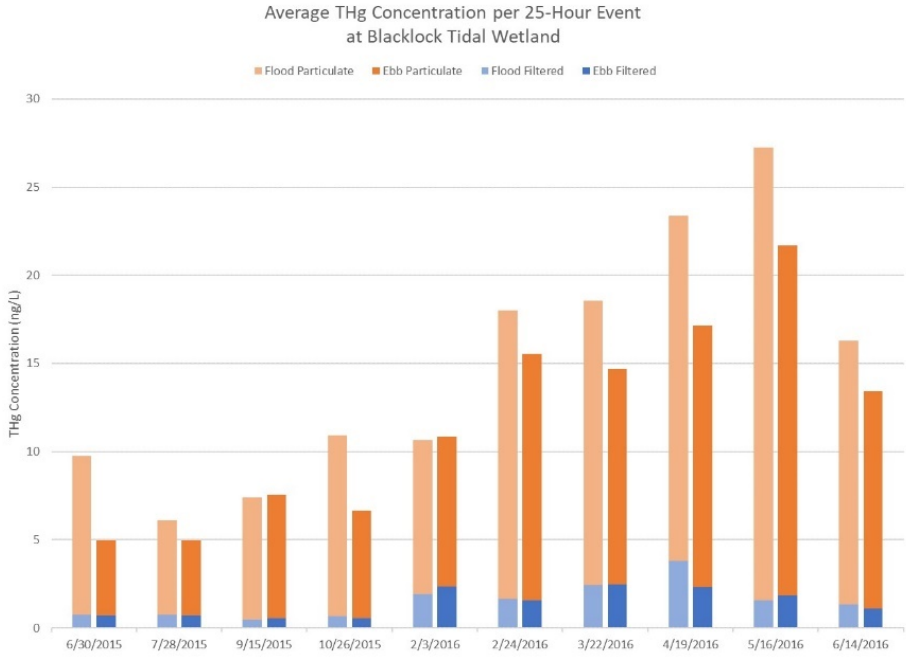


Figure 30 – THg flow-weighted average concentrations per 25-hour event at North Lindsey Slough Tidal Wetland. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction. The lighter shading indicates the flood tide concentration and the darker shading indicates the ebb tide concentrations.

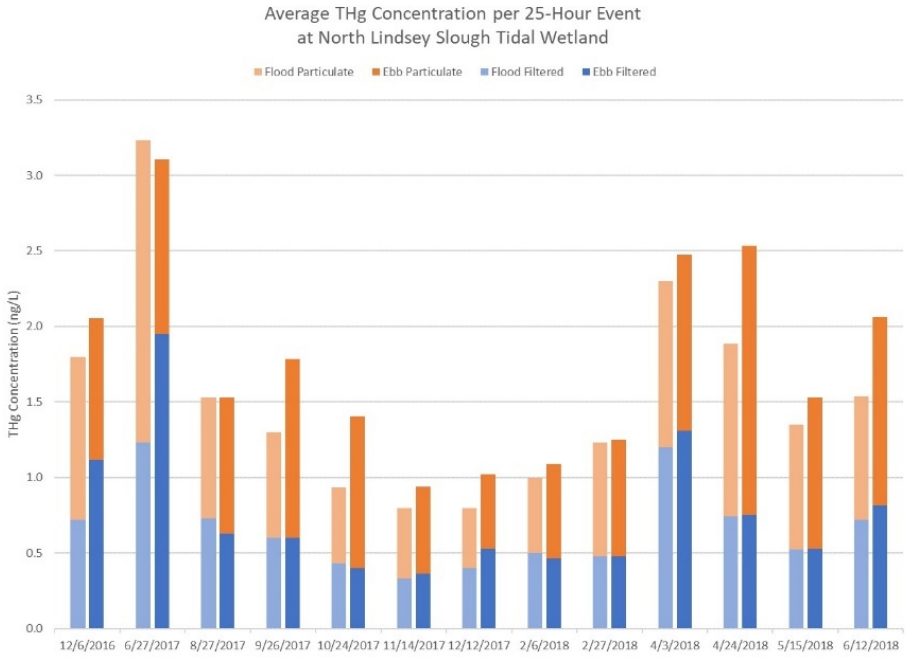
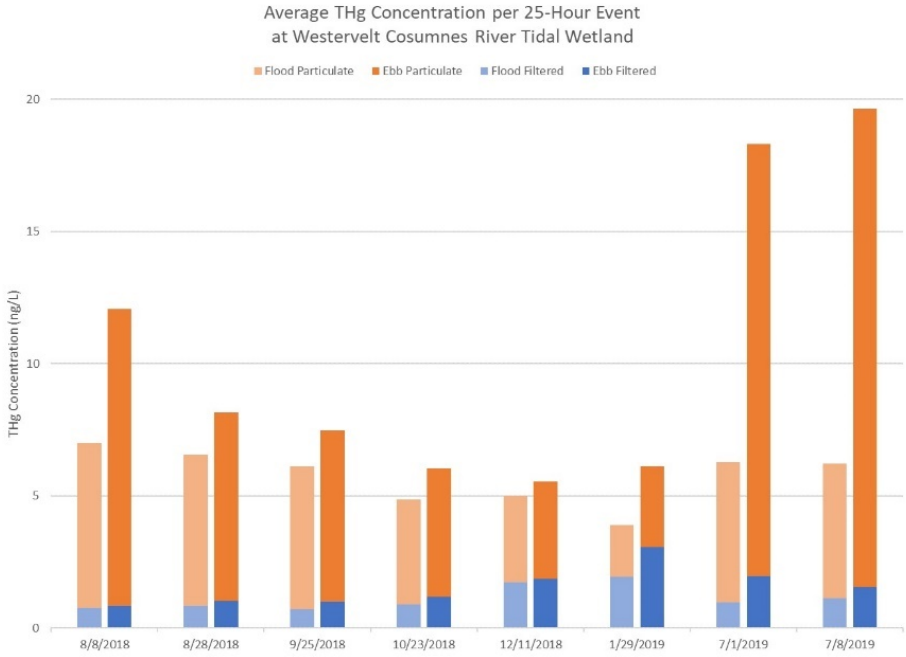


Figure 31 – THg flow-weighted average concentrations per 25-hour event at Westervelt Cosumnes River Tidal Wetland. The blue portion of each bar is the filtered fraction and the orange portion of each bar is the particulate fraction. The lighter shading indicates the flood tide concentration and the darker shading indicates the ebb tide concentrations.



Hypothesis 3 – Tidal wetlands have higher total (unfiltered) and dissolved MeHg exports during the warmer, summer months.
Objective 2 – Measure and calculate monthly and/or bimonthly MeHg imports and exports to determine if seasonal differences occur.

While none of the tidal wetlands were significant annual sources of MeHg, some of the wetlands were a source of MeHg over shorter periods of times, such as tidal cycles, days, weeks, or months.

Mercury is an expensive and difficult water quality contaminant to collect and process, so DWR was only able to collect a small number of 25-hour events per wetland, $n < 20$. Because we are working with a small set of data, we could not test significance if we attempted to analyze each wetland by season. Therefore, we relied on observations to evaluate this hypothesis

In general, none of the wetlands showed a seasonal pattern of increased MeHg exports during warmer months except possibly Blacklock. Blacklock exported MeHg during the months of June through September 2015 and was mostly a sink the rest of the year. Figure 32, Figure 33, Figure 34, and Figure 35 show MeHg graphs of each tidal wetland through time, both in the particulate and filtered phase. Bar graphs of each event's data are shown in Figure 8, Figure 9, Figure 10, and Figure 11 in Hypothesis 1.

Another pattern seen at Yolo was after a flood event. The wetland showed an increase in the percent of filtered MeHg concentrations for two months after the Yolo Bypass flooded in December 2014. Before and several months after the flood event, the wetland had an approximately 30% filtered MeHg fraction. After the two sampling events following the flood, the median percent of filtered MeHg was 50% (Figure 16).

Because THg is also important, we looked for seasonal patterns in the THg loads as well. Yolo showed a slight seasonal pattern as particulate THg loads were higher in May-August 2014 and April 2015, for a total of about five months. The other three wetlands did not appear to have a seasonal THg load pattern. Figure 36, Figure 37, Figure 38, and Figure 39 show graphs of particulate and filtered THg through time. Bar graphs of each event's data are shown in Figure 20, Figure 21, Figure 22, and Figure 23 in Hypothesis 2.

Although our data did not show a seasonal pattern, it does not suggest that seasonal patterns do not exist. Collecting more frequent data points over a year and/or over multiple years would be useful in determining any seasonal differences.

Figure 32 – MeHg loads per 25-hour event at Yolo Wildlife Area Tidal Wetland. Filtered MeHg loads are shown in blue, and particulate MeHg loads are shown in orange.

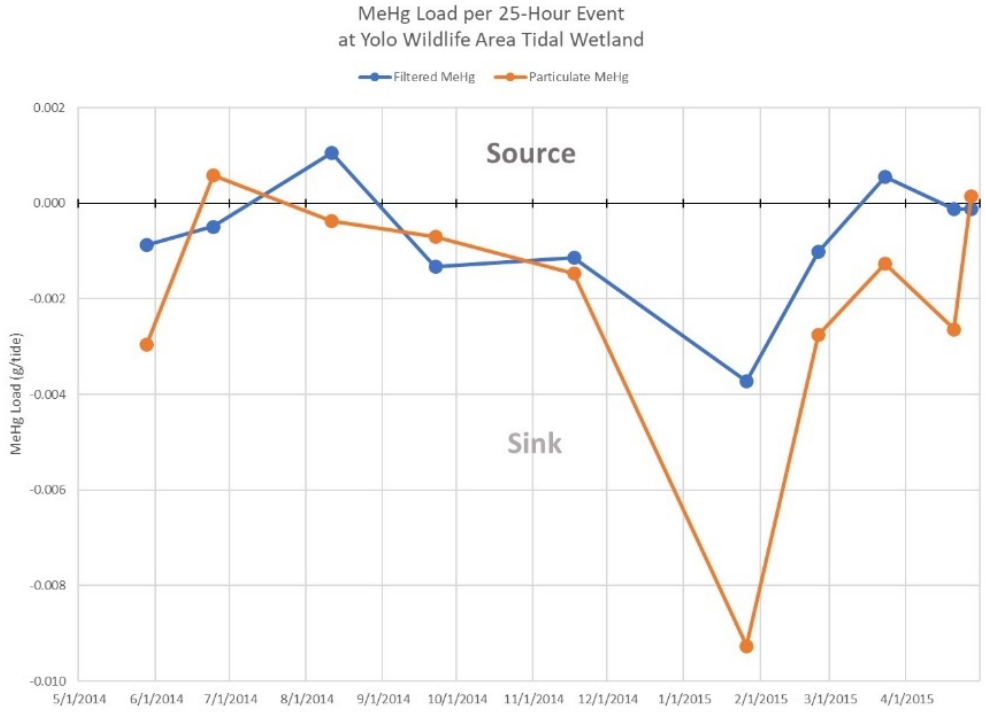


Figure 33 – MeHg loads per 25-hour event at Blacklock Tidal Wetland. Filtered MeHg loads are shown in blue, and particulate MeHg loads are shown in orange.

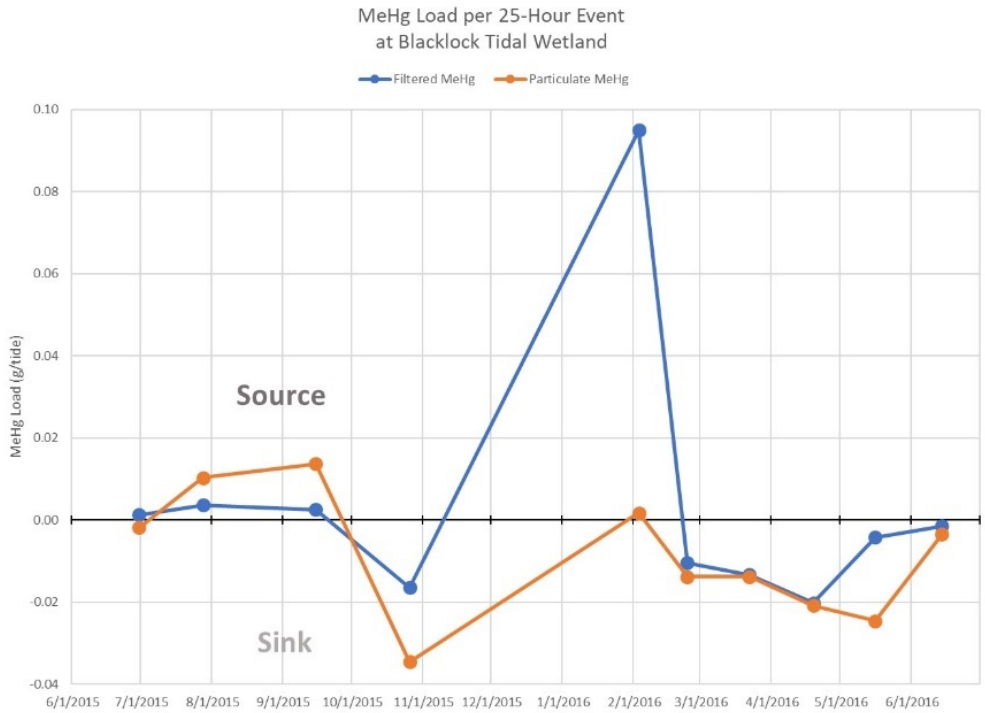


Figure 34 – MeHg loads per 25-hour event at North Lindsey Tidal Wetland. Filtered MeHg loads are shown in blue, and particulate MeHg loads are shown in orange.

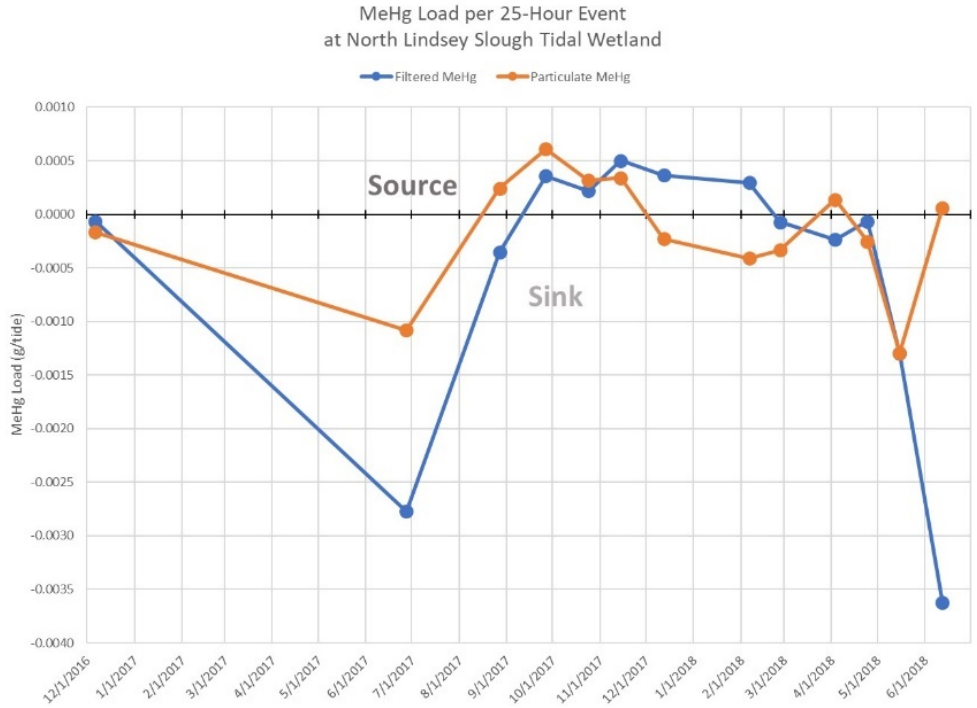


Figure 35 – MeHg loads per 25-hour event at Westervelt Cosumnes River Tidal Wetland. Filtered MeHg loads are shown in blue, and particulate MeHg loads are shown in orange.

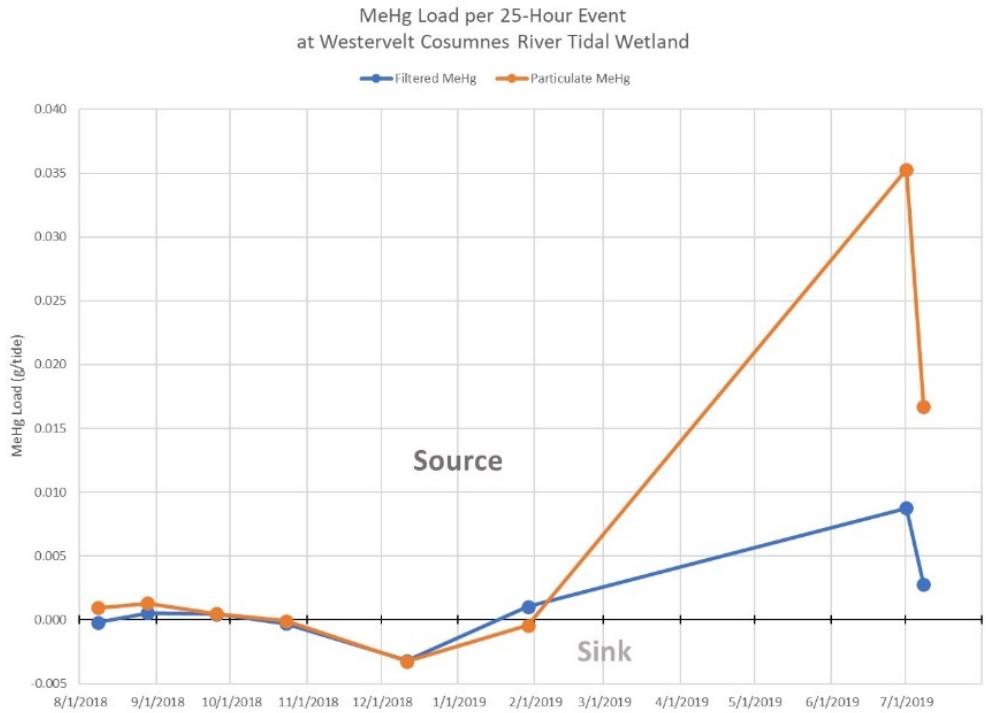


Figure 36 – THg loads per 25-hour event at Yolo Wildlife Area Tidal Wetland. Filtered THg loads are shown in blue, and particulate T Hg loads are shown in orange.

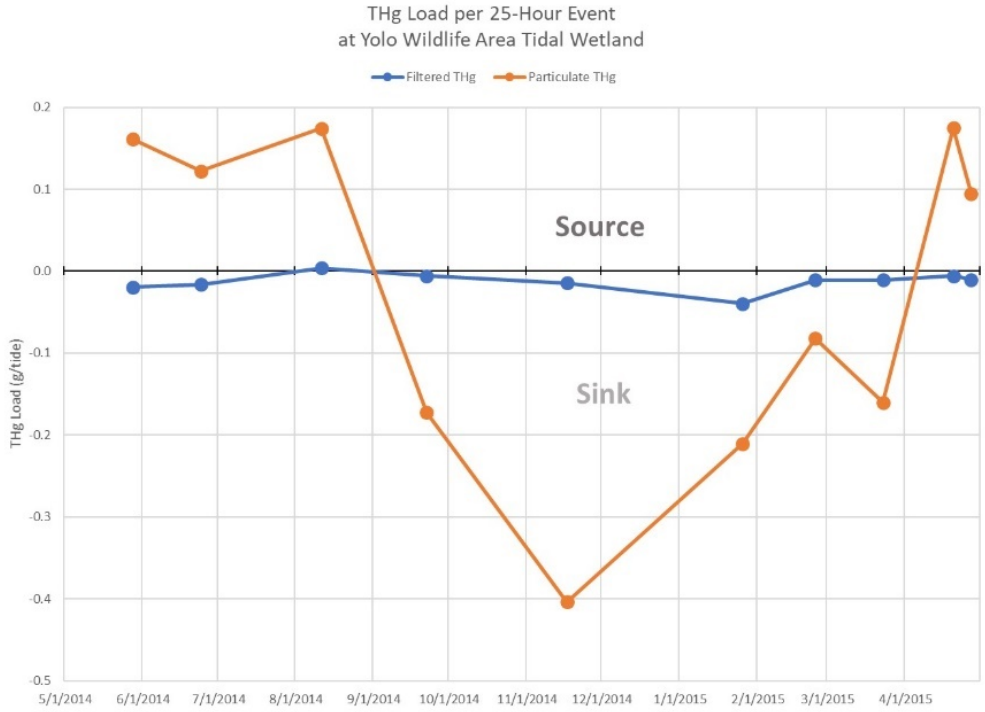


Figure 37 – THg loads per 25-hour event at Blacklock Tidal Wetland. Filtered THg loads are shown in blue, and particulate THg loads are shown in orange.

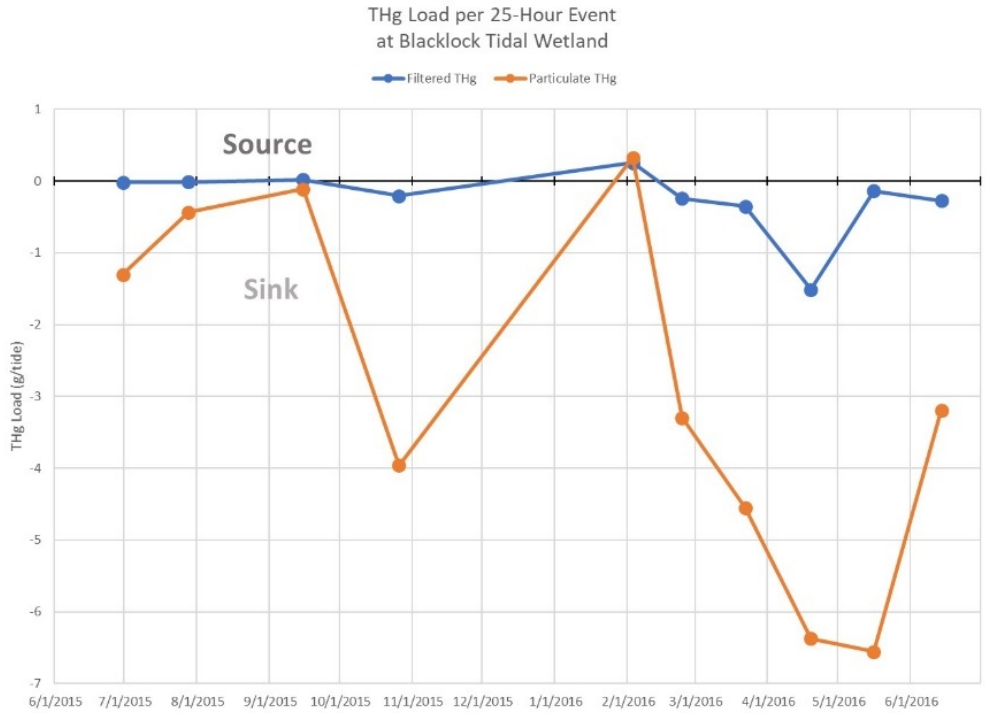


Figure 38 – THg loads per 25-hour event at North Lindsey Slough Tidal Wetland. Filtered THg loads are shown in blue, and particulate THg loads are shown in orange.

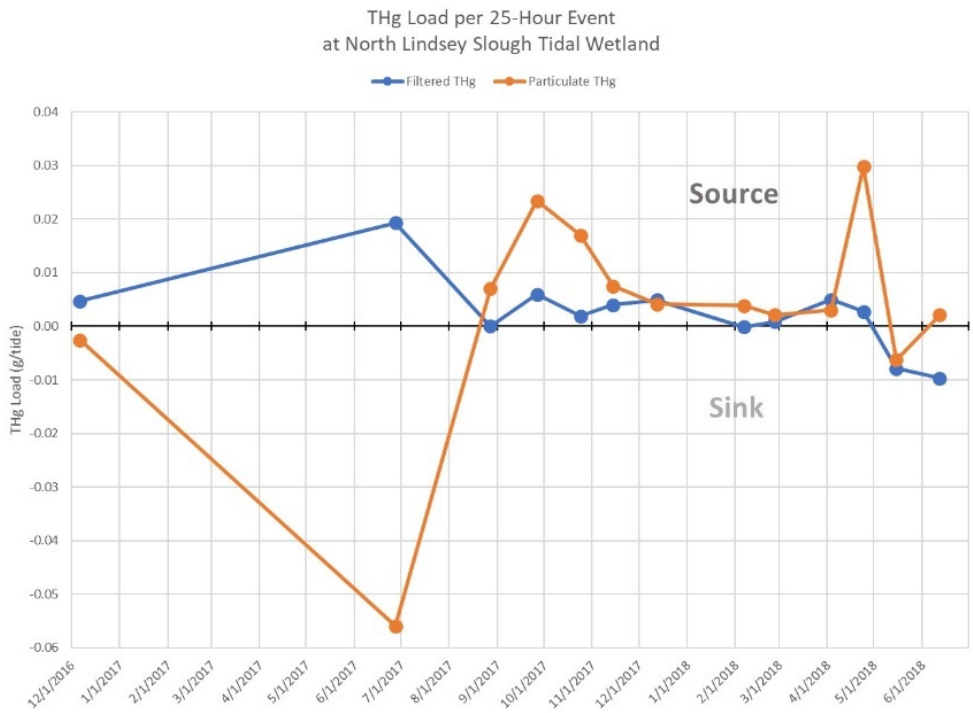
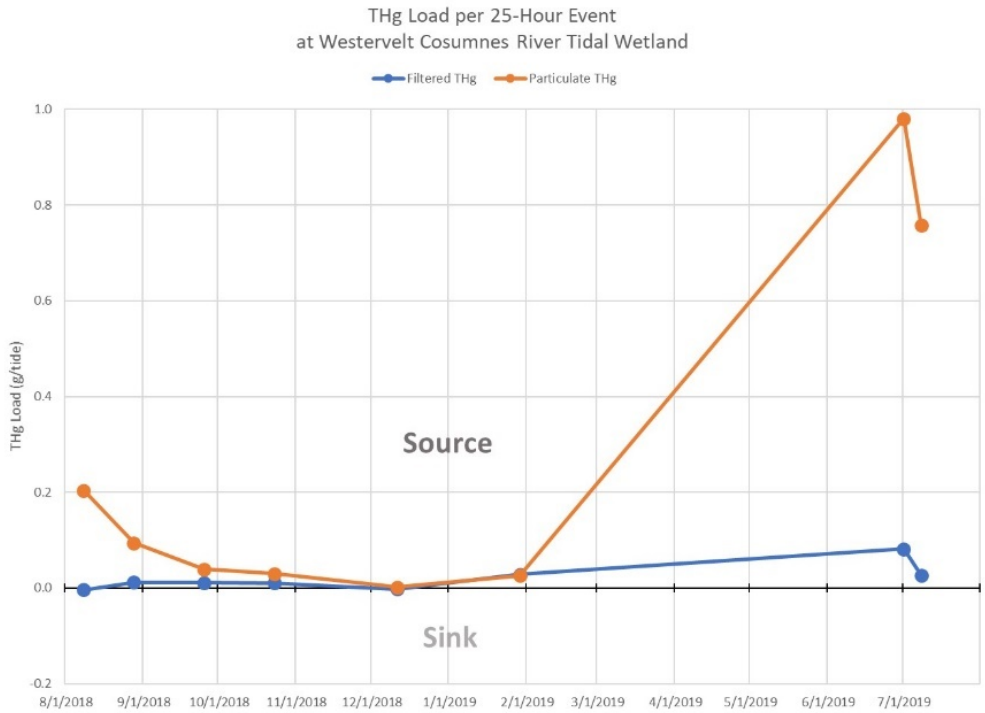


Figure 39 – THg loads per 25-hour event at Westervelt Cosumnes River Tidal Wetland. Filtered THg loads are shown in blue, and particulate THg loads are shown in orange.



Hypothesis 4 – Tidal wetlands are a net source of dissolved MeHg and a sink for particulate MeHg and THg on an annual basis.

As discussed more comprehensively in Hypothesis 1, none of the wetlands was a significant annual source (load) of particulate or filtered MeHg. In fact, Yolo and Blacklock were significant sinks of MeHg in all forms when we used the monthly estimated loads, and Yolo was a sink of particulate MeHg when using the 25-hour event load data.

In Hypothesis 2, we discussed significant annual particulate THg loads. Westervelt was a significant source of particulate THg when calculated using the 25-hour tidal event loads and between the ebb and flood tide particulate THg concentrations. Blacklock was a significant sink of particulate THg loads.

All in all, we did not see a trend of these four tidal wetlands being a net source of filtered or net sink of particulate MeHg. Any trends of particulate THg seem to be more nuanced and are discussed in more detail in Hypotheses 1 and 2. To detect any trends that may exist, we would have had to collect 25-hour load data more frequently than we did. Our data suggests there is no strong annual trend.

Hypothesis 5 – Organic carbon concentrations and MeHg concentrations are positively correlated.
Objective 4 – Determine if organic carbon and MeHg concentrations are correlated.

DWR analyzed the relationship between concentrations of filtered MeHg and DOC because previous research has indicated strong relationships between MeHg and organic material. However, the DOC measurement does not include quality measurements of any kind for organic carbon, the kind of which were examined by other researchers (Bergamaschi, et al., 2011; Bergamaschi, et al., 2011; Mitchell, Jordan, Heyes, & Gilmour, 2012). Additionally, we only collected composite samples during 25-hour events, which was at monthly (or less frequent) intervals. Because each of the four composited samples were collected within a day of each other, we could not assume independence, and therefore calculated one flow-weighted concentration value per 25-hour event to use for our correlation calculations. The Methods section briefly describes how we composited our samples, and a more complete description can be found in the Monitoring Plan attached to this report.

Because our data set is small ($n < 20$), we could not assume a distribution and therefore used Kendall's Tau Rank Correlation Coefficient to analyze our data ($\alpha = 0.05$). We looked at the relationships between filtered MeHg and DOC, unfiltered MeHg and TOC, and particulate MeHg and particulate organic carbon (POC). The data analysis is presented below.

Filtered MeHg and Dissolved Organic Carbon

Using Kendall's Tau, DWR calculated correlation coefficients between paired filtered MeHg and DOC concentrations for each wetland. Yolo and North Lindsey had a positive correlation between filtered MeHg and DOC (Kendall's Tau = 0.69 p-value = 0.007, and Kendall's Tau = 0.64 p-value = 0.003, respectively). Blacklock and Westervelt showed no significant correlation. At this time, we cannot recommend using DOC concentrations as a predictor of filtered MeHg concentrations without more data, but our data suggests that they may be linked in some circumstances based on our flow-weighted concentration values. Collecting more frequent, non-composited samples that are not autocorrelated would be useful to prove or disprove this hypothesis. See Table 10 for Kendall's Tau coefficients and p-values per wetland and Figure 41 shows the correlation graphs with a regression line.

Table 10 – Kendall's Tau correlation coefficient and p-values for filtered MeHg and DOC. Light purple highlighting indicates significant correlation of $\alpha \leq 0.05$.

Wetland	Kendall's Tau	p-value
Yolo	0.69	0.01
Blacklock	0.39	0.18
North Lindsey	0.64	0.00
Westervelt	0.36	0.27

Unfiltered MeHg and Total Organic Carbon

When examining unfiltered MeHg versus TOC, DWR found two out of four wetlands were significantly correlated, Yolo and North Lindsey. Blacklock and Westervelt were not correlated. This pattern unsurprisingly matches that of filtered MeHg and DOC since DOC appears to be the dominant fraction of TOC. See Table 11 for Kendall's Tau coefficients and p-values per wetland and Figure 42 for the correlation graphs with a regression line. See Figure 40 for a graph showing the median percentage of particulate and dissolved organic carbon concentrations for each wetland, which shows that the dominant fraction is filtered.

Table 11 – Kendall's Tau correlation coefficient and p-values for unfiltered MeHg and TOC. Light purple highlighting indicates significant correlation of $\alpha \leq 0.05$.

Wetland	Kendall's Tau	p-value
Yolo	0.78	0.00
Blacklock	0.50	0.08
North Lindsey	0.59	0.01
Westervelt	0.29	0.39

Particulate MeHg and Particulate Organic Carbon

The particulate fractions were calculated as the total/unfiltered fraction minus the filtered fraction. Blacklock and North Lindsey had significantly correlated fractions, whereas Yolo and

Westervelt did not. Particulate organic matter is a relatively small percentage of the organic carbon fraction, which is dominated by DOC. See Table 12 for Kendall's Tau coefficients and p-values per wetland and Figure 43 for the correlation graphs with a regression line.

Table 12 – Kendall's Tau correlation coefficient and p-values for particulate MeHg and POC. Light purple highlighting indicates significant correlation of $\alpha \leq 0.05$.

Wetland	Kendall's Tau	p-value
Yolo	-0.02	1.00
Blacklock	0.67	0.02
North Lindsey	0.50	0.02
Westervelt	-0.11	0.80

Figure 40 – Median percent organic carbon fractions for each wetland. The blue portion of the bar is dissolved organic carbon, and the particulate organic carbon is indicated in orange.

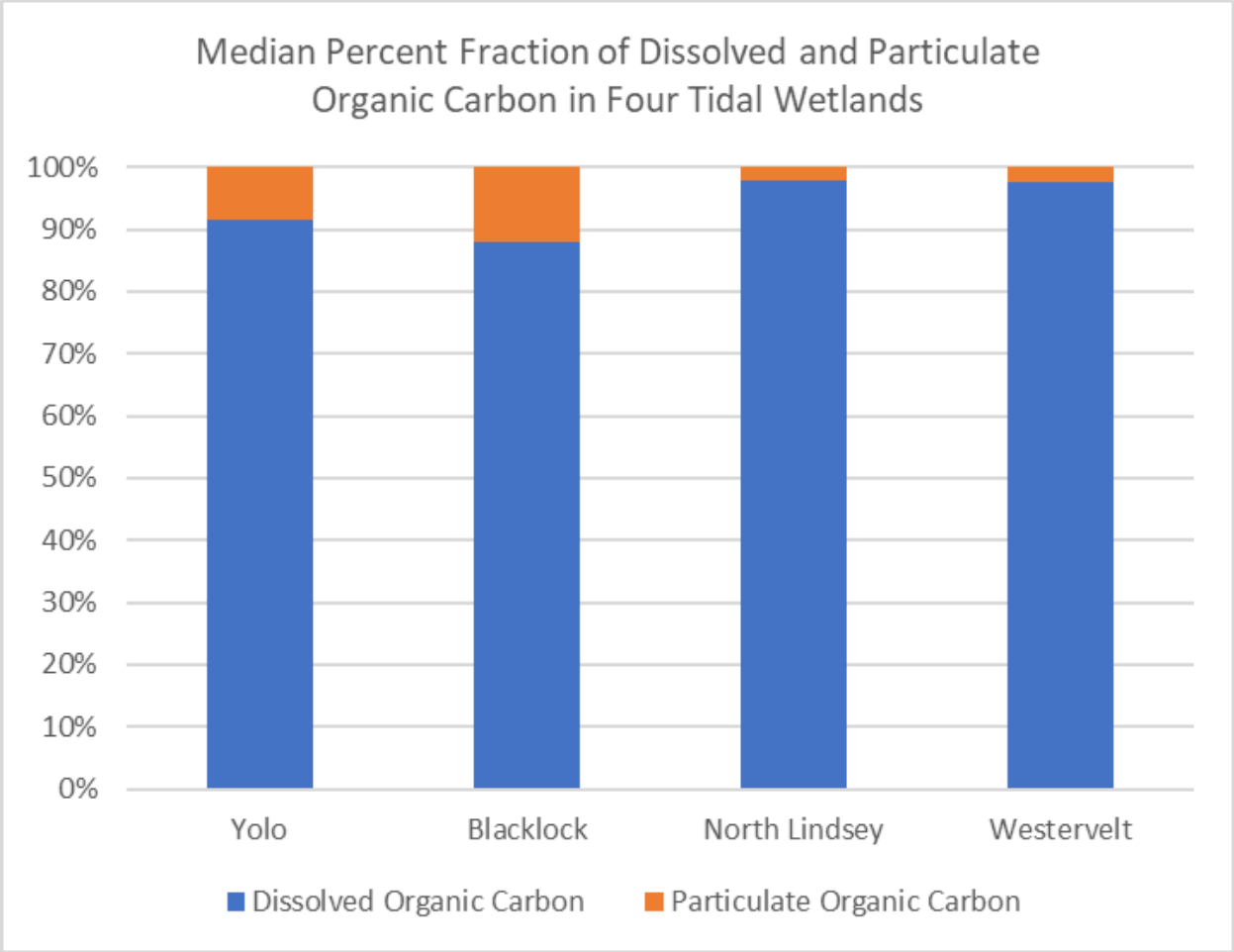


Figure 41 – Filtered MeHg vs dissolved organic carbon concentration correlation graphs and p-value. The blue dots are paired data points and the red line is the regression line.

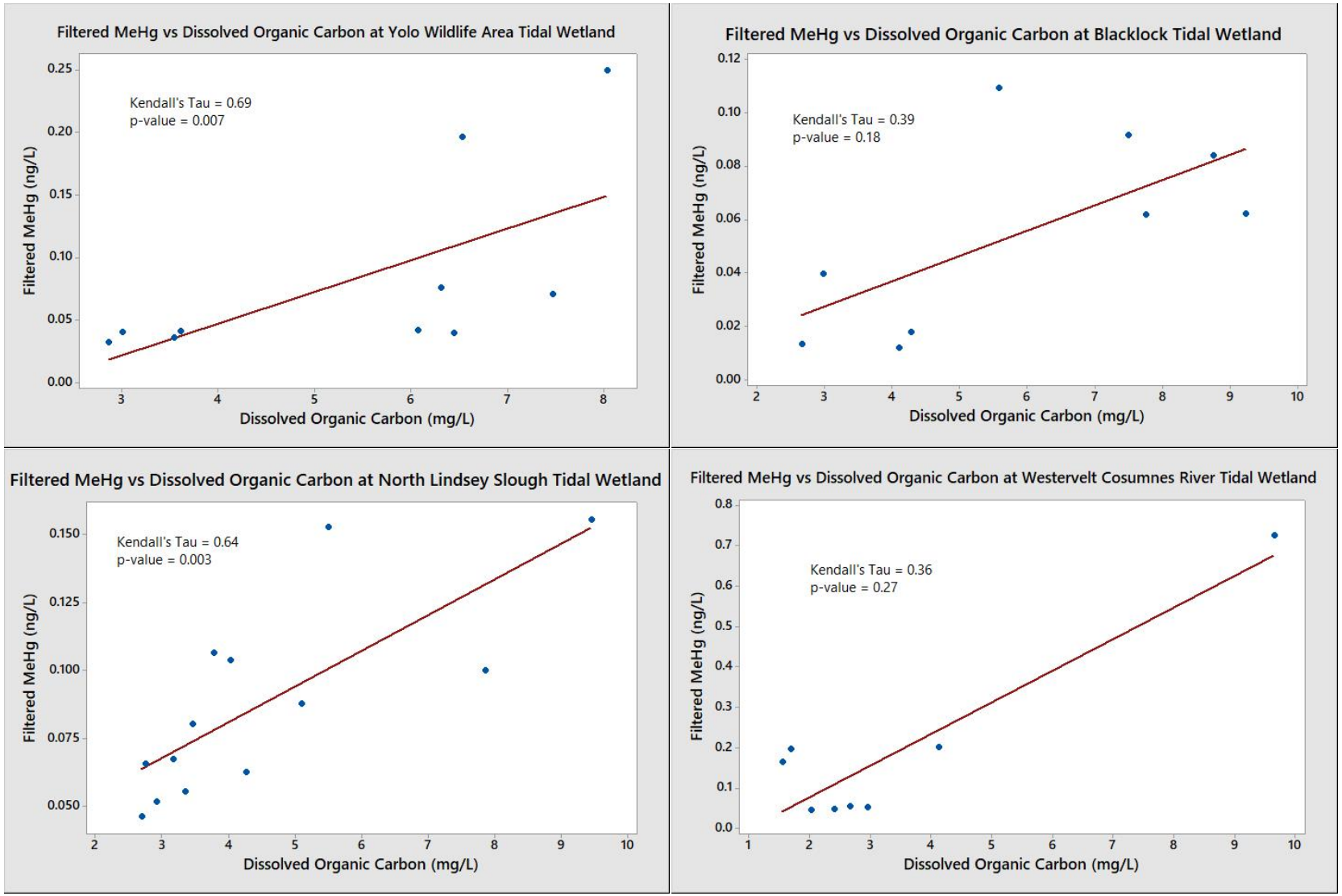


Figure 42 – Unfiltered MeHg vs total organic carbon concentration correlation graphs and p-value. The blue dots are paired data points and the red line is the regression line.

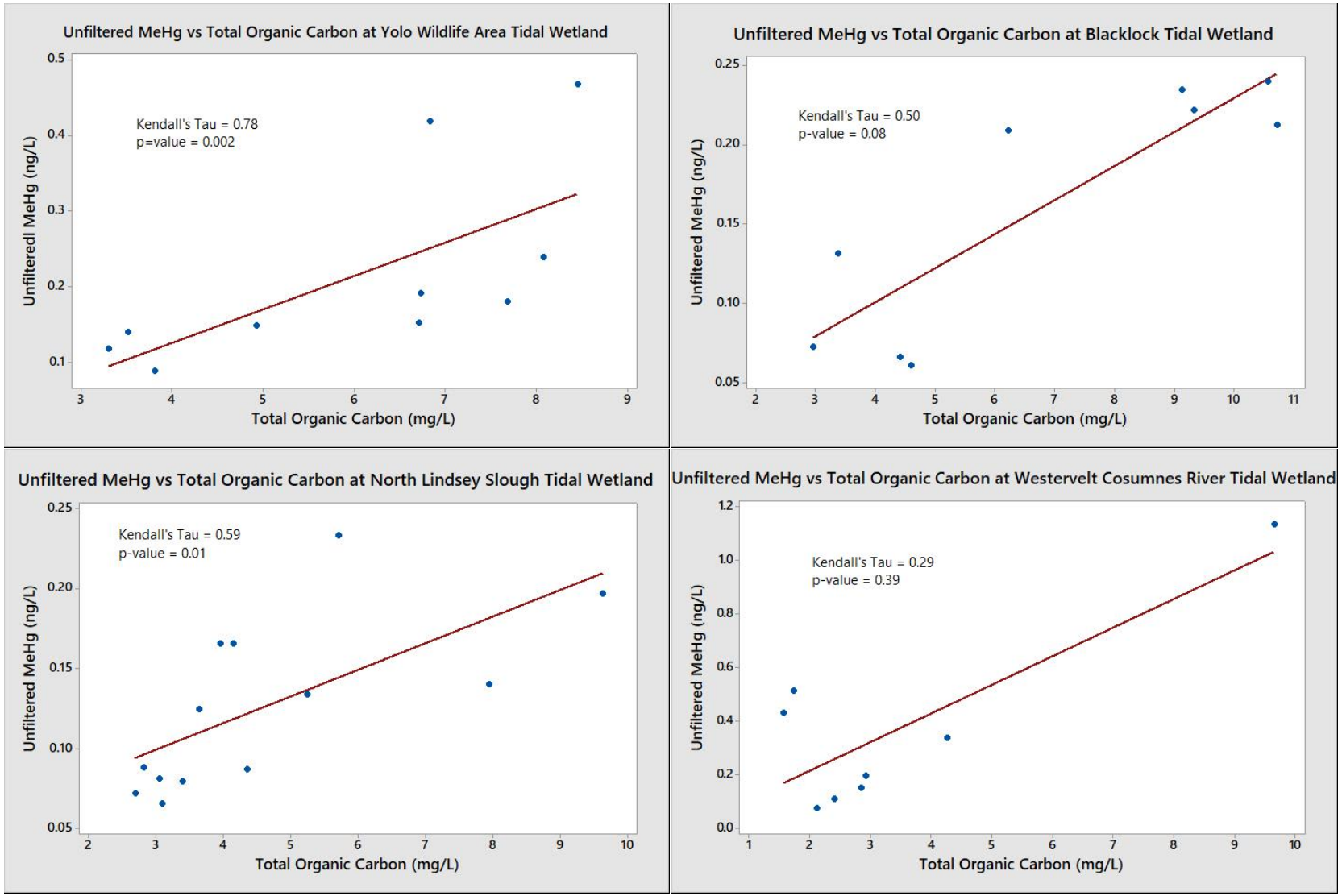
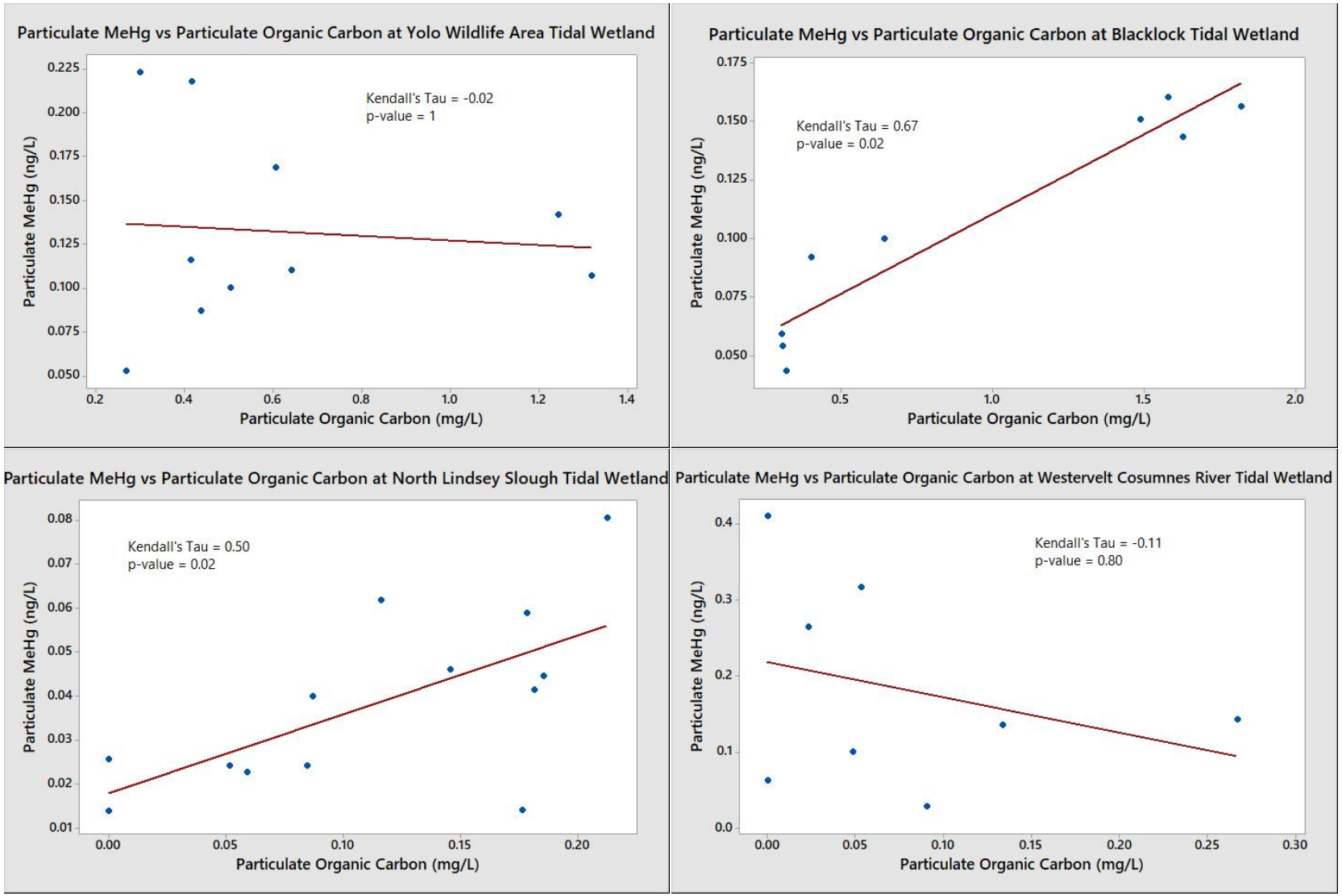


Figure 43 – Particulate MeHg vs particulate organic carbon concentration correlation graphs and p-value. The blue dots are paired data points and the red line is the regression line.



