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October 20, 2015

Pamela Creedon, Executive Officer
Central Valley Regional Water Quality Control Board
11020 Sun Center Drive, Ste 200
Rancho Cordova, California 95670-6114

Submittal of Delta Mercury Control Progress Report for Tidal Wetlands

Dear Ms. Creedon,

In fulfillment of the requirements of the Delta Mercury Control Program (DMCP), the Department of Water Resources (DWR) is submitting a Tidal Wetland Progress Report (Progress Report) for approval. This Progress Report contains study updates, outlines progress, and has a preliminary analysis of data collected at one freshwater tidal wetland. DWR staff will continue to work with your staff throughout the study.

Please contact Petra Lee at (916) 376-9735 or Petra.Lee@water.ca.gov for any questions about the Progress Report.

Sincerely,

Haidi Rooker for Dean Messer

Dean F. Messer, Chief
Division of Environmental Services

Enclosure

Progress Report

Delta Mercury Control Program

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

October 20, 2015

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Executive Summary

In December 2013, the Department of Water Resources (DWR) submitted a workplan to the Central Valley Regional Water Quality Control Board (Regional Board) detailing a proposed study of several tidal wetlands in the Sacramento-San Joaquin Delta and Suisun Marsh. This workplan was in compliance with the Delta Mercury Control Program (DMCP) requirements.

After the workplan was approved, DWR began the largest and most comprehensive import/export freshwater tidal wetland study to date, in May 2014, starting with the Yolo Wildlife Area (YWA) Tidal Wetland. Monitoring of this wetland began in May 2014 and ended in April 2015 with a total of 10 sampling events. Currently, DWR is studying the second tidal wetland, Blacklock, a brackish tidal wetland located in Suisun Marsh, to the west of the Sacramento-San Joaquin Delta. Monitoring of this wetland began in June 2015 and will continue through May 2016. Tentatively, we plan to study the Westervelt Cosumnes Tidal Wetland as the third wetland and if time permits, we will study a fourth wetland depending on discussions with Regional Board staff.

Some changes have been made to the study as outlined in the original workplan, and these changes have been discussed with Regional Board staff. The changes include increasing the amount of sampling events for each wetland, clarifying the current and future wetlands to be studied, and updating the number of wetlands to be monitored.

Based upon mass load calculations of each of the 10 sampling events, the YWA Tidal Wetland was a sink of THg and MeHg during a majority the events. For the events in which the YWA Tidal Wetland was a source of THg, it was generally in the particulate fraction. The YWA Tidal Wetland was a source of total suspended solids (TSS) loads during the warmer months and a sink during the cooler months; however, it is unclear at this point if this apparent seasonal trend would be repeated in other years or wetlands. The YWA wetland had a strong correlation between TSS and particulate THg loads (Spearman's $\rho=0.855$, $p=0.002$), and a weaker correlation between TSS and particulate MeHg (Spearman's $\rho=0.685$, $p=0.029$). There was no correlation between DOC and dissolved MeHg (Spearman's $\rho=0.085$, $p=0.815$).

For the final report required by the DMCP, we will be able to fully test our hypotheses. We will also do a more thorough data analysis by including data from multiple wetlands and looking at correlations between more water quality constituents.

Introduction and Background

The Department of Water Resources (DWR) began the study of tidal wetlands for Phase 1 compliance of the Delta Mercury Control Plan (DMCP) in April 2014. This import/export study of freshwater tidal wetlands is the largest and most comprehensive to have been attempted thus far. The hypotheses in the original workplan remain unchanged from the original workplan (DWR 2013).

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

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.

Because we have only partially completed the study, we will not be fully testing the hypotheses in this report. For more information and background, please reference to the Methylmercury Import and Export Studies on Tidal Wetlands in the Sacramento-San Joaquin Delta and Yolo Bypass Workplan (DWR 2013).

Changes to Workplan

Few changes were made to the original workplan, and those have been discussed with Regional Board staff. The changes include the following:

- DWR will collect data from three to five wetlands, depending on timing. Due to the numerous unanticipated equipment failures and site challenges, we expect to study a total of three tidal wetlands by the October 2018 deadline. With a deadline extension of two years, and unless there are extensive equipment failures and additional site challenges, DWR could collect data from up to two more wetlands, for a total of five.
- DWR studied the Yolo Wildlife Area Tidal Wetland (YWA Tidal Wetland) first, is currently working on monitoring Blacklock Tidal Wetland, and is next planning on studying the Westervelt Cosumnes Tidal Wetland.
- DWR changed sampling frequency and timing. Rather than sampling four times a year during back-to-back spring and neap tides, we have been sampling more consistently throughout the year.
 - Generally, we sampled the YWA Tidal Wetland on a monthly basis during the warmer months, and bimonthly during the winter, which is similar to the study design of Mitchell and others (2014).

- We were unable to sample during back-to-back spring and neap tides due to staff availability and site access restrictions during hunting season at the Yolo Wildlife Area.

Preliminary Methods

Study Area

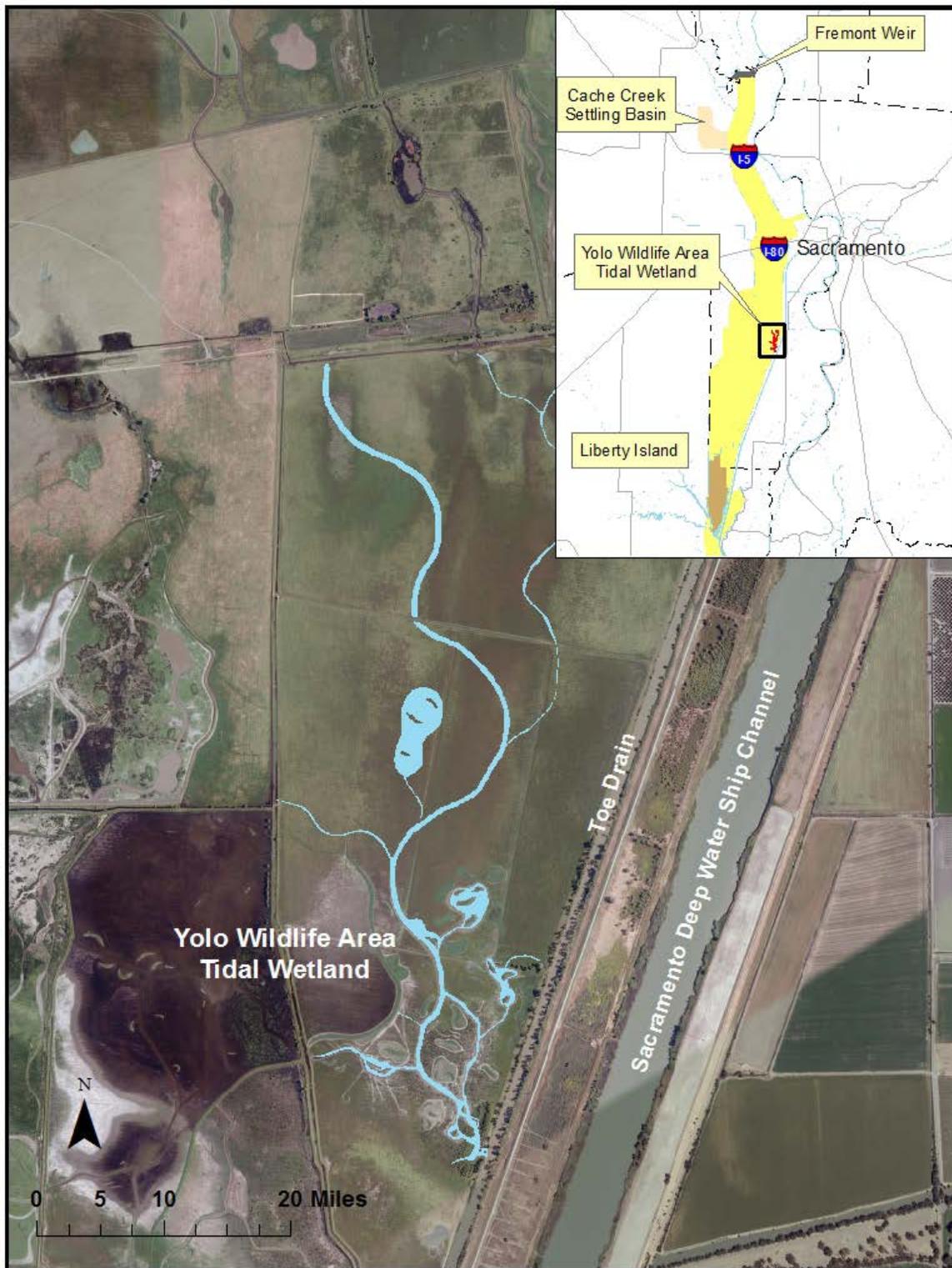
Yolo Wildlife Area Tidal Wetland

The first wetland that DWR studied is the YWA Tidal Wetland, which is located in the southern portion of the Yolo Wildlife Area (see Figure 1). The wetland is a freshwater tidal wetland with one opening (mouth) to the Toe Drain in the Yolo Bypass.

This site had several limitations and items of note:

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 was only able to access the island within the mouth of the wetland about every other month during the hunting season.
2. The tidal wetland is relatively new and was beginning to have a more mature plant population, making it a good candidate as a newer wetland, but not ideal for the study of mature wetlands.
3. The wetland was a water sink, and possibly connected to some agricultural drains.
4. The wetland was flooded during a Yolo Bypass mini-flooding event in December 2014 and, to prevent damage, we had to remove our equipment for about a month. Even if we had been able to collect data during the mini-flood event, the flow data would not have been accurate once the wetland channels were overtopped.

Figure 1 – Location of Yolo Wildlife Area Tidal Wetland



Blacklock Tidal Wetland

In June 2015, DWR staff began studying Blacklock tidal wetland, which is located in the Suisun Marsh, west of the DMCP. The Blacklock property is approximately 70 acres of tidal wetland and was acquired by DWR in December 2003. In July 2006, an unplanned breach occurred on the northwest levee, followed by a planned breach in October 2006, near the first breach. Figure 2 shows the location of Blacklock and the two breaches.

Figure 2 – Location of Blacklock Tidal Wetland



Study Design

Yolo Wildlife Area Tidal Wetland

DWR staff deployed an Acoustic Doppler Current Profiler (ADCP), located on the channel bed in the middle of the main channel, to collect velocity, stage, and flow data. A transect that was slightly more internal to the wetland than the ADCP was used to collect data to develop a flow rating curve to calculate flow data. See Figure 3 for the location of the flow and water quality equipment. More information about data collection can be found in the Monitoring Plan, which is located in Appendix A.

Figure 3 – Yolo Wildlife Area Tidal Wetland Equipment Locations



Throughout the study of the wetland, multiple problems occurred with collecting flow data. The first ADCP failed after being deployed for approximately three months, and the second began getting buried in sediment after two months. We purchased a newer unit with a longer cord in September 2014, which allowed us to place it in a location where it would not be buried by settling sediment. The cord was cut in late October 2014 and a new cord was attached to the ADCP, which was redeployed in November 2014. Each time an ADCP was removed and replaced or the cord was cut, we had to develop another rating curve in order to calculate flow data. As mentioned previously, the station was temporarily suspended from December 2014 through January 2015 due to minor flooding in the Yolo Bypass.

The water quality sonde was located in the water near the ADCP and experienced few to no problems with data collection. The sonde collected four parameters at 15-minute intervals: temperature, specific conductance, turbidity, and chlorophyll. More information about sonde data collection can be found in the Monitoring Plan in Appendix A.

The autosamplers were located on the shore and the intake of the tubing was located near the sonde, as shown in Figure 3. More specific details about how the autosamplers were set up to collect samples, equipment used in the autosamplers, cleaning methods, etc., can be found in the Monitoring Plan in Appendix A.

We monitored the YWA Tidal Wetland for approximately one year and were able to collect data for a total of 10 events. During one event beginning April 20, 2015, an autosampler collected only enough samples to measure half a tidal cycle. Because we only were able to collect samples for half of a tidal event, we decided to do a second event the next week beginning April 27, 2015. During the second April 2015 event, an autosampler failed to collect three samples during the Ebb 1 subset of samples on April 27-28, 2015.

Blacklock Tidal Wetland

As was done in the YWA Tidal Wetland, DWR is collecting continuous flow data with an ADCP, continuous water quality sonde data, and discrete THg, MeHg, and organic carbon data via autosampler on a monthly or bimonthly basis; additionally, we are collecting TSS via autosampler, which was not done with the YWA Tidal Wetland. Collecting flow data has been a particular challenge as the levees containing Blacklock are being allowed to erode. DWR staff is watching for additional breaches, and Blacklock is being studied early in the study period to decrease the risk that additional levee breaches will occur during the study.

An ADCP was mounted to a concrete block and lowered to the bottom of the channel of each breach. The telemetry equipment is located on the south banks of each of the breaches. See Figure 4 for the location of the flow and telemetry equipment. The ADCPs have been challenging to deploy and maintain for various reasons. In the southern breach, the brand-new ADCP was not functional and, after several attempts at deployment, it was replaced by Sontek. In addition, the ADCPs had a poorly designed attachment point at the cord, and several cords

were damaged through normal use. As a result, DWR had to redeploy the ADCPs and develop several new rating curves to calculate flow. Eventually, most of the problems were resolved and a rating curve for flow was developed for each of the ADCPs. The study began at the end of June 2015, several months after our anticipated start date.

The autosamplers are deployed on the south shores of each breach at the locations shown in Figure 4. The tubing intakes are deployed in the deepest part of the channels, approximately 20 feet away from where the ADCPs are located to avoid interfering with them. Occasional malfunctions of one or more of the autosamplers have led to some missing data, which could happen again in the future.

The water quality sondes were deployed in April 2015. Because of strong currents and soft sediment, the pipes that housed the sondes nearly fell over. As a result, the sondes were removed in June 2015 and the housing was removed in July 2015. Consequently, sonde data will not be collected until the new installation occurs. We plan to install them at the locations indicated in Figure 4 and we will set them up to collect temperature, specific conductance, pH, dissolved oxygen, turbidity, and chlorophyll at 15-minute intervals. The sonde sensors will be approximately one meter below the surface at all times.

Figure 4 – Blacklock Tidal Wetland Breaches and Equipment Locations



Autosampler Bias Mini-Study

Before beginning the DMCP study, we needed to verify that the autosamplers would not bias the samples. DWR staff contacted Dr. Carl Mitchell, whose sampling study we were mostly emulating (Mitchell and others 2012), and discussed his sampling methods with. Dr. Mitchell used the same sampling devices (ISCO 6712 Autosampler) and did extensive quality assurance to determine that the samplers were acceptable to use (Dr. Carl Mitchell, University of Toronto-Scarborough, pers. comm. September 8, 2013). In addition, we did a “Mini-Study” at the Toe Drain at Lisbon Weir to determine if using the autosamplers would bias our samples compared to a grab sample with a sampling pole. We determined that the autosamplers were not biasing the mercury samples and documented the methods and results. Information about the “Mini-Study” can be found in Appendix I of the Monitoring Plan (Appendix A of this report).

Flow-Weighted Compositing Pre-Study

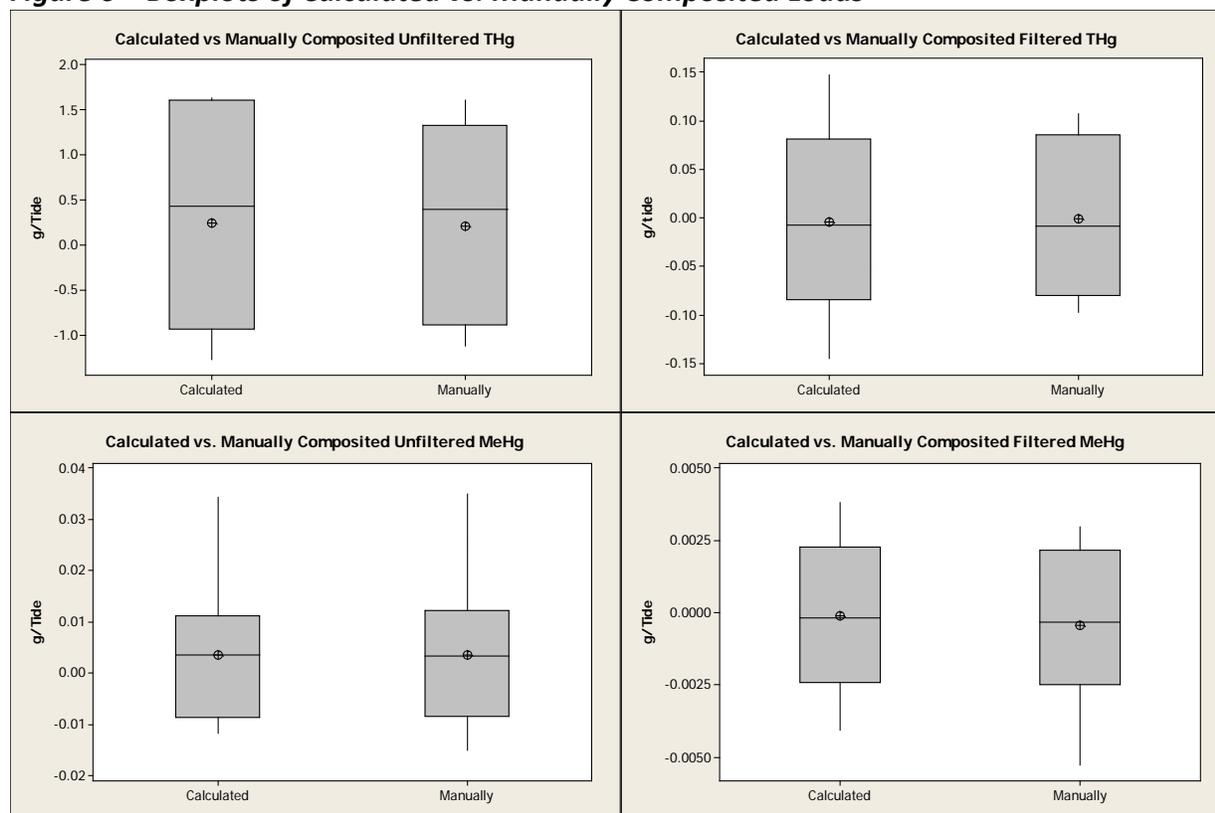
DWR staff collected and analyzed samples for two 25-hour tidal cycles at the YWA Tidal Wetland to assess the flow-weighted compositing used in Mitchell and others (2012). We analyzed the hourly samples and calculated a composite value using flow data. We compared the calculated composite value (calculated composites) to the composites that we manually composited in the lab (manual composites).