Objective 3 – Measure and calculate net yearly organic carbon, chlorophyll-a, and total suspended solids imports and exports.

DWR collected load data in addition to MeHg and THg data that we will present in this section. We calculated loads for organic carbon, chlorophyll-a, and TSS using 25-hour event loads and estimated monthly loads. The two methods are described in the Methods section.

Organic Carbon

DWR collected flow-weighted composited organic carbon samples during 25-hour sampling events. We collected TOC and DOC and then calculated POC by subtracting DOC from TOC (TOC - DOC = POC). We calculated estimated monthly loads for organic carbon using the same method as we used for mercury monthly loads, by using the 25-hour event data along with the continuous 15-minute flow data. More details about how we calculated loads are located in the Methods section

Seasonal trends among the wetlands were not apparent, though the majority of the organic carbon was in the dissolved form for all four wetlands. Yolo had a higher percentage of POC during the months of April-July 2014, and the wetland was only a source of TOC during April and May 2014 (Figure 44). Blacklock was a slight source of TOC from June-October 2015, but a larger sink during June 2016 (Figure 45). North Lindsey was a source of TOC from September 2017 through April 2018, with several months being large sinks of TOC, predominantly DOC (Figure 46). Westervelt was nearly always a sink of TOC, although after the wetland flooded in early 2019, it was a source of organic carbon in June and July 2019 (Figure 47).

Figure 44 – Estimated organic carbon monthly loads at the Yolo Wildlife Area Tidal Wetland. The graph shows estimates of organic carbon loads made using data collected from the 25-hour events and the continuous flow data.

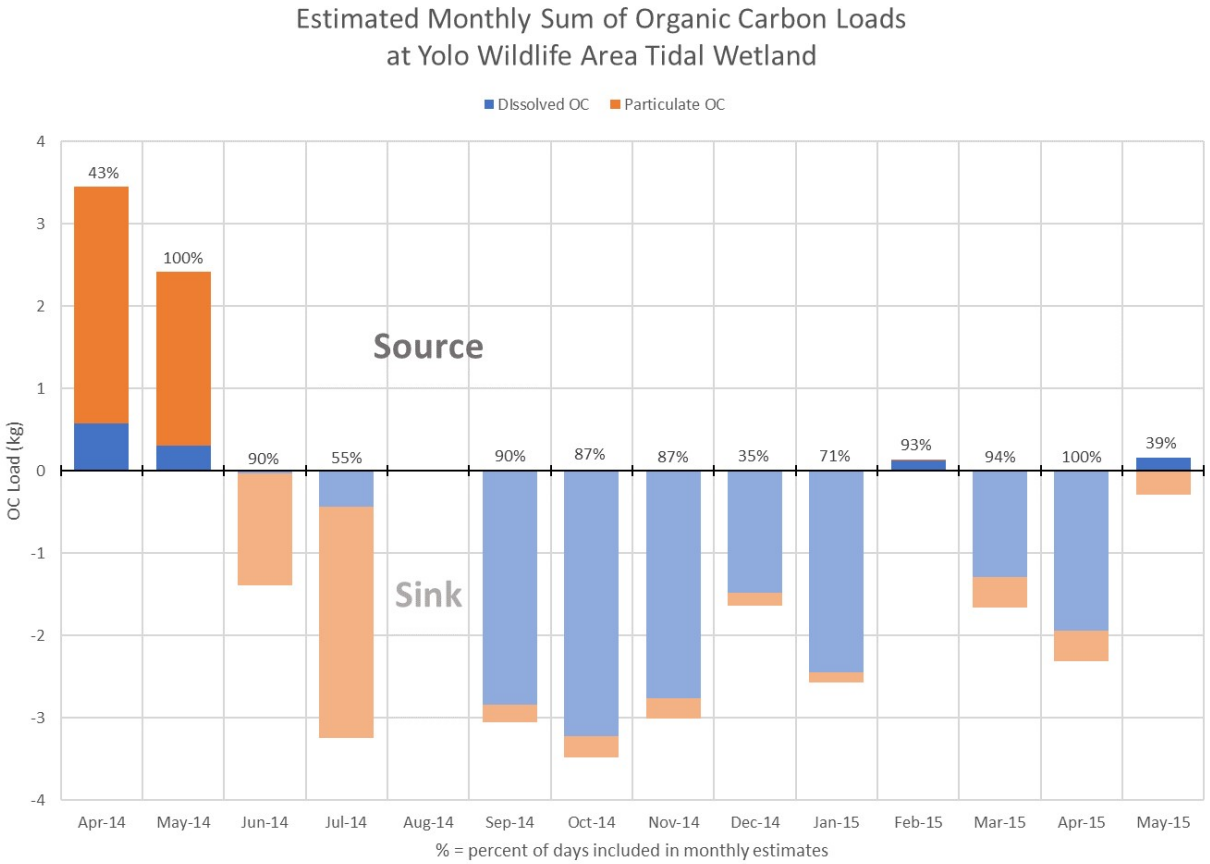


Figure 45 – Estimated organic carbon monthly loads at the Blacklock Tidal Wetland. The graph shows estimates of organic carbon loads made using data collected from the 25-hour events and the continuous flow data.

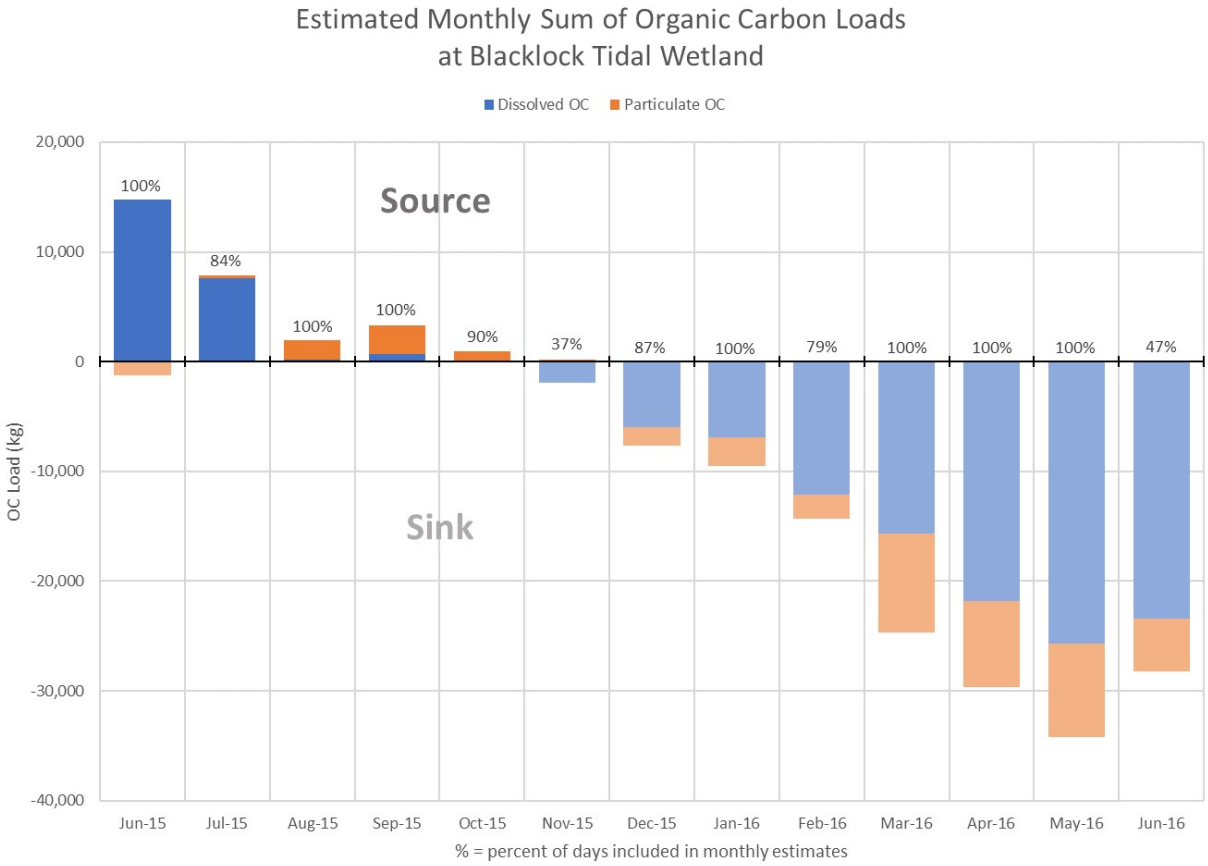


Figure 46 – Estimated organic carbon monthly loads at the North Lindsey Slough Tidal Wetland. The graph shows estimates of organic carbon loads made using data collected from the 25-hour events and the continuous flow data.

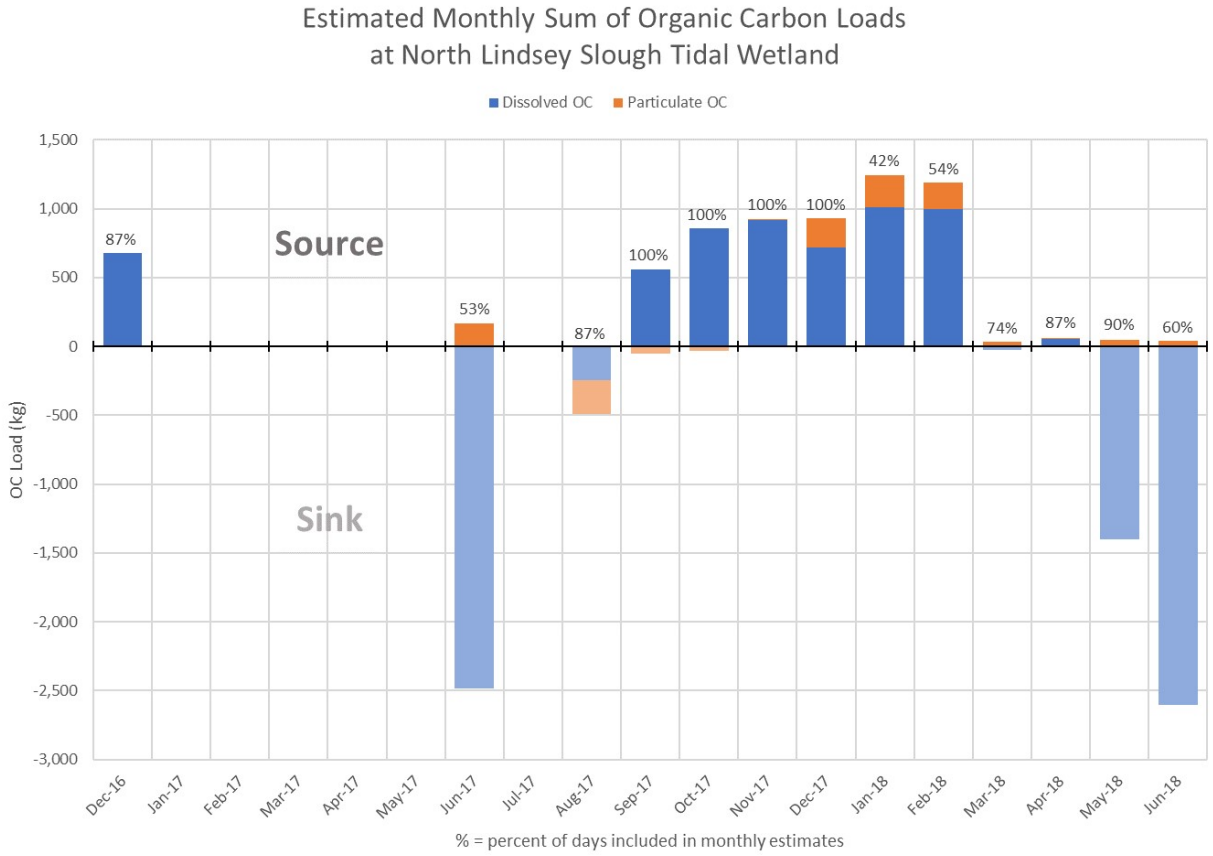
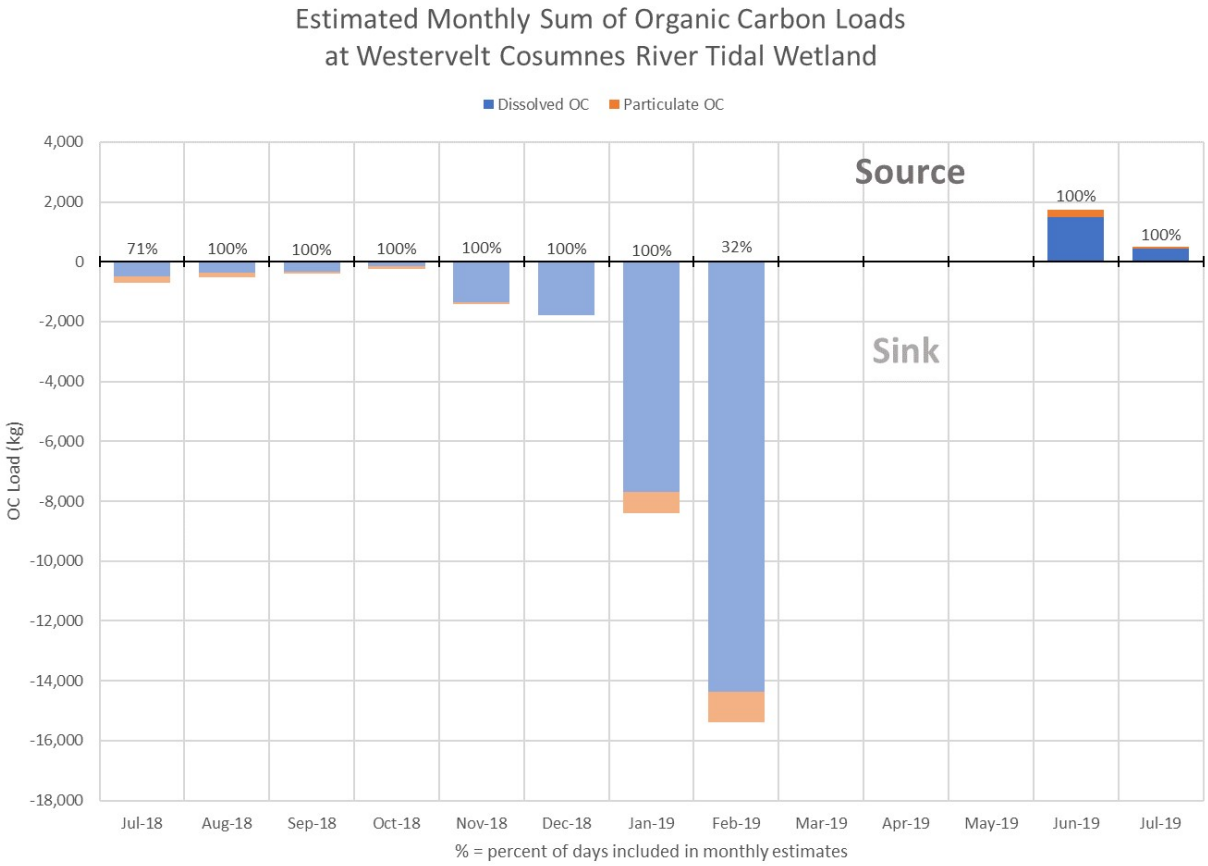


Figure 47 – Estimated organic carbon monthly loads at the Westervelt Cosumnes River Tidal Wetland. The graph shows estimates of organic carbon loads made using data collected from the 25-hour events and the continuous flow data.



Chlorophyll-a

Chlorophyll-a grab samples were collected approximately weekly along with a "total chlorophyll" measurement using the YSI EXO water quality sondes from all wetlands except Blacklock. Because chlorophyll-a load estimates were included in the original workplan and objectives, we will include them here but not discuss them further because of methodological errors while filtering chlorophyll-a samples. Figure 48, Figure 49, and Figure 50 show the estimated chlorophyll-a loads.

Figure 48 – Estimated monthly chlorophyll-a loads at Yolo Wildlife Area Tidal Wetland. The masses are estimated.

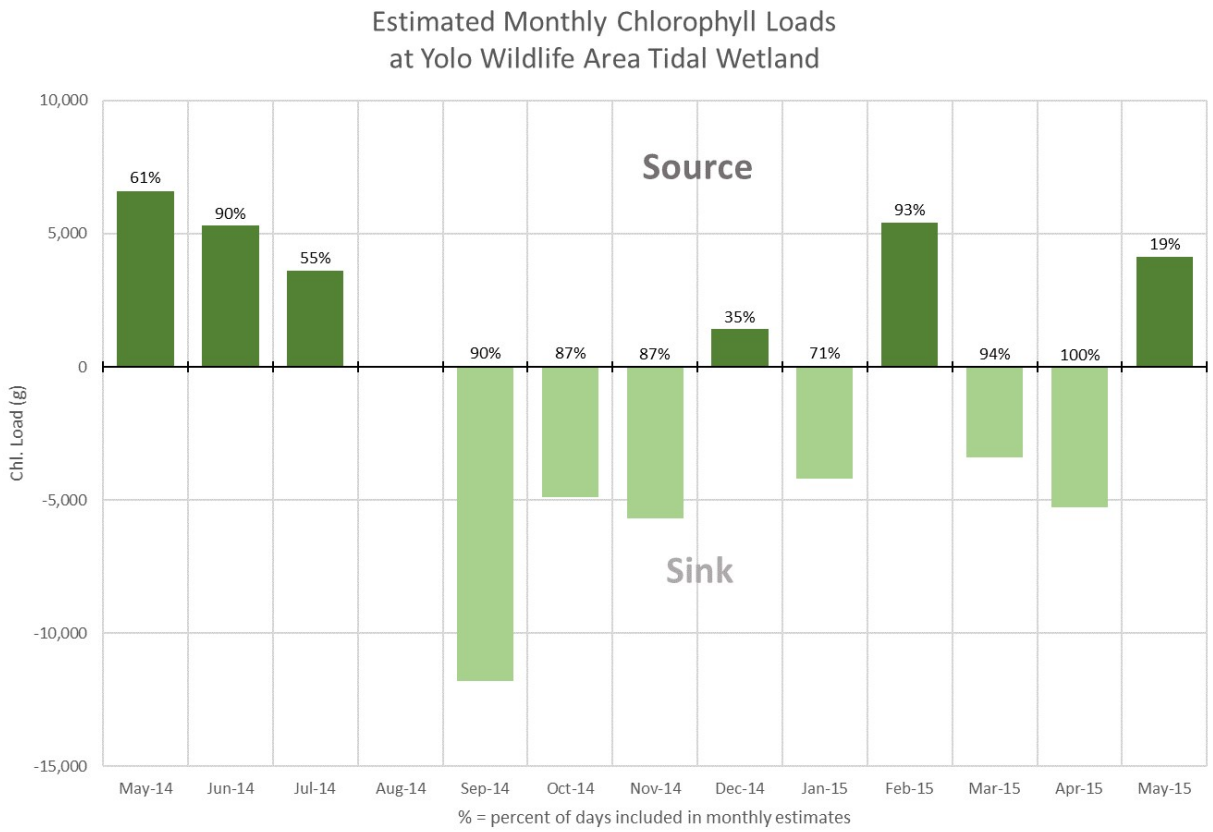


Figure 49 – Estimated monthly chlorophyll-a loads at North Lindsey Slough Tidal Wetland. The masses are estimated.

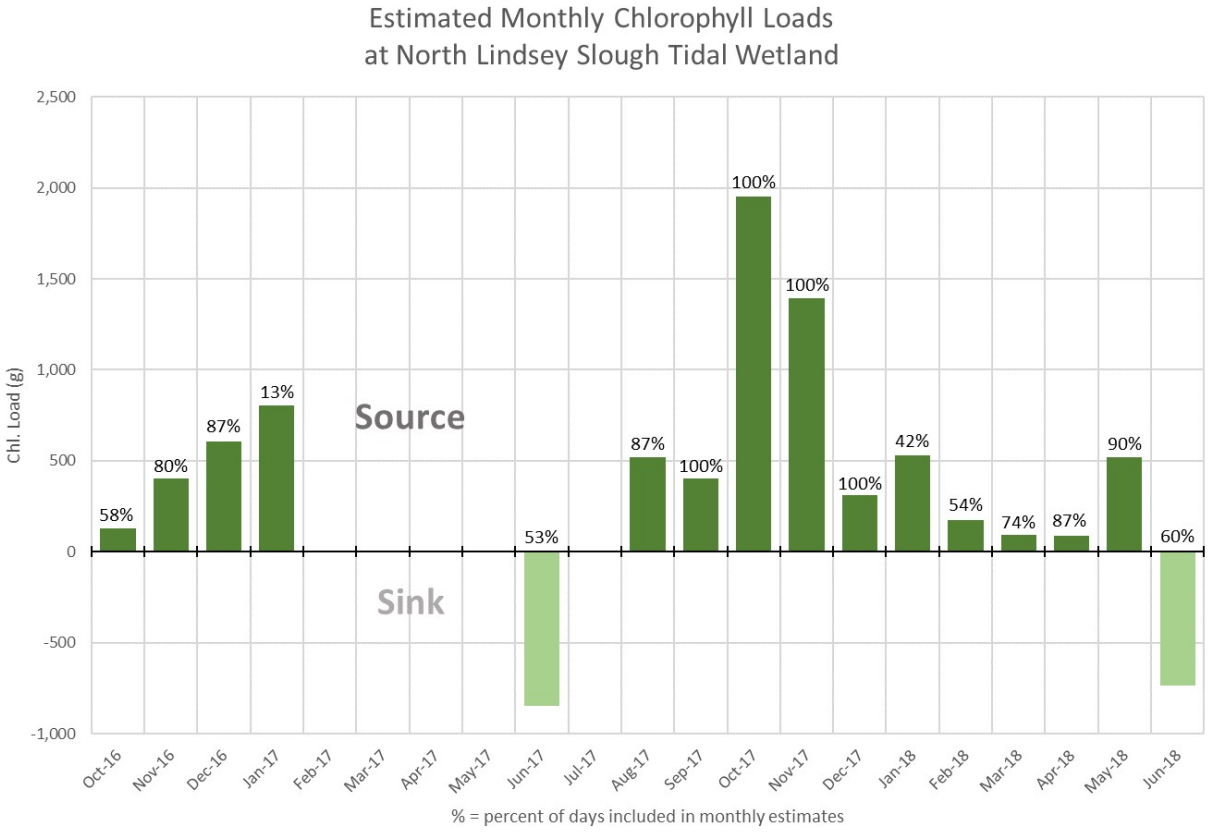
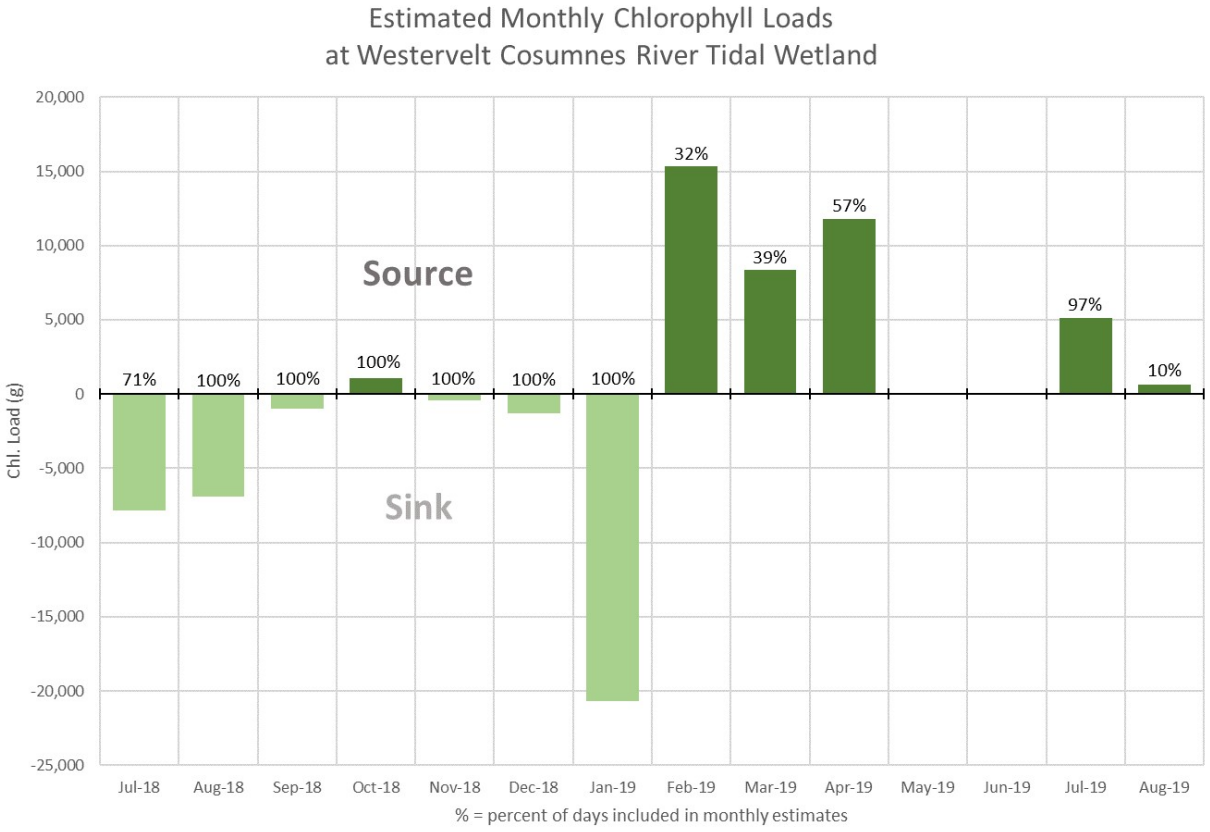


Figure 50 – Estimated monthly chlorophyll-a loads at Westervelt Cosumnes River Tidal Wetland. The masses are estimated.



Total Suspended Sediment

As a reminder from the Methods section, TSS was calculated using two methods with two sets of TSS data. We present both methods to illustrate the difference between using continuous versus 25-hour concentration data. The first method involved using estimated TSS concentrations that were calculated using continuous turbidity water quality data. The calculated continuous TSS value was then paired with the continuous flow data of the same dates and times to estimate 15-minute loads, which we used to calculate monthly loads. The second method used the 25-hour TSS event data with the continuous flow data to estimate 15-minute loads which were added together to calculate monthly loads.

The first method of using estimated continous TSS data was used at Yolo, North Lindsey, and Westervelt only, as we could not deploy sondes at Blacklock; sondes were required to collect continuous turbidity data that could be used to estimate TSS concentrations. The second method of using the 25-hour TSS event data with the continuous flow data was used for Blacklock, North Lindsey, and Westervelt, but not Yolo as we did not collect TSS water samples during the 25-hour sampling events.

There did not seem to be any consistent patterns of TSS among the four wetlands, but there were individual patterns at each wetland. Yolo was a sink of TSS from September 2014 through February 2015, and a source of TSS the rest of the time (Figure 51). Blacklock was a sink of TSS the majority of the time, at an order of magnitude more than Yolo; the TSS data used at Blacklock was from the 25-hour events only and the loads were less reliable estimates than from the sonde data (Figure 52). North Lindsey showed similar patterns between the two estimated TSS loads. In both estimates, the wetland was mostly a source of TSS, except for June 2017 which was a notable sink in both estimates (Figure 53 and Figure 54). The TSS loads were much smaller at North Lindsey than any of the other three wetlands, understandably, since North Lindsey is a smaller wetland than the others. Unlike North Lindsey, Westervelt did not show very similar patterns between the two estimated TSS loads. In both estimates, Westervelt was a source of TSS in July through September, and a sink in February 2019, though the estimated sources and sinks varied depending on the method used to calculate monthly TSS loads (Figure 55 and Figure 56). At North Lindsey, we collected data from thirteen 25-hour events, and from Westervelt, we only collected data from eight 25-hour events, which might help explain the differences. The loads estimated using the continuous 15-minute sonde data at Westervelt (Figure 55) are more likely to be accurate.

Figure 51 – Estimated total suspended solids monthly loads at the Yolo Wildlife Area Tidal Wetland. Estimates of TSS loads were made using continuous 15-minute sonde data and continuous 15-minute flow data.

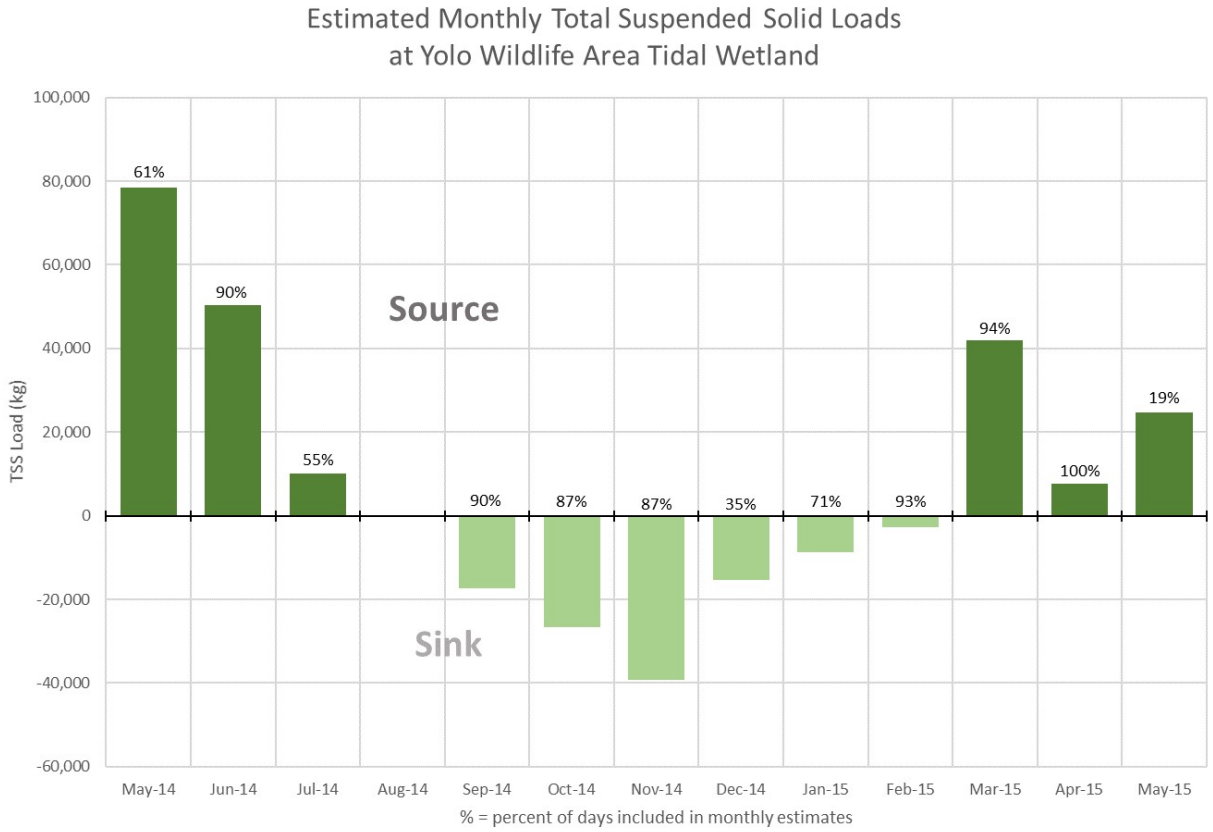


Figure 52 – Estimated total suspended solids monthly loads at the Blacklock Tidal Wetland. Estimates of TSS loads were made using 25-hour tidal event TSS concentration data with continuous flow data.

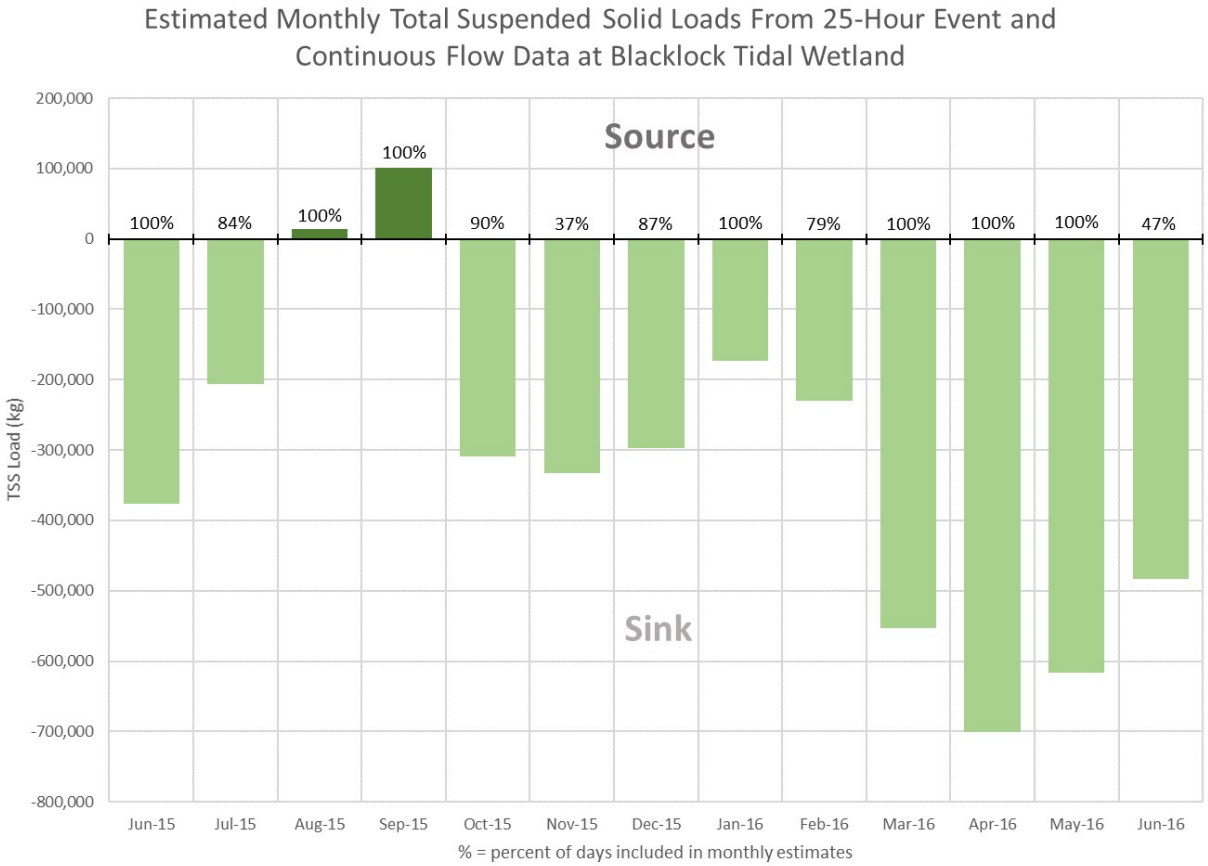


Figure 53 – Estimated total suspended solids monthly loads at the North Lindsey Slough Tidal Wetland. The graph shows estimates of TSS loads made using continuous 15-minute sonde data and continuous 15-minute flow data.

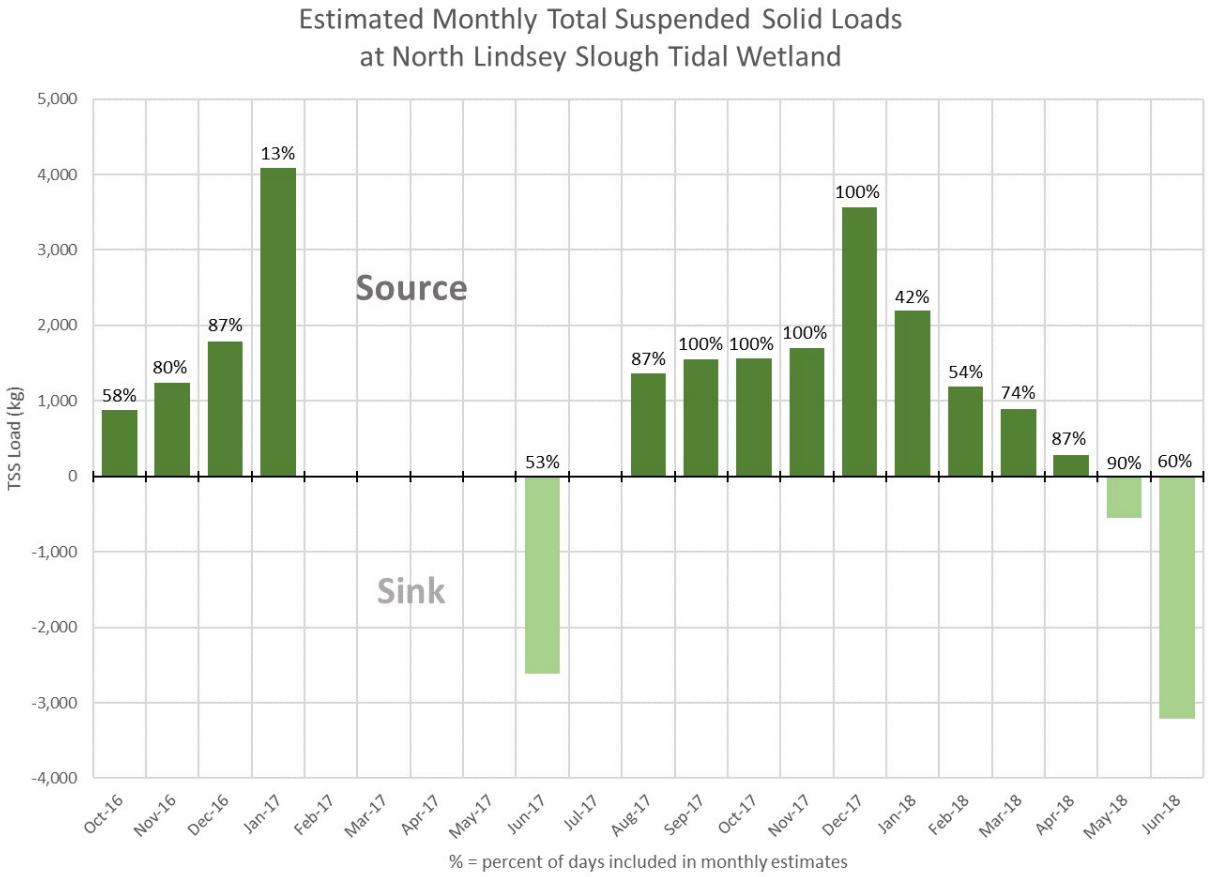


Figure 54 – Estimated total suspended solids monthly loads at the North Lindsey Slough Tidal Wetland. The graph shows estimates of TSS loads using 25-hour tidal event TSS concentration data with continuous flow data.

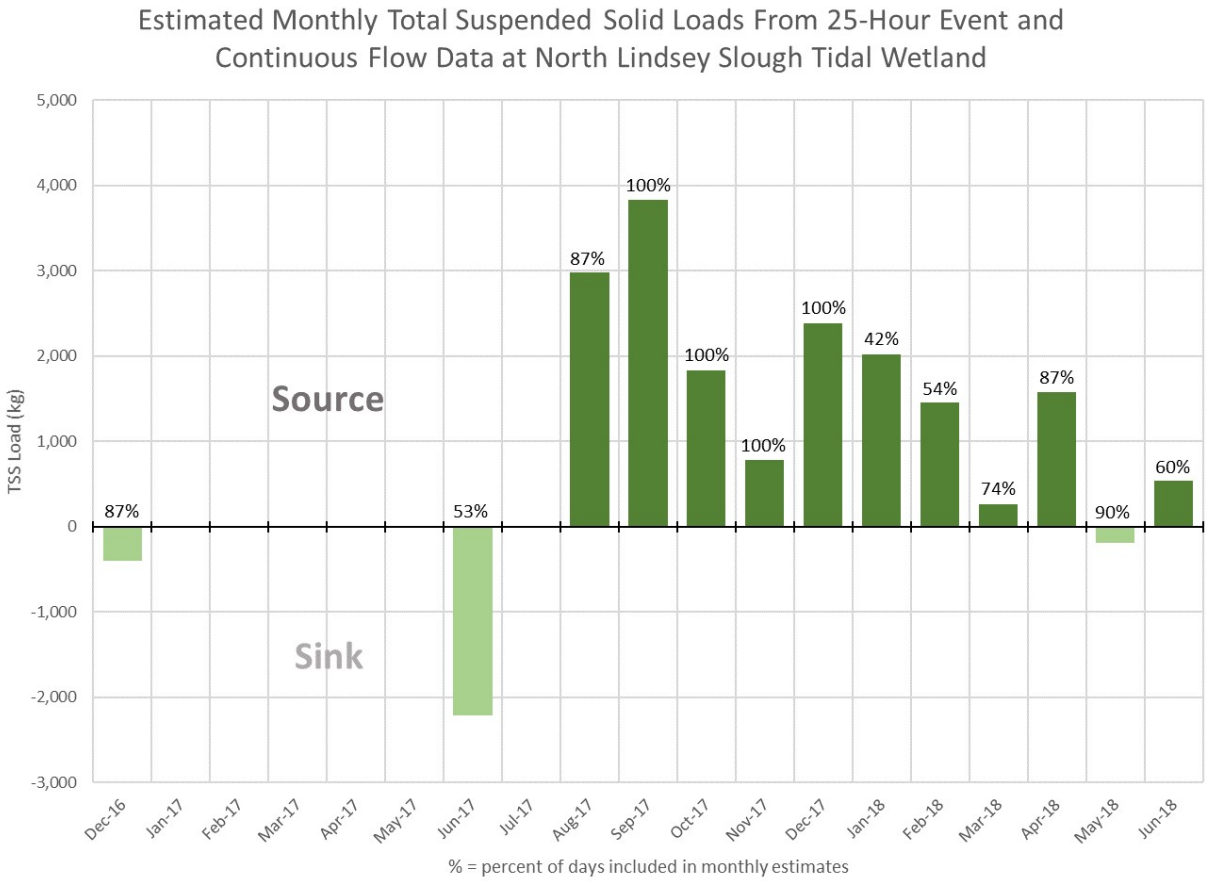


Figure 55 – Estimated total suspended solids monthly loads at the Westervelt Cosumnes River Tidal Wetland. The graph shows estimates of TSS loads made using continuous 15-minute sonde data and continuous 15-minute flow data.

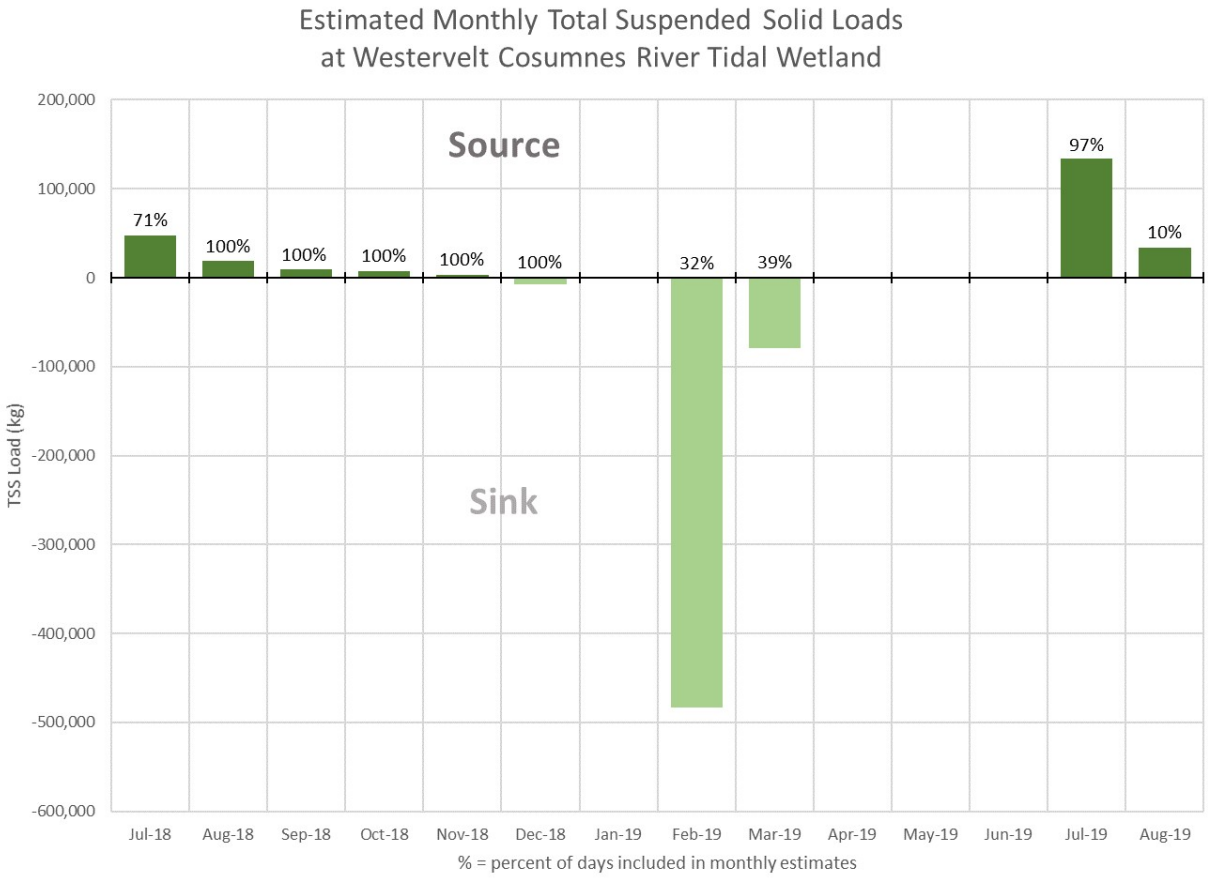
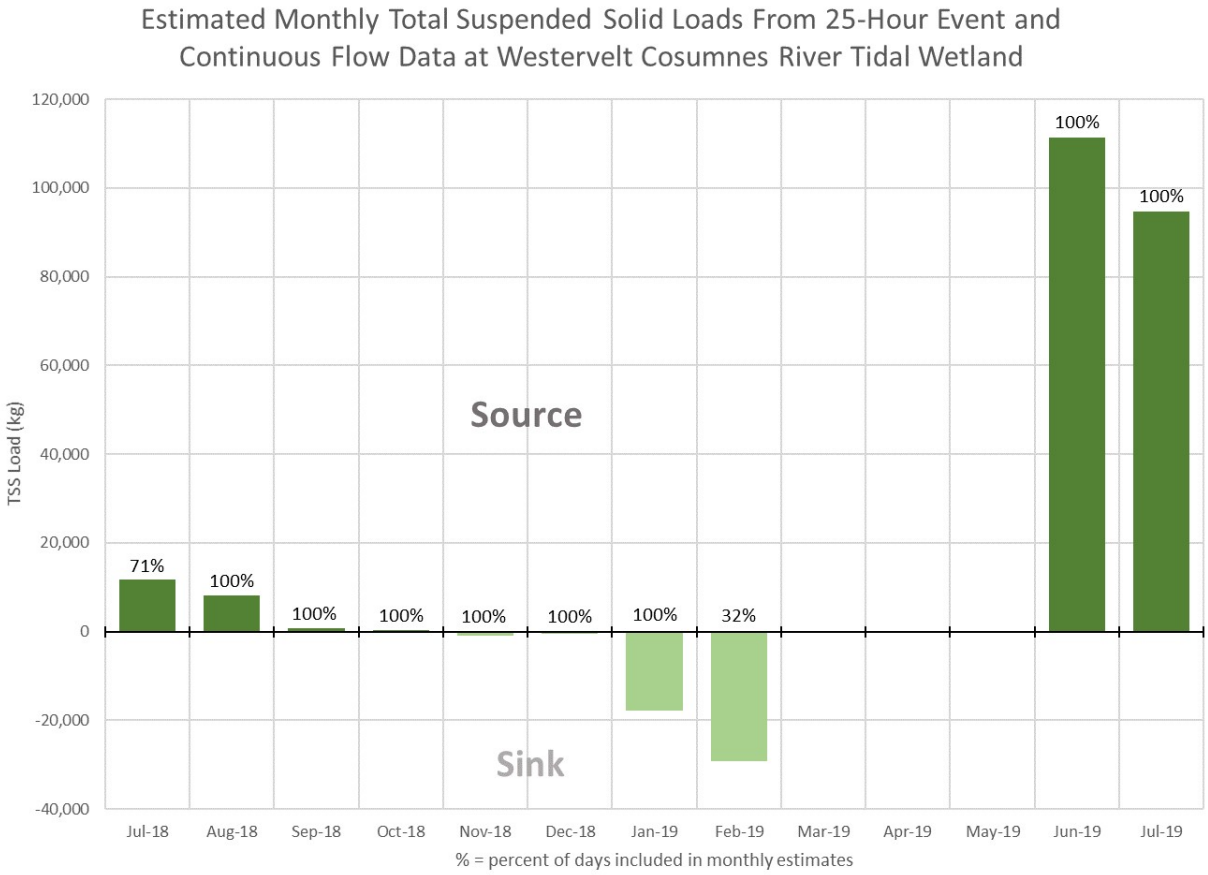


Figure 56 – Estimated total suspended solids monthly loads at the Westervelt Cosumnes River Tidal Wetland. The graph shows estimates of TSS loads using 25-hour tidal event TSS concentration data with continuous flow data.



Other Tidal Wetland Observations

This section contains additional information that is beyond what DWR addressed in the hypotheses and objectives of the workplan (CDWR, 2013). While we focused on collecting data to fulfill the workplan obligations, we collected other pertinent data and performed selected additional analyses.

<u>Particulate and Filtered Mercury Fractions</u>

We briefly examined the percentage of mercury in the particulate and filtered phases. Depending on whether the mercury is in the particulate or filtered phase can suggest a direction for control measures, if deemed necessary. For example, if the majority of the mercury is in the particulate phase, controlling sediment might be a viable solution for controlling mercury export.

Percentages of filtered and particulate species of THg and MeHg varied somewhat amongst wetlands, although some trends exist. We calculated a median filtered and particulate THg and MeHg percentage for each wetland based on the 25-hour event loads, which showed that the dominant fraction of both MeHg and THg was generally the particulate fraction, with the notable exception being at North Lindsey. Particulate THg was approximately 90% of the THg, except for North Lindsey which was approximately 57% in the particulate form. MeHg tended to be in the particulate form around 60-70% at the wetlands, although North Lindsey had only 30% in the particulate form. See Table 13 and Figure 57 and Figure 58 for percentages and a graph depicting the particulate and filtered fractions. Figure 59 and Figure 60 show box plots of unfiltered, filtered, and particulate THg and MeHg.

North Lindsey was a notable exception to the trend of the percentage of THg and MeHg in the particulate and filtered forms. North Lindsey was also unique in several ways. First, North Lindsey had the slowest velocity water entering and exiting the tidal wetland (Huston, 2020). Second, we observed that the majority of the tidal wetland contained vegetation, mostly tules, to a higher degree than any of the other tidal wetlands we studied. Lastly of note, North Lindsey was a relic of a historical tidal wetland that was fully reconnected to tidal flow in 2014 (Carrothers, Email communication, 2020).

Table 13 – Calculated median percentages of filtered and particulate THg and MeHg for four tidal wetlands.

Wetland	Filtered THg	Particulate THg	Filtered MeHg	Particulate MeHg
Yolo	8%	92%	29%	71%
Blacklock	10%	90%	29%	71%
North Lindsey	43%	57%	70%	30%
Westervelt	13%	87%	41%	59%

Figure 57 – Bar graphs of median percentages of filtered and particulate THg and MeHg comparing four tidal wetlands.

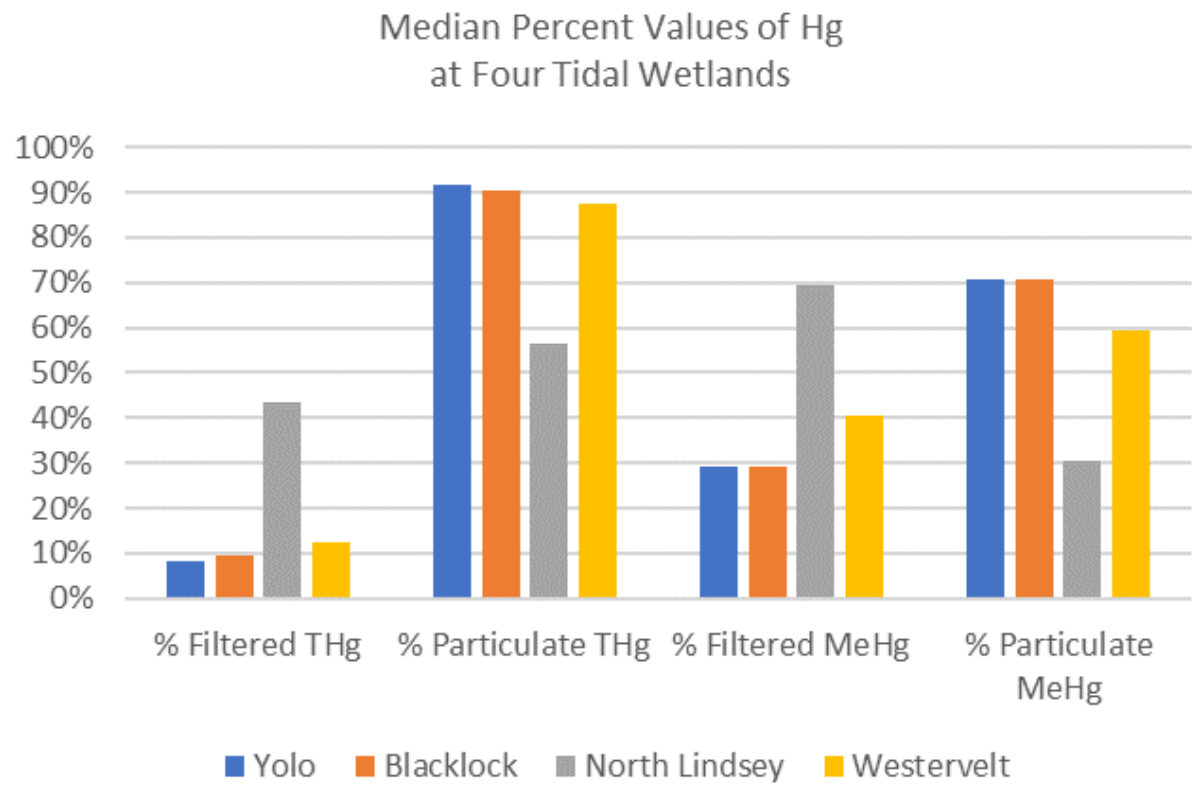


Figure 58 – Median percent of filtered and particulate fractions of THg and MeHg presented for each tidal wetland. The orange portion of the bar graph is particulate THg fraction and the blue is the filtered THg fraction.

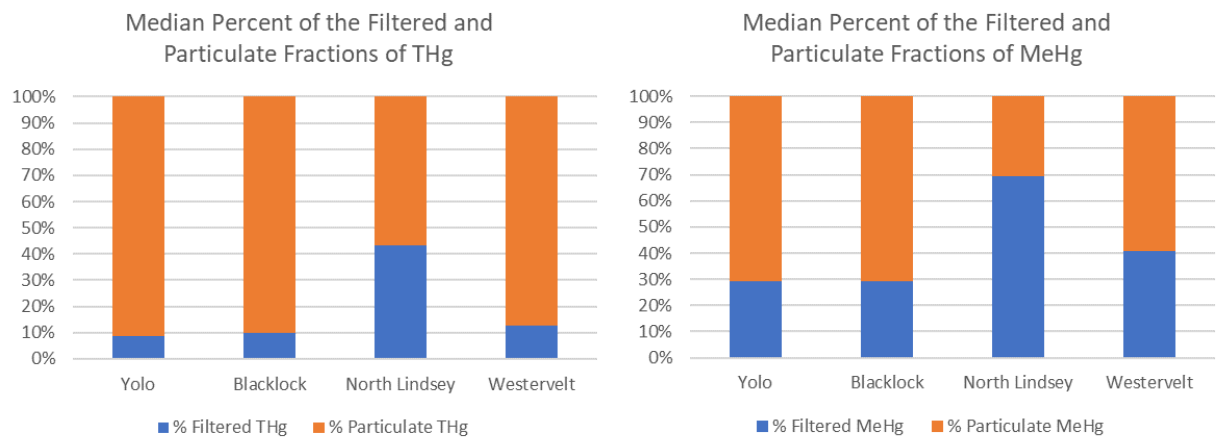


Figure 59 – THg concentration box plots at four tidal wetlands.

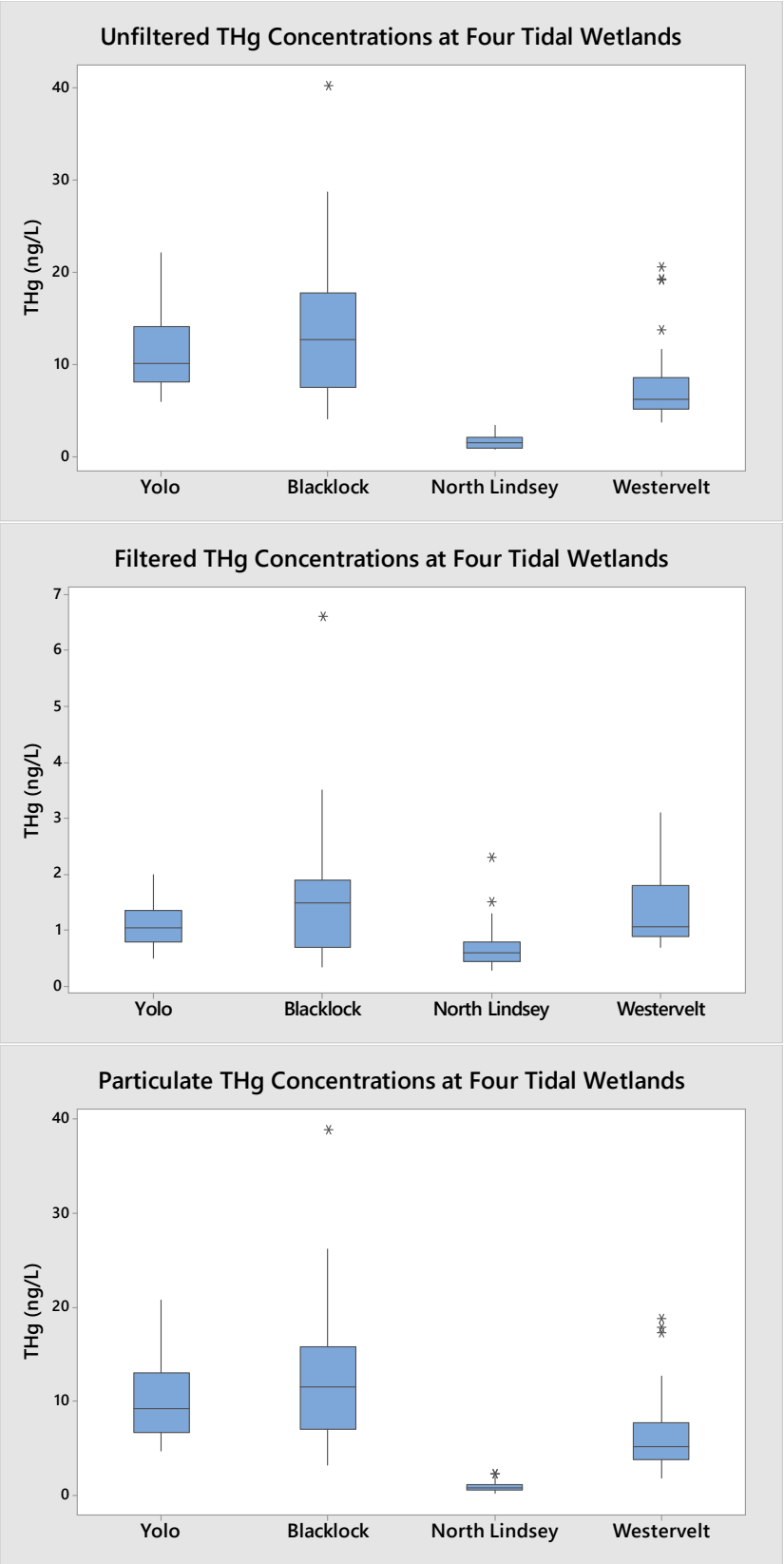
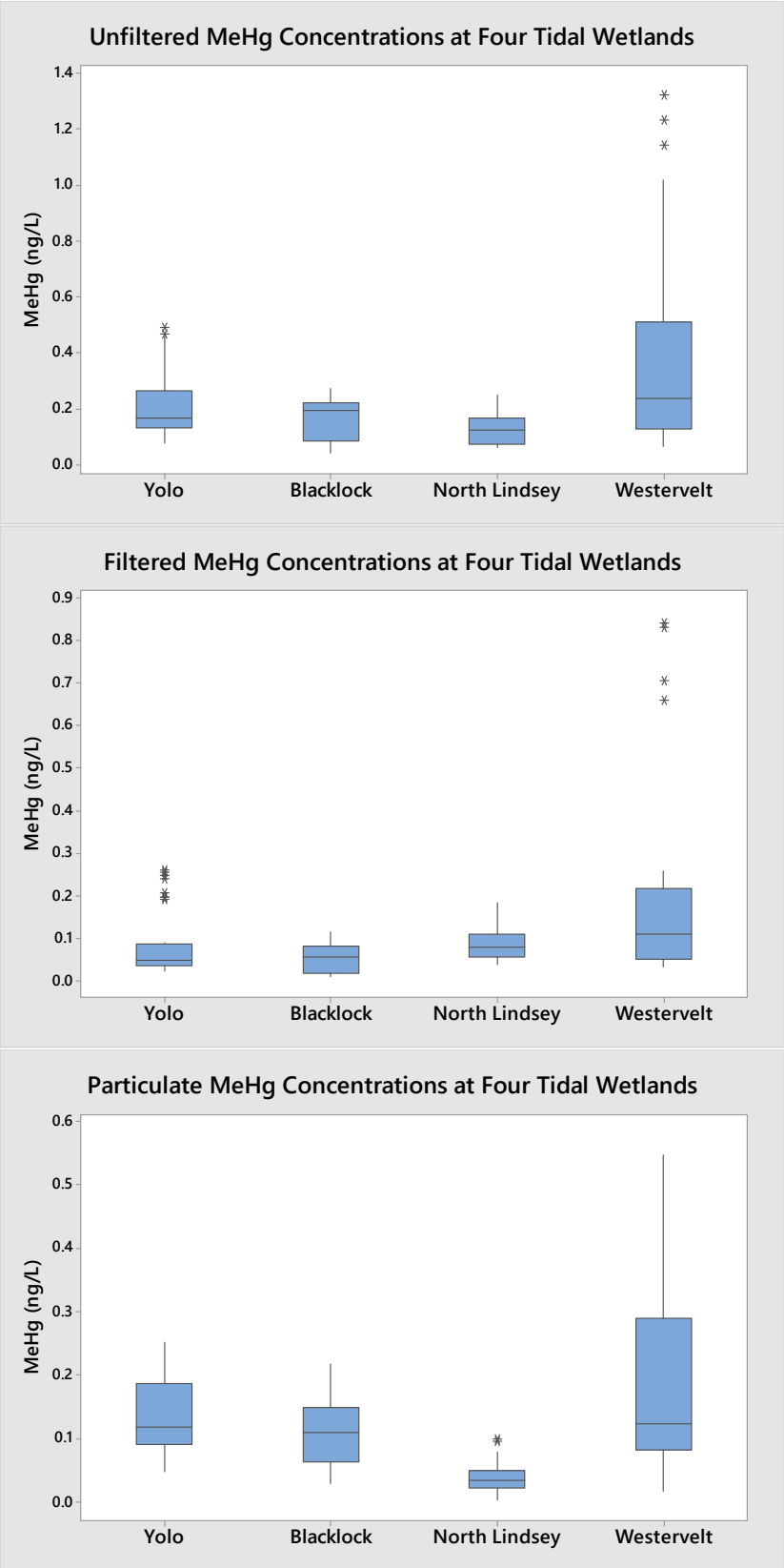


Figure 60 – MeHg concentration box plots at four tidal wetlands.



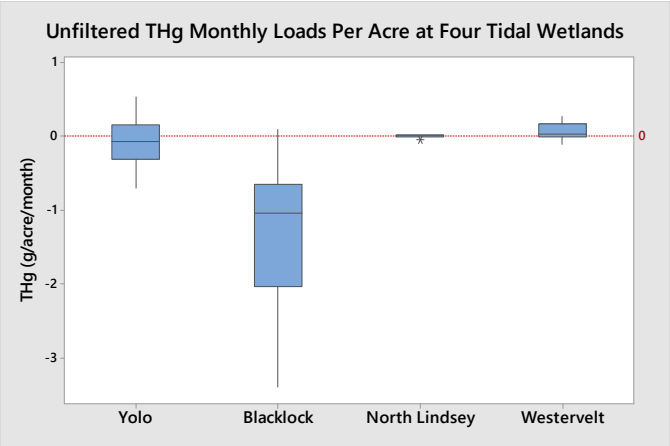
Exports and Imports of THg and MeHg Per Area

Each of the four tidal wetlands studied was a different acreage, so we used ArcGIS to estimate square area. Because the wetlands were tidal, the area of the wetland varied depending on the water level of the tide; therefore these numbers ***are only a rough estimate***.

Each wetland presented its own challenges in calculating area due to tidal changes, edge slopes, flooding, wetland elevation, and other variables. Yolo was highly channelized and circuitous, and water did not leave those channels except when the Yolo Bypass flooded, which was outside of our project scope. Blacklock was easier to estimate area as it is bounded by levees, always wet, not circuitous, and merely has occasional mudflats at low tide. Calculating acreage for North Lindsey was challenging because it had a main channel that always contained water, and then a slightly more elevated area covered with tules that was wet, but not always covered in water. We used the larger area that was covered by tules to calculate mercury per acre as the higher elevation area still had some water flow. Lastly, Westervelt was the most challenging as it was designed to flood when water levels rose. Water was channelized when the Cosumnes River was not flooding and water levels were low, but when the water level increased, the water in the wetland would leave the 22.5 acres of channels and flood an area between 22.5 and 492 acres. We calculated mercury imports and exports per acre using the 22.5 acres of channels during times when the wetland water level was lower. When the wetland flooded, we had no way to determine area so could not estimate imports and exports per acre (Gause, 2020).

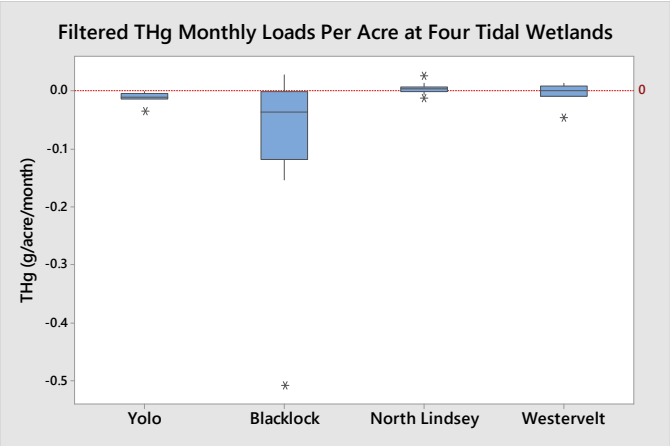
Blacklock was the largest importer/sink of THg per acre whereas North Lindsey and Westervelt were the largest exporters/source of THg per acre, . Westervelt was primarily a sink in the particulate phase and North Lindsey was a source in the filtered phase. Per acre, Blacklock was also the largest importer/sink of MeHg per acre, and none of the wetlands were a net exporter or source. The maximum, minimum, and median grams per acre are presented in Figure 61, Figure 62, Figure 63, Figure 64, Figure 65, and Figure 66 below.

Figure 61 – Median monthly unfiltered THg loads per acre at four tidal wetlands. Negative values indicate the wetland imported and was a sink of unfiltered THg, and the positive values indicate the wetland exported and was a source of unfiltered THg.



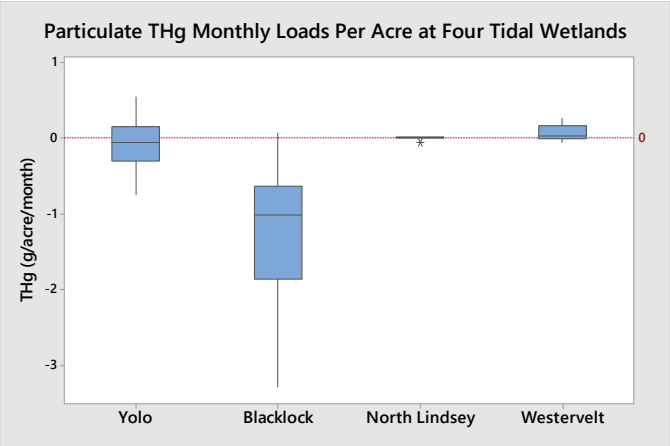
Unfiltered Monthly THg Loads			
Tidal Wetland Site	**Minimum (g/acre)**	**Median (g/acre)**	**Maximum (g/acre)**
Yolo	-0.697	**-0.072**	0.538
Blacklock	-3.384	**-1.038**	0.092
North Lindsey	-0.057	**0.016**	0.033
Westervelt	-0.104	**0.033**	0.264

Figure 62 – Median monthly filtered THg loads per acre at four tidal wetlands. Negative values indicate the wetland imported and was a sink of filtered THg, and the positive values indicate the wetland exported and was a source of filtered THg.



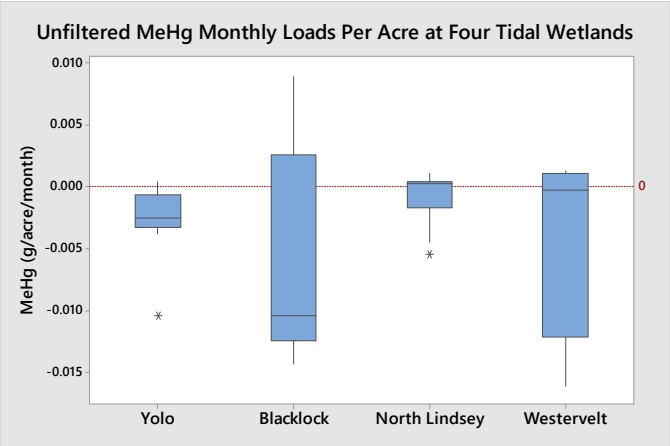
Filtered Monthly THg Loads			
Tidal Wetland Site	**Minimum (g/acre)**	**Median (g/acre)**	**Maximum (g/acre)**
Yolo	-0.0356	**-0.0110**	-0.0006
Blacklock	-0.5080	**-0.0361**	0.0282
North Lindsey	-0.0137	**0.0036**	0.0255
Westervelt	-0.0465	**-0.0004**	0.0126

Figure 63 – Median monthly particulate THg loads per acre at four tidal wetlands. Negative values indicate the wetland imported and was a sink of particulate THg, and the positive values indicate the wetland exported and was a source of particulate THg.



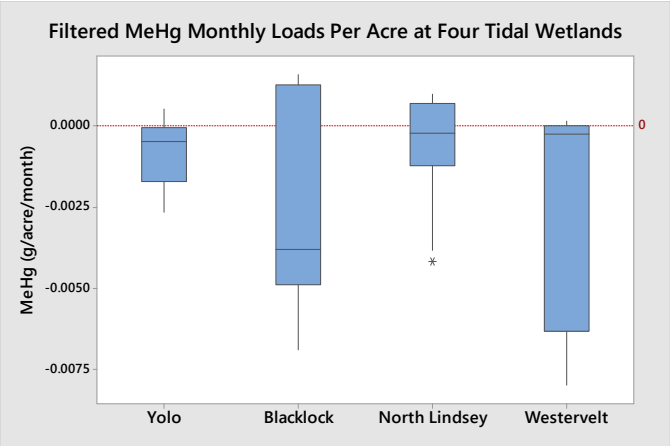
Particulate Monthly THg Loads			
Tidal Wetland Site	**Minimum (g/acre)**	**Median (g/acre)**	**Maximum (g/acre)**
Yolo	-0.744	**-0.061**	0.542
Blacklock	-3.280	**-1.008**	0.063
North Lindsey	-0.066	**0.008**	0.025
Westervelt	-0.057	**0.023**	0.266

Figure 64 – Median monthly unfiltered MeHg loads per acre at four tidal wetlands. Negative values indicate the wetland imported and was a sink of unfiltered MeHg, and the positive values indicate the wetland exported and was a source of unfiltered MeHg.



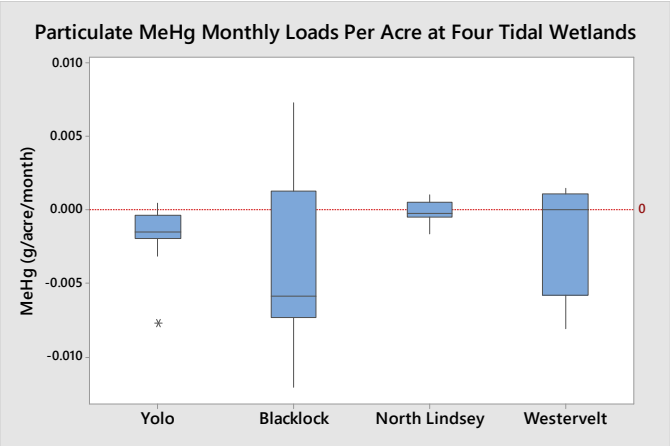
Unfiltered Monthly MeHg Loads			
Tidal Wetland Site	**Minimum (g/acre)**	**Median (g/acre)**	**Maximum (g/acre)**
Yolo	-0.0104	**-0.0025**	0.0004
Blacklock	-0.0143	**-0.0103**	0.0089
North Lindsey	-0.0055	**0.0003**	0.0011
Westervelt	-0.0160	**-0.0002**	0.0013

Figure 65 – Median monthly filtered MeHg loads per acre at four tidal wetlands. Negative values indicate the wetland imported and was a sink of filtered MeHg, and the positive values indicate the wetland exported and was a source of filtered MeHg.



Filtered Monthly MeHg Loads			
Tidal Wetland Site	**Minimum (g/acre)**	**Median (g/acre)**	**Maximum (g/acre)**
Yolo	-0.0026	**-0.0005**	0.0005
Blacklock	-0.0069	**-0.0038**	0.0016
North Lindsey	-0.0042	**-0.0002**	0.0010
Westervelt	-0.0080	**-0.0002**	0.0001

Figure 66 – Median monthly particulate MeHg loads per acre at four tidal wetlands. Negative values indicate the wetland imported and was a sink of particulate MeHg, and the positive values indicate the wetland exported and was a source of particulate MeHg.



Particulate Monthly MeHg Loads			
Tidal Wetland Site	**Minimum (g/acre)**	**Median (g/acre)**	**Maximum (g/acre)**
Yolo	-0.0077	**-0.0015**	0.0005
Blacklock	-0.0120	**-0.0058**	0.0073
North Lindsey	-0.0016	**-0.0003**	0.0010
Westervelt	-0.0081	**0.0000**	0.0015

Upcoming DWR Tidal Wetland Restorations

DWR has five tidal wetland restoration projects either in planning or under construction. Here we list the upcoming tidal restoration projects and provide general information about each. We also very briefly discuss if their design and locations are similar to any of the tidal wetlands analyzed in this report.

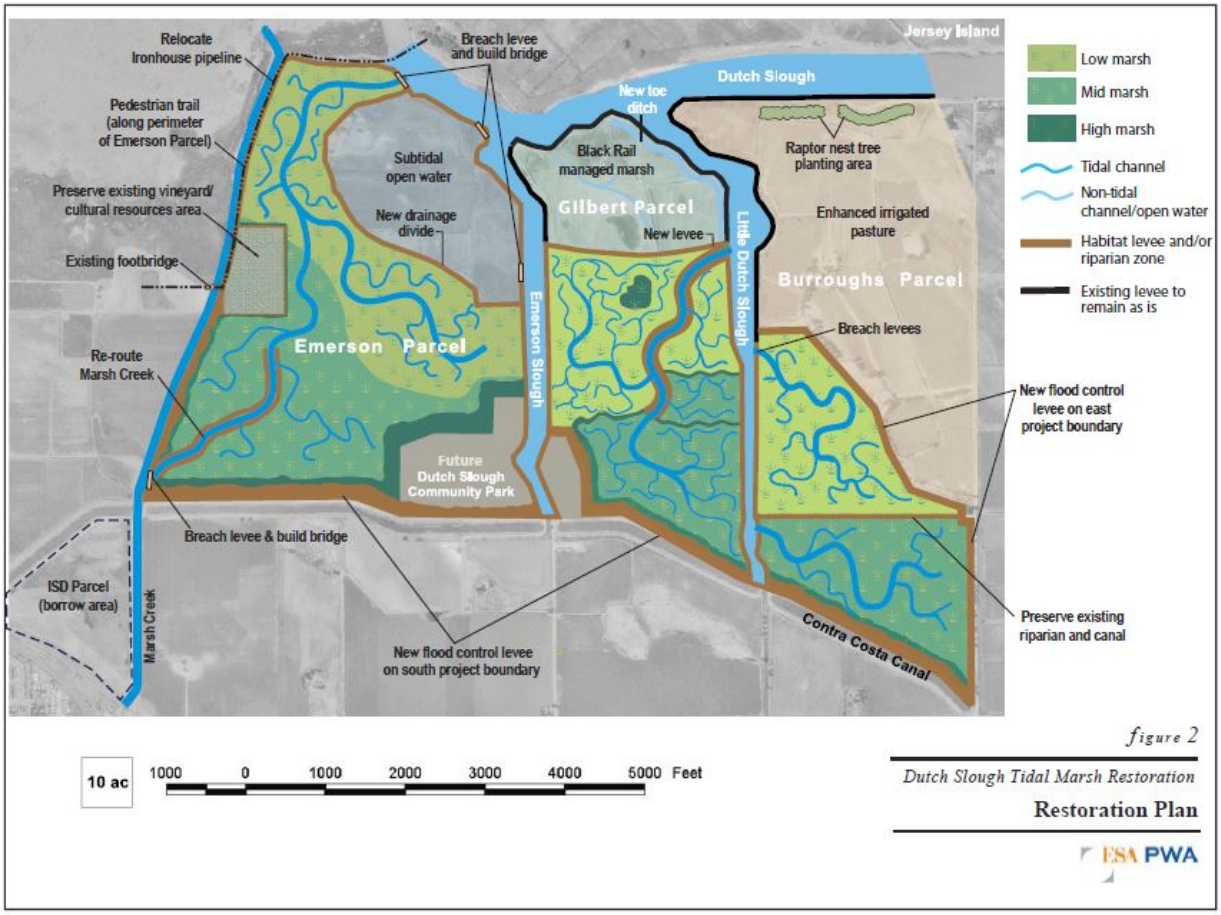
Dutch Slough Tidal Marsh Restoration Project

The Dutch Slough Tidal Marsh Restoration Project (Dutch Slough) is a 1,187-acre project located in Oakley, California in the western Delta DMCP subarea; this subarea is in compliance with the DMCP. Dutch Slough is comprised of three parcels, which will include tidal/subtidal habitat,

riparian forest, and managed marsh. Construction on the Emerson and Gilbert parcels were completed January 2020 and include 410 acres of tidal marsh that will open to Marsh Creek and Little Dutch Slough. These parcels have not yet been breached.

The tidal marsh area will be primarily low marsh and mid marsh with a very small amount of high marsh along the margins and will be most similar to Blacklock in that it is submerged and does not dry out. Also similar to Blacklock, the wetland vegetation community will be dominated by tules. Unlike Blacklock in Suisun Marsh, which is brackish, the source water is fresh and comes from the western Delta. Figure 67 shows the concept design of Dutch Slough.

Figure 67 – Planned Dutch Slough Tidal Marsh Restoration map



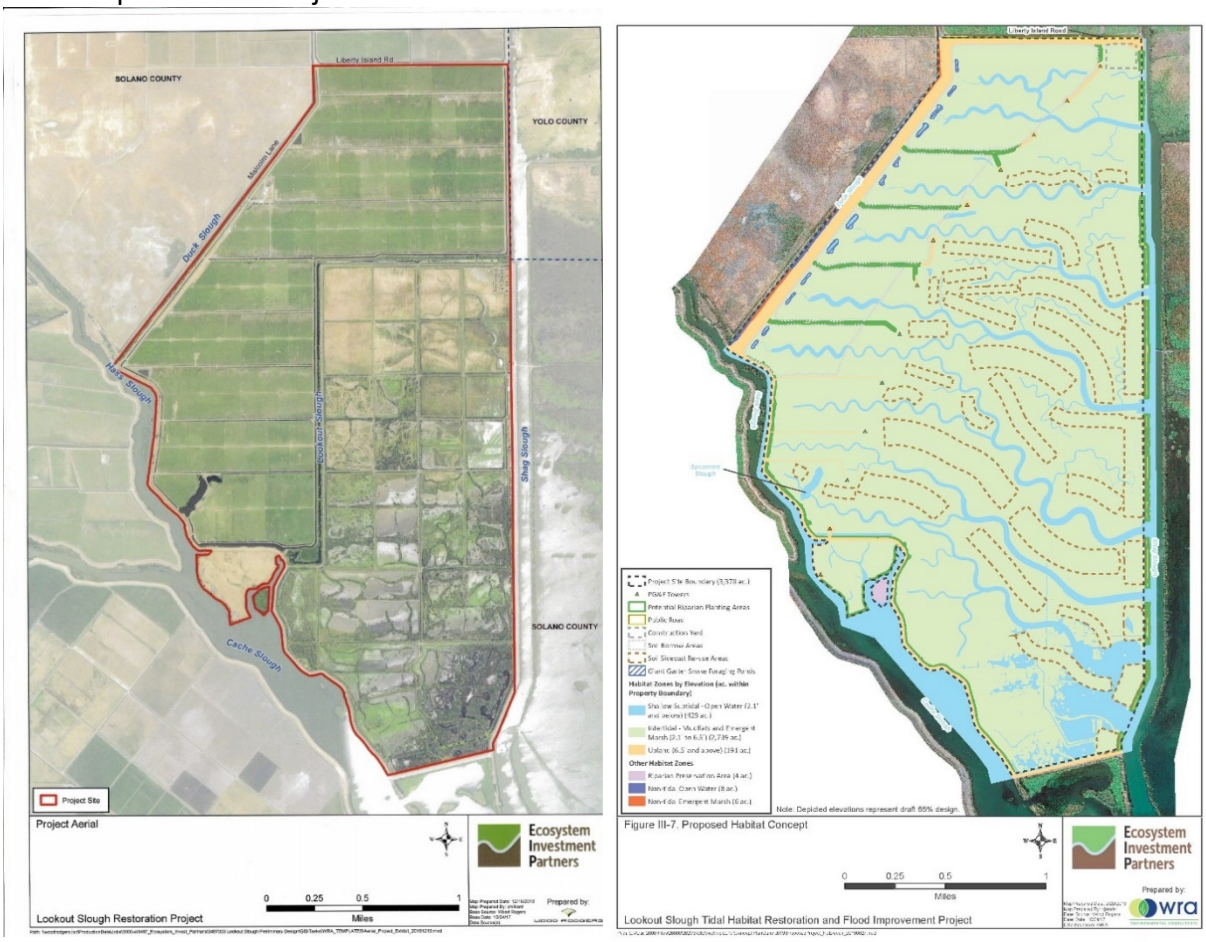
Lookout Slough Tidal Habitat Restoration and Flood Improvement Proposed Project

The Lookout Slough Tidal Habitat Restoration and Flood Improvement Proposed Project (Lookout Slough) is an approximately 3,400-acre site in the Cache Slough Complex which is in the southern Yolo Bypass DMCP subarea. The draft Environmental Impact Report (EIR) was released in December 2019, and DWR expects the final EIR to be released during the summer of 2020; construction is projected to begin in late 2020.

Lookout Slough would be the Delta's largest single tidal habitat restoration project to date, with over 3,000 acres of intertidal and associated subtidal wetland habitat created. Multiple breaches would be constructed along the eastern Shag Slough levee. Over 20 miles of channels would be constructed in the interior of the site.

Lookout Slough is located in the Cache Slough Complex near North Lindsey, which DWR studied. The source water will be most similar to North Lindsey, although the overall tidal wetland function will be similar to the proposed Prospect Island Tidal Habitat Restoration Project (see below). When the Yolo Bypass floods, Lookout Slough will be inundated through the constructed levee breaches and channels, in addition to two areas on the Shag Slough levee that will be degraded to facilitate flood waters flowing onto and draining from the site. Figure 68 shows the upcoming plans and area of the wetland.

Figure 68 – Overview and concept design of the Lookout Slough Tidal Habitat Restoration and Flood Improvement Project

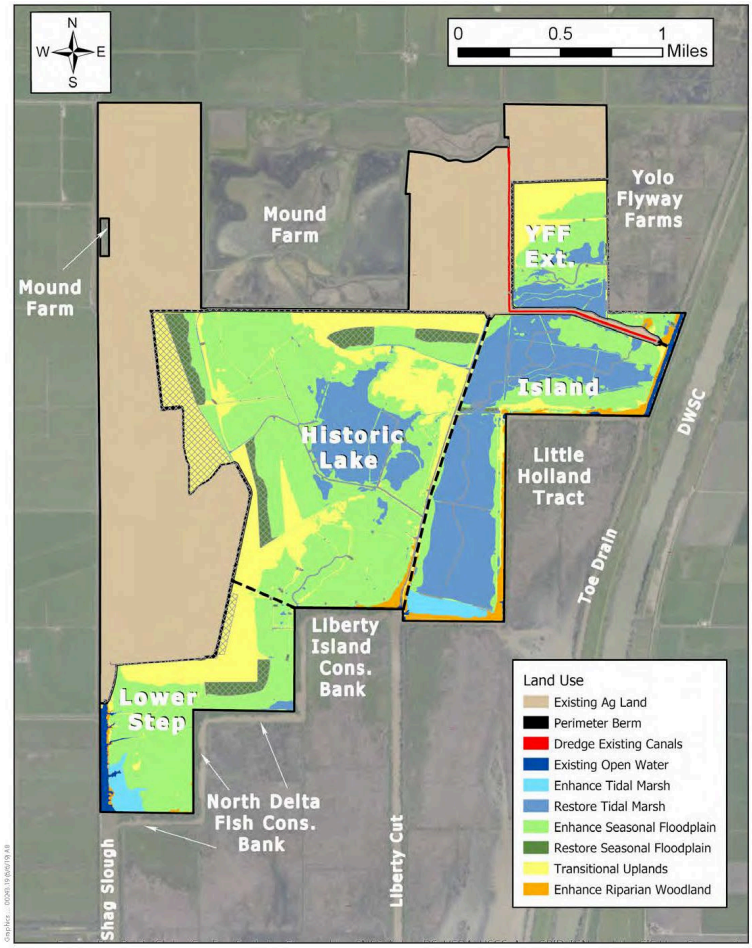


Lower Yolo Ranch Restoration Project

The Lower Yolo Ranch Restoration Project (Lower Yolo Ranch) is an approximately 3,400-acre site located in the southern Yolo Bypass DMCP subarea, north of Liberty Island, and is designed to flood when the Yolo Bypass is inundated. The project will restore an estimated 1,680 acres of agricultural land to intertidal and subtidal wetland, which includes approximately 12 acres of new tidal channels and swales. Shag Slough will be the primary source of water and will run through an existing central north-south channel feeding into the tidal marsh through adjacent smaller channels. Currently, the area is partially inundated through existing channels with water from Shag Slough and the Toe Drain through tidal flap gates.

While the water source will be similar to the Yolo and possibly North Lindsey, the design is not similar to either of those wetlands, so we are unsure how project design will affect MeHg imports and exports. Figure 69 shows the upcoming project area for Lower Yolo Ranch.

Figure 69 – The project area for the Lower Yolo Ranch Restoration Project.