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, neither unfiltered nor filtered MeHg were different ($p=0.477$ for unfiltered MeHg, and $p=0.294$ for filtered MeHg). Bar graphs of the loads (Figure 5) indicate that, while there were some visual differences, the values tracked fairly well on the whole. Additionally, we graphed the data using box plots and, visually, they appeared to be similar. See Figure 6 for the associated boxplots.

The details of how the flow-weighted compositing and comparison were done are found in Section 5.1.1.4 of the Monitoring Plan in Appendix A.

Figure 5 – Calculated versus Manually Composited Loads



Figure 6 – Boxplots of Calculated vs. Manually Composited Loads

Load Calculations

THg, MeHg, and Organic Carbon

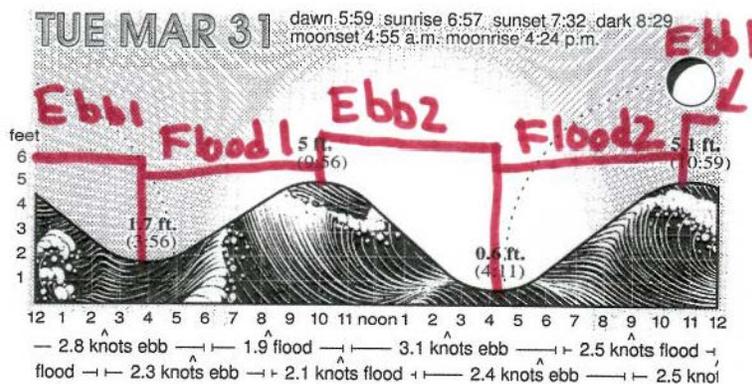
In this report, we will be referring to mercury and carbon species using several terms. Unfiltered samples are derived from the analyzed unfiltered water sample, and includes all THg, MeHg, and carbon species. Unfiltered THg and MeHg samples will be referred to as “unfiltered” and organic carbon samples will be referred to as total organic carbon (TOC). Filtered samples are referred to as “dissolved”, and are the fractions that remain after being filtered through a 0.45 μm filter. These fractions are referred to as “filtered” or “dissolved” THg and MeHg or “dissolved” organic carbon (DOC). We did not measure particulate fractions directly as in other publications, but the “particulate” mercury is represented as the filtered concentration subtracted from the unfiltered concentration. In summary we will refer to the THg and MeHg as “total,” “dissolved,” and “particulate,” and the organic carbon as TOC and DOC.

Using flow and concentration data, we calculated loads for unfiltered THg and filtered THg, and then did a subtraction of unfiltered THg minus filtered THg to calculate an estimate for particulate THg. The same process was used with MeHg and organic carbon using filtered and unfiltered species.

The flow data from the ADCP and the autosampler collection times were matched (e.g. sampler collected at 12:30, so we used flow data for 12:30). The flow data used for the sample was collected as cubic feet per second and was derived from averaged values for a 15-minute interval (e.g. 12:30-12:44). We used the 15-minute flow value, extrapolated that value to the hour, and used that value to do a flow-weighted composite for each of the four tides (Ebb 1, Ebb 2, Flood 1, and Flood 2).

Usually we started collecting the hourly samples in the middle of a tide, so we combined tides from the beginning and end to make a complete tide. Occasionally, we were able to begin collecting at slack tide, before an ebb or flood tide began, but that was rare and difficult to achieve. See Figure 7 for an example of how we collected and divided our hourly samples into flood and ebb tides.

Figure 7 – Example of Tide Collection Times



During the April 27-28, 2015 event, three hourly samples were not collected by the autosampler, so we had to estimate the missing concentrations. To estimate the missing concentrations, we calculated the mean concentration for all the concentrations in the subset of samples, and used that mean value in place of the missing three samples.

Total Suspended Solids

Unlike our THg, MeHg, and organic carbon data, the total suspended solids (TSS) data were calculated from continuous turbidity values collected by a YSI EXO water quality sonde. The data is continuous and matches times with the flow data collected with the ADCP. Neither the ADCP nor the sonde collected a 100% complete data set. Missing data gaps less than six hours within the flow data record were estimated and filled using a cubic spline interpolation. For the sonde turbidity data, we estimated the missing concentrations using the average of the last value before the data gap and the first value after the data gap.

Values Below the Detection Limit

In the YWA Tidal Wetland data, there were very few mercury concentrations less than the detection limit (non-detects), far fewer than 10%. Because there were so few non-detects, we used one-half of the detection limit as a substitute value in statistical analyses.

Currently, there are no non-detects for the small amount of data we have collected from Blacklock Tidal Wetland. If more than 15% of the values are non-detects, we will use statistics that accommodate those non-detects.

Preliminary Results

Yolo Wildlife Area Tidal Wetland

THg and MeHg loads for the individual events at the YWA Tidal Wetland are shown in Table 1 and Table 2, respectively. In the tables, red highlighting and positive numbers indicate a source, green highlighting and negative numbers indicate a sink, and yellow highlighting indicates that the wetland was neither a source nor a sink during that event. Loads for organic carbon are in Table 3, and monthly estimated loads for TSS are in Table 4.

Tidal Water Balance

As seen in Table 1, Table 2, and Table 3, the tidal wetland was a sink of water during our 10 events, meaning more water was imported into the wetland than was exported. We are unsure of why the tidal wetland is a sink of water, although when discussing the water sink with the Yolo Wildlife Area Manager, Jeff Stoddard, he mentioned several factors that could affect tidal water balances. Apparently, there are many pumps in the Toe Drain to the north and south of the YWA Tidal Wetland, which pump water into and out of the Toe Drain. Jeff also mentioned that the tidal wetland is connected to one particular field, but that no water was pumped directly into or out of the field, so it is currently unclear whether the field affects the MeHg in the tidal wetland (Jeff Stoddard, California Department of Fish and Wildlife, pers. comm. September 14, 2015). These connections will be investigated more thoroughly for the final report.

THg and MeHg

In four out of 10 sampling events, the wetland was a source of THg. On all four occasions, the particulate fraction was the source, while the dissolved (filtered) portion was a sink. The majority of the THg was in the particulate phase. See Table 1.

During the 10 sampling events, the tidal wetland was never a source of total (or unfiltered) MeHg. However, on one occasion, the wetland was neither a source nor a sink of MeHg. However, on four different occasions, while not a source of total MeHg, the tidal wetland was twice a source of particulate MeHg and, on other occasions, twice a source of dissolved MeHg.

Organic Carbon

For all 10 sampling events, the tidal wetland was a sink of TOC (unfiltered). In two instances, while the DOC was a sink, the particulate organic carbon (TOC minus DOC) was a source, but the TOC was still negative and a sink. Unlike in the mercury species, for the most part, the majority of the organic carbon occurred in the dissolved phase, rather than in the particulate phase. See Table 3.

Total Suspended Solids

Overall, the wetland was a source of TSS with a net annual load of approximately 94,000 kg (Table 4 and Figure 8). The loads changed seasonally and the wetland was a sink of TSS from September 2014 through February 2015, and a source the rest of the year. Figure 8 shows TSS loads per month and includes the number of days of actual data that were used to estimate the entire month's load.