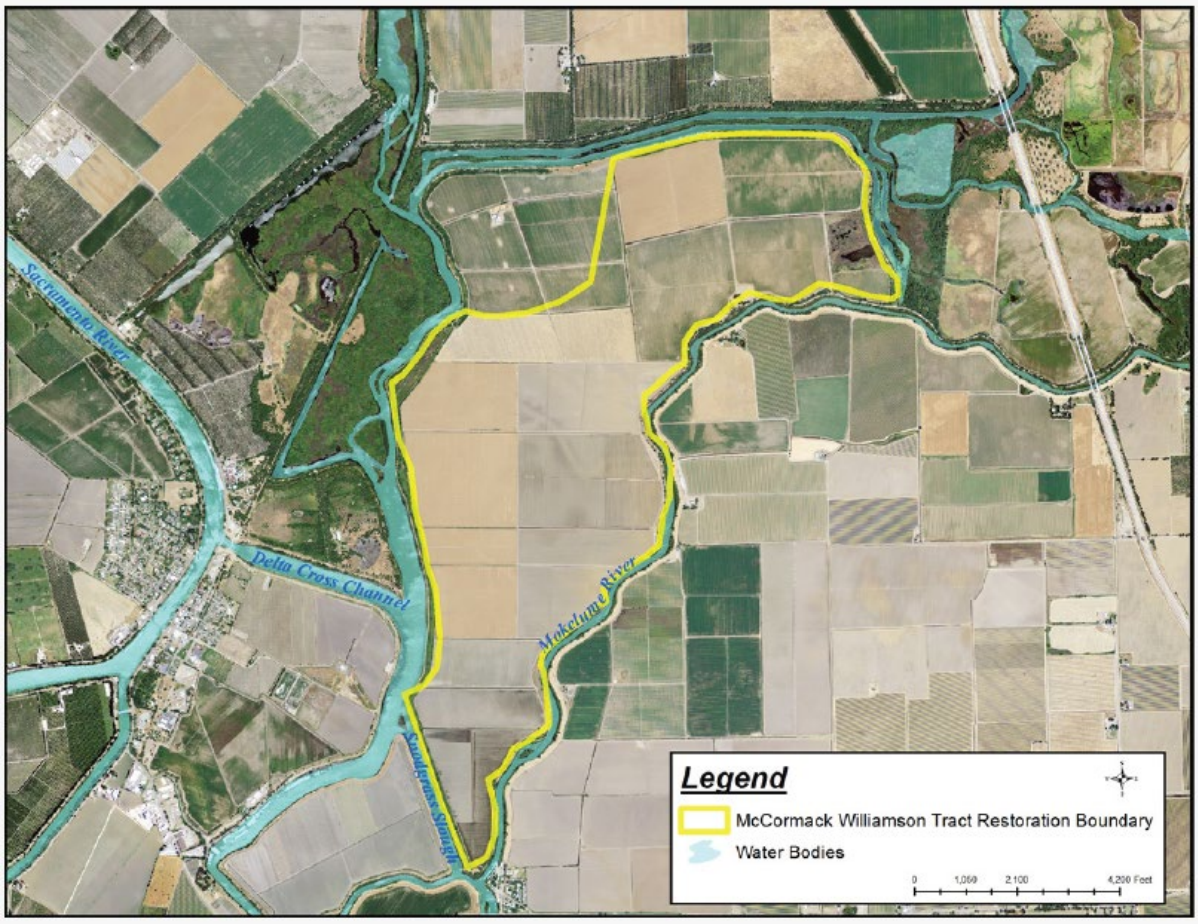
ICF

Figure 17
Proposed Restoration Design

McCormack-Williamson Tract Restoration Project

The McCormack-Williamson Tract Restoration Project (MWT) is a 1,489-acre multi-benefit project in the Cosumnes/Mokelumne River subarea that combines flood management with habitat creation. MWT will provide critical tidal freshwater marsh and floodplain habitat by returning a reclaimed wetland to its nearly historical condition. The phased project consists of building up interior levees to create an enhanced riparian fringe, while weirs and a breach near the confluence of the Cosumnes Mokelumne Rivers allow flooding of the interior, allowing both tidal and floodplain processes to shape the tracts interior. Most of the area will remain wetted and the entire area will flood during flood events. As part of the Cosumnes Preserve, MWT will contribute to the nearly contiguous riparian floodplain corridor along the Lower Cosumnes River. This corridor includes a variety of existing and planned riparian floodplain/tidal marsh projects on the edge of the Delta and is located near the Westervelt Cosumnes River Tidal Wetland and will have a similar water source. The design of these wetlands is similar in that they combine tidal marsh with a floodplain to work with the area's natural propensity for flooding. Figure 70 is a map of the project area of MWT.

Figure 70 – The project area for the McCormack-Williamson Tract Restoration Project.

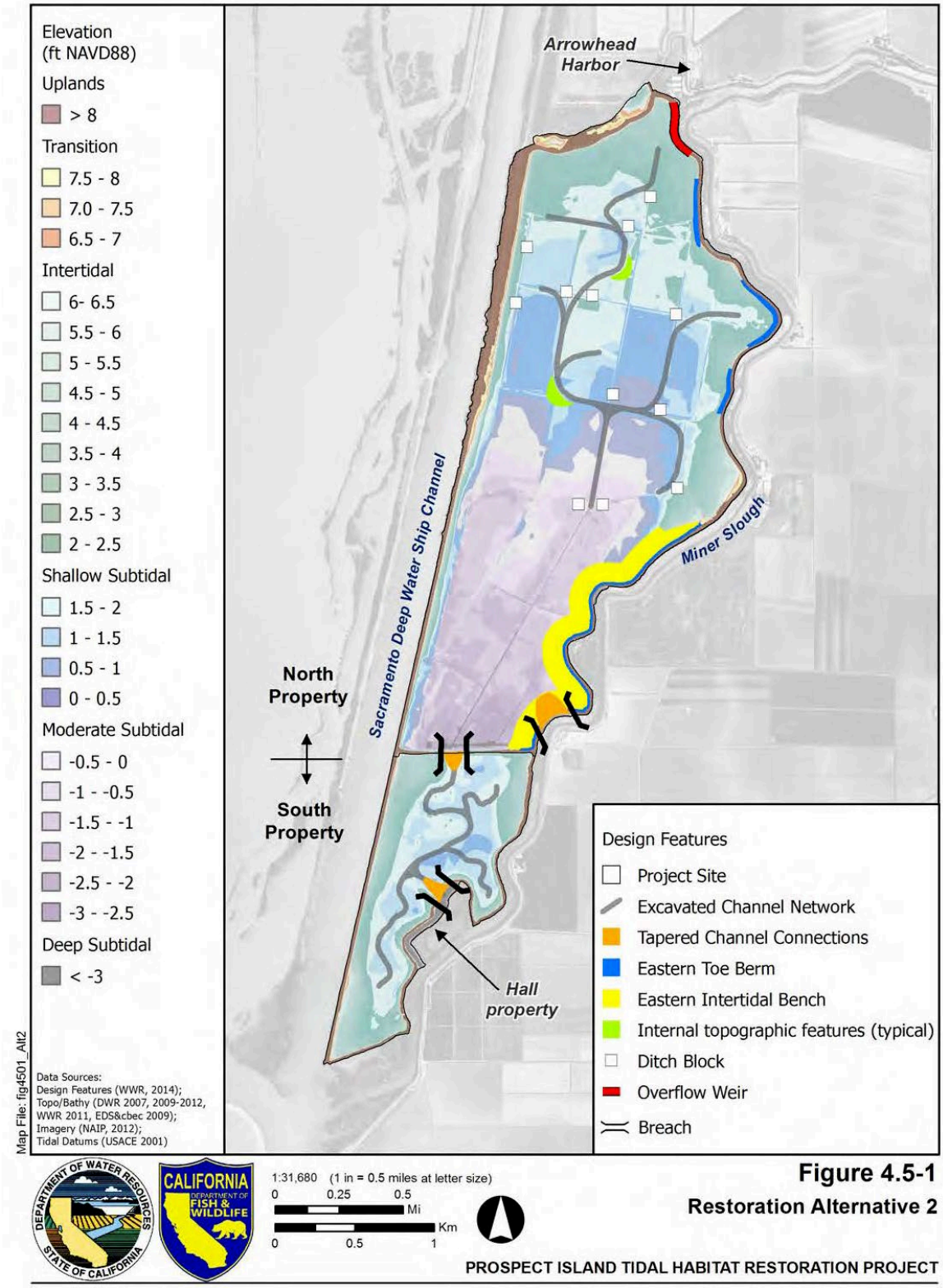


Prospect Island Tidal Habitat Restoration Project

The Prospect Island Tidal Habitat Restoration Project (Prospect Island) is roughly 1,500-acres of planned tidal wetland located in the Sacramento DMCP subarea. The restoration area was historically tidal marsh before being converted to agriculture in the 1960s through 1994 and is currently inundated and connected to Miner Slough through a flap gate, negating any tidal action. To restore the wetland, two breaches would be made along Miner Slough and an interior channel network created. The source water from Miners Slough is fresh and the wetland will not dry out. Figure 71 shows the concept design for Prospect Island.

The most similar wetland design that we studied is Blacklock, although the source water from Blacklock is brackish. Source water greatly affects MeHg, and MeHg imports and exports are difficult to predict.

Figure 71 – Concept design for the Prospect Island Tidal Habitat Restoration Project.



Next Steps

DWR characterized mercury imports and exports of four wetlands as proposed in our workplan. The purpose was to determine whether the tidal wetlands were exporting MeHg as was assumed in the DMCP (Wood, Morris, Cooke, & Louie, 2010; Wood, Foe, Cooke, & Louie, 2010), and if so, if any control measures might be suggested by our data. As mentioned above, it does not appear that the tidal wetlands that we studied are net exporters of MeHg, so no control measures appear to be needed. Collecting more data to expand knowledge about tidal wetlands and mercury import and export would be useful to confirm or refute these findings.

There are several future directions suggested by this study. First, this study only looked at loads and concentrations of mercury in water and did not examine the impacts on biota. Because the biota is ultimately what is harmed by high mercury concentrations, understanding what is occurring in the biota is important. Using biosentinels would help identify bioaccumulation and understand mercury toxicity in local species rather than in exotic species and by using lab toxicity testing. The Delta Regional Monitoring Program has proposed placing biosentinel organisms near proposed tidal wetland restoration sites (DiGiorgio, 2020). Testing mercury concentrations of biota that lived primarily in tidal wetlands would also be useful, particularly once toxic mercury concentrations have been determined by toxicity testing.

Second, this study collected mercury water samples approximately monthly (or less frequently in some instances) at four tidal wetlands, and we were only able to collect data for eight 25-hour events at Westervelt. Winter collection was especially challenging, and we consequently have fewer 25-hour event data points during winter. Collecting mercury samples more frequently would give us better resolution data which would be helpful for a number of reasons. Having better resolution would give us a better idea of diel, seasonal, tidal, and any other short-term patterns that were missed in our study. Ideally, continuous mercury data could be collected, and if and when that technology becomes available, the mercury data could be paired with the continuous flow data for a far more accurate estimate of loads.

Third, this study can provide a better estimate of tidal wetland mercury imports and exports to any mercury models that need such data. DWR is working on a mercury model of the Delta and Yolo Bypass, and this data can be used for any future work involving tidal wetlands and mercury.

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Methylmercury Import and Export Studies of Tidal Wetlands In the Sacramento-San Joaquin Delta, Yolo Bypass, and Suisun Marsh

Environmental Monitoring Plan

California Department of Water Resources

Completed by:
Petra Lee, Senior Environmental Scientist – Specialist
Julianna Manning, Environmental Scientist

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1. Introductions and Overview

To address mercury contamination in the Delta and Yolo Bypass, the Central Valley Regional Water Quality Control Board (Regional Board) adopted the Sacramento-San Joaquin Delta Methylmercury Total Maximum Daily Load and Basin Plan Amendment that established a Delta Mercury Control Program (DMCP) (Wood, Morris, Cooke, & Louie, 2010; Wood, Foe, Cooke, & Louie, 2010). Under the DMCP, the Department of Water Resources (DWR) and the Department of Fish and Wildlife (CDFW) are required to develop control measures to minimize the discharge of methylmercury (MeHg) from wetlands.

Because future restoration efforts will focus heavily on tidal wetlands throughout all seven DMCP subareas and within Suisun Marsh, understanding the role of tidal wetlands on MeHg production is important. Few studies have focused specifically on tidal wetlands and the quantity of their MeHg and total mercury (THg) imports and exports (Mitchell, Jordan, Heyes, & Gilmour, 2012; Bergamaschi, et al., 2011; Langer, Fitzgerald, Visscher, & Vandal, 2001). Because MeHg production in tidal wetlands is not understood, no management practices to decrease MeHg production have been developed. DWR and CDFW have chosen to focus on tidal wetlands before major restoration occurs because their MeHg imports and exports are so poorly understood. Therefore, it is important to improve our understanding of MeHg dynamics before tens of thousands of acres of tidal wetland restorations occur.

DWR proposes to do an in-depth study of 3-6 tidal wetlands within the DMCP area, the largest and most comprehensive study of freshwater tidal wetlands to date. The study will follow selected methodologies developed by Mitchell and others (2012) but will be scaled to the amount of funding available. We will do this study in hopes of better characterizing MeHg imports and exports of tidal wetlands within the DMCP area. In addition to characterizing and analyzing the data of several individual tidal wetlands, we will be looking at the aggregate data of all the tidal wetlands to see if patterns emerge. This data will add significant amounts of information about MeHg loads of tidal wetlands and will be provided to the Regional Board to assess TMDL allocations and plan for future tidal wetlands.

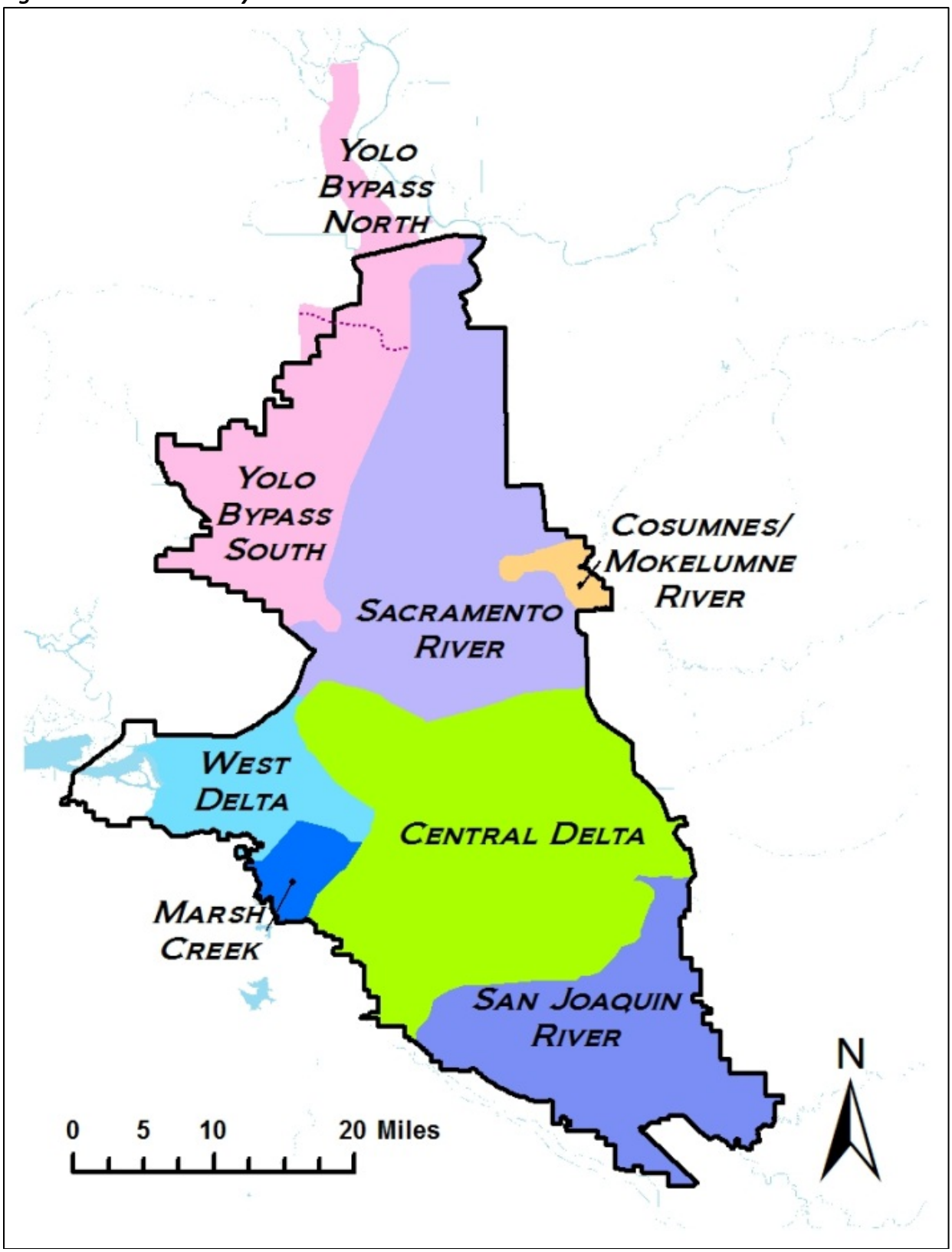
In this monitoring plan, the sampling plan details will be outlined for staff from DWR's Mercury Monitoring and Evaluation Section (MME), as well as other relevant parties.

2. Problem Statement and Monitoring Objectives

2.1 Geographical Setting

Most of the study will be done in the DMCP area outlined by the Regional Board (Wood, Morris, Cooke, & Louie, 2010; Wood, Foe, Cooke, & Louie, 2010) (Figure 1). However, one tidal wetland in the Suisun Marsh, which is west of the DMCP, will also be studied. See Section 5.1.2 for a description of the tidal wetlands that will be studied in this project.

Figure 1 – Delta Mercury Control Plan Area



2.2 Problem Statement

Because it is not known whether various types of tidal wetlands are net sources or net sinks of MeHg, the first step is to study a variety of tidal wetlands and characterize the magnitude of imports and exports of MeHg and other related water quality parameters in each wetland and then study the wetlands as a group. In this way we can hope to determine if trends of imports and exports of MeHg exist and whether tidal wetlands are net sources or sinks of MeHg.

2.3 Monitoring Objective and Study Question

DWR will be studying 3-6 tidal wetlands and will be analyzing data at two different levels. First, we will be analyzing the data of each individual wetland, and second, we will be analyzing the data of all the wetlands as a group to determine if any trends exist within the aggregated data. Because of this multi-level approach, we will be analyzing the data using the following objectives and hypotheses.

Objectives of the study are the following:

1. Determine whether these tidal wetlands are net sources or net sinks of MeHg and THg by measuring and calculating imports and exports;
2. Measure and calculate monthly and/or bimonthly MeHg imports and exports to determine if seasonal differences occur;
3. Measure and calculate net yearly organic carbon, chlorophyll *a*, and total suspended solids imports and exports;
4. Determine if organic carbon and MeHg concentrations are correlated; and
5. Provide data to the Regional Board for a revision of the MeHg allocations.

These hypotheses will be applied to each wetland and the group of tidal wetlands:

1. Tidal wetlands are a net source of total MeHg* on an annual basis;
2. Tidal wetlands are a net source of total THg* on an annual basis;
3. Tidal wetlands have higher total and dissolved MeHg** exports during the warmer, summer months;
4. Tidal wetlands are a net source of dissolved MeHg** and a sink for particulate MeHg and THg on an annual basis; and
5. Organic carbon concentrations and MeHg concentrations are positively correlated.

*We used the terms “total THg” and “total MeHg and they are also referred to as “unfiltered THg” and “unfiltered MeHg”, respectively throughout this document.

** We used the terms “dissolved THg” and “dissolved MeHg” and they are used synonymous with “filtered THg” and “filtered MeHg”, respectively.

3. Project Personnel, Roles, and Responsibilities

3.1 Project Personnel

DWR personnel will be working on this study. DWR is providing the funding for lab analyses through Moss Landing Marine Laboratories and Bryte Laboratory, as well as funding for field and office staff. CDFW provided funding for MeHg sample design expertise and access to tidal wetlands that will be studied. Table 1 lists the personnel.

Petra Lee, the Project Manager, is responsible for assisting with study design, implementing the study, including writing and maintaining the monitoring plan and other documentation, managing laboratory contracts, and oversight of the project progress. The Project Manager will consult with the Technical Advisor to implement the study. Additionally, the Project Manager will work with the Laboratory Liaisons to ensure that the labs are aware of sample analysis requirements, that chain of custodies, QA/QC, and reporting requirements are understood and implemented. The Project Manager will be responsible for ensuring that the appropriate supplies have been purchased and are available for sampling staff. The Project Manager will also act as Safety Leader for leading safety moments, a safety plan, and safety briefings, or tailgate meetings before field work. Lastly, the Project Manager will manage field teams and events as well as sample deliveries, and overall event logistics.

Mark Stephenson, the Technical Advisor of the Project, was responsible for assisting with study design, providing technical information, and study guidance. The Technical Advisor worked with the Project Manager to ensure that the study was designed appropriately.

Wes Heim is the Moss Landing Marine Laboratories Laboratory (MLML) Liaison and will consult with DWR about sampling. He will also be a point of contact for the MLML contract with DWR. Autumn Bonnema is the MLML QA Officer and will be in contact with the Project Manager to arrange sample analysis and provide sample supplies and will answer QA related questions.

Allan Wong is the Bryte Laboratory Liaison and QA officer and will be in contact with the Project Manager to arrange sample analysis and provide sampling supplies. He will provide laboratory expertise.

Julianna Manning, David Bosworth, and Carol DiGiorgio are part of the Project Team that will assist with the field work for the project as well as with sample design and implementation. In addition, personnel from the Water Quality Evaluations Section (WQES) in DWR's North Central Region Office (NCRO) may be assisting with field work. Dave Huston, the Senior Engineer of the Flow Monitoring Section in NCRO, will be coordinating the flow measurements at each of the wetlands.

3.2 Other Parties Associated with the Project

Table 2 lists individuals who will be associated with the Project in various capacities but will not be a part of Project Personnel.

Janis Cooke was the Regional Board Liaison for Delta Methylmercury TMDL implementation and was replaced by Jennifer Fuller midway through the project. They guide the "dischargers" in their studies to meet regulatory compliance.

Chris Wilkinson is the Project Sponsor and will be briefed and will make high level decisions.

Table 1 – Roles and Contact Information

Name	Affiliation	Role	Phone	Email
Petra Lee	DWR	Project Manager	916-376-9735	Petra.Lee@water.ca.gov
Mark Stephenson	MLML & CDFW	Technical Advisor	831-771-4177	MStephenson@mlml.calstate.edu
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Autumn Bonnema	MLML	MLML QA Officer	831-771-4175	bonnema@mlml.calstate.edu
Allan Wong	DWR Bryte Lab	Bryte Laboratory Liaison & QA Officer	916-375-6008	Allan.W.Wong@water.ca.gov
Julianna Manning	DWR	Project Team	916-376-9816	Julianna.Manning@water.ca.gov
David Bosworth	DWR	Project Team	916-376-9847	David.Bosworth@water.ca.gov
Carol DiGiorgio	DWR	Project Team	916-376-9743	Carol.DiGiorgio@water.ca.gov
Dave Huston	DWR NCRO	Flow Monitoring Lead	916-376-9654	Dave.Huston@water.ca.gov

Table 2 – Other Roles

Name	Affiliation	Phone	Email
Janis Cooke	Regional Board	916-464-4672	Janis.Cooke@waterboards.ca.gov
Jennifer Fuller	Regional Board	916-464-4646	Jennifer.Fuller@waterboards.ca.gov
Chris Wilkinson	DWR	916-376-9704	Christopher.Wilkinson@water.ca.gov

4. Project Tasks and Schedule

A rough schedule of the study is outlined in Table 3. Each tidal wetland that we study will take place over a 12 to 15-month period. A status report to the Regional Board is due in 2015 and a

final report is due in 2020 with an extension granted by the Regional Board Executive Officer (CRWQCB-CV, 2011).

Table 3 – Approximate Study Schedule

Task	Anticipated Schedule
Initial Project Planning	June 2013 – May 2014
Data Collection	April 2014 – July 2019
Data Analysis	March 2015 – December 2019
Status Report for Regional Board	October 2015
Final Report for Regional Board	April 2020

5. Monitoring Strategy and Design

5.1 Ebb and Flood Tide Characterization

DWR will do in-depth studies of 3-6 tidal wetlands to determine MeHg and THg imports and exports. At each tidal wetland studied, DWR staff will 1) take continuous flow measurements at the mouth(s), and 2) intensely measure both dissolved and particulate MeHg and THg for 8-12 25-hour periods to estimate MeHg and THg loads over an approximately one-year period. The MeHg and THg data generated from the 25-hour sampling periods will be used to calculate whether the wetland is a net source or a sink of MeHg and THg as well as determine some basic mechanisms of import and export of dissolved and particulate MeHg and THg between wetlands and adjacent waterbodies.

5.1.1 Sample Timing and Hydrology

5.1.1.1 Flow Data

Acoustic Doppler Current Profilers (ADCPs) will be placed in the mouth(s) of the wetland and will collect continuous flow data every 15 minutes on the hour, quarter hour, half hour, and three quarters hour, throughout the study period of each wetland. This flow data will be used in two main ways; first, it will help us calculate percentages of water to use in our flow weighted composited samples, and second, along with concentration data, it will help us determine loads into and out of the wetland.

Because flow is a value calculated from level and velocity, the team must collect transect data over the range of tides to develop a rating curve, which will be used to calculate flow. The DWR team will collect flow data over a 25-hour tide cycle to develop a rating curve. Flow calculations will follow Levesque and Oberg (2012).

5.1.1.2 Continuous Water Quality Data

A YSI EXO water quality sonde will be placed at the mouth(s) of the wetland, near the ADCP(s), but not close enough to affect flow around the ADCP. The sonde will collect continuous water quality data, every 15 minutes, on the hour, half hour, quarter hour, and three quarters hour. Water quality parameters collected will always include temperature, salinity/specific conductance, turbidity, and total chlorophyll. The continuous water quality data will be collected within 1-3 minutes of the collection time of the ADCP and will be collected throughout the study period of each wetland, generally 12-15 months. Sonde data will be quality checked and then uploaded to DWR's Water Data Library via the Hydstra database.

5.1.1.3 THg and MeHg Sampling Events

At each wetland studied, DWR will collect THg and MeHg samples during a minimum of 8 sampling events over approximately a year. Each event will consist of collecting water samples over 25-hours to capture an entire tide cycle. These samples will be collected hourly and will be matched with sonde and flow data that is being taken every 15 minutes. The ADCP data will be used to determine ebb and flood tide, in addition to flow, and will be used to calculate masses and loads of various water quality constituents, including THg, MeHg, TOC, DOC, TSS, and chlorophyll *a*.

Because hourly sampling over a 25-hour tide cycle is intense, we will make use of ISCO 6712 autosamplers. The autosamplers will be programmed to collect water samples every hour. We will use glass bottle sets of four 4-L (Figure 2) or eight 1.8 L (Figure 3) bottles per autosampler, with a total sample capacity of between 14 and 15 L for each autosampler.

Figure 2 – The ISCO 4-Bottle Set

Figure 3 – The ISCO 8-Bottle Set

To collect samples the autosampler will be placed on the bank at the mouth(s) of the wetland, near the ADCP and sonde, but not close enough to interfere with their readings. The autosampler will be set up on a level surface and the suction tube (which pulls the water into the autosampler) will be attached to a cleaned CPVC plastic-coated weighted strainer, made by ISCO. The autosampler will rinse the tubing three times before collecting each sample, and the tubing will be purged of water after every collection.

In wetlands with water shallow enough to wade into, the PTFE suction lines will be attached to a stake in the mouth of the wetland and the strainers will be attached to a float. See Figure 4 for a photo of the deployment.

In wetlands with deeper water, the PTFE suction lines will be cable tied together with a plastic covered stainless-steel cable (Figure 5). The end of the cable will be attached to a float and weight set up, which will keep the PVC strainers suspended in the water column during sampling (Figure 6). Figure 7 shows the float, weight and suction line set up in approximately 4-5 feet of water.

Figure 4 – Autosamplers deployed at the Yolo Wildlife Area Tidal Wetland with PTFE suction lines attached to stakes and a float in the water

Figure 5 – Suction lines and strainers cable tied together with stainless steel cable

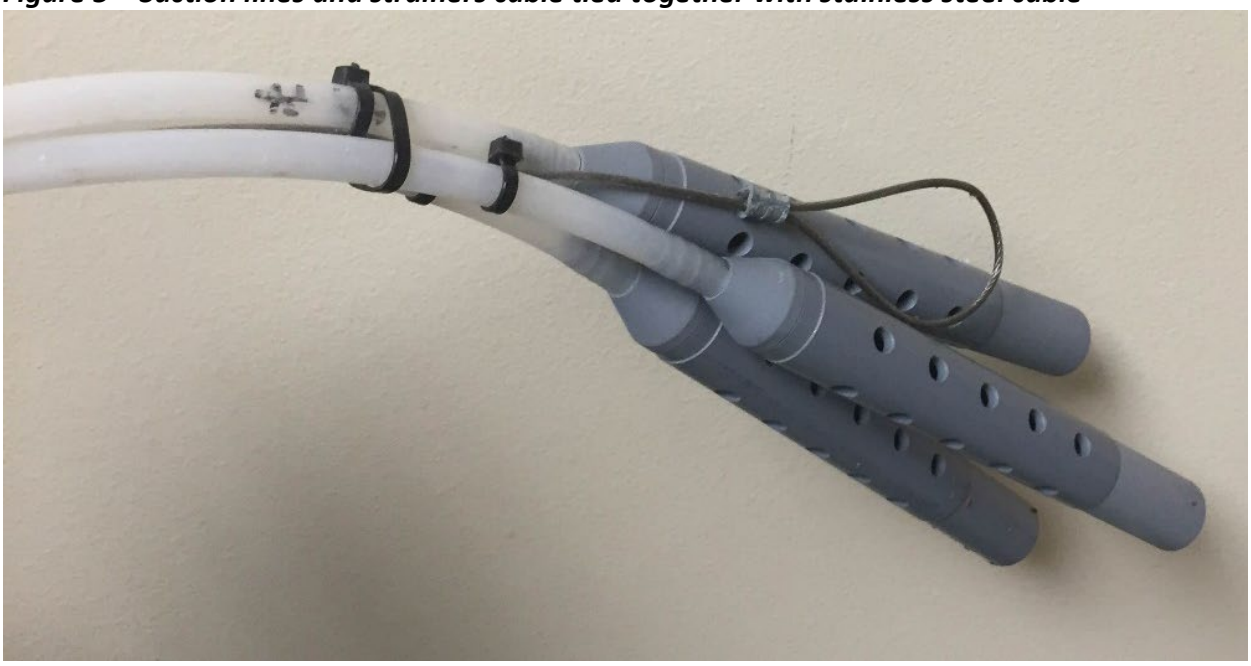
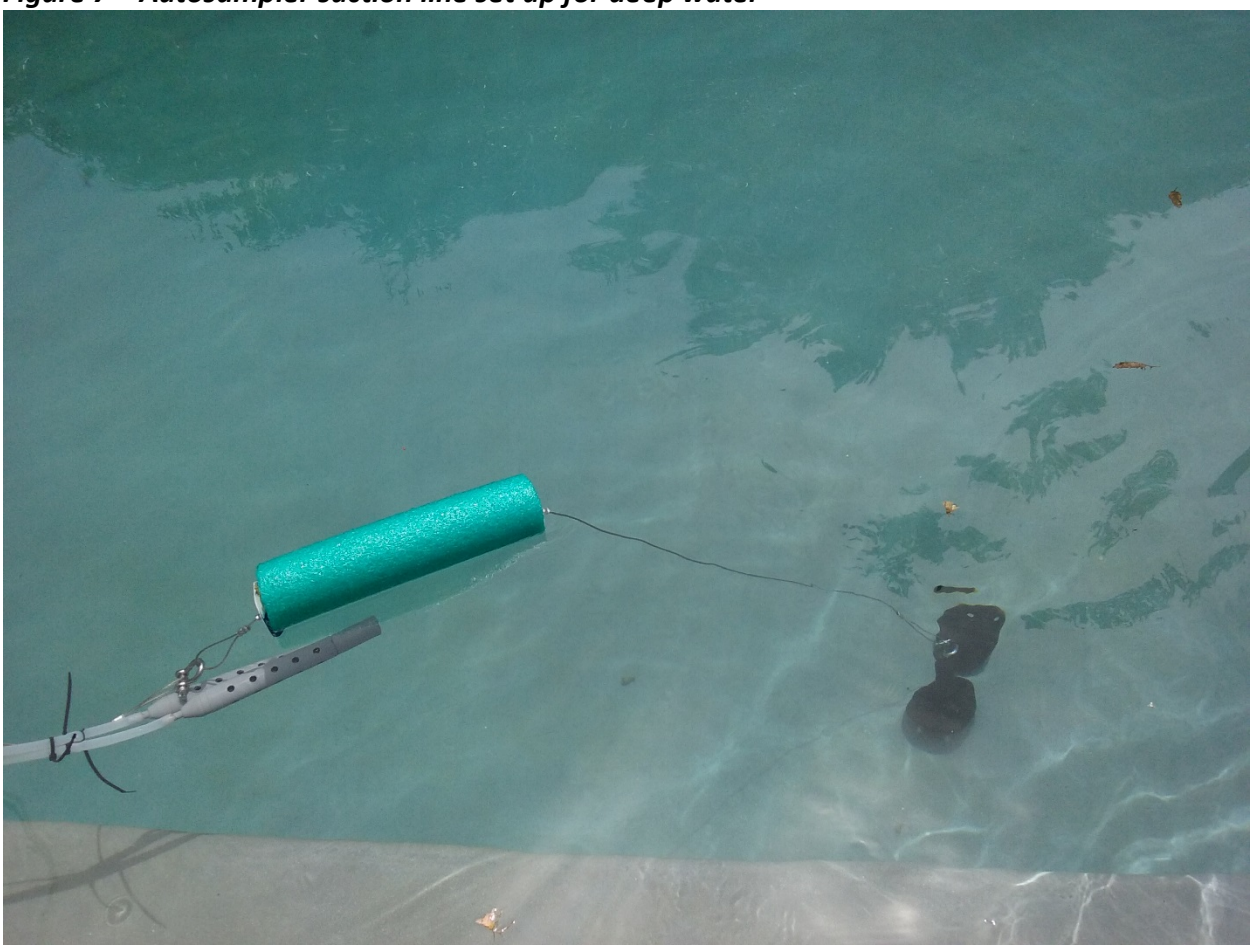


Figure 6 – Float and weight set up

Figure 7 – Autosampler suction line set up for deep water



5.1.1.4 Manually Composited Flow-Weighted Samples

To reduce the cost and number of THg and MeHg samples being analyzed, we will be manually compositing samples using flow data, tides, and a flow-weighting technique. DWR will download flow data from the ADCP and calculate flow-weighted composite "recipes" using the compositing worksheet. An example of the output is shown in Figure 8. The study area has a mixed semidiurnal tidal cycle, meaning there are two high and two low tides of varying heights per 25-hour tidal cycle. We will composite the hourly samples into one set of samples per high tide and one set of samples per low tide, for a total of four sets of samples per 25-hour sampling period. If ebb and flood tides are not clear, we may have fewer than four composited samples. Figure 9 shows an example of the four potential sample groups that could occur.

Figure 8 – Example of Flow-Weighted Compositing Recipe

Tidal Cycle: Ebb Tide 1

Bottle #	Collection Time	Flow (cfs)	Proportion of Total Flow during Tidal Cycle	Weight of subsample required (g)
1	6/24/2014 23:00	7.582138	0.009	34
8	6/25/2014 6:00	207.541	0.235	939
9	6/25/2014 7:00	162.8851	0.184	737
10	6/25/2014 8:00	158.8693	0.180	719
11	6/25/2014 9:00	124.2403	0.141	562
12	6/25/2014 10:00	93.11139	0.105	421
13	6/25/2014 11:00	57.21869	0.065	259
14	6/25/2014 12:00	41.41427	0.047	187
15	6/25/2014 13:00	31.16578	0.035	141

Tidal Cycle: Flood Tide 1

Bottle #	Collection Time	Flow (cfs)	Proportion of Total Flow during Tidal Cycle	Weight of subsample required (g)
2	6/25/2014 0:00	-83.5458	0.095	381
3	6/25/2014 1:00	-171.478	0.196	783
4	6/25/2014 2:00	-211.594	0.241	966
5	6/25/2014 3:00	-200.361	0.229	915
6	6/25/2014 4:00	-195.474	0.223	892
7	6/25/2014 5:00	-13.7974	0.016	63

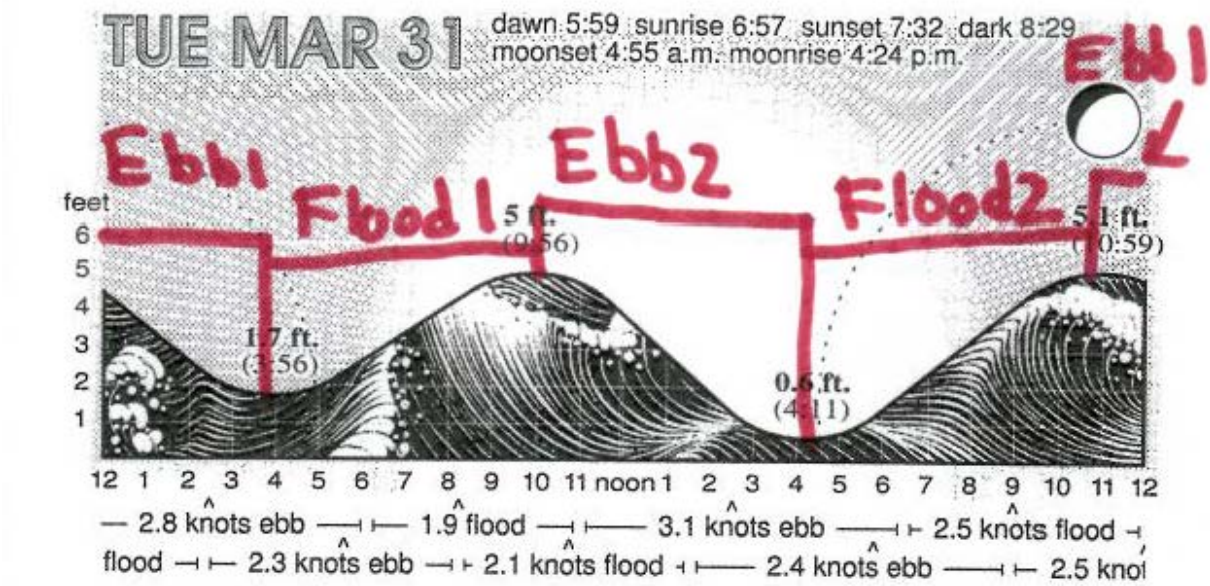
Tidal Cycle: Ebb Tide 2

Bottle #	Collection Time	Flow (cfs)	Proportion of Total Flow during Tidal Cycle	Weight of subsample required (g)
21	6/25/2014 19:00	12.28465	0.028	113
22	6/25/2014 20:00	132.8415	0.305	1220
23	6/25/2014 21:00	122.2913	0.281	1123
24	6/25/2014 22:00	97.9128	0.225	899
25	6/25/2014 23:00	70.1516	0.161	644

Tidal Cycle: Flood Tide 2

Bottle #	Collection Time	Flow (cfs)	Proportion of Total Flow during Tidal Cycle	Weight of subsample required (g)
16	6/25/2014 14:00	-27.4708	0.051	205
17	6/25/2014 15:00	-62.7364	0.117	469
18	6/25/2014 16:00	-144.556	0.270	1080
19	6/25/2014 17:00	-161.499	0.302	1207
20	6/25/2014 18:00	-139.001	0.260	1039

Figure 9 – Example of Potential Sample Groups



5.1.1.5 Comparing Hourly Calculated Composited and Manually Composited Flow-Weighted Samples

Before studying any wetlands, DWR completed a proof of concept that the manually composited samples provide the same loads as hourly data. We collected and analyzed samples for two 25-hour tidal cycles at the Yolo Wildlife Area tidal wetland. We analyzed the hourly

samples and calculated a composite value using flow data. We compared the calculated composite value to the composites that we manually composited in the lab.

We used a 1-Sample Wilcoxon Signed Rank test to determine if there were any differences between the calculated composites and the manual composites. Unfiltered and filtered THg composites were not significantly different ($p=0.906$ for unfiltered THg, $p=0.624$ for filtered THg). Importantly, both unfiltered and filtered MeHg also were not different ($p=0.477$ for unfiltered MeHg, and $p= 0.294$ for filtered MeHg). Figure 10 shows bar graphs of the loads, which shows that while there were some visual differences, overall the values tracked well. Additionally, we graphed the data using box plots (Figure 11) and visually, they appeared to be similar.

Figure 10 – Calculated vs. Manually Composited Loads

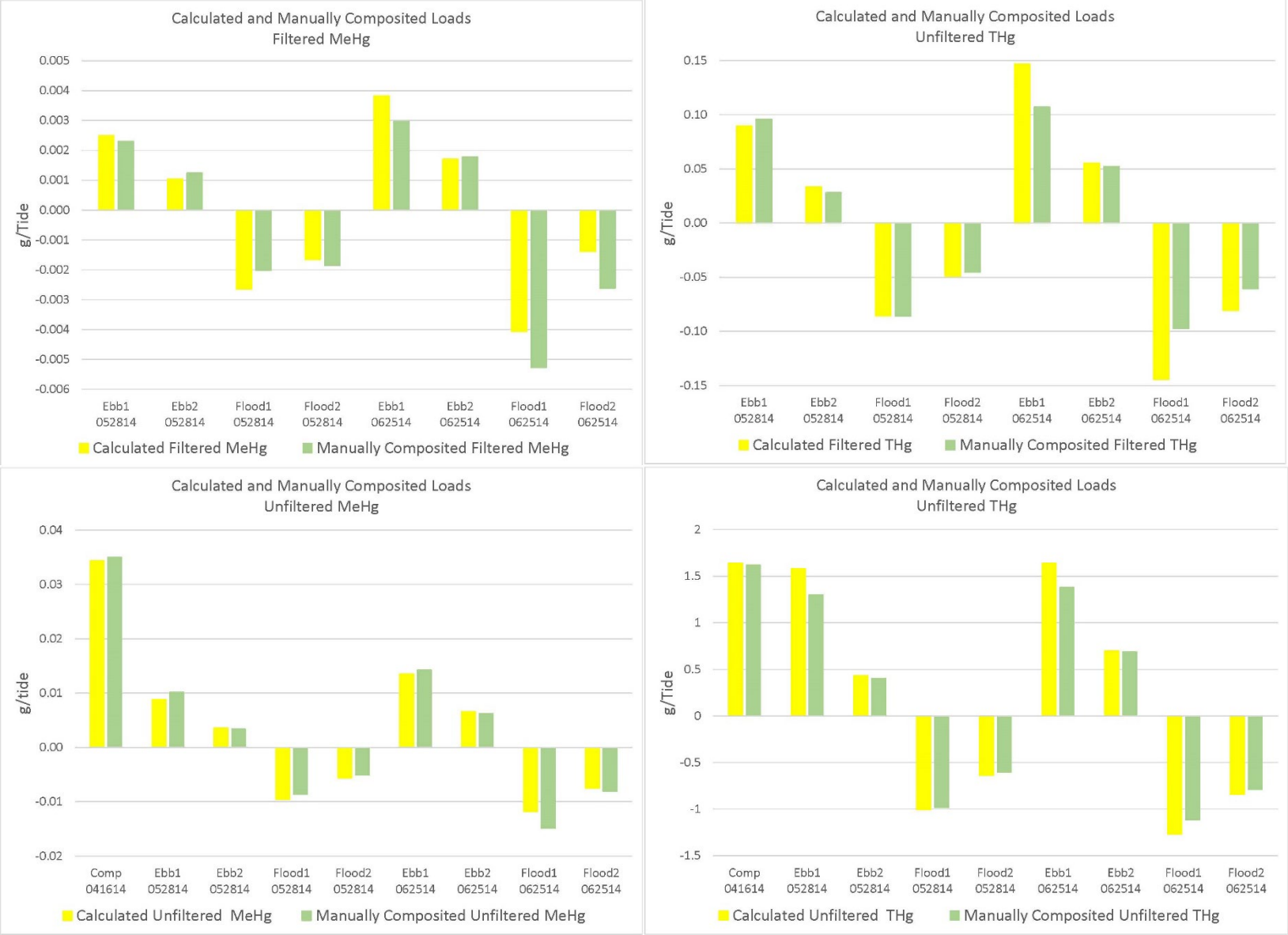
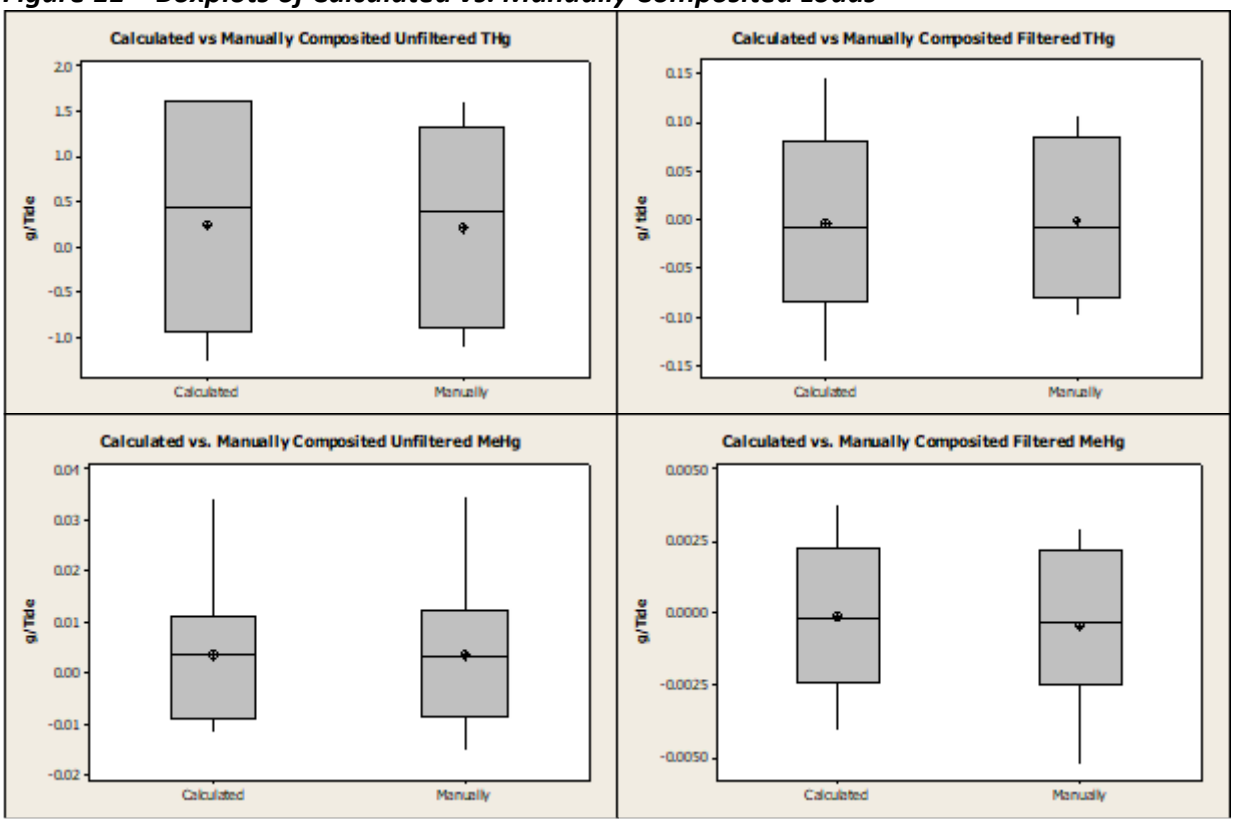


Figure 11 – Boxplots of Calculated vs. Manually Composited Loads



5.1.2 Sampling Locations

DWR plans to study 3-6 tidal wetlands and will choose them year to year and include them in this monitoring plan as they are chosen. Currently, we plan on studying the wetlands that are described below.

5.1.2.1 Yolo Wildlife Area Tidal Wetland

The first wetland we will be studying is the Yolo Wildlife Area tidal wetland, which is in the southern portion of the Yolo Wildlife Area and the Yolo Bypass – South subarea (see Figure 12). The wetland is tidal, has one opening (mouth), and contains fresh water. It is located close to the DWR office and can be monitored more frequently so we can refine methods.

This site has several limitations:

1. The wetland is located within the Yolo Wildlife Area, which is open to hunting from September 1st through the first full weekend of February. DWR staff may not be able to access the land portion of the wetland during the hunting season.
2. Employees must get permission from the Wildlife Area manager before setting foot onto the land.
3. The wetland is located within the Yolo Bypass which can flood during winter months, and we will not be able to collect samples while it is flooding.

4. The wetland is relatively new and has very little vegetation, making it not ideal for the study of mature wetlands.

The ADCP, which will be used to collect velocity, stage, and flow data, will be located on the bed in the middle of the main channel. The transect that will be used to collect data to develop a rating curve to calculate flow using the ADCP will be slightly more internal to the wetland. The water quality sonde will be located in the water, off the shore, near the ADCP. See Figure 13 for the location of the flow and water quality equipment.

Figure 12 – Location of Yolo Wildlife Area Tidal Wetland

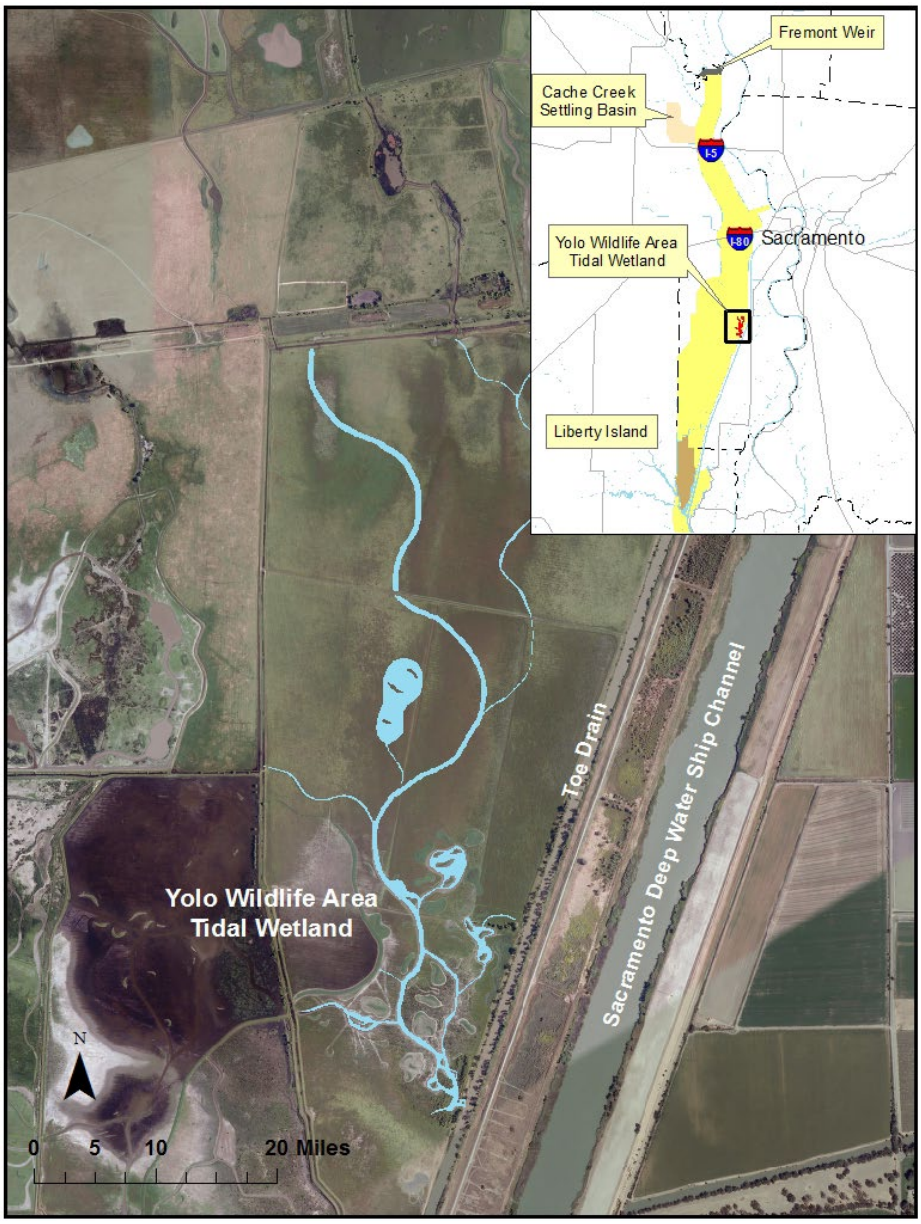


Figure 13 – Yolo Wildlife Area Tidal Wetland Equipment Locations

5.1.2.2 Blacklock Area Tidal Wetland

The second wetland we will be studying is Blacklock tidal wetland, in the Suisun Marsh, west of the DMCP. The Blacklock property was acquired by DWR in December 2003 and is approximately 70 acres of tidal wetland. In July 2006, an unplanned breach occurred on the northwest levee, followed by a planned breach in October 2006, near the first breach. Figure 14 shows the location of Blacklock and the two breaches.

Because DWR will be measuring flow, having defined levees that bound the flow of water in and out of the tidal wetland is important. Because of this, the main limitation for this study is that the levees containing Blacklock are being allowed to erode. DWR staff will continue to watch for additional breaches, and as a precaution, Blacklock is being studied early to decrease the chance that additional levee breaches will occur prior to or during the study.

Water quality sondes will not be placed at this wetland for several reasons. First, the velocities and depth of the mouths make a free-standing placement of a temporary sonde station very difficult. Second, the banks are unstable as they are being allowed to erode, so mounting the sondes off the shore is a good way to lose our sondes.

The ADCPs, which will be used to collect velocity, stage, and flow data, will each be mounted on a weighted platform on the bottom of the channel and placed in the mouths. The telemetry equipment and water quality station will be off the south banks of each of the breaches, far from the eroding portions of the levees. See Figure 15 for the location of the flow and water quality equipment.

Figure 14 – Location of Blacklock Tidal Wetland

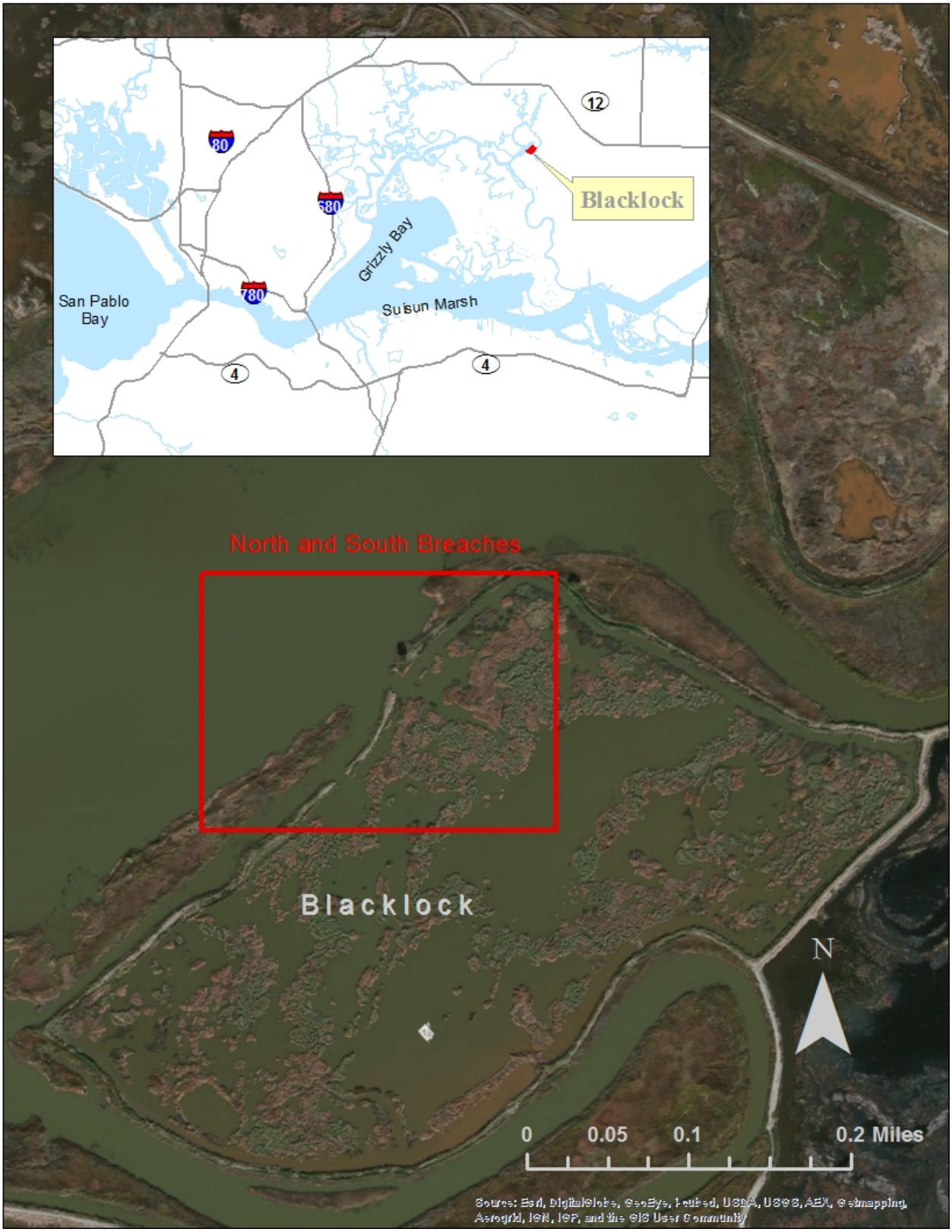
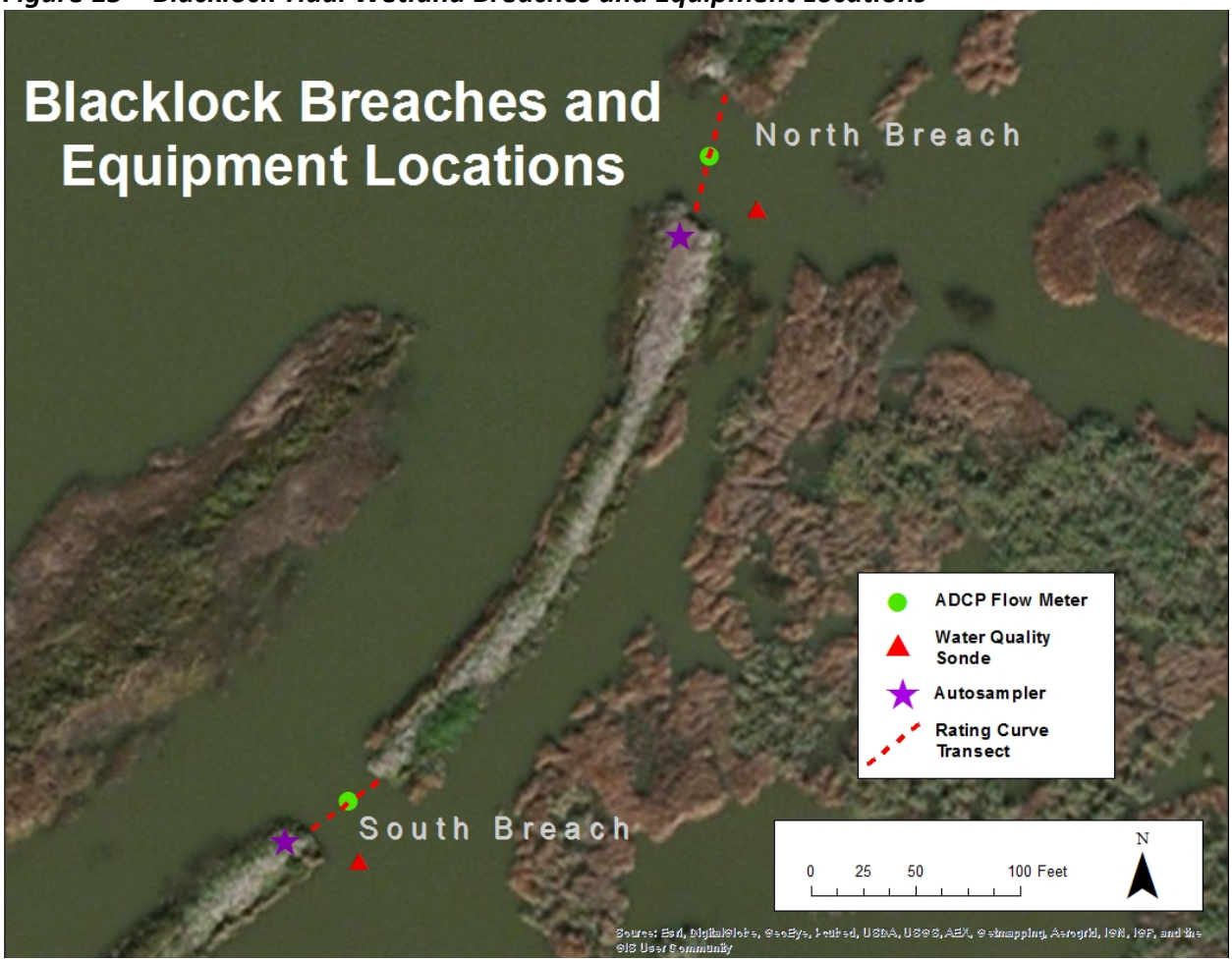


Figure 15 – Blacklock Tidal Wetland Breaches and Equipment Locations



5.1.1.3 North Lindsey Tidal Wetland

The third wetland we will be studying is North Lindsey tidal wetland, located in the Cache Slough Complex and Yolo Bypass – South subarea. The wetland is in an area that was historically back water sloughs and marsh and the mouth is open to Calhoun Cut to the south. See Figure 16 for location. It is densely covered with emergent tules and has the lowest maximum water velocity out of all the wetlands we plan to study. The wetland was officially breached in 2014 by the California Department of Fish and Wildlife though it had been muted tidal previously due to a broken flap gate.

The ADCP, which will be used to collect velocity, stage, and flow data, will be located on the bed of the main channel near the mouth. The telemetry equipment and water quality station will be off the shore, slightly further inside the wetland (Figure 17).

Figure 16 – Location of North Lindsey Slough Tidal Wetland

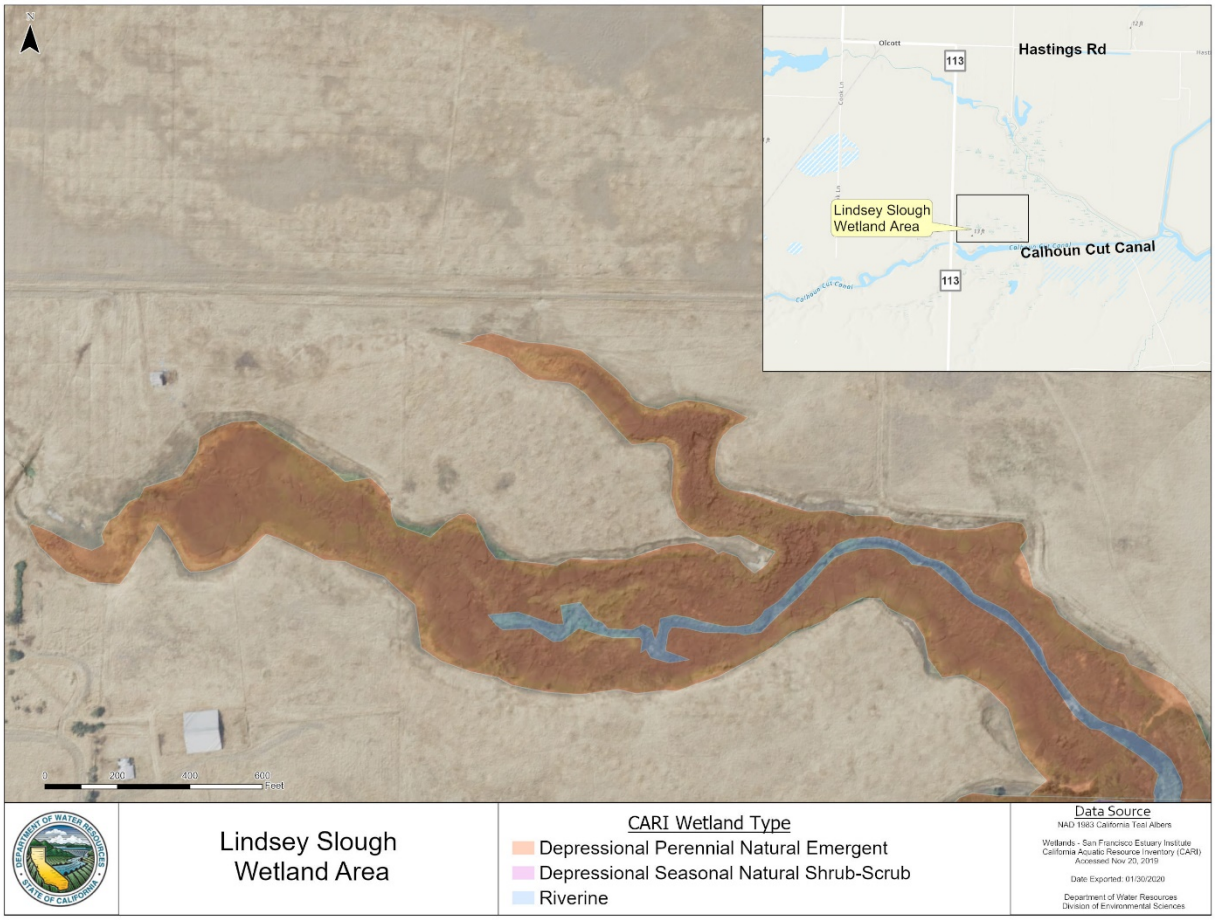


Figure 17 – North Lindsey Slough Tidal Wetland Equipment Locations

5.1.1.4 Westervelt Cosumnes River Tidal Wetland

The fourth wetland we will be studying is Westervelt Cosumnes River tidal wetland, located on the Cosumnes River just east of the confluence with the Mokelumne River. See Figure 18 for location. It is freshwater, and it was designed to have 9-acres of defined channels when the water levels were lower. As the water level increases in the winter months, the wetland's flood plain gradually fills up to fill the entire area which is bounded by levees.

This wetland is unusual in that it is our only wetland that was designed to include a portion that floods out of channel when the water rises but is also bounded by levees. This differs from the Yolo Wildlife Area tidal wetland which is in the middle of the Yolo Bypass flood plain that is more of a flow through system.

The ADCP, which will be used to collect velocity, stage, and flow data, will be located on the bed of the main channel near the mouth. The telemetry equipment and water quality station will be off the shore, slightly further inside the wetland (Figure 19).

Figure 18 – Location of Westervelt Cosumnes River Tidal Wetland

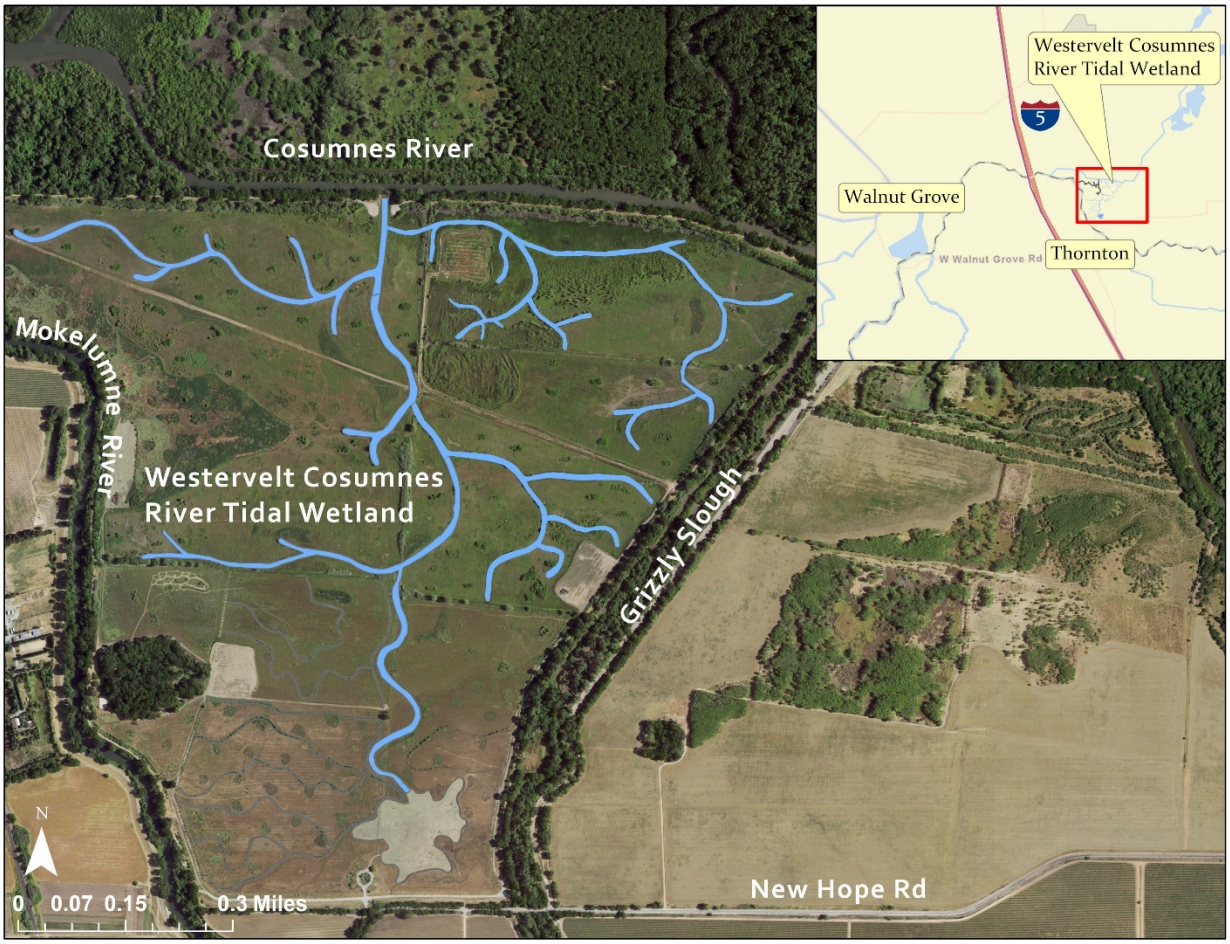


Figure 19 – Westervelt Cosumnes River Tidal Wetland Equipment Locations

5.1.3 Sample Types and Analytes

All sample bottles will be labeled with waterproof labels displaying the sample ID, station name, date, sample matrix, analyte(s), fraction, and sample collection depth. These labels and the chain of custody forms (COC's) are generated by the DWR Bryte Laboratory's Field and Laboratory Information Management System (FLIMS). DWR staff will enter sampling information including field personnel, station name, sampling date and time, and associated field measurements into the FLIMS Field Module, which will then generate the labels and COC's.

The water quality parameters collected can be grouped into three types:

1. The following analytes will be measured in water collected from the mouth of the wetland via auto-sampler:
   - THg, unfiltered and filtered
   - MeHg, unfiltered and filtered
   - Total and Dissolved Organic Carbon

- Total Suspended Solids (Except Yolo Wildlife Area tidal wetland)

2. The following physical parameters will be measured at the mouth of the wetland via water quality sonde (YSI EXO2):
   - Temperature
   - Specific conductance
   - Dissolved Oxygen
   - Turbidity
   - Total chlorophyll

3. While sampling, field crews will collect the following field measurements with calibrated handheld meters (YSI ProPlus and Hach Turbidimeter, for Westervelt, a YSI EXO 1) and will collect samples to submit to the lab:
   - Temperature
   - Specific conductance
   - Dissolved Oxygen
   - Turbidity
   - Chlorophyll *a*
   - Total Suspended Solids

5.1.4 Grab Sample Water Collection

Samples will be collected using either the autosampler, wading out with an acid cleaned bottle, or by using a sampling pole to collect samples. Some samples will be decanted directly from the auto sampler collection bottles, and others will be composited using a flow-weighting method. All bottles from which samples are distributed will be shaken thoroughly before sample distribution. Sample handling is outlined in Table 4. See Appendix B for sample splitting and filtering instructions.

Table 4 – Sample Handling and Lab Information

Parameter	Sample Container	Lab Submittal Container	Analytical Method	Filtered?	Preservation	Hold Time	Analytical Lab
Total Mercury, unfiltered	Acid-cleaned glass autosampler bottle or acid-cleaned 4L glass bottle	Acid-cleaned 250mL glass bottle	EPA 1631 E	No	2.5 mL BrCl at lab within 48 hours, <4°C	90 days	Bryte Lab
Total Mercury, filtered	Acid-cleaned glass autosampler bottle or acid-cleaned 4L glass bottle	Acid-cleaned 250mL glass bottle	EPA 1631 E	Yes, 0.45µm capsule filter	2.5 mL BrCl at lab within 48 hours, <4°C	90 days	Bryte Lab
Methylmercury, unfiltered	Acid-cleaned glass autosampler bottle, or acid-cleaned 4L glass bottle	Acid-cleaned 250mL glass bottle	EPA 1630 Modified	No	1.25 mL HCl within 48 hours, <4°C	180 days	Moss Landing Marine Lab
Methylmercury, filtered	Acid-cleaned glass autosampler bottle, or acid-cleaned 4L glass bottle	Acid-cleaned 250mL glass bottle	EPA 1630 Modified	Yes, 0.45µm capsule filter	1.25 mL HCl within 48 hours, <4°C	180 days	Moss Landing Marine Lab
Total Suspended Solids	Acid-cleaned glass autosampler bottle, acid-cleaned 4L glass bottle, or 1-quart HDPE bottle	Polyethylene 1-quart bottle	EPA 160.2	No	<4°C	7 days	Bryte Lab
Total Organic Carbon	Acid-cleaned glass autosampler bottle, or acid-cleaned 4L glass bottle	40mL glass vial	EPA 415.1	No	H3PO4 to <pH 2, <4°C	28 days	Bryte Lab
Dissolved Organic Carbon	Acid-cleaned glass autosampler bottle, or acid-cleaned 4L glass bottle	40mL glass vial	EPA 415.1	Yes, rinsed 0.45um capsule filter	H3PO4 to <pH 2, <4°C	28 days	Bryte Lab

Parameter	Sample Container	Lab Submittal Container	Analytical Method	Filtered?	Preservation	Hold Time	Analytical Lab
Chlorophyll *a*	Acid-cleaned glass autosampler bottle, acid-cleaned 4L glass bottle, or 1-pint HDPE bottle	Frozen glass filter folded inside coin envelope	Standard Method 102	Yes, glass fiber filter	Freeze	28 days	Bryte Lab

5.1.4.1 THg and MeHg Sample Collection Methods

Samples will be collected in acid-cleaned 1.8 or 3.7 L autosampler bottles, or 4 L acid-cleaned glass sample bottles. Both filtered and unfiltered THg and MeHg samples will be submitted to the lab in acid-cleaned clear glass 250mL sample bottles.

The 1.8L and 3.7 L autosampler bottles will be acid cleaned by DWR staff using methods described in Appendix A. The double-bagged 250 mL and 4 L sample bottles used for THg will be purchased from O2Si, or MLML. The 250 mL double-bagged MeHg bottles will be purchased from O2Si, MLML, or Environmental Sampling Supply (ESS). O2Si uses the cleaning method appropriate to the EPA's "Specifications and Guidance for obtaining Contaminant-Free Sample Containers" and EPA method 1631E in which they rinse bottles with 50% HCl acid. O2Si tests one bottle per 12, which is a rate of approximately 8%, and guarantees levels lower than 0.5 ng/L of THg. See Figure 20 for an example of their certificate of analysis. MLML follows stringent glass cleaning procedures which are described in Appendix H. Before the study began, ESS sample bottles were tested for MeHg and THg. While the bottles had contamination for THg, they did not have contamination for MeHg (2% were tested by MLML and had concentrations less than 0.03 ng/L), so the bottles will be used for MeHg only.

The 250 mL and 4 L glass bottles will arrive from the suppliers acid cleaned and in two closed resealable bags. The bottles will be stored in our laboratory or warehouse in their original cardboard box packaging inside an additional large plastic bag to protect them from airborne mercury contamination.

Because of the low concentrations of THg and MeHg that are being measured in samples, collection and processing must be done with care to keep from being contaminated. The samples will be collected and processed using the EPA's "clean hands, dirty hands" method, and all 250 mL and 4 L glass bottles will be rinsed three times with sample water before being filled. To preserve the integrity of the samples once they've been collected, samples will be kept in a dark refrigerator or on wet ice in an ice chest and kept at 4°C or less. The samples will be processed and filtered using methods outlined in Appendix B. Composited samples will be processed using methods outlined in Appendix C.

The MeHg samples will be preserved with 1.25 mL 12N HCl and stored in a cold, dark place, at less than 4°C while in DWR's custody; the labs will also keep samples below 4°C in a dark place. See Appendix D for the MeHg sample preservation standard operating procedure. Hold time is 180 days, but samples should be sent to MLML within seven days if possible. The THg samples will be submitted to Bryte lab as quickly as possible and will be preserved by lab personnel with BrCl. Hold time for THg samples is 90 days. See Table 4 for lab methods.

Figure 20 – O2Si Example Certificate of Analysis

o2si smart solutions®

Quality System Audited & Registered by NSF-ISR to ISO 9001:2008

Certificate of Analysis

Rev

Catalog No: 190007-29-DB

Description: 4 Liter Amber Glass for Method 1631 Low Level Mercury Sampling, 4/cs

Container Lot No.: 21021400

Lot No: 1063186

Glove Lot No: N/A

Date Received: _____

This certificate verifies that this Lot was cleaned to the recommended EPA wash procedure as set forth in EPA's "Specifications and Guidance for obtaining Contaminant-Free Sample Containers" and EPA Method 1631E. This Lot was tested and found to comply with or be lower than the EPA specification.

Hg <0.5 ng/L

Certified By: Kasey West

Kasey West Inorganics

This container was analyzed by Atomic Fluorescence Spectrometry in accordance with EPA Method 1631E.

2030 Savage Road • Charleston, SC 29407
Phone: 866.272.0932 • Fax: 866.509.5146
www.o2si.com

5.1.4.2 Total Suspended Solids Sample Collection Methods

Total Suspended Solids (TSS) will be collected in a 1-quart HDPE sample bottle. The bottle and inside of the cap will be rinsed three times with sample water before being filled. TSS samples will be placed on wet ice or in a fridge and kept at 4°C or less. The samples will be submitted to Bryte Lab within three days of collection because the hold time is seven days. See Table 4 for lab methods.

If the sample is not collected directly from the waterbody, the container that the water is poured from will be thoroughly shaken before water is decanted from the container. The sample container will still be rinsed three times before a final sample is poured.

5.1.4.3 Total Organic Carbon and Dissolved Organic Carbon Sample Collection Methods

Generally, total organic carbon (TOC) and dissolved organic carbon (DOC) samples will be decanted from a larger sample container into a 40mL glass vial containing preservative. Because the vials contain preservative, it is important to *not rinse or overfill the vials.* TOC samples will be collected from water decanted from the larger sample container. To collect DOC samples, sample water will be filtered directly into the sample vial, using filtering methods outlined in Appendix B. TOC and DOC samples will be placed on wet ice or in a fridge, kept at 4°C or less, and submitted to Bryte Lab within seven days of collection. Sample hold time is 28 days. See Table 4 for lab methods.

5.1.4.4 Chlorophyll *a* Sample Collection Methods

Sample water will be filtered through a glass fiber filter (47 mm) and the chlorophyll will be caught on the filter for analysis. Any bottle that the water is transferred to, will be rinsed three times with sample water before being filled. The filter will be frozen and submitted to Bryte Lab for analysis within seven days. Sample holding time is 28 days. See Appendix E for filtering methods and Table 4 for lab methods.

6. Measurement Quality Objectives

Measurement quality objectives consist of five components: accuracy, precision, representativeness, comparability, and completeness. Following is a brief description of each of these components:

- Accuracy is a measure of how close the measurement is to the true value. In a laboratory, it is typically evaluated by analysis of laboratory control standards (LCS), certified reference materials (CRM), and matrix spikes (MS), where the result can be compared to the expected value. LCS, CRM, and MS will be discussed in greater detail in Section 8.4.1.

- Precision measures the ability to repeat results and is determined by the analysis of duplicate samples or repeated measurements.
- Representativeness is how well a single sample can describe the conditions of an entire sample population and is controlled by the overall design of the project and by using standard sampling and analytical procedures.
- Comparability looks at how variable one set of data is to another and indicates the amount of consistency among data sets. This is also affected by using standard sampling and analytical procedures.
- Completeness is a measure of how many data points collected for the project are useable and reliable. The acceptable value for completeness for all field measurements and laboratory analyses collected for this project is greater than or equal to 90%.

Both representativeness and comparability are qualitative objectives, and therefore cannot by evaluated by numerical criteria. On the other hand, accuracy and precision are quantitative objectives, and there are various numerical criteria that can be used to evaluate them. The numerical quality objectives for the field measurements and laboratory analyses for this study are listed in Table 5 and Table 6, respectively. These measurement quality objectives depend on the amount of error that can be tolerated and the anticipated concentrations.

In addition to the quality objectives for accuracy and precision, Table 5 and Table 6 also contain other important data quality objectives including resolution for the field measurements and target reporting limits for the lab analyses. Resolution is the smallest change in a measured value that the field instrument can detect. A reporting limit is the minimum level that can be reliably measured by the analytical method within specified limits of precision and accuracy during routine laboratory operating conditions.

Table 5 – Measurement Quality Objectives for Field Measurements

Parameter	**Unit**	**Accuracy** (unit or Percent)[(a)]	**Precision** (unit or RPD)[(a)]	**Resolution**	**Measuring Range**
Specific Conductance	uS/cm	±1 or ±0.5%	±1 or ±0.5%	1	0 to 4,000
Dissolved Oxygen	mg/L	±0.2 or ±2%	±0.2 or ±2%	0.01	0 to 30
Temperature	°C	±0.2	±0.2	0.1	-5 to 40
Turbidity	NTU	±2%	±		0 to 1,000

[(a)]The accuracy and precision objectives are expressed as either a unit or percentage. In the cases where both are provided, we will use the objective that is greater. The relative percent difference (RPD) is the difference between two repeated measurements expressed as a percentage of their average.

Table 6 – Measurement Quality Objectives (MQOs) and Other Quality Objectives for Laboratory Analyses

Parameter	Unit	**Accuracy** (LCS or CRM Recovery)[a]	**Precision** RPD[b]	**Matrix Spike Recovery**	**Target Method Detection Limit (RL)**
Total Mercury	ng/L	75-125%	≤ 25%	75-125%	0.5
Methylmercury	ng/L	70-130%	≤ 25%	70-130%	0.03
Total Suspended Solids	mg/L	--	≤ 25%	--	1.0
Total Organic Carbon	mg/L as C	75-125%	≤ 30%	75-125%	0.5
Dissolved Organic Carbon	mg/L as C	75-125%	≤ 30%	75-125%	0.5
Chlorophyll *a*	µg/L	--	--	--	0.05

[a] A laboratory control sample (LCS) is a control matrix spiked with a known quantity of an analyte. A certified reference material (CRM) is purchased from an outside entity and has undergone extensive validation by several labs to be certified to have a recovery value within a specified confidence level. The LCS or CRM is the same matrix (water, sediment, tissue) as the sample set. An LCS or CRM is periodically analyzed by the laboratory, and the percent recovery is the amount of the analyte measured by the instrumentation expressed as a percentage of the expected or true value.

[b] The relative percent difference (RPD) is the difference between two field duplicates or lab replicates (sample or matrix spikes) expressed as a percentage of their average. *The precision MQO's for field duplicates or sample lab replicates only apply to paired samples with results greater than 10 times the Reporting Limit.*

7. Instruments and Methods for Field Measurements and Laboratory Analysis

This section describes the measurement systems that will be used to collect the data for this study. The term "measurement system" refers to the instruments used for field measurements and the processes used for water sample collection and lab analyses.

The DWR mercury monitoring group has two YSI Professional Plus handheld multi-parameter field meters that measure temperature, specific conductance, and dissolved oxygen. In addition, we have two Hach 2100Q portable turbidimeters that will be used to measure turbidity in Nephelometric Turbidity Units (NTU). The instrument specifications for our YSI multi-parameter field meters and turbidimeters are shown in Table 7.

Measurement systems that involve water sampling and lab analysis have a set of specifications that must be followed for the system to achieve its performance criteria and yield valid data. Table 8 shows the details for sample handling including filtering and preservation for all the analytes that will be collected for this study. Information about laboratory operations for this study including methods used, reporting limits, and performance criteria is presented in Table 9.

Table 7 – Instruments Used for Field Measurements

Parameter	Type/Method	Units	Model	Calibration Mode	Range	Resolution	Accuracy (unit or Percent)
Specific Conductivity	Four electrode cell	µS/cm, mS/cm	YSI 5560	1 point	0 to 200 mS/cm (auto range)	Range dependent: 0-500 µS/cm=1 µS/cm 501-50,000 µS/cm=10 µS/cm 50.01-200 mS/cm=100 µS/cm	±1 µS/cm or ±0.5%
Temperature	Thermistor	°C, °F, °K	YSI 5560	non-adjustable	-5 to 70°C	0.1˚C	±0.2˚C
Turbidity	Ratio turbidimetric determination	NTU	Hach 2100Q	1-4 point, user selectable calibration curve	0 to 1,000 NTU	0.01 NTU on lowest range	±2% plus stray light

Table 8 – Specifications for Sample Handling

Parameter(s)	Sample Preparation	Preservation and Storage	Holding Time
Total Mercury (total)	Unfiltered	0.5% BrCl within 28 days of collection, store <4˚C	90 days
Total Mercury (dissolved)	Filter within 24 hours of collection with a 0.45 µm capsule, prior to preservation	0.5% BrCl within 28 days of collection, store <4˚C	90 days
Methylmercury (total)	Unfiltered	0.5% 12N HCl within 48 hours of collection, store <4˚C in the dark	180 days
Methylmercury (dissolved)	Filter within 24 hours of collection with a 0.45 µm capsule, prior to preservation	0.5% 12N HCl within 48 hours of collection, store <4˚C in the dark	180 days
Total Suspended Solids	Unfiltered	No preservation, store <4˚C	7 days
Total Organic Carbon	Unfiltered	Vial contains H_3PO_4 to bring sample to pH <2, store <4˚C	28 days
Dissolved Organic Carbon	Filter within 24 hours of collection with a pre-rinsed 0.45 µm capsule filter	Vial contains H_3PO_4 to bring sample to pH <2, store <4˚C	28 days
Chlorophyll *a*	Filter within 24 hours through a 1.0 µm glass fiber filter at a pressure of 10 in. Hg	Store water sample <4˚C in the dark until filtered, then freeze filter <-20˚C	28 days

Table 9 - Methods Selected for Laboratory Analyses and their Performance Criteria

Analyte	Unit	Method # [(a)]	Method Name/Principle	Reporting Limit	LCS Recovery (Lab Control Chart Limits)	MS Recovery (Lab Control Chart Limits)	Laboratory Repeatability (RPD of lab replicates)
Total Mercury (total and dissolved)	ng/L	EPA 1631, Revision E	Oxidation, Purge, and Trap; Cold-Vapor Atomic Fluorescence Spectrometry	0.5	71-125%	71-125%	≤ 25%
Methylmercury (total and dissolved)	ng/L	EPA 1630 (MLML Modified)	Distillation, Aqueous Ethylation, Purge and Trap; Cold-Vapor Atomic Fluorescence Spectrometry	0.031	80-120%	70-130%	≤ 25%
Total Suspended Solids	mg/L	EPA 160.2	Gravimetric, Dried at 103-105˚C	1.0	Not Applicable	Not Applicable	≤ 25%
Total Organic Carbon	mg/L as C	EPA 415.1	Wet Oxidation	0.5	80-120%	80-120%	≤ 30%
Dissolved Organic Carbon	mg/L as C	EPA 415.1	Wet Oxidation	0.5	80-120%	80-120%	≤ 30%
Chlorophyll *a*	µg/L	SM 10200 H	Extraction, Spectrophotometry	0.05	Not Applicable	Not Applicable	Not Applicable

[(a)] SM indicates a method from the Standard Methods for the Examination of Water and Wastewater, 20th edition (APHA, 1998).

8. Quality Assurance Plan

This section describes how the quality of the data collected for this study will be assured. Good quality data depends upon competent operators, thorough documentation, and effective protocols. These three factors are described below, followed by a discussion of the procedures that we will use to affect and check data quality, and how the quality of the data will be recorded and reported. This section also communicates further information about data processing, including data verification and data validation.

8.1 Competent Operators

The competence of field staff will be assured by training. In addition to all field staff reading and comprehending this monitoring plan and all relevant SOP's, we will conduct hands-on training to instruct relevant personnel on sample collection, field meter use and calibration, sample compositing, filtration, and splitting methodology, and any other appropriate information. This training will be done on an as-needed basis. Field staff will be expected to conduct their work in an accurate and thorough manner and to ask questions when uncertainty in the correct methodology arises. Lastly, field staff will work in pairs (minimally) and observe each other's work to ensure consistency.

8.2 Documentation

Documentation for this study includes recording field observations and measurements, documenting calibration and accuracy check information for the field instruments, recording notes about filtering and compositing of samples, and communicating transfer of water samples with chain of custody documents (COC's).

Examples of the paper data sheets that will be used during this study include, but are not limited to:

- Autosampler field sheets for use during 25-hour events;
- Water Quality Collection Field Record
- Sonde Pre-Deployment Record
- Sonde Post-Deployment Calibration Check Record
- Filtering Notes
- Compositing Notes and Recipe

The paper data sheets to record field observations and measurements during 25-hour events and sonde checks, other water collection events, and field instrument calibration and accuracy check information are in Appendix F. Examples of COC forms for transferring sample custody to Bryte Lab and MLML are found in Appendix G.

Field staff will record all relevant field information on the field data sheets tailored to this study, which include placeholders for the following:

- Sampling location and event information
- Date, time (in Pacific Standard Time or PST), station name, sampling event, personnel
- Visual observations including weather and water conditions
- Field measurements and the time they were taken (if measurements were taken)
- Water sampling information including time of collection (if samples were taken)
- Field instrument identification and data file name (if measurements were taken)
- Autosampler notes
- Grab sample notes
- Other relevant field observations and notes

In addition to recording the field measurements on the field data sheets, DWR staff will also store the field readings in the instrument as an electronic copy to be downloaded after returning to the office. Therefore, the file names for the measurements stored in the field meters will also be recorded on the field data sheets.

DWR Flow Monitoring and Special Studies staff will document when they measure flow in the mouth(s) of the wetlands with an ADCP.

DWR staff will document calibration and accuracy check records for field instruments on the data sheet shown in Appendix F, which includes placeholders for the following information:

- Date, Time, Reason (pre-event or post event)
- Instrument ID
- Standard Material (ID of Standard solution, humid air, NIST thermometer)
- 'True' Value of Standard Material
- Reading of the Instrument before calibration
- Reading of the Instrument after calibration (for calibrations only)
- Operator

Each field instrument has a unique Instrument ID that will be used to track its performance during calibrations and accuracy checks. In addition, field staff will record the ID's of the meters that are used to take field measurements on the field data sheets.

The COC's for the samples submitted to Bryte Lab will be generated by the FLIMS Field Module, which electronically tracks sample submittal, processing, and analysis. FLIMS allows the user to print the specific COC for a field run, which will then be submitted with the samples when they are delivered to the lab. The COC will be signed by both the relinquishing and receiving personnel, and the signed COC will then be scanned and sent electronically to the DWR mercury monitoring group, where it will be stored electronically and as a paper copy, indefinitely. An example of a signed COC is in Appendix G.

FLIMS is used to keep track of all DWR samples, including samples analyzed by contract labs such as MLML. As a consequence, any samples sent to MLML will not only have a FLIMS tracking number but will also be assigned an MLML tracking number.

A signed copy of the MLML COC with FLIMS sample numbers will be included with the samples when they are shipped to MLML, and an electronic version of the COC will be emailed to MLML. When MLML receives the samples, their receiving personnel will sign the COC, and then send a scanned electronic copy to the DWR mercury monitoring group. DWR staff will fill out the FLIMS COC, using information from the MLML COC, and submit it to Bryte Lab, where it will be checked into the FLIMS database. Both COC's will be stored electronically and as a paper copy, indefinitely.

Physical copies of field sheets, calibration and accuracy check records, compositing records, filtering notes, and COCs will be stored in binders in the Project Manager's cubicle. Electronic copies of these documents will be stored on the DWR shared server on the Mercury folder.

8.3 Protocols

Field staff will follow all Standard Operating Procedures for sample collection and equipment cleaning, including flow-weighted compositing, mercury, organic carbon, and chlorophyll filtering, autosampler and equipment cleaning, and sample shipping, which can be found in the Appendices. The DWR Flow Monitoring and Special Studies staff will use their established methods for measuring flow with an ADCP described in (Mueller & Wagner, 2009). In addition, Bryte Laboratory and MLML will use their established SOPs and protocols for each analysis, which are available from the labs.

8.4 Procedures to Affect and Check Quality

Table 10 lists the different aspects of data quality that need to be addressed for this monitoring effort, and then shows the actions necessary in order to affect and check these data quality aspects. These actions will help to ensure production of data of known and defensible quality.