Table 1 – Load Calculations of Filtered and Unfiltered Total Mercury at the Yolo Wildlife Area Tidal Wetland

Sample ID	Flow (L/tide)	Unfiltered THg (g/tide)	Filtered THg (g/tide)	Unfilt-Filt THg (g/tide)
Ebb_Total_052814	87465550	1.71	0.12	1.58
Flood_Total_052814	-99198982	-1.59	-0.13	-1.46
Ebb+Flood_Total_052814	-11733432	0.12	-0.01	0.13
Ebb_Total_062414	134511687	2.07	0.16	1.91
Flood_Total_062414	-143890679	-1.91	-0.16	-1.75
Ebb+Flood_Total_062414	-9378992	0.16	0.00	0.16
Ebb_Total_081214	126469904	-1.42	0.11	1.31
Flood_Total_081214	-134479806	-1.31	-0.12	-1.19
Ebb+Flood_Total_081214	-8009902	0.11	-0.01	0.12
Ebb_Total_092214	84154581	0.53	0.06	0.47
Flood_Total_092214	-93517866	-0.70	-0.06	-0.64
Ebb+Flood_Total_092214	-9363285	-0.18	-0.01	-0.17
Ebb_Total_111714	33342141	0.23	0.00	0.22
Flood_Total_111714	-59388308	-0.66	-0.01	-0.63
Ebb+Flood_Total_111714	-26046166	-0.43	-0.01	-0.42
Ebb_Total_012615	77313415	0.58	0.11	0.47
Flood_Total_012615	-94076541	-0.83	-0.15	-0.68
Ebb+Flood_Total_012615	-16763126	-0.24	-0.04	-0.20
Ebb_Total_022415	72809459	0.63	0.14	0.49
Flood_Total_022415	-76032252	-0.70	-0.14	-0.55
Ebb+Flood_Total_022415	-3222793	-0.07	-0.01	-0.06
Ebb_Total_032315	56254996	0.57	0.05	0.53
Flood_Total_032315	-76211116	-0.79	-0.06	-0.73
Ebb+Flood_Total_032315	-19956120	-0.22	-0.02	-0.20
Ebb_Total_042015*	16107193	0.24	0.02	0.22
Flood_Total_042015*	-21663715	-0.48	-0.03	-0.45
Ebb+Flood_Total_042015*	-5556521	-0.24	-0.01	-0.23
Ebb_Total_042715**	28244929	0.46	0.02	0.44
Flood_Total_042715**	-32507106	-0.38	-0.04	-0.34
Ebb+Flood_Total_042715**	-4262177	0.08	-0.02	0.10
Key	Sink	Source	Neither source nor sink	

*Half a tidal cycle only

**Used mean concentration values for Ebb 1 due to missing samples.

Table 2 – Load Calculations of Filtered and Unfiltered Methylmercury at the Yolo Wildlife Area Tidal Wetland

Sample ID	Flow (L/tide)	Unfiltered MeHg (g/tide)	Filtered MeHg (g/tide)	Unfilt-Filt MeHg (g/tide)
Ebb_Total_052814	87465550	0.0136	0.0035	0.0100
Flood_Total_052814	-99198982	-0.0138	-0.0039	-0.0099
Ebb+Flood_Total_052814	-11733432	-0.0002	-0.0003	0.0002
Ebb_Total_062414	134511688	0.0205	0.0047	0.0157
Flood_Total_062414	-143890679	-0.0230	-0.0079	-0.0151
Ebb+Flood_Total_062414	-9378992	-0.0025	-0.0031	0.0006
Ebb_Total_081214	126469904	0.0155	0.0049	0.0106
Flood_Total_081214	-134479807	-0.0155	-0.0038	-0.0117
Ebb+Flood_Total_081214	-8009902	0.0000	0.0011	-0.0011
Ebb_Total_092214	84154581	0.0160	0.0061	0.0100
Flood_Total_092214	-93517866	-0.0179	-0.0074	-0.0105
Ebb+Flood_Total_092214	-9363285	-0.0019	-0.0013	-0.0006
Ebb_Total_111714	33342141	0.0028	0.0011	0.0017
Flood_Total_111714	-59388308	-0.0055	-0.0023	-0.0032
Ebb+Flood_Total_111714	-26046166	-0.0027	-0.0012	-0.0015
Ebb_Total_012615	77313415	0.0298	0.0151	0.0146
Flood_Total_012615	-94076541	-0.0415	-0.0185	-0.0230
Ebb+Flood_Total_012615	-16763126	-0.0117	-0.0033	-0.0084
Ebb_Total_022415	72809459	0.0334	0.0184	0.0151
Flood_Total_022415	-76032252	-0.0360	-0.0188	-0.0173
Ebb+Flood_Total_022415	-3222793	-0.0026	-0.0004	-0.0022
Ebb_Total_032315	56254996	0.0149	0.0047	0.0101
Flood_Total_032315	-76211116	-0.0167	-0.0046	-0.0122
Ebb+Flood_Total_032315	-19956120	-0.0019	0.0002	-0.0020
Ebb_Total_042015*	16107193	0.0029	0.0007	0.0022
Flood_Total_042015*	-21663715	-0.0039	-0.0008	-0.0032
Ebb+Flood_Total_042015*	-5556521.497	-0.0010	-0.0001	-0.0010
Ebb_Total_042715**	28244929	0.0046	0.0012	0.0034
Flood_Total_042715**	-32507106	-0.0047	-0.0014	-0.0033
Ebb+Flood_Total_042715**	-4262177	-0.0001	-0.0002	0.0000
Key	Sink	Source	Neither source nor sink	

*Half a tidal cycle only

**Used mean concentration values for Ebb 1 due to missing samples.

Table 3 – Load Calculations for Total and Dissolved Organic Carbon in the Yolo Wildlife Area Tidal Wetland

Sample ID	Flow (L/tide)	TOC (kg/tide)	DOC (kg/tide)	TOC-DOC (kg/tide)
Ebb_Total_052814	87465550	477	324	154
Flood_Total_052814	-99198982	-439	-351	-88
Ebb+Flood_Total_052814	-11733432	-87	-27	66
Ebb_Total_062414	134511687	430	417	13
Flood_Total_062414	-143890679	-518	-421	-97
Ebb+Flood_Total_062414	-9378992	-87	-4	-83
Ebb_Total_081214	126469904	425	365	59
Flood_Total_081214	-134479806	-451	-383	-67
Ebb+Flood_Total_081214	-8009902	-26	-18	-8
Ebb_Total_092214	84154581	573	539	34
Flood_Total_092214	-93517866	-622	-583	-39
Ebb+Flood_Total_092214	-9363285	-49	-44	-5
Ebb_Total_111714	33342141	128	119	9
Flood_Total_111714	-59388308	-226	-210	-16
Ebb+Flood_Total_111714	-26046166	-98	-91	-7
Ebb_Total_012615	77313415	528	508	21
Flood_Total_012615	-94076541	-643	-611	-31
Ebb+Flood_Total_012615	-16763126	-114	-104	-11
Ebb_Total_022415	72809459	616	585	32
Flood_Total_022415	-76032252	-641	-611	-30
Ebb+Flood_Total_022415	-3222793	-25	-26	1
Ebb_Total_032315	56254996	445	416	28
Flood_Total_032315	-76211116	-628	-575	-53
Ebb+Flood_Total_032315	-19956120	-183	-158	-25
Ebb_Total_042015*	16107193	126	105	21
Flood_Total_042015*	-21663715	-165	-139	-26
Ebb+Flood_Total_042015*	-5556521	-39	-34	-5
Ebb_Total_042715**	16107193	126	105	21
Flood_Total_042715**	-21663715	-165	-139	-26
Ebb+Flood_Total_042715**	-5556521	-39	-34	-5

Key	Sink	Source
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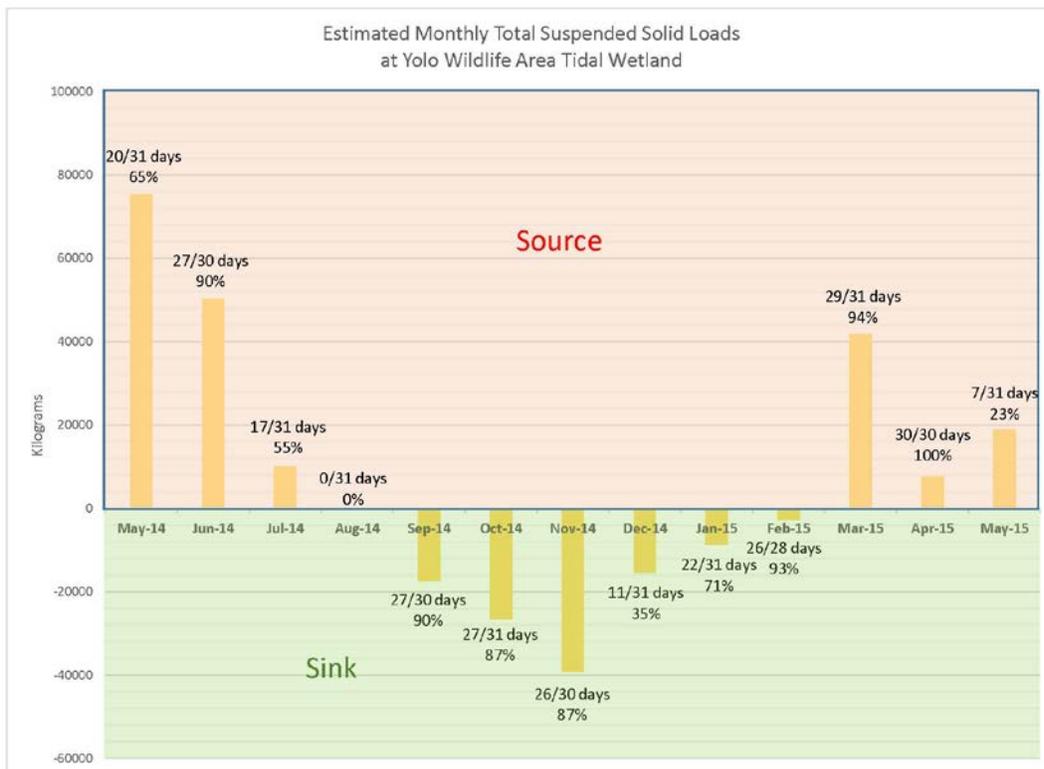
*Half a tidal cycle only