Table 10 – Summary of Actions to Affect and Check Data Quality

Activity	Data quality aspect	Affect (act to influence outcome)	Check (test to evaluate or verify)
All	operator's competence	train, refresh, supervise	review work products
Field measurements	accuracy	calibrate (adjustable-reading instruments)	conduct accuracy check (all instruments)
	precision	use consistent procedures	repeat measurements
Sample collection and handling	lack of contamination	use clean sampling equipment and containers, clean the sampling equipment adequately between sampling events, follow "clean hands-dirty hands" procedures when sampling and filtering Hg samples; use other proper sampling and filtering methods for other analytes	collect and analyze bottle, tubing, trip (field), filter, and equipment blanks; collect samples (mini-study) to check if sample bias occurs due to autosampler vs. grab sample collection
	lack of deterioration	if necessary, filter the samples within the proper amount of time; preserve samples with ice and acid as appropriate within proper hold times; keep samples cold and in the dark during field collection; ship or transport the samples cold;	measure temperature upon arrival at laboratory; determine if sample was filtered and preserved in the proper amount of time
Lab analyses	accuracy	calibrate lab equipment; use certified calibration standards	run lab control spikes, certified reference materials, and matrix spikes
	precision	use consistent lab procedures	run lab replicates, matrix spike duplicates
	lack of contamination	decontaminate lab equipment; clean lab technique	analyze lab method blanks
	lack of deterioration	samples stored properly, preserved with acid if appropriate, and analyzed within holding time	record refrigerator and freezer temperatures used for sample storage daily; confirm that sample was preserved in the proper amount of time and analyzed within the holding time
Sample collection and analysis	reproducibility	use consistent sampling and lab procedures	collect field duplicates

8.4.1 Accuracy

In order to assure accuracy of field measurements DWR staff will calibrate the field instruments at least as often as the manufacturer's recommendation, which is the most effective way to minimize the instrument's drift from the calibrated state. In addition, field staff will check the accuracy of the field instruments by conducting periodic accuracy checks. Accuracy checks are done by placing the instrument in a standard with a known value, and then recording the difference between the value measured by the instrument and the expected value of the standard. DWR staff will calculate the instrument drift, which is the difference between the instrument's reading and the standard value expressed in measurement units or as a percentage of the value of the standard, for every calibration adjustment and accuracy check conducted. Table 11 shows the frequency at which the field instruments will be calibrated and checked for accuracy during this study. Because measurement accuracy is as accurate as the standards used for instrument calibration, DWR staff will only use standard solutions that are:

- certified, or traceable to NIST or ASTM
- used within expiration date
- stored in proper conditions at a non-extreme temperature
- compared with fresh standards before being used up

For laboratory analyses, accuracy will be assured by lab instrument calibration using reliable standards and will be checked by the analysis of LCS, CRM, and MS as specified in the method and SOP for the particular analyte. Following is a brief description of these laboratory QA procedures:

- An LCS or CRM is in the same matrix (water or sediment) as the sample set and contains a known quantity of an analyte. A CRM is purchased from an outside entity and has undergone extensive validation by several labs to be certified to have a recovery value within a specified confidence level. Typically, an LCS is prepared in the laboratory, and is a control matrix spiked with a known quantity of an analyte. An LCS or CRM is periodically analyzed by the laboratory, and the recovery is the amount of the analyte measured by the instrumentation expressed as a percentage of the expected or true value.
- An MS is an environmental sample that is spiked with a known amount of an analyte. It is used to check for any matrix effects or interferences on the accuracy of an analytical measurement. MS recovery is calculated by the difference between the spiked and unspiked sample concentrations divided by the concentration of the spike added and is expressed as a percentage.

Recovery values for the LCS, CRM, and MS analyses should not exceed the measurement quality objectives shown in Table 6. Table 12 shows the frequency at which the laboratory will conduct accuracy checks (LCS, CRM, and MS) for each method.

Table 11 – Frequency of Calibration Adjustments, Accuracy Checks, and Repeated Measurements for Field Instruments

Parameter	Mode	Standard Material	Frequency of Calibration & Accuracy checks	Frequency of repeated field measurements
Specific Conductivity	adjustable	Salt Standard solution (KCl), 1-point calibration: 2767 µS/cm	Calibration once a month; periodic accuracy checks	20% or 2 per Trip
Dissolved Oxygen	adjustable	Humid Air or saturated water; 1-point calibration: 100% saturation	Calibration before each field run; accuracy check after each field run	20% or 2 per Trip
Temperature	non-adjustable	NIST thermometer	Accuracy check once a month	20% or 2 per Trip
Turbidity	adjustable	Formazin; 4-point calibration: <0.1, 20, 100, 800 NTU	Calibration every 3 months; accuracy check with a 10 NTU standard once a week [(a)]	10% or 1 per Trip

[(a)] It is not necessary to perform an accuracy check on the turbidimeter if it is not used during the particular week.

Table 12 – Frequency of Checks for Sample Integrity, Laboratory Accuracy, Laboratory Precision, and Process Reproducibility

Analyte	**Field blank frequency [a]**	**Field duplicates frequency [a]**	**Lab Method blank frequency [b]**	**Lab Control Sample type, concentration, and check frequency [b]**	**Matrix Spike /MS Duplicate frequency [b]**	**Lab replicate frequency [b]**
Total Mercury	1 per sampling event	5% or 1 per sampling event, whichever is greater	1 per lab batch of 20 samples	5 ng/L Hg standard, 1 pair per lab batch of 20 samples	2 pair per lab batch of 20 samples	1 per lab batch of 20 samples
Methylmercury	1 per sampling event	5% or 1 per sampling event, whichever is greater	3 per lab batch of 20 samples	1 ppm MeHg standard, 1 per lab batch of 20 samples	2 pair per lab batch of 20 samples	1 per lab batch of 20 samples
Total Suspended Solids	1 per 3 sampling events	5% or 1 per sampling event, whichever is greater	1 per lab batch of 20 samples	Not Applicable	Not Applicable	1 per lab batch of 20 samples
Total Organic Carbon	1 per sampling event	5% or 1 per sampling event, whichever is greater	1 per lab batch of 20 samples	1 per lab batch of 20 samples	1 pair per lab batch of 20 samples	1 per lab batch of 20 samples
Dissolved Organic Carbon	1 per sampling event	5% or 1 per sampling event, whichever is greater	1 per lab batch of 20 samples	10 mg/L TOC standard, 1 pair per lab batch of 20 samples	1 pair per lab batch of 20 samples	1 per lab batch of 20 samples
Chlorophyll *a*	1 per 3 sampling events	5% or 1 per sampling event, whichever is greater	1 per lab batch of 20 samples	Not Applicable	Not Applicable	Not Applicable

[a] A sampling event is field work conducted in one day to collect samples.

[b] A Lab Batch is a group of samples analyzed on one day by one lab instrument between calibrations.

8.4.2 Precision

Field and laboratory staff will be properly trained and will use consistent procedures to achieve good precision of field measurements and lab analyses. Precision of field measurements will be checked by repeated measurements, and laboratory precision will be checked by lab replicates and matrix spike duplicates. The reproducibility of the entire sampling and analysis process will be assessed by analyzing field duplicate samples. DWR staff will collect field duplicates at the tidal wetland being studied during an hour during the 25-hour tidal cycle collection event, or once every set of three samples collected for sonde verification. Table 11 and Table 12 show the frequency of precision checks for the field measurements and the lab analyses, respectively.

Precision will be calculated by the relative percent difference (RPD) between the duplicates, replicates, or any repeated measurements. RPD is calculated by the difference between the two paired values expressed as a percentage of their average. The RPD's for the repeated field measurements should not exceed 25 percent. For the field duplicates, lab replicates, and matrix spike duplicates, RPD's should not exceed the measurement quality objective for precision for the analyte, which can be found in Table 6. For most of the analytes, the measurement quality objective for precision is an RPD that is no greater than 25 percent; however, for low concentrations (less than five times the Reporting Limit), the RPD may be an artificially high value of greater than 25 percent.

8.4.3 Sample Integrity-Lack of contamination

Before and during field operations, lack of contamination will be assured by proper storage of pre-cleaned sample bottles, thorough cleaning of sampling equipment, sample processing equipment, autosampler bottles, tubing, and accessories, and by training operators on all aspects of the sampling process. To assure lack of contamination of THg and MeHg samples, field staff will follow "clean hands-dirty hands" procedures when sampling, compositing, filtering, and preserving. The cleaning procedure for equipment not in direct contact with samples will include scrubbing the surfaces with laboratory detergent and then rinsing with tap water. Equipment may also be rinsed with deionized water and ambient water as well, if appropriate. Equipment that may be in direct contact with samples will be cleaned according to SOPs in Appendices A and H.

DWR staff will check for contamination by routinely conducting various blank checks including bottle blanks, equipment blanks, field blanks, and filter blanks. We will use Type 1 blank water that has been tested for the constituents of concern.

A percentage of the sample bottles that we will use for the THg and MeHg analyses will be tested as bottle blanks to check if they have the potential to introduce contamination. O2Si tests one bottle per 12 (approximately 8%) for THg to 0.5 ng/L. Before using O2Si bottles for MeHg, we will send 1% or three of the bottles from each cleaning lot or batch, whichever is

greater, to MLML to be tested as MeHg bottle blanks. For the THg bottle blanks, we will send the same percentage or number of each lot of bottles from O2Si to Bryte Lab.

If we receive 4 L or 250 mL bottles from MLML for THg and MeHg samples, they test bottle blanks for these bottles at the same rate. All the bottles that we receive from MLML will be from lots with clean bottle blanks (all the results are below the method detection limit).

Field blanks are used to assess the contamination from field sources such as airborne materials, containers, and preservatives. Field crews will collect one set of field blanks during each event at each tidal wetland in the same manner that the sample will be collected; the field blanks will be collected in an acid-cleaned autosampler bottle filled with Type 1 water. Instead of using another autosampler to collect a field blank, we will use a five-gallon bucket or ice chest to replicate conditions in the autosampler. The field blank autosampler bottle will be placed with the lid removed into the loosely covered clean five-gallon bucket or ice chest for the same duration as sample collection (approximately 25 hours). The field blanks will be processed using "clean hands-dirty hands" and the sample bottles that are submitted to the lab will be rinsed three times with the field blank water before the bottle is filled. TOC field blanks will be poured directly into the vial without rinsing.

In addition to field blanks, equipment blanks will be collected to assess contamination from equipment. The filtered THg, MeHg, and DOC samples will be run through the appropriate filtering apparatus and then run into the sampling container; the sample bottles for filtered THg and MeHg will be rinsed three times before being filled with blank water.

The limit that field blanks should not exceed is either the Reporting Limit or one-fifth the concentration of the sample collected at the same location as the field blank, whichever is greater. If the field or other blanks do exceed the Reporting Limit or one-fifth the concentration of the sample collected, the data can only be used with caution, recognizing that the data may be biased high.

The autosamplers that are used to collect water samples may introduce contamination to the water samples. We will collect unfiltered THg and MeHg autosampler tubing and bottle blanks. To collect the tubing blanks, we will follow the procedures outlined in Appendix A to clean the tubing, rinse it three times with Type 1 water, and then collect an unfiltered THg and MeHg sample using the "clean hands, dirty hands" method. To do an autosampler bottle blank, we will randomly choose one autosampler bottle, put Type 1 water in it for 24 hours and keep it cold (< 4°C), and then decant unfiltered THg and MeHg samples using the "clean hands, dirty hands" method. We will conduct tubing and bottle blanks before each sampling event. If the tubing and/or bottle blanks indicate contamination, we will identify the source of contamination and correct the problem. The data can only be used with caution, recognizing that samples may be biased high.

Because DWR staff is using composited samples and an autosampler, we will be collecting duplicates of hourly samples to be analyzed, rather than using duplicates of the composited

samples. In this way, we can attempt to measure autosampler sampling variation that may occur. One set of duplicates will be collected for each analyte for each sampling event.

In the laboratory, lack of contamination will be assured by using highly cleaned laboratory equipment and by following proper laboratory practices when preparing samples and performing analytical procedures. Lack of sample contamination by the laboratory will be checked by analyzing method blanks at the frequency shown in Table 12.

8.4.4 Sample Integrity-Lack of deterioration

Lack of sample deterioration by field staff will be assured by following proper sample handling procedures including filtering (if necessary) and preserving the samples within the proper amount of time and keeping the samples cold and in the dark during storage, transport, and shipping. This will be checked by noting sample temperatures during staging and upon arrival at the laboratory and measuring the pH of samples upon receipt at the laboratory if there is reason to suspect that the proper acidification may not have occurred. DWR staff will use MLML procedures to acidify MeHg samples, and Bryte Lab staff will preserve THg samples according to their procedures. Appropriate nutrient samples will also be acidified by DWR field staff following Bryte Lab procedures. Additionally, lack of sample deterioration in the laboratory will be assured by proper sample storage below either 4 or -20˚C, proper and timely preservation, and analysis within the holding time. This will be checked by noting refrigerator and freezer temperatures used for sample storage daily and calculating if a sample was preserved within the proper amount of time and analyzed within its holding time.

8.5 Procedures to Record and Report Quality

As mentioned in Section 8.2, DWR staff will record the data from field instrument calibrations and accuracy checks onto data sheets (Appendix F). In addition, we will record the repeated field measurements on our field data sheets. For the analytical water samples, records for the data quality checks for accuracy, precision, and sample integrity will be provided to us in the COC forms and in reports provided by the labs which will include analysis results and lab QA data.

8.6 Data Verification and Validation

The process of data verification involves checking whether all monitoring activities have been performed as planned, all samples have been properly tracked, accounted for, and analyzed, and all the results have been recorded and entered correctly. Data validation is assuring that the sampling process was conducted properly and that the field and analytical instruments were functioning correctly. This is assessed by determining if the accuracy and precision performance measures met their associated measurement quality objectives and by reviewing the results of other QA samples and information (blanks, field duplicates, method detection limits, sample handling, and hold times). The results from the validation process will inform

DWR staff on which data is considered reliable, which data should not be used, or which data should be used with qualifications.

9. Data Management, Interpretation, and Reporting

9.1 Data Integrations and Management

DWR staff will store all data, including data from Bryte Lab, MLML, the water quality sonde, and the flow station, in DWR's Water Data Library (WDL) (http://www.water.ca.gov/waterdatalibrary/), which is accessible to the public.

Data collected from the flow station will be QA/QC'd by DWR's Flow Monitoring Section, uploaded into the Hydstra database, and then uploaded into the WDL. Data collected from the water quality sonde will be QA/QC'd by MME staff, uploaded into the Hydstra database, and then uploaded into the WDL. Analytical data from DWR's Bryte Lab will be directly uploaded into the WDL via FLIMS. MeHg data from MLML will be entered into FLIMS by MME or Bryte Lab staff, which will allow it to be uploaded into the WDL.

9.2 Statistical Analyses

Tentatively, the below statistical analyses will be run to attempt to answer our hypotheses or suggest trends. As staff completes work, we will consult with a statistician to determine final analyses.

Table 13 – Possible Statistical Analyses

Variable 1	Variable 2	Statistical Test 1	1 wetland	All wetlands
Unfiltered THg		Kruskell Wallace		X
Dissoled MeHg		Kruskell Wallace		X
Unfiltered THg		Kruskell Wallace		X
Unfiltered MeHg		Kruskell Wallace		X
Unfiltered and Filtered MeHg	Unfiltered and Filtered THg	Regression	X	
Filtered MeHg	Unfiltered MeHg	Regression	X	
Filtered THg	Unfiltered Hg	Regression	X	
Unfiltered and Filtered MeHg	Chlorophyll	Regression	X	X
Unfiltered MeHg	DOC	Regression	X	
Unfiltered MeHg	TOC	Regression	X	
TSS	Turbidity	Regression	X	

Variable 1	Variable 2	Statistical Test 1	1 wetland	All wetlands
Total chlorophyll	Chlorophyll a	Regression	X	
Filtered MeHg	Season	Kruskell Wallace	X	X
Unfiltered MeHg	Season	Kruskell Wallace	X	X
Filtered THg	Season	Kruskell Wallace	X	X
Unfiltered THg	Season	Kruskell Wallace	X	X
Unfiltered and Filtered MeHg	Vegetation	Regression		X
Unfiltered Hg	TSS	Regression	X	X
Unfiltered and Filtered MeHg	Salinity	Regression	X	X
Particulate THg	TSS	Ratio	X	

9.3 Status and Final Reports

The DMCP requires a status report by October 2015 (CRWQCB-CV, 2011). An extension was granted by the Regional Board Executive Officer for the final report to April 2020. The reports will be prepared by the Project Manager, with technical assistance from the Technical Advisor and Project Team and submitted to the Regional Board Liaison.

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Appendices for Methylmercury Import and Export Studies on Tidal Wetlands In the Sacramento-San Joaquin Delta, Yolo Bypass, and Suisun Marsh Environmental Monitoring Plan

Appendix A
Standard Operating Procedure
Autosampler, Accessory, and Bottle Cleaning

Department of Water Resources
Originated by: Petra Lee and Julianna Manning
February 6, 2015

1. Scope and Application

Methylmercury and total mercury samples must be collected using clean equipment; most importantly the autosamplers that are being used to collect samples must have clean collection bottles and tubing, which must be acid-cleaned prior to sampling. This SOP describes the procedures used to clean the autosampler body, bottle racks, and strainers, as well as how to dilute the acid to the appropriate concentration before acid-cleaning the autosampler bottles, accessories, and tubing.

2. Summary of Method

The autosampler bodies and racks will be cleaned with liquid dish soap and tap water to remove any dirt and debris. Since they are not directly touching the samples, they do not need to be rinsed with more than tap water.

The strainers will be cleaned with Micro-90, then rinsed with tap water, then Type 2 water, then placed into a clean resealable bag.

The autosampler bottles, lids, and PTFE lid liners will be cleaned inside and outside with Micro-90, then rinsed with tap water, then Type 2 water. They will then be bagged and taken to DWR's Bryte Lab. The liners will be soaked in a 10% hydrochloric acid (HCl) solution then rinsed with Type 1 water. Then the liners will be replaced in the lids and the bottles will be filled with 10% HCl. After the bottles have soaked, the acid will be removed and the interior of the bottles and lids will be rinsed with Type 1 water, then placed into a clean resealable bag.

The accessories, which include glass beakers and PTFE funnels, will be cleaned with Micro-90, then rinsed with tap water, then Type 2 water, then soaked in 10% HCl, then rinsed with Type 1 water, then placed into a clean resealable bag.

The outside of the silicone and PTFE tubing will be cleaned with Micro-90, then rinsed with tap water. Once the outside is cleaned, the inside of the tubing will be cleaned with Micro-90, then rinsed with tap water, then Type 2 water, then 10% HCl, then rinsed with Type 1 water, then placed into a clean resealable bag or garbage bag. The tubing ends will be sealed to prevent contamination inside the tubing.

3. Contamination and Interferences

Because of the low concentrations of mercury and methylmercury that are being measured, and the ubiquitous nature of low concentrations of mercury in the environment, sample contamination is a very real and challenging possibility. During the procedures discussed in this SOP, sampling equipment that touches the water sample, such as the interior of the tubing and the interior of the bottles, must be kept clean and only handled by staff wearing clean gloves.

4. Safety

This procedure involves working with glass bottles which can easily break under impact with hard surfaces. Please use caution when working with glass, especially when the glass bottles are heavy and the outside is wet.

This procedure also involves working with concentrated and 10% HCl, so precautions, such as protective gear, should be used. Staff should read DWR's Bryte Laboratory Safety Manual and read and sign any relevant safety documents before working with acid.

5. Apparatus and Materials

Reagents for equipment cleaning:

- Liquid dish soap, such as Dawn
- Micro-90, Cole-Parmer, Part #18100-20
- Hydrochloric Acid (HCl), Baker Analyzed, 12N, VWR Part #JT9535-3
- Hydrochloric Acid (HCl), 10%, prepared by adding 1 part 12N to 9 parts Type 2 water
- Type 1 water
- Type 2 water

***Note**: 10% HCl may be used a total of 6 times to clean equipment, then it must be neutralized with sodium bicarbonate. The neutralized acid can be poured down the drain with plenty of water for dilution.*

Equipment to clean:

- Autosampler
- Autosampler bottle rack
- PVC strainers
- 1.8 L and/or 3.7 L glass bottles with plastic lids and PTFE lid liners
- PTFE funnels
- 50 mL and/or 100 mL glass beakers
- Silicone pump and discharge tubing
- PTFE suction line

Equipment used to clean:

- Acid carboys
- Large glass container with lid
- Large HDPE container for cleaning the inside of the tubing
- Secondary storage containers
    - Plastic tub with lid
    - Bucket with lid
- Peristaltic autosampler pump, battery cable, and charged battery
- Barbed tubing connectors
- Various sizes of resealable plastic bags
- Large garbage bags
- Zip ties, large and small
- Hydrochloric acid stickers
- Permanent marker
- Parafilm

Safety equipment:

- Lab coat
- Eye protection
- PVC apron
- Polyethylene gloves that are stored inside a resealable plastic bag
- Nitrile gloves that are stored inside a resealable plastic bag

6. Detailed Procedures:

6.1 Cleaning Autosampler Body and Bottle Racks

1. Scrub the plastic parts of the autosampler and bottle racks with liquid dish soap.

2. Rinse with tap water and allow them to dry in a clean area that does not have excessive dirt (inside a lab, for example, not a warehouse). After they dry, place racks into a cleaned autosampler.

6.2 Cleaning Strainers

1. Scrub each strainer with a dilute Micro-90/tap water solution then rinse very thoroughly with tap water.

2. Put on new poly gloves and rinse with Type 2 water.

3. Place strainers into a new clean, appropriately sized resealable plastic bag and close. Label and date the bag with a permanent marker.

6.3 Making Dilute Acid Solution

1. Determine amount of hydrochloric acid necessary. It is recommended not to make and store more than 3.5 gallons per carboy as the weight makes the carboys unwieldy.

2. Use the initial acid concentration and calculate acid to water ratio.

3. Fill carboy with appropriate amount of Type 2 water from Bryte.

Note*: The next step should only be done in an acid fume hood wearing personal protective equipment.*

4. Carefully add appropriate amount of acid into carboy, using pre-calculated volume markings on the side of the carboy. For safety, only pour acid directly from original container into carboy full of water, do not use graduated cylinder or any other measuring device. The measurement markings on the side of the carboy are adequate. Replace the cap with a plastic bag under it to seal it fully, and gently shake until acid is mixed. Make sure the spigot is closed during mixing.

5. Make sure carboy is labeled appropriately with "10% Hydrochloric Acid", and a hydrochloric acid sticker.

6. Store in a safe area in a secondary container, such as a large HTPE plastic tub. Make sure container is also labeled with "Hydrochloric Acid".

6.4 Cleaning Autosampler Bottles

At West Sacramento Lab Facility:

1. Remove the lids from the bottles and the liners from the lids. Scrub the inside and outside of each part with a dilute Micro-90/tap water solution. Rinse lids, liners, and bottles with tap water, inside and out, very thoroughly.

2. Put on new poly gloves and rinse lids, liners, and bottles three times with Type 2 water.

3. Place lids on bottles and place each into an appropriately sized resealable plastic bag and close. Place liners in a separate bag and close. Label and date the bags with a permanent marker. The next steps will be done in Bryte Lab's clean room.

At Bryte Laboratory:

4. Read, understand, and sign the safety documents associated with this project. The safety documents and this Standard Operating Procedure (SOP) are living documents and will be updated as necessary.

5. Put on protective gear, including eye protection, a lab coat, nitrile gloves, a PVC apron, closed toe shoes, and long pants. Staff can also wear shoulder-length poly gloves if necessary, particularly if a lab coat is not available.

6. In the clean room, in the sink of the acid hood with the glass sash pulled down as far as possible and the hood turned on, place liners into a large glass container with a lid. They can be placed together with the small glass beakers and/or PTFE funnels if there is room. Then fill with 10% HCl until everything is submerged. Acid will be dispensed from a carboy or carefully poured from another container.

7. Place lid on container and cover the seams with parafilm. Rinse the outside of the container with Type 2 water and place in a secondary container, such as a bucket with a lid. With a permanent marker, write contents and how many times the acid has been used on the parafilm.

8. Place the entire container, including the secondary container in a safe place and allow liners to soak for a minimum of three days.

9. After a minimum of three days, to finish cleaning of liners, repeat step 5 to put on safety gear. Working in an acid hood in a clean room using clean gloves, remove each liner and rinse each three times with Type 1 water.

10. After the liners are rinsed, place liners into appropriately sized new resealable plastic bag and close. Label and date the bags with a permanent marker.

11. Pour remaining acid from the glass container into an acid carboy. Rinse the inside and outside of the glass container and lid with Type 2 water and store in secondary container until next use.

12. Rinse the outside of the carboy with Type 2 or tap water and label with the number of times acid has been used. If the acid has been used 6 times then neutralize, dilute, and dispose it.

13. Once the lid liners are acid-clean, the bottles can be acid-cleaned. Working in an acid hood in a clean room and wearing clean gloves and other protective gear, fill each bottle with 10% HCl. Acid will be dispensed from a carboy or carefully poured from another container.

14. Replace liner in lid and cap the bottle. Rinse the outside of the bottle with Type 2 water then place into a new appropriately sized resealable plastic bag and close. Label and

date the bag with a permanent marker. Then place into a secondary container, such as an HTPE plastic tub.

15. Repeat steps 13 and 14 until all bottles are filled with acid. Place the secondary container in a safe place and allow bottles to soak for a minimum of three days.

16. After a minimum of 3 days, repeat step 5 and put on protective gear. Working in an acid hood in a clean room and wearing clean gloves, empty a bottle of acid into another bottle ready to be soaked or into an acid carboy. Rinse the outside of the bottle with Type 2 water and set aside.

17. Once the carboy is full, rinse the outside with Type 2 or tap water and label with the number of times acid has been used. If the acid has been used 6 times then neutralize, dilute, and dispose it.

18. Rinse the inside of each empty bottle and lid three times with Type 1 water then place into an appropriately sized resealable plastic bag and close. Label and date the bag with a permanent marker. These bottles are ready to use in autosamplers to collect samples.

6.5 Cleaning Small Glass Beakers and PTFE Funnels

At West Sacramento Lab Facility:

1. Scrub the inside and outside of each beaker and funnel with a dilute Micro-90/tap water solution. Rinse beakers and funnels with tap water, inside and out.

2. Put on new poly gloves, and rinse beakers and funnels three times with Type 2 water.

3. Place beakers and funnels into an appropriately sized resealable plastic bag and close. Label and date the bags with a permanent marker. The next steps will be done in Bryte Lab's clean room.

At Bryte Laboratory:

4. Read, understand, and sign the safety documents associated with this project. The safety documents and this Standard Operating Procedure (SOP) are living documents and will be updated as necessary.

5. Put on protective gear, including eye protection, a lab coat, nitrile gloves, a PVC apron, closed toe shoes, and long pants. Staff can also wear shoulder-length poly gloves if necessary, particularly if a lab coat is not available.

6. In the clean room, in the sink of the acid hood with the glass sash pulled down as far as possible and the hood turned on, place beakers and/or funnels into a large glass container. They can be placed together with the PTFE lid liners if there is room. Then fill with 10% HCl until everything is submerged. Acid will be dispensed from a carboy or carefully poured from another container.

7. Place lid on container and cover the seams with parafilm. Rinse the outside of the container with Type 2 water and place in a secondary container, such as a bucket with a lid. With a permanent marker, write contents and how many times the acid has been used on the parafilm.

8. Place the entire container, including the secondary container in a safe place and allow liners to soak for a minimum of three days.

9. After a minimum of three days, repeat step 5, and work in an acid hood in a clean room. Wearing new clean gloves, remove each beaker and funnel and rinse each three times with Type 1 water.

10. Place small beakers and funnels into appropriately sized resealable plastic bags and close. Label and date each bag with a permanent marker.

11. Pour remaining acid from the glass container into an acid carboy. Rinse the inside and outside of the glass container and lid with Type 2 water and store in secondary container until next use.

12. Rinse the outside of the carboy with Type 2 or tap water and label with the number of times acid has been used. If the acid has been used 6 times then neutralize, dilute, and dispose it.

6.6 Cleaning Autosampler Tubing

At West Sacramento Lab Facility:

1. Scrub the outside of both types of tubing (PTFE suction line and silicone autosampler tubing) with a dilute Micro-90/tap water solution. Rinse thoroughly with tap water.

2. Inspect the length markings on the PTFE tubing. If they have been removed or are faded, rewrite tubing lengths on both ends with a permanent marker. Coil each length of tubing tightly and secure with large zip ties.

3. If precleaning the insides of the tubing at West Sacramento lab facility, skip this step and perform steps 4-9 before going to Bryte Lab. If precleaning the insides of the tubing at Bryte Laboratory, place PTFE tubing into a clean garbage bag and silicone tubing into an

appropriately sized new resealable plastic bag and close. Label and date the bags with a permanent marker. The next steps will be done in an acid hood at Bryte Lab.

At Bryte Laboratory:

4. Wearing clean gloves, carefully install a length of silicone pump tubing in an autosampler. Use barbed connectors to connect each end to another piece of silicone tubing and secure with small zip ties. Connect to PTFE tubing by pushing the end of the PTFE tubing slightly inside the silicone tubing and secure with a small zip tie.

5. Continue connecting all the PTFE and silicone tubing to create a continuous line. Make sure that each end of the line has at least one length of silicone tubing.

6. Place a large glass or HDPE container in the sink and fill with a dilute Micro-90/tap water solution.

7. Place both ends of tubing (intake and outtake) into the container and run pump in a loop, ensuring that the inside of the tubing is rinsed at least three times. Generally, you can measure how long it takes for the liquid to go through once, and then triple that amount of time for an appropriate minimum rinse time; more rinse time is acceptable. Make sure volume of solution is large enough to fill tubing entirely, so no gaps occur.

8. After a minimum of three rinses, pull both ends out of solution and allow tubing to drain completely. Thoroughly rinse the container with tap water while keeping the ends of the tubing away from touching sources of contamination (such as in and around the sink).

9. Fill container with tap water, and place intake into container. Pump water through tubing for three total volume rinses. Then remove intake from container and allow tubing to drain completely. Repeat with Type 2 water.

10. If precleaning the insides of the tubing at Bryte Laboratory, skip this step. If precleaning the insides of the tubing at West Sacramento lab facility, detach one piece of silicone tubing near the pump and remove from autosampler. Place a clean bag or poly glove around each end of tubing and secure with a small zip tie. Coil all the tubing together and bundle with large zip ties. Place them all in a clean garbage bag and transport everything to Bryte Lab. In an acid hood, remove the bags/gloves from each end and reassemble the tubing in an autosampler.

11. For the next steps, make sure you have read, understood, and signed the living safety documents, which will be updated as necessary.

12. Put on protective gear, including eye protection, a lab coat, nitrile gloves, a PVC apron, closed toe shoes, and long pants. Staff can also wear shoulder-length poly gloves if necessary, particularly if a lab coat is not available.

13. After verifying that the volume of acid is sufficient, place tubing intake and outtake into acid carboy. Turn the acid hood on, then pump acid through tubing for a minimum of three rinses. After the tubing has been rinsed with acid sufficiently, remove intake from carboy and allow tubing to drain free of acid completely.

14. Rinse the outside of the carboy with Type 2 or tap water and label with the number of times acid has been used. If the acid has been used 6 times then neutralize, dilute, and dispose it.

15. Fill a large acid-cleaned glass container or bottle with Type 1 water and place intake into container. Pump water through tubing for a minimum of three rinses. Then remove intake from container and allow tubing to drain completely.

16. Using a new set of poly gloves, detach each piece of tubing. Place a clean bag or poly glove around each end of PTFE tubing, secure with a small zip tie, and place into a clean garbage bag. Place silicone tubing into an appropriately sized resealable plastic bag and close. Label and date the bags with a permanent marker.

Appendix B
Standard Operating Procedure
Sample Filtering and Splitting

Department of Water Resources
Originated by: David Bosworth and Petra Lee
November 20, 2013

1. Scope and Application

After collecting or compositing samples into 4 L glass bottles, DWR staff will filter and split samples from the 4 L bottles into smaller individual bottles to be analyzed by the labs. This SOP describes the techniques that we will use to filter and split the samples. See the "Flow-Weighed Compositing SOP" in Appendix C for flow-weighted compositing procedures.

2. Summary of Method

We will use the "clean hands-dirty hands" method for trace metals while filtering and splitting samples for total mercury (THg) and methylmercury (MeHg) analyses. This "ultra-clean" handling procedure is not necessary for the remaining analytes.

The individual bottles for the unfiltered analytes will be filled first from the 4 L bottle. We will begin with the bottles for the unfiltered THg and MeHg analyses, then the bottles for all the other unfiltered analytes such as total organic carbon (TOC) and any additional unfiltered samples that we may be collecting. The 4 L bottle will be constantly agitated during this sample splitting procedure to ensure that the sample is thoroughly mixed.

The remaining water in the 4 L bottle will then be filtered into individual bottles for the filtered analytes using a peristaltic pump, a combination of acid-cleaned Teflon and C-Flex tubing, and a 0.45 µm capsule filter. After rinsing the tubing and filter with Type 1 water and then the sample water, the sample will first be filtered into the bottles for filtered THg and MeHg analyses and then the bottles for all the other filtered analytes such as dissolved organic carbon (DOC) and then any additional filtered samples that we may be collecting. As a note, capsule filters must be pre-rinsed with a minimum of 1 L of water before collecting DOC, so that the filter does not contaminate the DOC sample.

3. Contamination and Interferences

Because of the low concentration of mercury and methylmercury that are being measured, and the ubiquitous nature of low concentrations of mercury in the environment, sample contamination is a very real and challenging possibility. During the procedures discussed in this SOP, samples can become contaminated by the sample bottles, filtering equipment, and through dirt and dust in the air and surrounding environment.

Please be diligent and use the utmost care to minimize contamination when following the procedures described in this SOP. We will be using the "clean hands-dirty hands" method while filtering and splitting samples for THg and MeHg analyses. While following this methodology, remember that the clean hands person only touches the following, but nothing besides these items:

- The inner bag of a double-bagged container;
- The 4 L and 250 mL sample containers;
- The ends of the filter tubing set;
- The 0.45 µm capsule filter and;
- Anything else that comes in direct contact with the water sample

The dirty hands person handles everything else but does not touch any of the clean hand's items listed above. If at any point something occurs that you suspect will compromise the cleanliness of the polyethylene gloves worn by the clean hands personnel, replace those gloves with a clean pair immediately. Always change your gloves before working with a different water sample to prevent cross-contamination.

The lab where DWR staff will be filtering and splitting the samples must be free of dirt and dust as much as possible. The filter tubing will be acid-cleaned by Moss Landing Marine Laboratories (MLML) using the method described in their MPSL-101 SOP in Appendix H.

Some of the mercury in a water sample is associated with particulates which can settle rapidly. In addition, mercury can stick to the glass of a sample container. Therefore, samples in the 4 L bottles must be mixed as thoroughly as possible when splitting the sample into the containers used for the unfiltered analyses.

4. Safety

This procedure involves working with glass bottles which can easily break under impact with hard surfaces. Please use caution when working with glass, especially when the glass bottles are heavy and the outside is wet.

Since these procedures involve pouring water from one bottle to another and running water through filters, please be aware of water spilling on the lab floor as it may be slippery. Clean up water spills to minimize slipping hazards.

5. Apparatus and Materials

- Peristaltic pump
- Polyethylene or nitrile gloves that are stored inside a clean resealable plastic bag
- Large plastic bag to cover lab bench where filtering is conducted

- Waste bucket or sink for rinse water
- One 1000 mL graduated cylinder to measure rinse water
- Ice chest filled with wet ice or refrigerator and freezer to store samples

For each water sample:

- 4 L bottle of sampled water that is stored double-bagged and on wet ice or in a refrigerator
- One acid-cleaned and double-bagged C-Flex and Teflon tubing set from MLML
- One 0.45 µm Pall High Capacity In-Line Groundwater Sampling Capsule (Product #121780)
- The following individual sample containers pre-labeled with waterproof labels printed from the Bryte Lab FLIMS system:
    - filtered and unfiltered THg and MeHg acid-cleaned 250 mL glass bottles that are double-bagged
    - other sample bottles including 40 mL glass vials for total and dissolved organic carbon (TOC and DOC)

6. Detailed Procedures

6.1 Lab Work Bench Setup for Filtering

1. Wipe down the area where you will be filtering and working with the water samples with a clean cloth to remove dust and dirt that can contaminate the total mercury samples.

2. Rip open a clean, new large plastic bag, not touching the inside, and cover the work area. The inside of the large plastic bag should be exposed and facing up towards the work area. Typically, the same plastic bag will be used for the duration of the filtering and splitting process for all samples collected during that sampling event; however, if excessive sample water spills on the plastic or something else occurs which compromises the cleanliness of the plastic surface, replace the plastic bag with a new one.

3. Set up the peristaltic pump on the work area, and plug it in.

4. Dedicate a spot on the plastic-covered lab bench near the peristaltic pump where you will place the 4 L amber bottles containing the water samples collected from the field. The outer bags of these bottles may be wet and/or dirty, so it is necessary to place these in a dedicated spot to keep the rest of the plastic-covered lab bench dry and clean.

6.2 Splitting the Sample into the Bottles for the Unfiltered Analyses

1. Process the unfiltered sample splitting over a sink or waste bucket.

2. Before proceeding with the next steps, decide who is going to be designated as the clean hands personnel and who will be dirty hands. Both will put on new, clean gloves. Remember that both personnel discard their old gloves and put on new ones before processing a new sample; this is especially important for clean hands.

3. Prepare the two 250 mL glass bottles pre-labeled for unfiltered THg and MeHg, a 40 mL glass vial for TOC, and any additional bottles to be filled with unfiltered sample water. The dirty hands person opens the outer bag of a 250 mL glass bottle without touching the inner bag and pushes the inner bag and bottle partly out of the outer bag, so that clean hands can access the inner bottles without dirty hand's assistance. The dirty hands person then places the prepared bottle on its side on the edge of the plastic-covered lab bench making sure that the inner bag is hanging off the edge and not touching any solid object. Complete these steps for both Hg bottles.

4. The dirty hands person then removes a double-bagged 4 L glass amber bottle or 1.8 L clear glass autosampler bottles that contains one of the hourly or composited water samples and opens the outer bag for the clean hands person.

5. For the 4 L amber glass bottle that is in two resealable bags, the clean hands person opens the inner bag, removes the 4 L bottle. For the 1.8 L clear glass autosampler bottle, remove the bottle as there is only one outer bag. The clean hands person shakes the capped bottle as vigorously as possible for a full minute. If the sample is particularly turbid, shake longer initially. Be careful because the bottle can be heavy and slippery from condensation.

6. The dirty hands person will then become a second clean hands person during steps #7-11 and will be referred to as clean hands #2. This transformation occurs when the dirty hands person replaces his/her gloves with a new pair. Alternatively, you can have a third person be the second clean hands and not have to do any switching of gloves or bag and bottle balancing.

7. After replacing their gloves, the clean hands #2 person opens the inner bag of one of the 250 mL glass bottles prepared in step 3 above, removes the 250 mL bottle for the unfiltered THg sample, and then pushes the inner bag into the outer bag enough to keep it from touching anything.

Note: *During steps #8-12 below, clean hands will continuously shake the capped 4 L bottle during times when sample water is not being poured from the bottle to keep the sample well mixed.* ***This is very important!***

8. After shaking the 4 L bottle for a full minute, the clean hands person pours approximately 15 mL of sample water into the 250 mL bottle held by clean hands #2. The clean hands #2 person then places the cap onto the 250 mL bottle and shakes it to ensure that the entire interior surface of the bottle and cap have been rinsed and coated with sample water.

After shaking the bottle, clean hands #2 removes the cap, pours the rinsate into the cap allowing the excess to spill into the waste bucket or sink, and then empties the contents of the cap. The 250 mL bottle will be rinsed two more times following the same procedures. Do this as quickly as possible to prevent sediment settling in the 4 L bottle.

9. After three rinses, the clean hands person will recap the 4 L bottle and shake it vigorously for 10-20 seconds. After shaking, the clean hands person fills the rinsed 250 mL bottle that clean hands #2 is holding with sample from the 4 L bottle, making sure to leave a small amount of headspace for the preservative to be added later. The clean hands #2 person then caps the 250 mL bottle and with places it back into the inner bag. Clean hands #2 will seal the inner bag and push the inner bag so that it is completely inside the outer bag. During this step clean hands #2 takes precaution to not touch the outer bag with his/her hands. The outer bag is left unsealed at this time and will later be closed after the other bottles that require "clean hands-dirty hands" procedures are filled.

10. The clean hands and clean hands #2 personnel then repeat steps #7-9 above to rinse and fill the 250 mL glass bottle for the unfiltered MeHg sample. Throughout these procedures, clean hands will continue to shake the capped 4 L bottle during times when sample water is not being poured from the bottle.

11. After all bottles requiring "clean hands-dirty hands" procedures are rinsed, filled, and placed back into their inner bags, clean hands #2 becomes dirty hands again, and closes all the outer bags of the filled containers. This step is unnecessary if you have three people and are working with two people who have clean hands as mentioned in step #6.

12. The clean hands person will continue to shake the 4 L bottle and will pour unfiltered water into the remaining bottles, including a 40mL vial for TOC, which will not be rinsed nor overfilled. Place filled bottles into a fridge or freezer. It is important that the 4 L bottle continues to be only handled by the clean hands person during this step to prevent contamination of the remaining sample in the 4 L bottle.

13. After all the bottles for the unfiltered analytes are filled and placed into a refrigerator or freezer, the clean hands person will put the capped 4 L bottle back into its inner bag and place in the fridge until sample is filtered.

6.3 Filtering the Remaining Sample into the Bottles for the Filtered Analyses

1. Clean hands and dirty hands personnel will put on a new set of gloves.

2. First, the tubing and filter will be set up on the peristaltic pump. The dirty hands person opens the outer bag of the cleaned and double-bagged C-Flex and Teflon tubing set from MLML, and clean hands opens the inner bag and removes the tubing. While the clean hands person holds onto the ends of the tubing, the dirty hands person threads the C-Flex portion of the tubing into the peristaltic pump head and then locks the head down.

3. While continuing to hold onto the end of the tubing with the long Teflon tube, clean hands uncaps the 4 L bottle containing type 1 water (for rinsing the filter), and then inserts the long Teflon tubing into the 4 L bottle making sure that the end of the tubing is near the bottom of the bottle and that it is securely wedged into the bottle.

4. Dirty hands opens the plastic bag of a new 0.45 µm Pall High Capacity In-Line Capsule Filter. The clean hands person carefully removes the filter making sure to not touch the outside of the bag, and then inserts the filter into the other end of the tubing set consisting of C-Flex tubing. The filter should be installed in the proper orientation using the marking on the filter that shows the direction of flow.

Note: *Depending on the length of the tubing, a bottle filled with water can be placed in front of the pump and the extra tubing can be wrapped around it, which will allow the filter to dangle off the edge of the plastic-covered lab bench. This way, the filter no longer needs to be touched and no hands are required to hold it. See Figure B1 for an example. To minimize leaks, the junction between the tubing and filter and between the C-Flex and Teflon tubing can be cinched with clean zip ties using a zip tie tightener.*

Figure B1 – Filtering Set Up

5. Before filtering the sample water into the individual sample bottles, the filter needs to be rinsed with 500-600 mL of type 1 water. Dirty hands will place a 1000 mL graduated cylinder in a waste bucket below the dangling filter. Making sure that the pumping direction is set correctly, the dirty hands person turns on the peristaltic pump and let type 1 water run through the filtering apparatus. Run 500-600 mL of type 1 water through the filter to rinse it thoroughly.

6. After filter is rinsed, clean hands will remove the Teflon end of the tubing in the type 1 water and allow water to drain using the pump. Afterwards, clean hands will place Teflon end into sample water and allow 100-200 mL of sample water to rinse the tubing and filter.

7. After the filter and tubing are rinsed, filter sample water from the 4 L amber glass bottle for the THg sample. Dirty hands opens up the outer bag of the 250 mL bottle pre-labeled for filtered THg, and clean hands opens up the inner bag, removes the bottle, and pushes the inner bag back into the outer bag. Dirty hands can place the bags on the counter. With the clean hands person holding onto the 250 mL bottle below the filter, dirty hands will operate the pump.

8. Fill the bottle with approximately 15 mL of sample water. The clean hands person then places the cap onto the 250 mL bottle and shakes it to ensure that the entire interior surface of the bottle and cap have been rinsed and coated with sample water. After shaking the bottle, clean hands removes the cap, pours the rinsate into the cap allowing the excess to spill into the waste bucket or sink, and then empties the contents of the cap. The 250 mL bottle will be rinsed two more times following the same procedures.

9. The 250 mL bottle is then filled, leaving a small amount of headspace for the preservative to be added later. With the assistance of the dirty hands person, clean hands puts the filled bottle back into the inner bag, seals this bag, and pushes the inner bag so that it is completely inside the outer bag. Dirty hands seals the outer bag and places the bottle into a fridge. Repeat for the filtered MeHg sample.

10. Once the THg and MeHg samples are filtered, the "clean hands-dirty hands" method is no longer necessary and does not need to be followed while filtering the sample into the remaining containers.

11. To fill the DOC, fill the pre-labeled 40 mL vial, but do not overfill or rinse.

12. After all the unfiltered and filtered bottles have been filled, processed, and stored in a fridge or freezer, that sample is completed. Remove and discard the tubing and filter from the pump and discard the remaining sample water from the 4 L bottle. Place the 4 L bottle in a container to be recycled, and both clean hands and dirty hands personnel will remove and discard their gloves.

6.4 Additional Steps

Repeat the sample splitting and filtering procedures described above for the remainder of the water samples using a new set of tubing, filter, bottles, and gloves for each sample.

Filter blanks will be processed in the same way a sample is, only type 1 water will be used in the place of sample water. A filter blank may be collected prior to a water sample being filtered using the same tubing and filter set. Note which filter blank was filtered before which water sample.