**Used mean concentration values for Ebb 1 due to missing samples.

Table 4 – Monthly Estimated and Calculated Loads of Total Suspended Solids

Date	Average Daily TSS Load (kg)	# of days included in load calculation	Total # of days in month	% of days included	Calculated Monthly TSS Load (kg)
May-14	2433	20	31	65%	75422
Jun-14	1675	27	30	90%	50263
Jul-14	325	17	31	55%	10068
Sep-14	-577	27	30	90%	-17311
Oct-14	-857	27	31	87%	-26571
Nov-14	-1307	26	30	87%	-39200
Dec-14	-496	11	31	35%	-15361
Jan-15	-281	22	31	71%	-8717
Feb-15	-97	26	28	93%	-2709
Mar-15	1353	29	31	94%	41930
Apr-15	255	30	30	100%	7663
May-15	610	7	31	23%	18921
Key	Sink	Source	Net TSS Load (kg):		94398

Figure 8 – Estimated Monthly Total Suspended Solid Loads in the Yolo Wildlife Area Tidal Wetland



Particulate and Dissolved THg and MeHg Concentrations and Seasonal Concentration Trends

Both Figure 9 and Figure 10 show the fractions of dissolved and particulate THg and MeHg concentrations for all 10 events. Also, for all events, we averaged the four concentrations (Ebb 1, Ebb 2, Flood 1, and Flood 2), except for the event on April 20, 2015, in which we had only data for one ebb and one flood event.

Because we have collected data only at one wetland, we were not able to do any statistical analyses to determine seasonal differences. However, we did graph the data and some visual trends were apparent. Hopefully, as we study more wetlands, we will be able to look at seasonal trends statistically.

Some seasonal variation in THg concentrations appeared to exist, mostly in the particulate form. Higher THg concentrations occurred in the spring through summer, and lower concentrations in the winter and fall. The THg was primarily in the particulate form during the entire year and the dissolved THg fraction was approximately 2-24% of the total THg concentration (Figure 9).

Figure 10 shows concentrations of MeHg for each of the 10 events. There were some seasonal patterns in MeHg concentrations, but the trend was not as strong as with THg. After the mini-flood event (as defined by Foe and others 2008) that occurred in the Yolo Bypass in December 2014, MeHg concentrations increased to their highest values collected during the study. During the January and February 2015 sampling events, the particulate MeHg concentrations increased, and the dissolved concentrations increased even more, so that the dissolved MeHg was almost equal to that of the particulate MeHg. This is consistent with the data collected during this mini-flood event for the Open Water modeling effort (Open Water Group 2015).

During the study, the MeHg concentration was 0.73-6.37% of the THg concentration and the dissolved MeHg portion was 0.15-3.29% of the unfiltered (total) THg concentration. The percentage of dissolved MeHg in the total MeHg concentration was 14-55%, which is higher than that of THg.

Figure 9 – Particulate and Dissolved Total Mercury Concentrations in the Yolo Wildlife Area Tidal Wetland

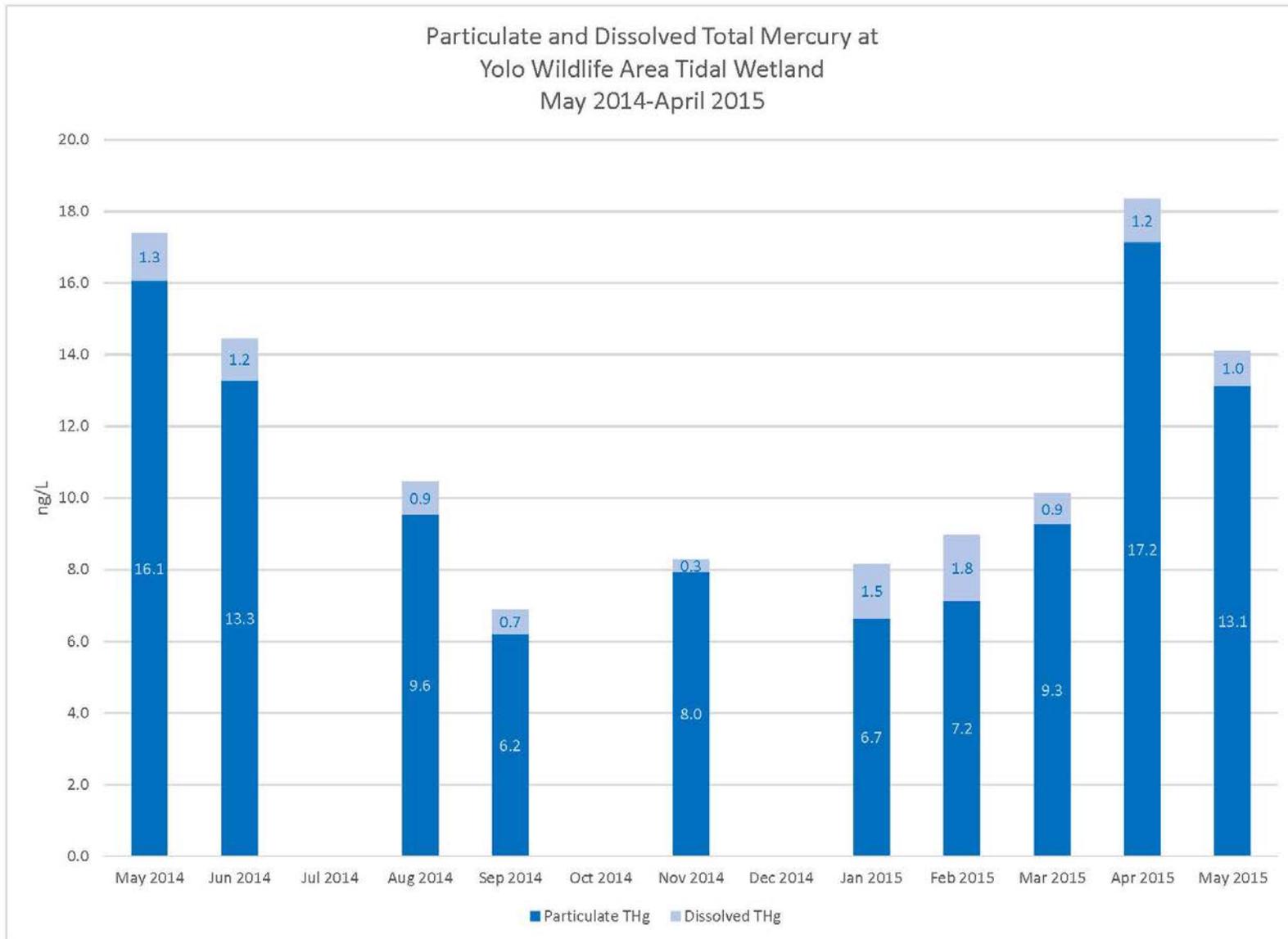
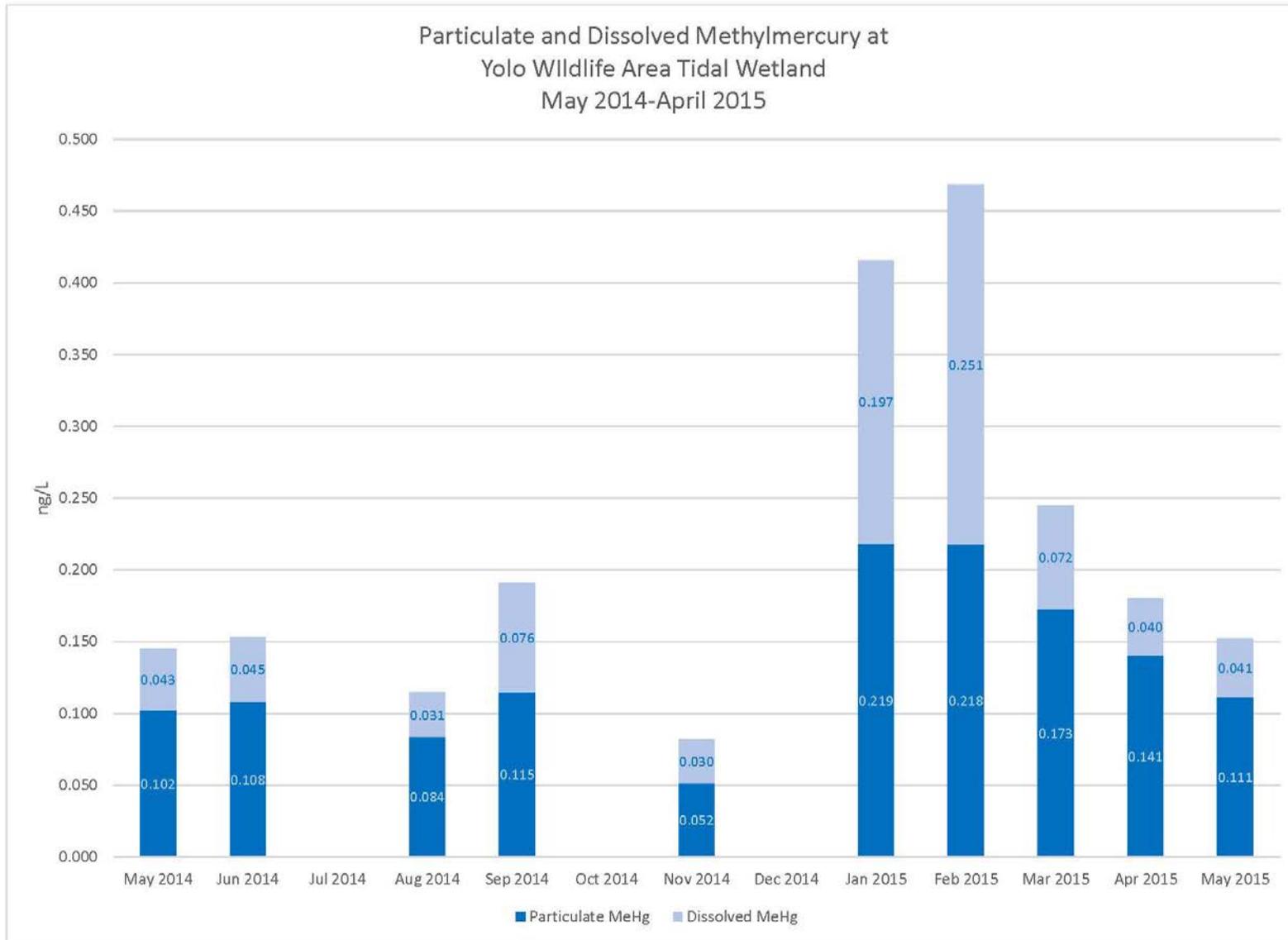


Figure 10 – Particulate and Dissolved Methylmercury Concentrations in the Yolo Wildlife Area Tidal Wetland



Ebb versus Flood

Because the tidal wetland was a sink of water, we thought it would be useful to determine if either the ebb or flood tide concentrations were higher. Visually, the average ebb and flood concentrations did not appear to be consistently different from each other; for example, ebb was not always higher than flood concentrations for any of the constituents (Figure 11, Figure 12, Figure 13, Figure 14, Figure 15, and Figure 16). This was corroborated by 1-Sample Wilcoxon Signed Rank tests on the ebb versus the flood concentrations. For all ebb and flood concentration comparisons (total, particulate, and dissolved MeHg and THg), there were no statistical differences ($p>0.05$, $n=10$).

There appeared to be a seasonal ebb and flood trend in the THg data, which was more pronounced in the particulate fraction. The concentrations of THg appeared to be consistently higher on the ebb tide (source) during the warmer months of May through August 2014 and April 2015 (Figure 11, Figure 13, and Figure 15). No such trend was apparent in the MeHg data.

Figure 11 – THg Ebb and Flood Concentrations in the Yolo Wildlife Area Tidal Wetland

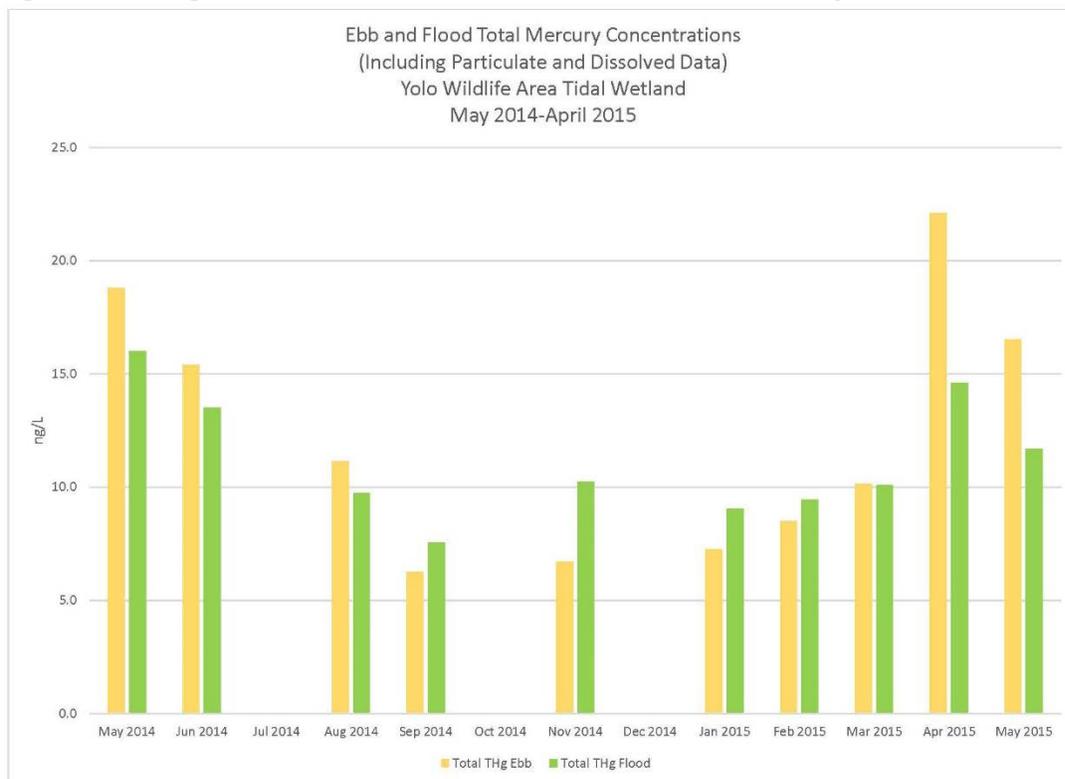


Figure 12 – Total MeHg Ebb and Flood Concentrations in the Yolo Wildlife Area Tidal Wetland

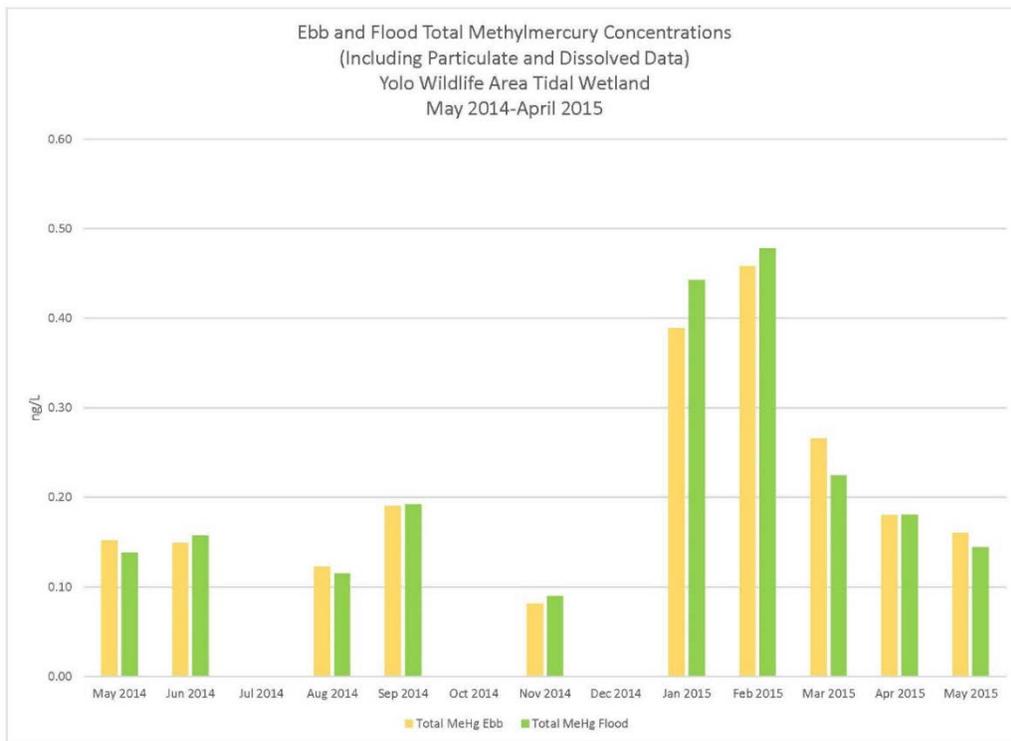


Figure 13 – Dissolved THg Ebb and Flood Concentrations in the Yolo Wildlife Area Tidal Wetland