After all the samples have been processed in this way, the individual sample bottles will be stored in a lab refrigerator or freezer in the dark until they are either shipped to MLML or transported to Bryte Lab.

DWR staff will preserve the MeHg samples within 48 hours of collection with HCl following the "Methylmercury Sample Preservation SOP" found in Appendix D. Bryte Lab will preserve the THg samples with BrCl within 28 days of collection.

Appendix C
Standard Operating Procedure
Flow-Weighted Compositing

Department of Water Resources
Originated by: Petra Lee and Julianna Manning
February 6, 2015

1. Scope and Application

Hourly water samples will be collected over the course of a 25-hour mixed semi-diurnal tidal cycle, meaning sample depth will vary depending on tide and the design of the sample intake float. To reduce the number of total mercury (THg) and methylmercury (MeHg) samples that DWR must have analyzed, we will be physically compositing samples using flow data, tides, and a flow-weighting technique. To composite the THg and MeHg samples using flow data, DWR will use the flow data and calculate flow weighted composites using the compositing recipe worksheet. This Standard Operating Procedure will describe how staff will manually flow-weight composite the hourly water samples.

2. Summary of Method

Autosamplers will collect 25 hourly samples into 25 separate sample bottles. Using a flow weighted calculation, samples will be proportionally dispersed from the 25 samples bottles into ebb and flood samples using flow data that has been collected simultaneously. Samples will be measured by mass. See the Monitoring Plan for more details.

3. Contamination and Interferences

Because of the low concentration of THg and MeHg that are being measured, and the ubiquitous nature of low concentrations of mercury in the environment, sample contamination is a very real and problematic possibility. During the procedures discussed in this SOP, samples can become contaminated by the sample bottles, processing equipment, and through dirt and dust in the air.

Please be diligent and use the utmost care to minimize contamination when following the procedures described in this SOP. We will be using the “clean hands-dirty hands” method while compositing samples for THg and MeHg analyses. While following this methodology, remember that the clean hands person only touches the following, but nothing besides these items:

- The inner bag of a double-bagged 4 L bottle;
- The 4 L sample bottle;
- The acid-cleaned PTFE funnel;

- The acid-cleaned 50 or 100 mL beaker and;
- Anything else that comes in direct contact with the water sample

The dirty hands person handles everything else but does not touch any of the clean hand's items listed above. If at any point something occurs that you suspect will compromise the cleanliness of the polyethylene gloves worn by the clean hands personnel, replace those gloves with a clean pair immediately. Always change your gloves before working with a different water sample to prevent cross-contamination.

The lab where DWR staff will be compositing the samples must be free of dirt and dust as much as possible. The funnels and small beakers will be cleaned by DWR staff as described in the "Autosampler, Accessory, and Bottle Cleaning SOP" in Appendix A.

Some of the mercury in a water sample is associated with particulates which can settle rapidly. In addition, mercury can stick to the glass of a sample container. Therefore, samples in the autosampler bottles must be mixed as well as possible when pouring the sample into the containers used for compositing.

4. Safety

This procedure involves working with heavy glass bottles which can easily break under impact with hard surfaces. Please use caution when working with glass, especially when the glass bottles are heavy, and the outside is wet.

Since these procedures involve pouring water from one bottle to another, please be aware of water spilling on the lab floor as it may be slippery. Clean up water spills when convenient to minimize slipping hazards.

5. Apparatus and Materials

- Scale with 1 gram resolution and greater than 12 pound maximum
- Autosampler bottles containing individual water samples
- Composite bottle, generally an acid cleaned amber 4 L bottle
- Polyethylene and/or nitrile gloves that are stored inside a resealable plastic bag
- Acid-cleaned PTFE funnel
- Acid-cleaned 50 mL and/or 100 mL glass beaker
- Kim wipes
- Compositing recipe

6. Detailed Procedures

6.1 Compositing Setup

1. Calculate mass of water to take from each bottle using flow data. This flow weighted composite will be called the "compositing recipe". Composite samples in chronological order (Hour 1, Hour 2, etc.).

2. Turn on scale by pushing the On/Zero key. Make sure scale is level and that the scale is measuring in grams and is clean.

3. Handling of the samples should be done using the "clean hands-dirty hands" method.

4. Dirty hands will put on a pair of poly gloves and open the outer bag of an acid-cleaned 4 L composite bottle. Clean hands will put on a pair of nitrile gloves and will open inner resealable bag and remove composite bottle and place it onto scale.

Note: *The nitrile gloves give better grip on the heavy wet bottle and are a safer choice than the poly gloves.*

5. Clean hands will unscrew the lid of composite bottle and with assistance from dirty hands, will place lid into the resealable inner bag. Clean hands will push bag inside of outer bag. Dirty hands can seal outside bag and place bags aside.

6. Dirty hands will open resealable bag with acid-cleaned Teflon funnel. Clean hands will remove one funnel from the bag and place it into the mouth of the composite bottle. Dirty hands can seal the bag and place aside.

7. Dirty hands will open bag with the acid-cleaned beaker (50 or 100mL, though 100mL is preferred) and clean hands will remove beaker from bag and hold it until dirty hands splits open beaker bag and places inner portion face up for a resting spot. Clean hands will place beaker on resting spot.

8. Dirty hands will tare scale by pressing the Tare button.

6.2 Initial Rinsing of Equipment

1. Dirty hands will open bag of first autosampler bottle and remove bottle from bag and begin shaking bottle for a minimum of 1 minute to mix contents well. If necessary, dirty hands may rinse outside of the autosampler bottle with type 2 water to rinse off dirt or debris. Clean hands will grab funnel and beaker and hold over sink.

2. Dirty hands will pour sample water over beaker, while clean hands makes sure beaker gets thoroughly rinsed, inside and out at least three times.

3. Once the beaker is rinsed, dirty hands will pour sample water into beaker and clean hands will use that water to rinse funnel at least three times, focusing on the inside cone and outer stem portions. Clean hands will gently shake excess water off funnel, and place rinsed funnel back into neck of composite bottle. Do not tare scale again; the rinse of the funnel only needs to be done with the initial sample in each group (each ebb or flood tide).

6.3 Pouring Each Autosampler Bottle

Note: *Keep autosampler bottle samples well mixed before and during compositing. Particles may settle quickly, so vigorously shake capped bottle between dispersals.* ***This is very important!***

1. You may do one of two things, depending on what is easier and the water level in the autosampler bottle. 1) Dirty hands will pour water from the autosampler bottle into the beaker and clean hands will pour that water into the composite bottle until it reaches the mass the compositing recipe calls for or 2) dirty hands will pour water from the autosampler bottle directly into the composite bottle until getting close to the mass called for by the composite recipe, then finish by using the beaker method in the first option. Be very careful as there's no turning back if you overfill. Error of ±0.5-1% is acceptable.

2. After pouring water into composite bottle, dirty hands will use a Kim Wipe to clean up any spilled water and drips on the scale and composite bottle. Be careful not to contaminate the sample water.

3. Once the mass is reached for that autosampler bottle, clean hands will place beaker on resting spot. Dirty hands will recap autosampler bottle, place back into labeled bag, then place back in the fridge.

4. Dirty hands will tare scale.

5. Dirty hands will open bag of the next autosampler bottle and remove bottle from bag and begin vigorously shaking bottle for a minimum of 1 minute to mix contents well. If necessary, dirty hands may rinse outside of the autosampler bottle with type 2 water to rinse off dirt or debris.

6. Clean hands will hold small beaker over sink. Dirty hands will pour well mixed water from the autosampler bottle over beaker, while clean hands makes sure beaker gets thoroughly rinsed, inside and out just once. Repeat steps #1-4.

7. Repeat steps #5-6 until finished with each autosampler bottle in the ebb or flood composite.

6.4 After Pouring All Autosampler Bottles in Compositing Set

1. Clean or dirty hands will remove the funnel from the composite bottle. The funnel and beaker can now be placed in the dirty glassware/equipment bin.

2. Dirty hands will open the outer bag for the 4L composite sample bottle. Clean hands will open inner bag, remove the composite bottle cap and screw onto composite bottle.

3. Clean hands will place composite bottle into inner bag with help from dirty hands. Clean hands will seal inner bag, and dirty hands will seal outer bag, label bag appropriately with sample ID and date, then place composite sample bottle into a fridge until sample is dispersed. See the "Sample Filtering and Splitting SOP" in Appendix B for those procedures.

Appendix D
Standard Operating Procedure
Methylmercury Sample Preservation

Department of Water Resources
Originated by: Petra Lee and Julianna Manning
February 5, 2015

1. Scope and Application

This SOP outlines the procedure in which DWR staff will preserve 250mL Methylmercury (MeHg) water samples with concentrated (12N) Hydrochloric acid (HCl).

2. Summary of Method

MeHg water samples will be collected and must be preserved to 0.5% hydrochloric acid (HCl) within 48 hours of collection. Water samples will be in 250mL acid-cleaned doubled bagged bottle, so 1.25mL of concentrated HCl will be added to reach a 0.5% solution.

3. Contamination and Interferences

Preventing water samples from mercury contamination during the preservation process is paramount. During the procedures discussed in this SOP, samples can become contaminated by staff mishandling, preservation equipment, and through dirt and dust in the air. Sample hold time is 48 hours and must be adhered to.

Please be diligent and use the utmost care to minimize contamination when following the procedures described in this SOP. We will be using the “clean hands-dirty hands” method while preserving samples for MeHg analyses. While following this methodology, remember that the clean hands person only touches the following, but nothing besides these items:

- The inner bag of a double-bagged container;
- The 250 mL sample bottles;
- The Teflon bottles filled with HCl and;
- Anything else that comes in direct contact with the water sample

The dirty hands person handles everything else but does not touch any of the clean hand’s items listed above. If at any point something occurs that you suspect will compromise the cleanliness of the polyethylene gloves worn by the clean hands personnel, replace those gloves with a clean pair immediately.

The lab and hood where we will be preserving the samples must be free of dirt and dust as much as possible.

Unless samples are actively being preserved, they should be kept cold and in a dark place as much as possible to prevent degradation.

4. Safety

This procedure involves working with glass bottles which can easily break under impact with hard surfaces. Please use caution when working with glass, especially when the glass bottles are heavy and the outside is wet.

This procedure also involves working with concentrated HCl, so precautions, such as protective gear, should be used. Staff should read the Bryte Laboratory Safety Manual and read and sign any relevant safety documents before working with acid.

5. Apparatus and Materials

- Hydrochloric Acid (HCl), Baker Analyzed, 12N, VWR Part #JT9535-3
    - One Teflon bottle filled with HCl, labeled “for preservation”
    - One Teflon bottle filled with HCl, labeled “for rinsing”
- Pipette adjusted to 1.25mL and tips
- 2 or 4L bottle filled with baking soda saturated water for acid neutralization
- Safety gear: lab coats, eye protection, PVC aprons, and nitrile and polyethylene gloves
- Methylmercury samples to be preserved
- A large plastic resealable bag
- Permanent marker

6. Detailed Procedures

6.1 Roles of Personnel

Ideally, three people should be involved in sample preservation. One person will handle the outer bags of the acid bottles, the pipette and tips, and will dispense acid and will be referred to as the “acid dispenser”. A second person will be clean hands and will handle the inner bag and bottles of the sample and acid. A third person will be dirty hands and will handle only the outer bags of the sample, as well as anything else that needs to be moved or used. However, two people can complete sample preservation with one person acting as clean hands and one person acting as both dirty hands and acid dispenser at the same time.

6.2 Preservation Setup

1. All preservation will be done in a fume hood. Turn on the lights, the air flow, and place bottle with baking soda and water into the sink for acid neutralization.

2. Wearing all appropriate protective gear, rip the large resealable bag open at the seams, not touching the inside, and lay it down inside the hood. The inside should be exposed and facing up towards the work area. Do all further work using this clean surface.

3. The acid dispenser, wearing protective gear and clean nitrile gloves, will put a pipette tip onto the pipette without touching the tip.

4. The acid dispenser will hold the outer bag of the acid to be used for rinsing and the clean hands person, who is wearing clean nitrile gloves, will open the inner bag and remove the bottle of acid. Clean hands will push the inner bag slightly inside of the outer bag to protect it, and the acid dispenser will put both bags aside. Clean hands will open the bottle and place it on the clean surface in a position that the acid dispenser can reach the bottle with the pipette.

5. The acid dispenser will then open the baking soda and water filled acid neutralization container and use the pipette (set to 1.25mL) to draw up acid and dispose of it in the acid neutralization container. The acid dispenser will do this three times, which will clean the pipette tip of any MeHg containing residues.

6. The acid dispenser and clean hands will put the bottle back into the inner bag, seal the inner bag, seal the outer bag, and place aside.

7. Repeat step #4 for the bottle of acid used for preservation.

6.3 Sample Preservation

1. Dirty hands will open the outer bag of the MeHg sample. Clean hands will open the inner bag and remove the sample bottle.

2. Clean hands will open the sample bottle in the hood and the acid dispenser will carefully add 1.25mL of acid to the sample.

3. Clean hands will cap the bottle, invert it, open the cap slightly again inside the hood to release any gasses, and then close the cap completely to seal the bottle.

4. Clean hands will place the bottle back into inner bag with dirty hands' help and will seal the inner bag.

5. Dirty hands will seal the outer bag and write "P" on the outer bag for preserved, using a permanent marker. Dirty hands will place bags and bottle aside, being careful not to mix the preserved samples with unpreserved samples.

6. Repeat steps #1-5 until all MeHg samples are preserved.

6.4 Clean Up and Acid Disposal

1. After all samples have been preserved, the acid dispenser will neutralize the pipette tip by drawing the baking soda and water solution into the pipette tip three times, and then expel the tip into the acid neutralization container. The acid dispenser may need to carefully push the tip into the water with a gloved finger.

2. The acid dispenser and clean hands can then work together to put the preservation acid bottle back into the inner and outer bags and seal them.

3. Clean up the hood and neutralize any acid that may have spilled. After acid is neutralized and diluted, it may be poured down the sink with plenty of tap water, and the pipette tip may be thrown away.

Appendix E
Standard Operating Procedure
Filtering Chlorophyll Samples

Department of Water Resources
Originated by: David Bosworth and Petra Lee
November 27, 2013

1. Scope and Application

This SOP describes the techniques that DWR staff will use to filter water samples collected in an HDPE bottle from the field to then be analyzed for chlorophyll *a*. See the Monitoring Plan for field collection procedures.

2. Summary of Method

DWR staff will transport samples collected in HDPE bottles back to our lab on wet ice. Depending on the turbidity of the sample, 100-500 mL of the sample will be filtered through a 1.0 µm glass-fiber filter using a vacuum pump set with a pressure between 7-10 inches of Hg. After the aliquot is completely passed through the filter, the filter is folded in half with the filtered-side facing inside, removed from the filter manifold, and placed into a pre-labeled manila envelope. The envelope containing the filter is labeled with the volume filter, then immediately placed into the lab freezer.

3. Contamination and Interferences

To prevent photodecomposition of chlorophyll *a*, keep samples in a cold and dark environment until filtering. The filtering procedure should also be carried out in subdued light. Samples should be filtered on the same day as they were collected or within 24 hours from collection if filtering on the same day is not possible. Water samples will be treated with an $MgCO_3$ solution during filtration to eliminate transformation of chlorophyll to its degradation product, pheophytin. Do not allow the vacuum pump to exceed a pressure of 10 inches of Hg at any time while filtering to prevent the rupture of phytoplankton cells.

4. Safety

Since these procedures involve pouring water into volumetric flasks or graduated cylinders and running water through filters, please be aware of water spilling on the lab floor as it may be slippery. Clean up water spills when convenient to minimize slipping hazards.

5. Apparatus and Materials

- Three-port vacuum manifold with plastic filter funnels
- Millipore vacuum pump with two 1-L flasks
- Whatman 47 mm glass-fiber filters with a 1.0 µm pore size
- One 500 mL volumetric flask or graduated cylinder
- Blunt filter forceps
- One 500 mL plastic squirt bottle with Deionized (DI) water
- One 500 mL plastic squirt bottle with a saturated $MgCO_3$ solution made with Type 2 water and $MgCO_3$ powder
- Waste bucket or sink for rinse water
- Manila envelopes pre-labeled with waterproof labels
- Permanent marker to write sample volume on the envelopes

6. Detailed Procedures

6.1 Lab Work Bench Setup

1. Set out the chlorophyll filtering set up, which includes the vacuum manifold and Millipore vacuum pump. Insert the rubber stopper from the 1 L flask that is not attached to the pump into the opening of the 1 L flask that is attached to the pump. Then insert the rubber stopper from the vacuum manifold into the opening of the 1 L flask that is not attached to the pump.

2. Inspect the filter funnels, their platforms, and the volumetric flask or graduated cylinder to make sure that they are clean. If not, rinse them with Type 2 water a few times.

6.2 Filtering the Water Sample Through the Filtering Apparatus

1. Using blunt forceps, place one 1.0 µm glass-fiber filter with the rough side facing downwards on a filter funnel platform. Attach the filter funnel and check to see that it is seated correctly. Open the appropriate filter manifold valve.

2. Shake the HDPE container containing the chlorophyll water thoroughly. Pour approximately 15 mL of sample water into the clean volumetric flask or graduated cylinder and shake the flask to rinse its inside surface with sample water. Pour the rinsate into the waste bucket or sink and rinse the volumetric flask two more times following the same procedure.

3. After rinsing the volumetric flask or graduated cylinder three times, pour and measure 100-500 mL of the sample water in the flask or cylinder. Make sure that the bottom of the meniscus lines up with the etched line. Pour the contents of the volumetric flask or graduated cylinder into the prepared filter funnel and add 1-2 mL of the $MgCO_3$ solution from the squirt bottle to the water sample.

4. Turn on the Millipore vacuum pump and set the pressure between 7-10 inches of Hg. Turn the pressure adjustment knob on the pump to change the pressure if necessary. As mentioned above, do not allow the vacuum pump to exceed 10 inches of Hg at any time while filtering.

5. Open the valve on the filter manifold and filter the sample water through the glass fiber filter, using vacuum suction. While the sample is passing through the filter, rinse the volumetric flask or graduated cylinder three times with DI water from the squirt bottle, and pour the contents into the filter funnel.

6. When most of the sample water has passed through the filter, rinse the inside of the filter funnel with DI water from the squirt bottle. Continue to run the vacuum pump to allow all the sample water to pass through the filter and to allow the filter to dry. When the filter is mostly dry remove the filter funnel.

7. With the vacuum pump running and using forceps, remove the filter by its edge, and fold the filter in half with the filtered-side inside. Take care to not touch the pigments with the forceps and avoid touching the filter paper with your fingers. Turn off the vacuum pump.

8. Insert the folded filter into the appropriate pre-labeled envelope and record the volume of the water filtered on the envelope with a permanent marker. Place the envelope with the filter in the laboratory freezer immediately.

9. The filtering process for this sample is now finished. Discard the remaining sample water from the HDPE container, and recycle the bottle. Before using the filter funnel for a new water sample, rinse it out with tap water and DI water. Rinse the volumetric flask or graduated cylinder a couple times with DI water before using it to measure another water sample.

6.3 Additional Steps

Repeat the chlorophyll filtering procedures described above for the remainder of the water samples using a new glass fiber filter for each sample. Samples with higher turbidity will take longer to filter, so a smaller volume of sample can be used. If a sample is taking a while to filter, it is possible to run multiple samples on the vacuum manifold at the same time. Keep the envelopes with the filters in the laboratory freezer until they are transported to Bryte Lab. Transport the envelopes in a cooler with wet ice to Bryte Lab within one week of collection.

Appendix F

Sampling and Processing Forms

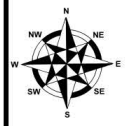
Figure F1 – Autosampler Field Sheet

Tidal Wetlands Autosampler Field Sheet

Sampling Location:_____Date:_____

Sampling Event:_____Personnel:_____

Weather/Water Conditions

Sky	Air Temperature	Rain	Precipitation (last 24 hrs)	Wind Conditions	Wind Direction	Tidal Cycle (if applicable)	Water Color	Water Odor
Clear/Sunny	Cold	None	None	None		Ebb	Colorless	None
Partly Cloudy	Cool	Light	<0.5"	Light Breeze		Slack (high)	Green	Sulfides
Hazy	Mild	Medium	0.5-1.5"	Windy		Slack (low)	Yellow	Sewage
Overcast	Warm	Heavy	>1.5"	Very Windy		Flood	Brown	Petroleum
Fog	Hot		Unknown	Gale				Other:_____

Autosampler Notes:

Grab Sample Notes:

Other Notes:

Figure F2 – Water Quality Collection Field Records, Old and New

Old

FIELD RECORD

CA Dept. of Water Resources

Division of Environmental Services, Mercury Monitoring and Evaluations Section

Station: _____ Date: _____ /_____ /_____ Time: _____:_____ (PST)

Performed by: _____ Sonde Removal Time: _____:_____ (PST)

Weather/Water Conditions

Sky	Rain	Air Temp.	Precipitation (last 24 hrs)	Wind Conditions	Wind Direction	Flow Direction	Water Clarity	Water Color	Overland Runoff (last 24 hrs)
Clear/Sunny	None	Cold	None	None	N	Downstream	Clear (see bed)	Colorless	None
Partly Cloudy	Light	Cool	<1"	Light Breeze	NW NE	Slack Tide	Cloudy (>4" vis)	Blue	Light
Hazy	Medium	Mild	>1"	Windy	W E	Upstream	Murky (<4" vis)	Green	Moderate
Overcast	Heavy	Warm	Unknown	Very Windy	SW SE			Yellow	Heavy
Fog		Hot		Gale	S			Brown	Unknown

Hand-Held and Sonde Data

Field Instrument IDs:

YSI 63: _____

HACH 2100P: _____

YSI ProODO: _____

Removed Probe/Sensor ID's:

Conductivity/Temperature: _____

Turbidity: _____

Chlorophyll: _____

(1) Hand-Held Data* At depth: _____ (m)	**(2) Sonde Data**	**Total Deviation (= 2 - 1)**
_____:_____ Time (PST)	_____:_____ Time (PST)	
_____ Water Temperature (°C)	_____ Water Temperature (°C)	+ / - _____ (°C)
_____ Specific Conductivity (µS/cm)	_____ Specific Conductivity (µS/cm)	+ / - _____ (µS/cm)
_____ Dissolved Oxygen (mg/L)	_____ Dissolved Oxygen (mg/L)	+ / - _____ (mg/L)
_____ Dissolved Oxygen (%)	_____ Dissolved Oxygen (%)	+ / - _____ (%)
_____ pH (units)	_____ pH (units)	+ / - _____ (units)
_____ Turbidity (NTU)	_____ Turbidity (NTU)	+ / - _____ (NTU)
_____ Salinity (ppt)	_____ Salinity (ppt)	

*Water samples should be collected near sonde depth, either at 1 meter (~3 feet) below the surface or 0.15 m in surface water 1 meter in depth

Biofouling: (very heavy) 7 6 5 4 3 2 1 (minimal/none)

Additional Samples Collected? If Yes, Please Specify: _____

Notes:

New

FIELD RECORD

CA Dept. of Water Resources

Division of Environmental Services, Mercury Monitoring and Evaluation Section

Station: _____ Date: _____ /_____ /_____

Performed by: _____ Arrival Time: _____:_____ (PST)

Weather/Water Conditions

Sky	Rain	Air Temp.	Precipitation (last 24 hrs)	Wind Conditions	Wind Direction	Flow Direction	Water Clarity	Water Color	Overland Runoff (last 24 hrs)
Clear/Sunny	None	Cold	None	None		Downstream	Clear (see bed)	Colorless	None
Partly Cloudy	Light	Cool	<1"	Light Breeze		Slack Tide	Cloudy (>4" vis)	Blue	Light
Hazy	Medium	Mild	>1"	Windy		Upstream	Murky (<4" vis)	Green	Moderate
Overcast	Heavy	Warm	Unknown	Very Windy				Yellow	Heavy
Fog		Hot		Gale				Brown	Unknown

Sonde Data

Sonde IDs:

Verification Sonde: _____

Replacement Sonde: _____

Sonde Removed: _____

Removal Details:

Sonde Removal Time: _____:_____ (PST)

Sonde Replacement Time: _____:_____ (PST)

Biofouling: (very heavy) 7 6 5 4 3 2 1 (minimal/none)

(1) Before Cleaning* At depth: _____ (m)	(2) After Cleaning	(3) Sonde Data	Total Deviation (= 3 - 1)
_____:_____ Time (PST)	_____:_____ (PST)	_____:_____ (PST)	
_____ Water Temperature (°C)	_____ (°C)	_____ (°C)	+ / - _____ (°C)
_____ Specific Conductivity (µS/cm)	_____ (µS/cm)	_____ (µS/cm)	+ / - _____ (µS/cm)
_____ Dissolved Oxygen (mg/L)	_____ (mg/L)	_____ (mg/L)	+ / - _____ (mg/L)
_____ Dissolved Oxygen (% sat)	_____ (% sat)	_____ (% sat)	+ / - _____ (% sat)
_____ Chlorophyll (µg/L)	_____ (µg/L)	_____ (µg/L)	+ / - _____ (µg/L)
_____ Turbidity (NTU)	_____ (NTU)	_____ (NTU)	+ / - _____ (NTU)
_____ Salinity (ppt)	_____ (ppt)	_____ (ppt)	

*Water samples should be collected near sonde depth, either at 1 meter below the surface or 0.15 m in surface water 1 meter in depth

Additional Samples Collected? If Yes, Please Specify: _____ Time: _____:_____ (PST)

Notes:

Figure F3 – Sonde Pre-Deployment Record

PRE-DEPLOYMENT RECORD: Maintenance and Calibration

CA Dept. of Water Resources

Division of Environmental Services, Mercury Monitoring and Evaluations Section

Station Name: _____

1. Probe/Sensor Maintenance and Calibration

Date: _____ /_____ /_____

Performed by: _____

Probe/Sensors Cleaned? Y / N

Probe/Sensor ID's:

Conductivity/Temperature: _____

Turbidity: _____

Chlorophyll: _____

Calibration-

Parameter	Before	Standard	After
Conductivity (µS/cm)		2767	
Chlorophyll (µg/L)		0.0	
Turbidity (NTU) 2-point - DI Std		0.0	
Turbidity (NTU) 2-point - High Std			

Cal Constant: _____

Temperature Accuracy Check-

Thermometer: _____ (°C)

Probe: _____ (°C)

Accuracy Verified? Y / N

Calibration and Maintenance Notes:

2. Sonde Maintenance and Logging (performed in the field)

Maintenance-

Date: _____ /_____ /_____

Performed by: _____

Sonde Body Cleaned? Y / N

Central Wiper Cleaned? Y / N

Central Wiper Parked Correctly? Y / N

Batteries Changed? Y / N

Battery Voltage: _____

Clock Checked/Set (PST) Correctly? Y / N

Logging-

File: _____

Logging Start Date & Time: ____/____/_____ ____:____ (PST)

Deployment Date & Time: ____/____/_____ ____:____ (PST)

Logging Active? Y / N

Sample Interval: 00: :00

SDI-12 Address: _____ ☐

Sample & Hold? Y / N ☐

Sonde Maintenance and Logging Notes:

Figure F4 – Sonde Post-Deployment Calibration Check Record

POST-DEPLOYMENT: Calibration Check Record

Sonde ID #: _____

CA Dept. of Water Resources

Division of Environmental Services, Mercury Monitoring and Evaluations Section

Laboratory Calibration Check

Location Removed From: _____ Biofouling: 7 6 5 4 3 2 1

Date Removed: _____ /_____ /_____ Time Removed: ____:____ (PST)

Date of Calibration Check: _____ /_____ /_____ Time of Calibration Check: ____:____ (PST)

1	2	3	4	5	6	7
Standard	**Sonde (pre-cleaning)**	**Total Deviation (= 2 - 1)**	**Ratings (Circle One for Each Constituent)**			
			Excellent	**Good**	**Fair**	**Poor**
***DO:** _____	_____ (% sat.)	+ / - _____ (% sat.)	≤ ± 3.0% sat.	> ± 3-6% sat.	> ± 6-10% sat.	> ± 10% sat.
EC: 2767	_____ (µS/cm)	+ / - _____ (µS/cm)	≤ ± 27 µS/cm	> ± 27-55 µS/cm	> ± 55-138 µS/cm	> ± 138 µS/cm
****pH:** 7.0	_____ (units)	+ / - _____ (units)	≤ ± 0.20 units	> ± 0.20-0.30 units	> ± 0.30-0.40 units	> ± 0.40 units
****pH:** 10.0	_____ (units)	+ / - _____ (units)	≤ ± 0.20 units	> ± 0.20-0.30 units	> ± 0.30-0.40 units	> ± 0.40 units
Turbidity: 0.3	_____ (NTU)	+ / - _____ (NTU)	≤ ± 2.0 NTU	> ± 2.0-3.0 NTU	> ± 3.0-4.0 NTU	> ± 4.0 NTU
Turbidity: _____	_____ (NTU)	+ / - _____ (NTU)	≤ ± 5.0 NTU	> ± 5.0-10.0 NTU	> ± 10.0-15.0 NTU	> ± 15.0 NTU
Chlorophyll: 0.0	_____ (µg/L)	+ / - _____ (µg/L)	≤ ± 2.0 µg/L	> ± 2.0-3.0 µg/L	> ± 3.0-4.0 µg/L	> ± 4.0 µg/L
Temperature: Therm: _____	Sonde: _____	+ / - _____ (°C)	≤ ± 0.2 °C	> ± 0.2-0.3 °C	> ± 0.3-0.4 °C	> ± 0.4 °C

***DO% Calculation:** DO%=100*Local Barometric Pressure/760

DO Charge: _____ (units)

Battery: _____ (V)

	8	9	10	11
	Sonde (post-cleaning)	**Drift (= 8- 1)**	**Fouling (= 2 - 8)**	**Shift (if [9] > [4] = 3, else = 10)**
****pH probe post-cal check**	DO: _____	_____	_____	+ / - _____ (% sat.)
pH 7 (mV): _____ (0 mV ideal)	EC: _____	_____	_____	+ / - _____ (µS/cm)
pH 10 (mV): _____ (-180 mV ideal)	pH: _____	_____	_____	+ / - _____ (units)
	pH: _____	_____	_____	+ / - _____ (units)
Slope (pH 7 mV - pH 10 mV): _____	Turbidity: _____	_____	_____	+ / - _____ (NTU)
(Take pH probe out of service, if slope < 160)	Turbidity: _____	_____	_____	+ / - _____ (NTU)
(Range 165 to 180, 177 ideal)	Chlorophyll: _____	_____	_____	+ / - _____ (µg/L)

NOTES:				Excellent	Good	Fair	Poor
An estimate of post-cal ratings in mg/L based on the DO saturation categories (i.e. > ± 3-6% sat. ~ > ± 0.3-0.5 mg/L)			DO	≤ ± 0.3 mg/L	> ± 0.3-0.5 mg/L	> ± 0.5-0.8 mg/L	> ± 0.8 mg/L
Percent difference of post calibration specific conductance value from a given standard			EC	≤ ± 1%	> ± 1-2%	> ± 2-5%	> ± 5%
Max allowable limits	DO ± 10% sat.	EC (2767) ± 277 µS/cm (10%)	pH ± 0.80 pH units		Turb. 0.3 NTU std: ± 6 NTU	Turb. ~100 NTU std: ± 15%	Chlorophyll ± 6.0 µg/L

Figure F5 – Filtering Notes for Hourly Samples and Composited Samples

Hourly Samples

Filtering Notes

Sampling Location:_____Sampling Dates:_____

Sampling Event:_____

	Date Sample Processed	Time Began Filtering	Filtering Team	Notes (incl blanks, reps, etc.)
Hour 1				
Hour 2				
Hour 3				
Hour 4				
Hour 5				
Hour 6				
Hour 7				
Hour 8				
Hour 9				
Hour 10				
Hour 11				
Hour 12				
Hour 13				
Hour 14				
Hour 15				
Hour 16				
Hour 17				
Hour 18				
Hour 19				
Hour 20				
Hour 21				
Hour 22				
Hour 23				
Hour 24				
Hour 25				
Ebb 1 Comp.				
Ebb 2 Comp.				
Flood 1 Comp.				
Flood 2 Comp.				

Composited Samples

Filtering Notes

Sampling Location:_____Sampling Dates:_____

Sampling Event:_____

	Date Sample Processed	Time Began Filtering	Filtering Team	Notes (incl blanks, reps, etc.)
Hour				
Hour Dup				
Ebb 1 Comp.				
Ebb 2 Comp.				
Flood 1 Comp.				
Flood 2 Comp.				
Notes:				

Figure F6 – Compositing Notes

Compositing Notes

attach to print-out of composite recipe

Sampling Location:_____ Sampling Dates:_____

Sampling Event:_____

Tidal Cycle: Ebb Flood 1 2 3 Samples Composite (circle tides & sample #s)

Date Composited:_____ 1 2 3 4 5 6 7 8 9 10 11 12 13

Time Composited Began:_____ 14 15 16 17 18 19 20 21 22 23 24 25

Time Composited Ended:_____ Sample Notes:

Tidal Cycle: Ebb Flood 1 2 3 Samples Composite (circle tides & sample #s)

Date Composited:_____ 1 2 3 4 5 6 7 8 9 10 11 12 13

Time Composited Began:_____ 14 15 16 17 18 19 20 21 22 23 24 25

Time Composited Ended:_____ Sample Notes:

Tidal Cycle: Ebb Flood 1 2 3 Samples Composite (circle tides & sample #s)

Date Composited:_____ 1 2 3 4 5 6 7 8 9 10 11 12 13

Time Composited Began:_____ 14 15 16 17 18 19 20 21 22 23 24 25

Time Composited Ended:_____ Sample Notes:

Tidal Cycle: Ebb Flood 1 2 3 Samples Composite (circle tides & sample #s)

Date Composited:_____ 1 2 3 4 5 6 7 8 9 10 11 12 13

Time Composited Began:_____ 14 15 16 17 18 19 20 21 22 23 24 25

Time Composited Ended:_____ Sample Notes:

Tidal Cycle: Ebb Flood 1 2 3 Samples Composite (circle tides & sample #s)

Date Composited:_____ 1 2 3 4 5 6 7 8 9 10 11 12 13

Time Composited Began:_____ 14 15 16 17 18 19 20 21 22 23 24 25

Time Composited Ended:_____ Sample Notes:

Other Notes:

Figure F7 – Example Compositing Recipe

Tidal Cycle:	Ebb Tide 1			
Bottle #	Collection Time	Flow (cfs)	Proportion of Total Flow during Tidal Cycle	Weight of subsample required (g)
1	2/6/2018 12:00	68.0	0.377	1507
2	2/6/2018 13:00	51.0	0.283	1130
3	2/6/2018 14:00	30.0	0.166	665
4	2/6/2018 15:00	18.0	0.100	399
5	2/6/2018 16:00	10.0	0.055	222
6	2/6/2018 17:00	3.5	0.019	78

Tidal Cycle:	Flood Tide 1			
Bottle #	Collection Time	Flow (cfs)	Proportion of Total Flow during Tidal Cycle	Weight of subsample required (g)
7	2/6/2018 18:00	-3.2	0.061	243
8	2/6/2018 19:00	-8.4	0.160	639
9	2/6/2018 20:00	-10.0	0.190	760
10	2/6/2018 21:00	-19.0	0.361	1445
11	2/6/2018 22:00	-12.0	0.228	913

Tidal Cycle:	Ebb Tide 2			
Bottle #	Collection Time	Flow (cfs)	Proportion of Total Flow during Tidal Cycle	Weight of subsample required (g)
12	2/6/2018 23:00	22.0	0.239	958
13	2/7/2018 0:00	27.0	0.294	1175
14	2/7/2018 1:00	18.0	0.196	783
15	2/7/2018 2:00	12.0	0.131	522
16	2/7/2018 3:00	9.0	0.098	392
17	2/7/2018 4:00	3.9	0.042	170

Tidal Cycle:	Flood Tide 2			
Bottle #	Collection Time	Flow (cfs)	Proportion of Total Flow during Tidal Cycle	Weight of subsample required (g)
18	2/7/2018 5:00	-1.0	0.006	23
19	2/7/2018 6:00	-9.6	0.056	225
20	2/7/2018 7:00	-15.0	0.088	352
21	2/7/2018 8:00	-32.0	0.188	750
22	2/7/2018 9:00	-44.0	0.258	1032
23	2/7/2018 10:00	-52.0	0.305	1219
24	2/7/2018 11:00	-17.0	0.100	399

Appendix G
Chain of Custodies

Figure G1 – Example of Moss Landing Marine Laboratories Chain of Custody

MPSL REQUEST FOR ANALYSIS AND CHAIN OF CUSTODY RECORD Page 1 of 1

Sampler	Phone	Send Results To	Phone
Julianna Manning DWR	916-376-9816	same	
Address: 3500 Industrial Blvd. 2nd Floor		Address	
City: West Sacramento	State: CA	Zip: 95691	City / State / Zip
		Email: julianna.manning@water.ca.gov	
Date Required/Reason: 60 days turn around			

Sample Identification/Location (Draw map on separate sheet if necessary)		Collection			Total/Unfiltered				Dissolved/Filtered									Sample Type			# of Containers			Preservation		
DWR Sample Code	Station Name	Date	Time (PST)	Salinity (ppt)	Trace Elements (Specify Below)	Total Hg	Total MMHg	Total Boron	Diss Trace Elements (Specify Below)	Diss Hg	Diss MMHg	Diss Boron	SSC	TSS	Chl-a	Pesticides (Specify Below)		Water	Soil	Tissue	Plastic	Glass	VOA Vial	Temp	Acid	
EH0814B0493	Ebb 1 Total	8/11/2014	12:30				x											x				1		x	x	
EH0814B0493	Ebb 1 Dissolved	8/11/2014	12:30								x							x				1		x	x	
EH0814B0494	Ebb 2 Total	8/11/2014	21:30				x											x				1		x	x	
EH0814B0494	Ebb 2 Dissolved	8/11/2014	21:30								x							x				1		x	x	
EH0814B0495	Flood 1 Total	8/11/2014	15:30				x											x				1		x	x	
EH0814B0495	Flood 1 Dissolved	8/11/2014	15:30								x							x				1		x	x	
EH0814B0496	Flood 2 Total	8/11/2014	3:30				x											x				1		x	x	
EH0814B0496	Flood 2 Dissolved	8/11/2014	3:30								x							x				1		x	x	
EH0814B0497	Trip Blank	8/11/2014	9:00				x											x				1		x	x	
EH0814B0498	Filter Blank	8/11/2014	9:00								x							x				1		x	x	
EH0814B0499	Ebb 1 Duplicate	8/11/2014	12:30								x							x				1		x	x	
EH0814B0500	Flood 2 Duplicate	8/11/2014	3:00				x											x				1		x	x	
EH0814B0515	Bottle Blank	8/5/2014	13:30				x											x				1		x	x	
EH0814B0516	Tubing Blank	8/5/2014	13:30				x											x				1		x	x	

Project Name: DWR Tidal Wetland Study - Yolo Bypass August 2014

Specify Trace Elements

Comments/Special Instructions Please send us a scanned copy of the signed COC, return the ice chest to the above address, and include the DWR Sample Code with the results.

Samples Relinquished By (Signature)	Print Name	Date	Received By (Signature)	Print Name	Date
Julianna Manning	Julianna Manning	8-18-14	[illegible]	S. MacDonald	8/19/14 @ 5.2°c

Shipping Address: MPSL-Cleanlab, 7544 Sandholdt Road, Moss Landing CA 95039. Tel: 831-771-4158, Fax: 831-633-0805

Figure G2 – Example of Bryte Lab Chain of Custody

State of California **Department of Water Resources** **The Resources Agency**

Bryte Chemical Laboratory Chain of Custody

Submittal ID & Run/Submittal Name: EH0614B0020 - Tidal Wetlands Monthly Equipment Blanks Hg(T)

Container Summary

Glass, Clear, 250 ml		2
Bottle Check: Lab Initials: MC	Field Initials: DB	Total: 2

Send Report To: Petra Lee
3500 Industrial Blvd
2nd Floor

West Sacramento CA 95691
Activity Unit: 0313

Instructions to Lab:

Notice: Please deliver samples to the lab as soon as possible. Allow time for lab handling and preparation after delivery. The lab is not responsible for missed holding times due to late delivery. SEE YOUR LAB ANALYSIS GROUPS FOR MINIMUM SAMPLE HOLD TIME. Samples must be transported in accordance with method and handling requirements, on ice and arrive below 6°C if transported overnight.

Submitted By: Signature: [illegible] Date Relinquished: 6/19/14
Print Name: David Bosworth Phone Number: 916-376-9847

Received By: Signature: Marta Carroll Print Name Marilyn Carroll
Date and Time Received: 6/19/14 1540 Condition When Received: 9 °C Iced? Yes X No

Submittal ID: EH0614B0020

DWR Sample Number **EH0614B0369** Collection Date 6/~~20~~19/2014 Collection Time: 15:30 EC:
Station No.: (None) Station Name: (None) Matrix: Water, Purified
Add'l Note: Auto Sampler Bottle Pre-Sampling Cost Code: VMERCURY0SWP

Total Mercury		

DWR Sample Number **EH0614B0370** Collection Date 6/~~20~~19/2014 Collection Time: 14:30 EC:
Station No.: (None) Station Name: (None) Matrix: Water, Purified
Add'l Note: Auto Sampler Pre-Sampling Tubing Blank Cost Code: VMERCURY0SWP

Total Mercury		

Submittal ID: EH0614B0020 Page 1 of 2

Figure G3 – Example of Bryte Lab Checklist Included with Chain of Custody

Submittal ID: EH0614B0020

Check List for Sample Submittal by Field Personnel

- [ ] Correct collection dates and times are on the COC.
- [ ] An EC result per collection event has been written on the COC.
- [ ] The number of containers being submitted matches the container count on the COC.
- [ ] * Please correct the count if it is not the same and initial the appropriate area to confirm.
- [ ] Container label's DWR Sample Number matches what is on the COC .
- [ ] Samples/sites not collected are crossed out and clearly marked as not sampled "N.S." with your initials.
- [ ] Volumes for chlorophyll samples are written on either the label or the packet.
- [ ] The "Send Report To:" contact on the COC is correct.
- [ ] The "Submitted By:" signature, printed name and phone number are on the COC.
- [ ] Sample submittal date and time are on the COC.

Check List for Bryte Lab Sample Receiving Personnel

- [ ] Collection dates and times are on the COC for every sample.
- [ ] The EC for each collection event is written on the COC.
- [ ] The Priority Code for the submittal/samples is 5. If not, alert Bryte management prior to field personnel leaving.
- [ ] The container count matches COC.
- [ ] The container count has been initialed on COC by both parties to confirm.
- [ ] Sites that are not collected are crossed out and clearly marked as not sampled "N.S." with field personnel initials.
- [ ] Corresponding analyses for containers not collected are crossed out on the COC. (Not necessary for collection events crossed out, flagged "N.S." and initialed.)
- [ ] The COC includes additional analyses collected or replicate samples added in the field.
- [ ] The DWR Sample Number on the container labels matches the COC.
- [ ] UNFROZEN sample temperature is written on the COC.
- [ ] Write a note on the COC regarding analyses requiring freezing either "…received frozen" or "…received not frozen." (See examples below)
- [ ] * Example 1: Samples are requiring freezing are frozen OR received same day as collected - Write "Chlorophyll received frozen" on the COC.
- [ ] * Example 2: Samples are not frozen and received >48hrs from collection date - Write "Nutrients received not frozen" on the COC.
- [ ] The volume for chlorophyll samples are written on the packet or label.
- [ ] All EC's are in FLIMS before the project is submitted.
- [ ] Collection date and time in FLIMS matches the COC.

Submittal ID: EH0614B0020 Page 2 of 2

Appendix H
Method # MPSL-101
Sample Container Preparation for Organics and Trace Metals, Including Mercury and Methylmercury
Moss Landing Marine Laboratories

1.0 Scope and Application

1.1 This procedure describes the preparation of sample containers for the determination of synthetic organics and metals including but not limited to: aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), selenium (Se), silver (Ag) and zinc (Zn) in tissue, sediment and water.

2.0 Summary of Method

2.1 Teflon, polyethylene, glass containers, and collection implements are detergent and acid cleaned prior to contact with tissue, sediment or water samples. Pre-cleaned containers may be purchased from the manufacturer in some instances.

3.0 Interferences

3.1 Special care must be used in selecting the acid(s) used for cleaning. Only reagent grade, or better, acids should be used. Prior to use, all acids should be checked for contamination.

3.2 If samples are to be analyzed for mercury, only Teflon or glass/quartz containers with Teflon-lined caps may be used. Use of other plastics, especially linear polyethylene, will result in Hg contamination through gas-phase diffusion through the container walls.

3.3 Colored plastics should be avoided, as they sometimes contain metal compounds as dyes (i.e., cadmium sulfide for yellow, ferric oxide for brown, etc.).

4.0 Apparatus and Materials

4.1 Crew Wipers: Fisher Scientific Part # 06-666-12
4.2 Disposable Filter Units, 250 mL: Nalge Nunc Inc. Part # 157-0045
4.3 Garbage Bag, clear 30 gallon
4.4 Glass Bottle Class 100 Amber, 4 L: I-Chem Part # 145-4000
4.5 Glass Bottle Class 200 Environmentally Cleaned, 250 mL: I-Chem Part # 229-0250
4.6 Glass Bottle Trace Clean, 250 mL: VWR Part # 15900-130
4.7 Glass Jar Class 100, 125 mL: I-Chem Part # 120-0125 (for use only when class 200 or 300 are not available)
4.8 Glass Jar Class 100, 500 mL: I-Chem Part # 121-0500 (for use only when class 200 or 300 are not available)
4.9 Glass Jar Class 200 Environmentally Cleaned, 125 mL: I-Chem Part # 220-0125

4.10 Glass Jar Class 200 Environmentally Cleaned, 500 mL: I-Chem Part # 221-0500
4.11 Glass Jar Class 300 Environmentally Cleaned, 125 mL: I-Chem Part # 320-0125
4.12 Glass Jar Class 300 Environmentally Cleaned, 500 mL: I-Chem Part # 321-0500
4.13 Heavy Duty Aluminum Foil
4.14 Homogenization Jar: Büchi Analytical Part # 26441
4.15 Immersion Heater: VWR Part # 33897-208
4.16 Lab Coats
4.17 Non-metal Scrub Brush
4.18 Non-metal Bottle Brush
4.19 Nylon Cable Ties, 7/16” wide x 7” long
4.20 Masterflex C-flex Tubing: ColeParmer Part # 06424-24
4.21 Plastic Knife
4.22 Polyethylene Bin, 63 L
4.23 Polyethylene Bin with Lid, 14.5”x10.5”x3.25”: Cole Parmer Part # 06013-80
4.24 Polyethylene Bucket with Lid, medium: ColeParmer Part # 63530-12 and 63530-53
4.25 Polyethylene Bucket with Lid, small: ColeParmer Part # 63530-08 and 63530-52
4.26 Polyethylene Caps, 38mm-430: VWR Part # 16219-122
4.27 Polyethylene Gloves: VWR Part # 32915-166, 32915-188, and 32915-202
4.28 Polyethylene (HDPE) Bottle, 30 mL: Nalgene-Nunc, Inc. Part # 2089-0001
4.29 Polyethylene (HDPE) Bottle, 60 mL: Nalgene-Nunc, Inc. Part # 2089-0002
4.30 Polyethylene (HDPE) Jar, 30 mL: Nalgene-Nunc, Inc. Part # 2118-0001
4.31 Polyethylene (HDPE) Jar, 125 mL: Nalgene-Nunc, Inc. Part # 2118-0004
4.32 Polyethylene Scoop: VWR Part # 56920-400
4.33 Polypropylene Centrifuge Tubes, 15 mL: Fisher Scientific Part # 05-521
4.34 Polypropylene Cutter Tool: Büchi Analytical Part #24225
4.35 Polypropylene Diaphragm Seal: Büchi Analytical Part # 26900
4.36 Polypropylene “Snap Seal” Containers, 45 mL: Corning Part # 1730 2C
4.37 Polypropylene Spacer: Büchi Analytical Part # 26909
4.38 Precision Wipes: Fisher Scientific Part # 19-063-099
4.39 Sapphire Thermowell: CEM Part # 326280
4.40 Shoe covers: Cellucap Franklin Part # 28033
4.41 Steel Cutting Blade, Bottom: Büchi Analytical Part # 26907
4.42 Steel Cutting Blade, Top: Büchi Analytical Part # 26908
4.43 Syringe, 50 ml Luer Slip Norm-Ject: Air-Tite Part # A50
4.44 Teflon Centrifuge Tube, 30 mL: Nalge Nunc, Inc. Part # 3114-0030
4.45 Teflon HP500+ Control Cover: CEM Part # 431255
4.46 Teflon HP500+ Cover: CEM Part # 431250
4.47 Teflon HP500+ Liner: CEM Part # 431110
4.48 Teflon Sheet, 0.002"x12"x1000': Laird Plastics Part # 112486
4.49 Teflon Tape (plumbing tape)
4.50 Teflon Thermowell Nut: CEM Part #325028
4.51 Teflon Tubing, 0.0625” ID 0.125” OD: ColeParmer Part # 06406-62
4.52 Teflon Tubing, 0.1875" ID 0.25"OD: ColeParmer Part # 06406-66
4.53 Teflon Vial with cap, 60 mL: Savillex Part # 0202
4.54 Teflon Vial with cap, 180 mL: Savillex Part # 0103L-2-2- 1/8”
4.55 Teflon Wash Bottle, 500 mL

4.56 Teflon Vent Nut: CEM Part # 431313
4.57 Titanium Cutter Screw: Büchi Analytical Part # 34376
4.58 Titanium Cutting Blade, Bottom: Büchi Analytical Part # 34307 DISCONTINUED
4.59 Titanium Cutting Blade, Top: Büchi Analytical Part # 34306 DISCONTINUED
4.60 Titanium Displacement Disc: Büchi Analytical Part # 26471
4.61 Ventilation Hood
4.62 Zipper-closure Polyethylene Bags, 4milx4”x6”: Packaging Store Part # zl40406redline
4.63 Zipper-closure Polyethylene Bags, 4milx6”x8”: Packaging Store Part # zl40608redline
4.64 Zipper-closure Polyethylene Bags, 4milx9”x12”: Packaging Store Part # zl400912redline
4.65 Zipper-closure Polyethylene Bags, 4milx12”x15”: Packaging Store Part # zl401215redline
4.66 Zipper-closure Polyethylene Bags, 4milx13”x18”: Packaging Store Part # zl401318redline

5.0 Reagents

Reagent grade chemicals shall be used in all cleaning procedures. Unless otherwise indicated, it is intended that all reagents shall conform to the specification of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.1 Tap water (Tap)
5.2 Deionized water (DI)
5.3 Type II Water (MilliQ): Use for the preparation of all reagents and as dilution water. (reference ASTM D1193 for more on Type II water)
5.4 All-purpose Cleaner, 409™
5.5 Hydrochloric Acid (HCl), BAKER ANALYZED, 36.5-38.0% (12N): VWR Part # JT9535-3
5.6 Hydrochloric Acid (HCl), BAKER ANALYZED, 6N: VWR Part # JT5619-3
5.7 Hydrochloric Acid (HCl), 6N (50%): prepared by adding 1 part Baker 12N HCl to 1 part MilliQ
5.8 Hydrochloric Acid (HCl), 4N (33%): prepared by adding 1 part Baker 12N HCl to 2 parts MilliQ
5.9 Hydrochloric Acid (HCl), 1.2N (10%): prepared by adding 1 part Baker 12N HCl to 9 parts MilliQ
5.10 Hydrochloric Acid (HCl), 0.06N (0.5%): prepared by adding 1 part Baker 12N HCl to 99.5 parts MilliQ
5.11 Methanol: VWR Part # JT9263-3
5.12 Micro Detergent: ColeParmer Part # 18100-20
5.13 Nitric Acid (HNO_3), concentrated redistilled: Seastar Chemicals Part # BA-01
5.14 Nitric Acid (HNO_3), BAKER INSTRA-ANALYZED’*, 69.0–70.0% (15N): VWR Part # JT9598-34
5.15 Nitric Acid (HNO_3), 7.5N (50%): prepared by adding 1 part Baker HNO_3 to 1 part MilliQ
5.16 Nitric Acid (HNO_3), 6%: prepared by adding 1 part Seastar HNO_3 to 16.67 parts MilliQ
5.17 Nitric Acid (HNO_3), 1%: prepared by adding 1 part Seastar HNO_3 to 99 part MilliQ
5.18 Petroleum Ether: VWR Part # JT9265-3

6.0 Sample Collection, Preservation and Handling

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in each analytical procedure.

6.2 All samples shall be collected and analyzed in a manner consistent with the sampling and analytical sections of this QA/QC document (MPSL QAP Appendix E).

7.0 Procedures

All chemicals must be handled appropriately according to the Moss Landing Marine Laboratories Health and Safety Plan. Rinsings must be neutralized to pH 5-10 prior to disposal through the sewer system.

Two forms of acid baths are used throughout these procedures: Cold Bath and Hot Bath. All acid baths must be lidded and secondarily contained. Allow hot acid to cool completely before removing cleaned equipment.

A cold bath may be created in any clean polyethylene container of appropriate size. A hot bath is created using a clean polyethylene bucket and lid, two 63 L polyethylene bins and an immersion heater. The two bins are put together, the outer serving as secondary containment. The acid filled bucket is placed inside the inner bin and water is added to surround the bucket, creating a water bath. The immersion heater is placed outside the acid bucket, but within the water bath. The immersion heater MUST be set in a Teflon cap or other heat resistant item of appropriate size to disperse the heat source and eliminate melting of the two outer bins.

7.1 Trace Metal (including, but not limited to: Al, As, Cd, Cr, Cu, Pb, Mn, Hg, Ni, Se, Ag, Zn) Sample Containers

7.1.1 Carboy

7.1.1.1 Fill completely with dilute Micro/Tap solution and soak for three days.

7.1.1.2 Rinse three times in Tap and three times in DI.

7.1.1.3 Fill completely with 50% HCl and soak for three days.

7.1.1.4 Remove acid and rinse three to five times in MilliQ.

7.1.1.5 Fill with 10% HNO_3 and soak for three days.

7.1.1.6 Remove acid and rinse three to five times in MilliQ.

7.1.1.7 If carboy is to be used immediately, fill with MilliQ and soak for 3 days. Collect solution in cleaned Trace Metal and Mercury water sample containers and test for contaminants.

7.1.1.8 If carboy is to be stored, fill with 0.5% HCl. Double bag in new garbage bags. Label the outer bag with “Acid Cleaned” and the date of completion.

7.1.2 Carboy Spigots and Tubing

7.1.2.1 Soak in dilute Micro/Tap solution overnight.

7.1.2.2 Rinse three to five times in Tap and DI, making sure to work the spigot valve to rinse all surfaces.

7.1.2.3 Submerge in 4N HCl cold bath for three days.

7.1.2.4 Rinse three to five times in MilliQ, making sure to work the spigot valve to rinse all surfaces.

7.1.2.5 Dry completely on crew wipers, then bag in new appropriately sized zipper-closure polyethylene bags. Label outer bag “Acid Cleaned” along with the date of completion.

7.1.3 Syringes for Field Filtration (not for Hg use)

7.1.3.1 Pull plungers out of syringes and place the outer tube in a 10% HCl bath. Swirl to ensure ink removal.

7.1.3.2 Once ink is completely gone, rinse three times with each Tap and DI.

7.1.3.3 Submerge all syringe parts in 4N HCl cold bath for three days.

7.1.3.4 Rinse three to five times with MilliQ.

7.1.3.5 Allow to completely dry on clean Crew Wipers.
7.1.3.6 Reassemble dry syringes and double bag in new appropriately sized zipper-closure polyethylene bags. Label outer bag "Acid Cleaned" along with the date of completion and the number of syringes within.
7.1.4 Polyethylene Water Containers (not for Hg use)
7.1.4.1 Fill each new 60 mL bottle with a dilute Micro/Tap solution. Place in a clean dissection bin and soak for one day.
7.1.4.2 Rinse three times in Tap, followed by three rinses in DI.
7.1.4.3 Fill each bottle with 50% HCl, soak for three days. (Note: HCl may only be used up to 6 times before it must be appropriately discarded.)
7.1.4.4 Pour out HCl and rinse each bottle and lid three to five times in MilliQ.
7.1.4.5 Fill each bottle with 1% Seastar HNO_3, cap. Allow outside of bottle to dry.
7.1.4.6 Double bag each bottle in new appropriately sized zipper-closure polyethylene bags. Label each outer bag with the date.
7.1.5 Polyethylene Tissue Dissection Containers
7.1.5.1 Fill each new 60 mL or 125 mL jar with a dilute Micro/Tap solution. Place in a clean dissection bin and soak for one day.
7.1.5.2 Rinse three times in tap water, followed by three rinses in DI.
7.1.5.3 Fill each jar with 10% HCl, soak for three days. (Note: HCl may only be used up to 6 times before it must be appropriately discarded.)
7.1.5.4 Pour out HCl and rinse each jar and lid three times in MilliQ.
7.1.5.5 Fill with MilliQ and soak for three days.
7.1.5.6 Remove MilliQ and place cleaned jars in a dissection bin lined with clean crew wipers to dry.
7.1.5.7 Once completely dry, pair lids and jars and place in a new appropriately sized zipper-closure polyethylene bag. Label bag "Acid Cleaned" along with the date of completion.
7.1.6 Polyethylene Scoops
7.1.6.1 (Performed by field crew) Thoroughly scrub new and used scoops in dilute Micro/Tap to ensure no residue remains in nicks and scratches. If soil cannot be completely removed, discard scoop.
7.1.6.2 (Performed by field crew) Rinse three times in Tap. Dry.
7.1.6.3 (In the lab) Submerge in 4N HCl cold bath for 3 days.
7.1.6.4 Rinse three to five times with MilliQ.
7.1.6.5 Let dry completely and double bag in new appropriately sized zipper-closure polyethylene bags. Label each outer bag with the date and number of scoops within.
7.1.7 Polypropylene Knives for Aliquoting
7.1.7.1 Scrub knives in dilute Mirco/Tap solution.
7.1.7.2 Rinse three times with Tap, followed by three rinses in DI.
7.1.7.3 Allow to completely dry on Precision Wipes. Roll in Precision Wipes, then place in new appropriately sized zipper-closure polyethylene bags. Label outer bag with "Micro Clean" and the date of completion.
7.1.8 Teflon Digestion Vessel and Lids
7.1.8.1 Using a soft, sponge-like bottle brush, scrub each vessel and lid with a dilute Micro/Tap solution.
7.1.8.2 Rinse three times with Tap, followed by three rinses with DI.
7.1.8.3 Submerge in 6% Seastar HNO_3 bath, heated for a minimum of 8 hours in a hotbath.
7.1.8.4 Rinse three to five times in MilliQ.

7.1.8.5 Place on new Crew Wipers under fume hood to dry.
7.1.8.6 Once completely dry, place in clean appropriately sized zipper-closure polyethylene bag. Label bag with the date of completion. (Note: You may use bags that have formerly contained clean digestion vessels or lids.)
7.1.9 Polyethylene Digestate Bottles
7.1.9.1 Fill each new 30 mL bottle with a dilute Micro/Tap solution. Place in a clean dissection bin and soak for one day.
7.1.9.2 Rinse three times in tap water, followed by three rinses in DI.
7.1.9.3 Fill each cup with 50% HCl, soak for three days. (Note: HCl may only be used up to 6 times before it must be appropriately discarded.)
7.1.9.4 Pour out HCl and rinse each bottle and lid three times in MilliQ.
7.1.9.5 Fill with MilliQ and soak for three days.
7.1.9.6 Remove MilliQ and place cleaned bottles and lids upside-down in a dissection bin lined with clean crew wipers to dry.
7.1.9.7 Once completely dry, pair lids and bottles and place in a new appropriately sized zipper-closure polyethylene bag. Label bag “Acid Cleaned” along with the date of completion.
7.1.10 Polypropylene Centrifuge Tubes, 15 mL (“ICP Tubes”)
7.1.10.1 Soak tubes in dilute Micro/Tap bath for three days.
7.1.10.2 Rinse three times in Tap, followed by three rinses in DI.
7.1.10.3 Submerge tubes and caps in 50% HCl cold bath for three days.
7.1.10.4 Rinse each tube and cap three times with MilliQ.
7.1.10.5 Place tubes and caps on clean crew wipers to dry.
7.1.10.6 Once completely dry, place in a new appropriately sized zipper-closure polyethylene bag. Label bag “Acid Cleaned” along with the date of completion.
7.2 Mercury Only Sample Containers
7.2.1 Water Composite Bottles, 4L
7.2.1.1 Caps do not get micro cleaned.
7.2.1.2 Scrub the outside of each bottle with a dilute Micro/Tap solution, rinse with Tap.
7.2.1.3 Place a small volume of the Micro/Tap solution inside the bottle. Shake vigorously to coat all surfaces.
7.2.1.4 Rinse with Tap until no more suds appear.
7.2.1.5 Rinse three times with DI.
7.2.1.6 Fill each bottle with 3N HCl. Cap and let stand on counter for three days. (Note: Acid may be used for a total of six cleaning cycles.)
7.2.1.7 Empty bottles and rinse three to four times with MilliQ, and fill.
7.2.1.8 Pipette in 20 mL HCl, BAKER ANALYZED, top off with MQ, replace caps and let dry.
7.2.1.9 Once completely dry, double bag in new appropriately sized zipper-closure polyethylene bags. Label outer bag with the date of completion.
7.2.1.10 Place in original boxes, labeled with date of completion. Bag entire box in a new garbage bag.
7.2.2 Tubing Sets
7.2.2.1 Cable Ties
7.2.2.1.1 Soak new cable ties in dilute Micro/Tap solution for three days.
7.2.2.1.2 Remove and rinse three times with Tap, followed by three rinses in DI and three rinses in MilliQ.

7.2.2.1.3 Allow to completely dry on Crew Wipers, then place in new appropriately sized zipper-closure polyethylene bags. Label outer bag with “Micro Clean” and the date of completion.
7.2.2.2 Polyethylene Caps with Holes
7.2.2.2.1 Drill a hole slightly smaller than 0.25 inches in the top of each new cap.
7.2.2.2.2 Soak in dilute Micro/Tap solution for three days.
7.2.2.2.3 Rinse three times with Tap, followed by three rinses in DI.
7.2.2.2.4 Soak in 4N HCl for 3 days.
7.2.2.2.5 Rinse three to five times in MilliQ. Let dry on Crew Wipers.
7.2.2.2.6 Once completely dry, place in new appropriately sized zipper-closure polyethylene bags until assembly. Label outer bag with “Acid Clean” and the date of completion.
7.2.2.3 Teflon Tubing
7.2.2.3.1 Using clean utility shears, cut one 3 foot and one 2 foot piece of tubing for each tubing set to be made.
7.2.2.3.2 Soak in dilute Micro/Tap solution for 3 days, ensuring that the tube is completely filled.
Note: Use Teflon tape to bind the two ends of each piece of tubing together. This will increase safety throughout the procedure.
7.2.2.3.3 Rinse three times in Tap, followed by three rinses in DI.
7.2.2.3.4 Submerge in 50% HNO_3 hot bath for 8 hours, ensuring that tubing is completely filled.
7.2.2.3.5 Rinse cooled tubing three to four times in MilliQ and let dry on clean Crew Wipers.
Note: Drying time may be decreased significantly by blowing reagent grade argon through the tubing to remove the water.
7.2.2.3.6 Once completely dry, place in new appropriately sized zipper-closure polyethylene bags until assembly. Label outer bag with “Acid Clean” and the date of completion.
7.2.2.4 C-Flex Tubing
7.2.2.4.1 Using clean utility shears, cut one 2 foot and one 4 inch piece of tubing for each tubing set to be made.
7.2.2.4.2 Soak in dilute Micro/Tap solution for one day, ensuring that the tube is completely filled.
7.2.2.4.3 Rinse three times in Tap, followed by three rinses in DI.
7.2.2.4.4 Submerge for three days in 12N HCl under a fume hood.
7.2.2.4.5 Rinse three to four times in MilliQ.
7.2.2.4.6 Submerge for three days in 0.5% HCl under a fume hood.
7.2.2.4.7 Rinse three to four times in MilliQ. Let dry completely on clean Crew Wipers.
Note: Drying time may be decreased significantly by blowing reagent grade argon through the tubing to remove the water.
7.2.2.4.8 Once completely dry, place in new appropriately sized zipper-closure polyethylene bags until assembly. Label outer bag with “Acid Clean” and the date of completion.
7.2.2.5 Tubing Set Assembly (using cleaned parts described above)
7.2.2.5.1 Using two cable ties, attach 2 foot Teflon tubing to 2 foot C-flex.
7.2.2.5.2 Next attach 4 foot Teflon to the other end of the 2 foot C-flex, again with 2 cable ties.
7.2.2.5.3 Add the 4 inch C-flex to the open end of the 4 foot Teflon tubing with 2 cable ties.
7.2.2.5.4 Put a drilled Poly cap on the open end of the 2 foot Teflon.
7.2.2.5.5 Coil the assembled tubing set, and double bag in new appropriately sized zipper-closure polyethylene bags. Label outer bag with “Acid Clean” and the date of completion.
7.2.2.6 In-Lab Mercury Filters
7.2.2.6.1 Fill upper reservoir with 10% HCl. Cap and apply vacuum.

7.2.2.6.2 Detach filter apparatus from vacuum manifold. Place finger over the valve and shake the unit to clean all surfaces of the lower reservoir.
7.2.2.6.3 Repeat two more times. Acid can be used 6 times.
7.2.2.6.4 Repeat wash three times with MilliQ. Cap and apply vacuum.
7.2.2.6.5 Discard MilliQ after each rinse.
7.2.3 Water Sample Bottles, 250 mL
7.2.3.1 Rinse new bottles in DI. Place the caps only in a MilliQ bath for the duration of the bottle cleaning.
7.2.3.2 Submerge in 50% Baker HNO_3 hot bath for 8 hours, ensuring that each bottle is completely filled.
7.2.3.3 Rinse cooled bottles three to four times in MilliQ, then fill each with MilliQ.
7.2.3.4 Pipette in 1.25 mL 100% HCl, replace caps and let dry completely.
7.2.3.5 Double bag in new appropriately sized zipper-closure polyethylene bags. Label outer bag with the date of completion.
7.2.3.6 Place in original boxes, labeled with date of completion.
7.2.4 Polypropylene "Snap Seal" Containers, 45 mL ("Trikona Tubes")
7.2.4.1 Rinse new tubes in dilute Micro/Tap.
7.2.4.2 Rinse three times in Tap, followed by three times in DI.
7.2.4.3 Submerge in 50% HNO_3 hot bath for 8 hours, ensuring that each tube is completely filled.
7.2.4.4 Rinse cooled tubes three to four times in MilliQ.
7.2.4.5 Let dry completely on clean Crew Wipers.
7.2.4.6 Place dry tubes in new appropriately sized zipper-closure polyethylene bags. Label outer bag with "Acid Clean" and the date of completion.
7.3 Methylmercury Only Sample Containers
7.3.1 Teflon Digestion or Distillation Vials
7.3.1.1 Scrub vials with 409™ to remove any organic residue. It may be necessary to also soak the vials in dilute Micro/Tap for 3 days.
7.3.1.2 Rinse three times in DI.
7.3.1.3 Submerge in 50% HCl bath. Heat overnight, or soak for 3 days in cold bath.
7.3.1.4 Rinse three to five times in MilliQ; dry completely on clean crew wipers.
7.3.1.5 Place dry tubes in new appropriately sized zipper-closure polyethylene bags. Label outer bag with "Acid Clean" and the date of completion.
7.3.2 Teflon Distillation Caps and Tubing
7.3.2.1 Scrub caps and tubing with 409™ to remove any organic residue.
7.3.2.2 Rinse three times in DI.
7.3.2.3 Submerge in 10% HCl hotbath overnight. Use a Teflon squirt bottle to fill the tubing with acid.
7.3.2.4 Rinse three to five times in MilliQ; dry completely on clean crew wipers.
Note: Hang tubing over a clean hook against crew wipers to speed drying time.
7.3.2.5 Place in new appropriately sized zipper-closure polyethylene bags. Label outer bag with "Acid Clean" and the date of completion.
7.4 Organic Sample Containers
7.4.1 Aluminum Foil Sheets
7.4.1.1 Using a clean scalpel, cut a 4 foot long section of aluminum foil.
7.4.1.2 Fold in half, with dull side out. (The bright side may contain oils from the manufacturing process.)

7.4.1.3 Under a fume hood, rinse both exposed sides of the folded foil three times with Petroleum Ether. Make sure all exposed surfaces are well rinsed.
7.4.1.4 Set against a clean surface under the fume hood to dry.
7.4.1.5 Once completely dry, fold the sheet in quarters, ensuring the un-rinsed shiny side does not come in contact with the now cleaned dull side.
7.4.1.6 Place into a new appropriately sized zipper-closure polyethylene bag. Label bag "PE Cleaned" along with the date of completion and the number of sheets within.
7.4.2 Dissection Jars (125mL, 500mL Glass Jars)
NOTE: Clean 100 series jars as follows below. 200 and 300 series jars may be used as is from the manufacturer, with a clean Teflon square (section 7.5.2) over the threads.
7.4.2.1 Using a clean scalpel, cut three inch squares from a sheet of new Teflon.
7.4.2.2 Fit Teflon square to the jar and lid, ensuring that the threads are completely covered and no leaks will occur.
7.4.2.3 Under a fume hood, rinse each jar and lid three times with Petroleum Ether by putting a small of amount in the jar, sealing it and then shaking the jar to coat all sides.
Note: It is easiest to clean four jars simultaneously. Use each volume of PE once in each of the jars; repeat. After cleaning the fourth jar, discard PE into evaporation bin under the hood, or into designated solvent waste container.
7.4.2.4 Set jars aside in the hood to dry.
7.4.2.5 When completely dry, match the lids to the jar and place back in the original box. Label box "PE Cleaned" along with the date of completion.
7.5 "Split" Sample Containers (for metals and organics)
7.5.1 Teflon sheets
7.5.1.1 Cut new Teflon to desired length (1 or 2 feet long depending on application)
7.5.1.2 Submerge crumpled sheets in a 10% Micro/Tap bath overnight.
7.5.1.3 Remove sheets from micro bath and flatten. Rinse all surfaces of each sheet three times in tap water, followed by three rinses in deionized water.
7.5.1.4 Crumple rinsed sheets and submerge in 10% HCl in a hot bath; heat at least 8 hours.
7.5.1.5 Remove sheets from acid bath and flatten. Rinse all surfaces of each sheet five times in MilliQ.
7.5.1.6 Layer rinsed Teflon sheets on new Crew Wipers, with new Precision Wipes between each sheet. Cover stack with new Precision Wipes. Let dry.
7.5.1.7 Once the sheets are completely dry, rinse each surface three times with Petroleum Ether.
7.5.1.8 Place on clean Crew Wipers and Precision Wipes, as before, under hood and let dry.
7.5.1.9 Once the sheets are completely dry, fold sheets and place into a new appropriately sized zipper-closure polyethylene bag. Label bag "PE Cleaned" along with the date of completion and the number of sheets within.
7.5.2 Teflon Squares for Dissection Jars
7.5.2.1 Using a cutting board and scalpel, cut Teflon sheet into 3-inch squares.
7.5.2.2 Soak in 6% Seastar HNO_3 coldbath overnight.
7.5.2.3 Rinse three times with MilliQ.
7.5.2.4 Rinse three times with Methanol, followed by three rinses with Petroleum Ether.
7.5.2.5 Lay on clean crew wipers to dry.
7.5.2.6 Once the squares are completely dry, place into a new appropriately sized zipper-closure polyethylene bag. Label bag "PE Cleaned" along with the date of completion.
7.5.3 Dissection Jars (125mL, 500mL Glass Jars)

NOTE: Clean 100 series jars as follows below. 200 and 300 series jars may be used as is from the manufacturer, with a clean Teflon square (section 7.5.2) over the threads.
7.5.3.1 Using a clean scalpel, cut three inch squares from a sheet of new Teflon.
7.5.3.2 Fit Teflon square to the jar and lid, ensuring that the threads are completely covered and no leaks will occur.
7.5.3.3 Under a fume hood, rinse each jar and lid three times with 6% HNO_3 by putting a small of amount in the jar, sealing it and then shaking the jar to coat all sides.
Note: It is easiest to clean four jars simultaneously. Use each volume of each chemical once in each of the jars; repeat. After cleaning the fourth jar, discard into the appropriate evaporation bin under the hood or into designated waste container.
7.5.3.4 Rinse each jar three times in MilliQ.
7.5.3.5 Rinse each jar three times in Methanol, let dry completely.
7.5.3.6 Rinse each jar three times in Petroleum Ether; set aside in the hood to dry.
7.5.3.7 When completely dry, match the lids to the jar and place back in the original box. Label box "Split Cleaned" along with the date of completion.
7.5.4 Homogenization Parts (Büchi) including glass, polypropylene, titanium and stainless steel
7.5.4.1 Scrub with dilute Micro/Tap, followed by 3 rinses with DI.
7.5.4.2 Rinse 3 times with 6% Seastar HNO_3 using a Teflon squirt bottle.
7.5.4.3 Rinse 3 times with MilliQ.
7.5.4.4 Rinse 3 times with Methanol, followed by 3 times with Petroleum Ether.
7.5.4.5 Allow parts to dry completely before assembly and homogenization.

8.0 Analytical Procedure

8.1 Tissue Preparation procedures can be found in Method # MPSL-105.
8.2 Trace Metal and Mercury Only digestion procedures can be found in EPA 3052, modified, and Method # MPSL-106, respectively.
8.3 Trace Metals are analyzed with ICP-MS according to EPA 200.8.
8.4 Mercury samples are analyzed by FIMS according to Method # MPSL-103 or by DMA and EPA 7473.
8.5 Methylmercury tissue samples are extracted and analyzed according to Method # MPSL-109.
8.6 Methylmercury sediment samples are extracted and analyzed according to Method # MPSL-110 and modified EPA 1630, respectively.

9.0 Quality Control

9.1 See individual methods.

10.0 Method Performance

10.1 System blanks are performed on Mercury Sample 250 mL and 4 L bottles and tubing sets to guarantee thorough cleaning.
10.2 Carboys are tested for all metals after cleaning.

Appendix I

Autosampler Mini-Study

Department of Water Resources

Originated by: Petra Lee

August 5, 2015

1. Hypotheses

1. THg and MeHg samples collected via autosampler and by grab sample, will not be significantly different.
2. Autosampler tubing will not affect THg and MeHg samples.
3. Using flow weighted composited samples based on tides and flow will give us equal THg and MeHg loads when compared to data collected and analyzed hourly.
4. Autosampler containers will not be contaminated with THg or MeHg due to being open in autosampler during study.

2. Assumptions Made

1. All our ISCO 6712 autosamplers will function equivalently. Because we will be using the same type of tubing, fittings, bottles, and autosamplers, we will not need to worry about them affecting the water quality samples in different ways. We will test one autosampler.
2. During the main study, no autosampler will be collecting more than 8 consecutive samples.
3. During the main study, we will be using ISCO 6712 portable autosamplers and their tubing and bottle sets, all purchased from ISCO.
4. If unfiltered THg and MeHg samples are unaffected by the autosampler, filtered THg and MeHg samples will also be unaffected.

3. Location

This study will be performed at the Lisbon Weir CDEC station (LIS, http://CDEC.water.ca.gov, 38.475, -121.587). The station has the advantages that it is 1) close to the Yolo Wildlife Area Tidal Wetland where we will begin our main study, 2) DWR has a flow station already installed that is telemetered to CDEC, so we can have access to almost instant flow data, 3) the concentrations of THg and MeHg are relatively high and will give us a good signal, and 4) the area is somewhat secure and has low to no boat traffic, so minimal interferences will occur. However, the LIS station does not always have a strong tidal influence because of high flows, so depending on whether a reverse/negative flow (ebb) occurs or not, we may only have positive flow that we will split into two composited samples for the positive flow (flood) tide.

4. Methods

In order to test our hypotheses, DWR staff from the Mercury Monitoring and Evaluation Section (MME) will collect 8 hourly samples, for a total of 8 sampling events. We will collect 1.8 liters of water using the auto samplers, once an hour, and we will concurrently collect grab samples as close to the intake of the autosampler, and as close in time to the autosampler, as possible. In this way, we will minimize the variation in the water collected.

4.1 Autosampler

DWR MME staff will be testing an ISCO 6712 portable autosampler that we retrofitted with an 8-glass bottle set with the appropriate sample holder, PTFE feed tubing, and a nylon barbed connector to replace the stainless-steel connector originally installed by ISCO.

DWR staff will clean the autosampler bottles, the autosampler, and the autosampler tubing according to methods outlined in Appendix A. We will operate the ISCO 6712 according to the manual to collect a 1.8L of sample water per hour.

Initially, we will collect two THg and MeHg autosampler equipment blanks: an equipment blank for the acid-cleaned tubing, and an equipment blank for the acid-cleaned bottles.

Next, we will set up the autosampler that has been cleaned, and in which clean tubing has been installed. The intake will be attached to a stake in the Toe Drain to anchor it in place and will also be attached to a float so that samples are taken approximately 30 cm below the surface of the water.

We will load 8 1.8L glass bottles into the rack in the base of the autosampler. The autosampler will collect the maximum number of samples that is likely during the main study.

To check for residue in the sample tubing after samples have been collected, we will run Type 1 water through the autosampler tubing and analyze it for THg and MeHg.

To determine whether having open containers in the autosampler will affect sample concentrations, we will place an uncapped acid-cleaned autosampler bottle filled with Type 1 water into an autosampler and allow it to remain for the duration of the study. The water will be analyzed for THg and MeHg after 8 hours.

4.2 Grab samples

Grab samples will be collected concurrently with the autosampler samples. In this way, we will have a direct comparison to determine whether using the autosampler to collect the samples affects THg and MeHg concentrations. Grab samples will be considered the “control” situation.

We will collect the grab samples directly into clean 250 mL glass bottles from the bank using a sampling pole. One set of duplicates will be taken. Total mercury samples will be submitted to DWR's Bryte Lab for analysis and methylmercury samples will be preserved with 12N HCl and then submitted to Moss Landing Marine Lab for analysis.

4.3 Flow-weighed composites

In addition to testing the autosampler's potential effect on MeHg and THg sample concentrations, we will be testing a flow-weighted compositing method. We will collect hourly samples that will be analyzed for THg and MeHg and multiply the concentration per hour with the flow, to determine loads. Additionally, we will composite samples based on flow, and calculate the loads using the composites. The loads of the flow weighted composited sample should be approximately equal to the loads of the hourly samples.

4.4 Statistical Analysis

To determine whether the autosampler is affecting the samples, we will use a paired hypothesis test to compare samples from the autosampler to the grab samples. If the two groups of data are statistically equal, we can assume two things; 1) collecting samples via autosampler is not affecting the concentrations and 2) the tubing is not getting fouled and affecting the samples significantly.

First, we will test the normality of the data in two ways; we'll do a box plot to visually observe whether the data appears symmetrical, and we'll do a Shapiro-Wilk normality test. If both tests show that the data is normal, we will use the paired t-test (parametric) to determine if the grab samples and autosampler samples are different. If the box plot and/or Shapiro-Wilk normality test show that the data is skewed or not normal, we will use the Wilcoxon-signed-rank test (nonparametric) to determine if the grab samples and auto sampler samples are different.

If the t-test or Wilcoxon-signed-rank test shows that the data is significantly different, we can investigate the following:

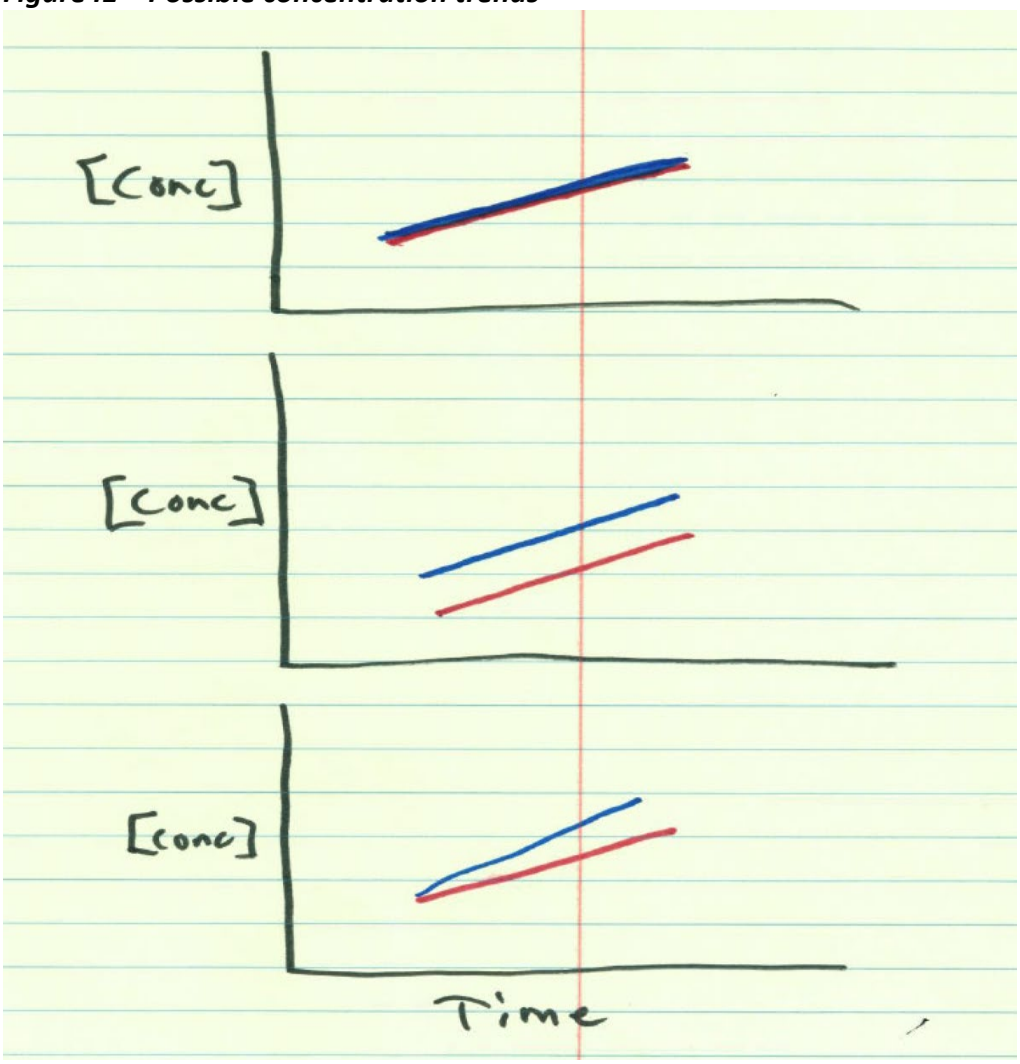
1. Which set of data is higher? The autosampler or the grab samples?
2. What could cause the grab samples or autosamplers to be higher?
3. Were both THg and MeHg higher or lower?

In addition, we will create time-series graphs of the MeHg or THg concentration data. The autosampler and grab samples will each be modeled separately with regression lines to examine whether concentration trends differ between the two groups. Figure I1 illustrates the possible scenarios. In these graphs, the x-axis is time and the y-axis is the concentration of either MeHg or THg. The following scenarios could occur:

1. The top scenario would likely indicate that the grab and autosampler samples are the same.
2. In the middle scenario, the grab and autosampler samples are different, and one is consistently higher, but the autosampler tubing is likely not affecting the samples.
3. In the bottom scenario, the autosampler and grab samples were initially the same, and then the tubing likely affecting the autosampler samples.

In addition to these three scenarios, a combination of these could occur. Beyond visually looking at the graphs, we may also perform analysis of covariance (ANCOVA) procedures to determine if the regression slopes of the two groups of samples are significantly different. A significant difference would indicate that the two groups of samples have statistically different trends of concentration through time.

Figure I1 – Possible concentration trends



5. Results and Conclusion

DWR staff plotted the data using box plots and did a Ryan-Joiner normality test (similar to Shapiro-Wilks) to look at normality for both MeHg and THg autosampler and grab sample data. Although some data appeared to be normal, not all data were, so we used the Wilcoxon Signed Rank test to see if there were any differences between manually grabbed water samples and samples collected via autosampler. We also calculated relative percent differences between the grab and autosampler data and they all were less than 25%. Figures I2 and I3 are graphs of the grab and autosampler data over the 8-hour period.

Figure I2 – THg data over an 8-hour time interval

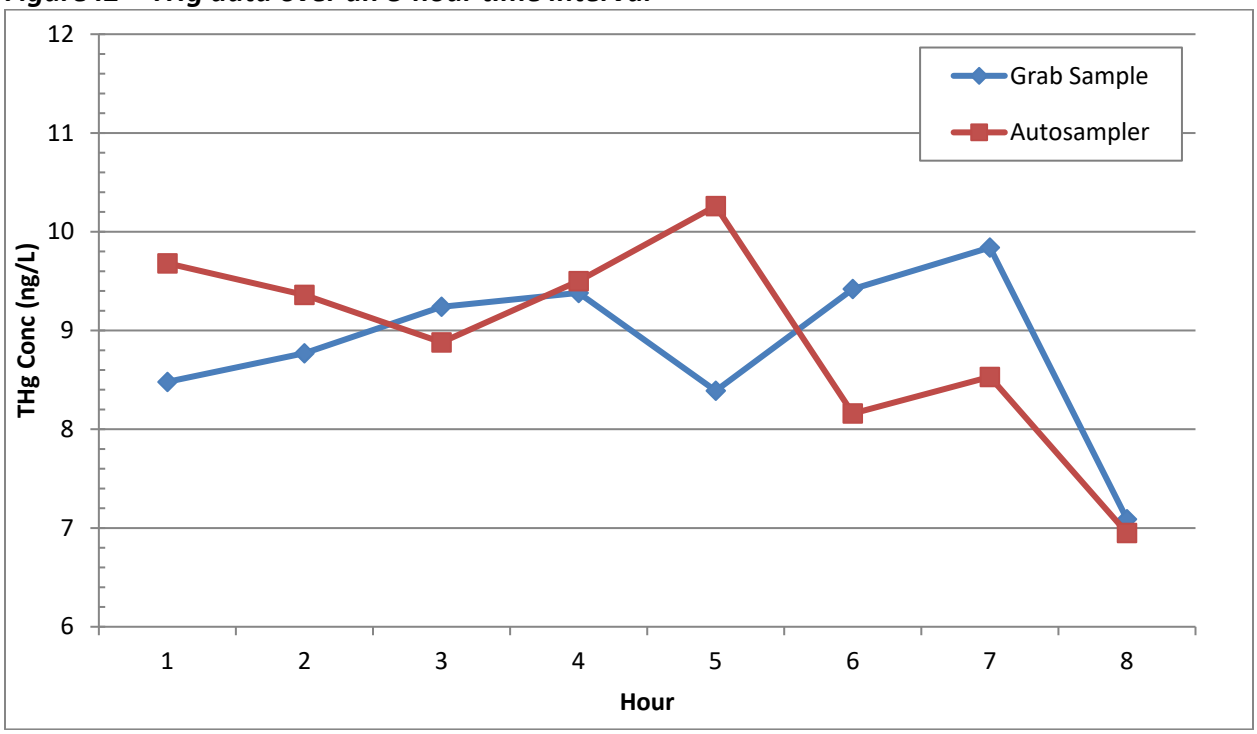
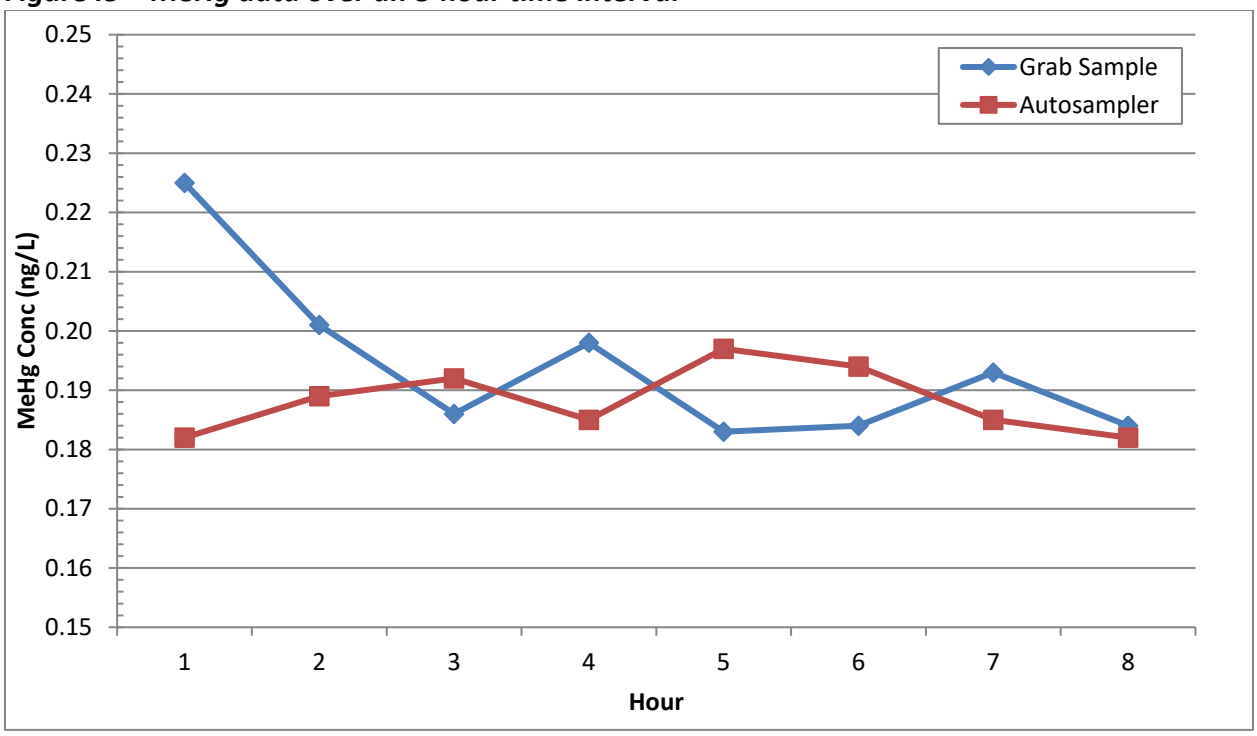


Figure I3 – MeHg data over an 8-hour time interval



For both the THg data and MeHg data sets, the p value > 0.05 (THg p=1.00 and MeHg p=0.529), which means that in both cases, the MeHg and THg grab samples were not significantly different than the samples collected via autosampler.

Additionally, we did an Equivalence test on the THg and MeHg data, which said that the grab and autosampler data sets were equivalent (THg p=0.804, MeHg p=0.378).

Staff collected pre and post-sampling tubing blanks, as well as a field blank. The pre-sampling tubing blank had a MeHg concentration of 0.011 ng/L, which is the method detection limit (the reporting limit is 0.031 ng/L), and the post-sampling tubing blank also had a concentration of 0.011ng/L, leading us to conclude that no residual MeHg was in the tubing. The pre-sampling tubing blank had a THg concentration of <0.500 ng/L (the method detection and reporting limit is 0.500 ng/L) and the post-sampling tubing blank had a THg concentration of <0.500 ng/L. The MeHg concentration of the field blank was <0.011 ng/L (the method detection limit), and a THg concentration of <0.500 ng/L. We concluded that neither the tubing nor leaving the samples open in the autosampler for 8 hours was biasing the samples. However, we will continue to do field blanks.

Using this data, we concluded that using the autosampler did not bias samples, and we will use this technique to collect samples in the future.