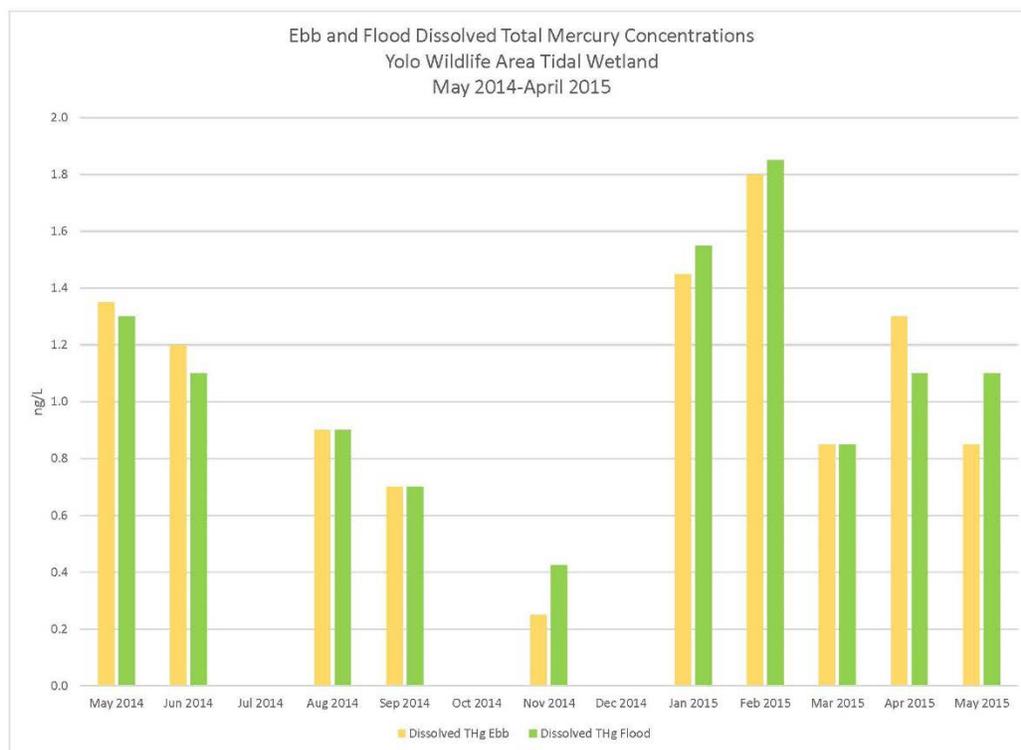


Figure 14 – Dissolved MeHg Ebb and Flood Concentrations in the Yolo Wildlife Area Tidal Wetland

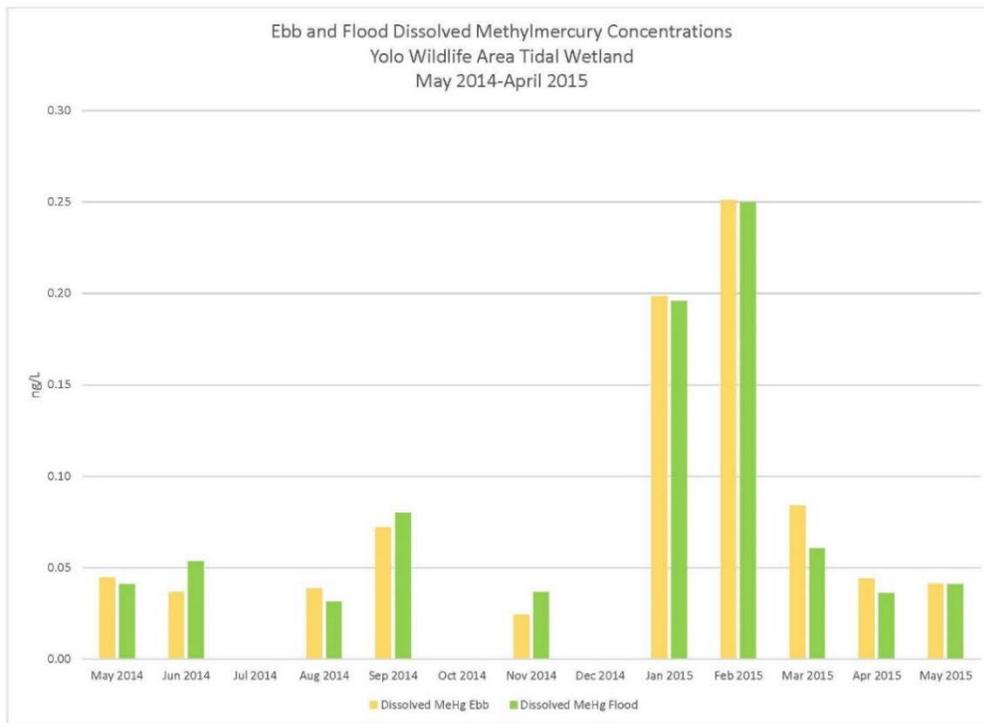


Figure 15 – Particulate THg Ebb and Flood Concentrations in the Yolo Wildlife Area Tidal Wetland

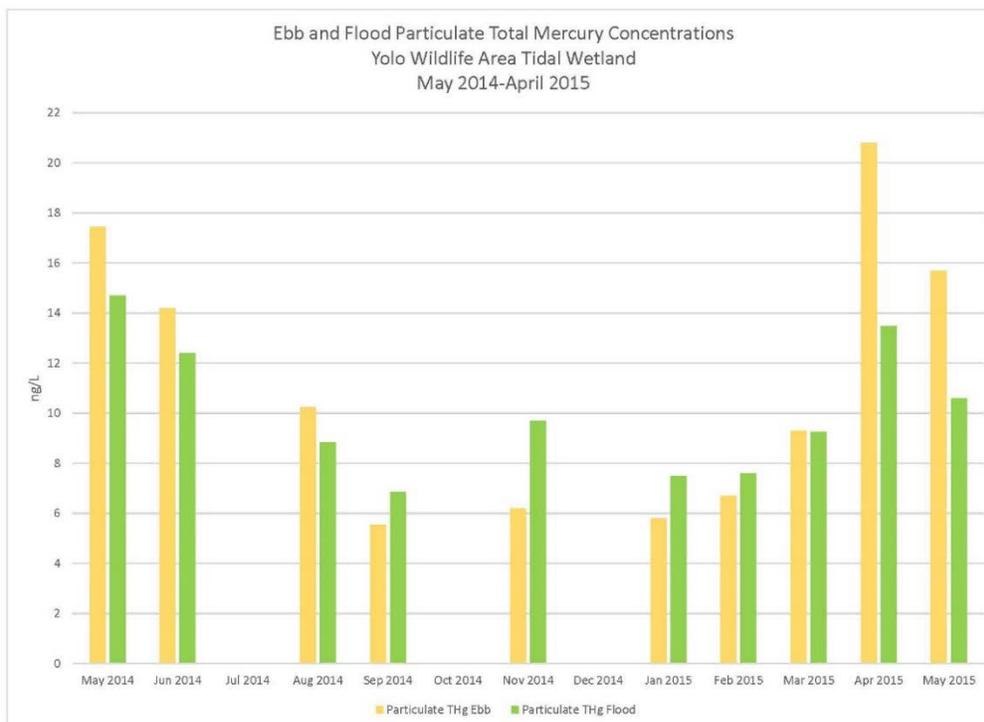
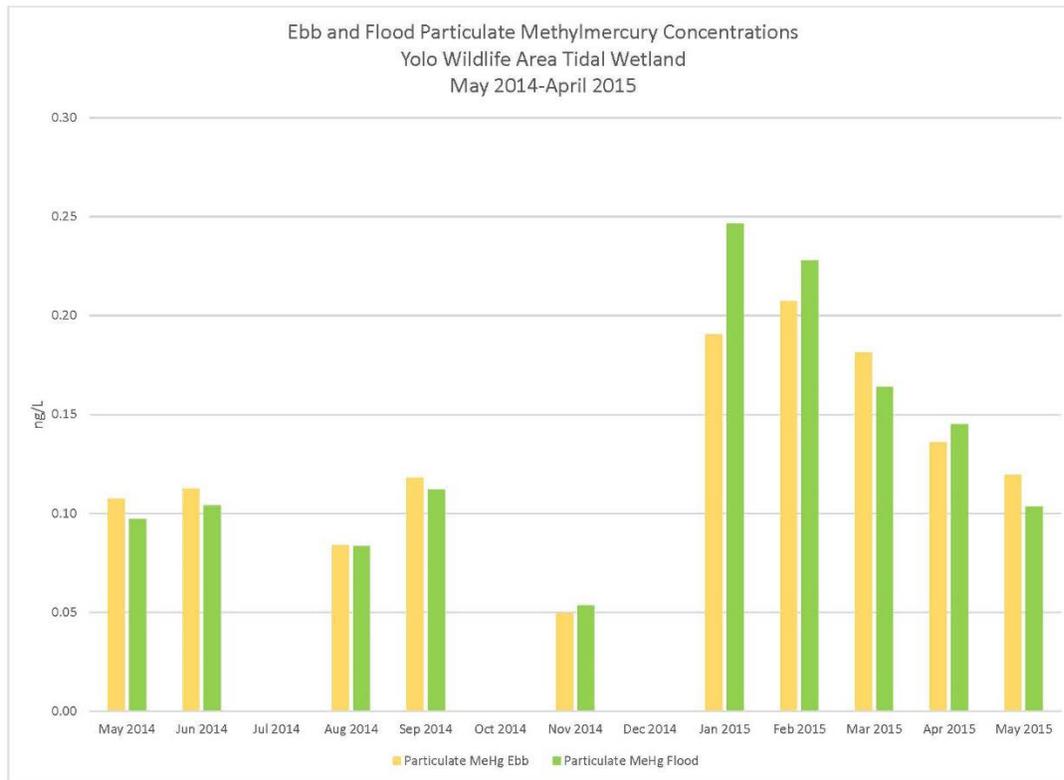


Figure 16 – Particulate MeHg Ebb and Flood Concentrations in the Yolo Wildlife Area Tidal Wetland



Constituent Relationships

DWR looked at a few of the important constituent relationships in this interim report: TSS vs. particulate THg, TSS vs. particulate MeHg, and DOC vs. dissolved MeHg. For this analysis, we looked at relationships between loads rather than concentrations. By the final report, we will look at correlations for loads and concentrations for all combinations of constituents.

Plots of each constituent relationship over time are shown in Figure 17, Figure 19, and Figure 21, scatterplots of each constituent relationship are shown in Figure 18, Figure 20, and Figure 22, and Spearman's rho correlation coefficients are provided in Table 5. Both the TSS vs. particulate THg ($p=0.002$) and TSS vs. particulate MeHg ($p=0.029$) relationships were significantly correlated, but the DOC vs. dissolved MeHg was not ($p=0.815$). Of note, whereas Mitchell and others (2012) found a correlation between DOC and dissolved MeHg at the wetland they studied, at the Yolo Wildlife Area Tidal Wetland, we did not.

Figure 17 – Total Suspended Solids and Particulate Total Mercury Loads in the Yolo Wildlife Area Tidal Wetland

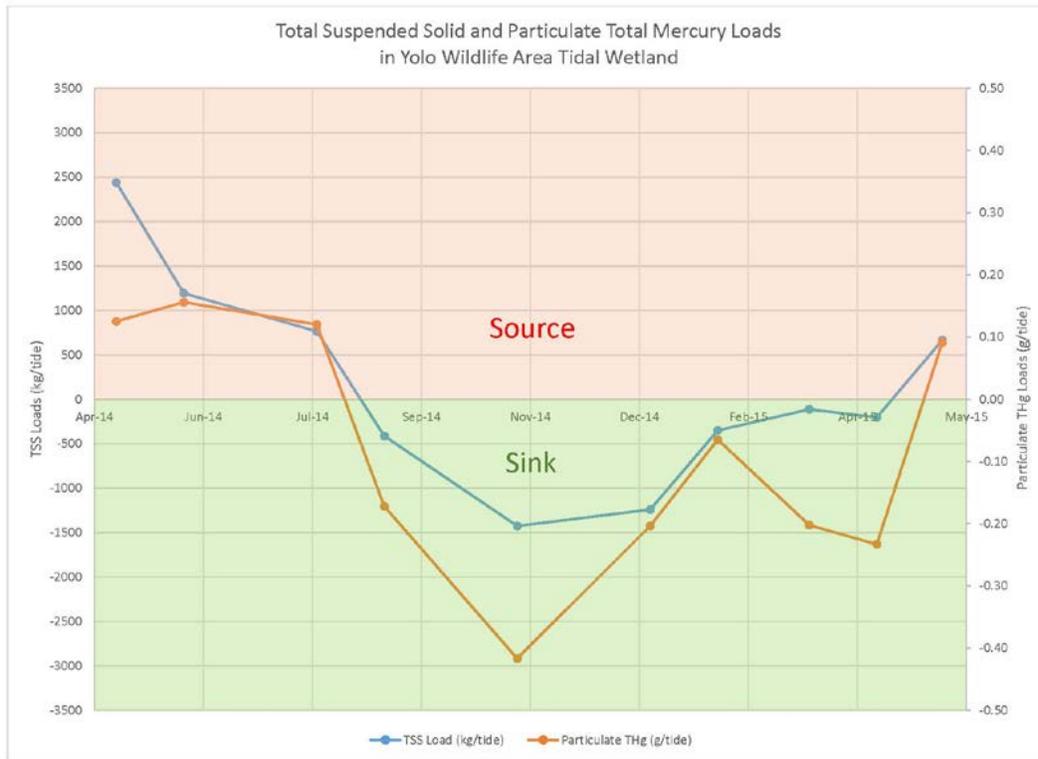


Figure 18 – Scatterplot of Total Suspended Solids versus Particulate Total Mercury Loads

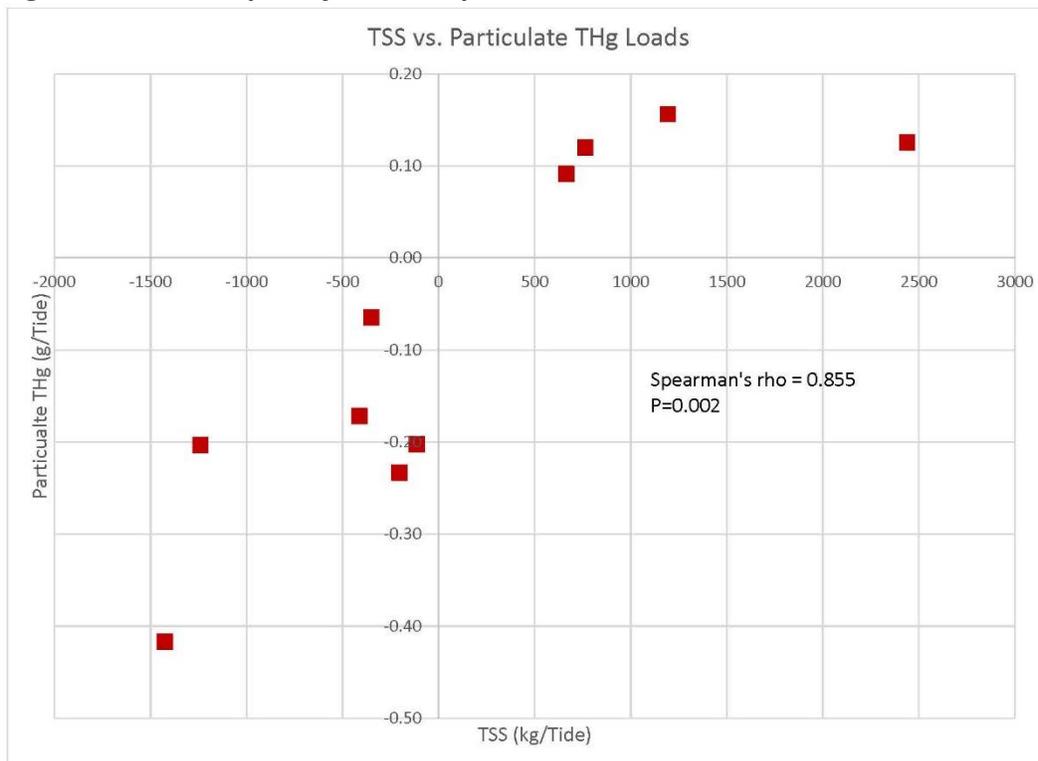


Figure 19 – Total Suspended Solids and Particulate Methylmercury Loads in the Yolo Wildlife Area Tidal Wetland

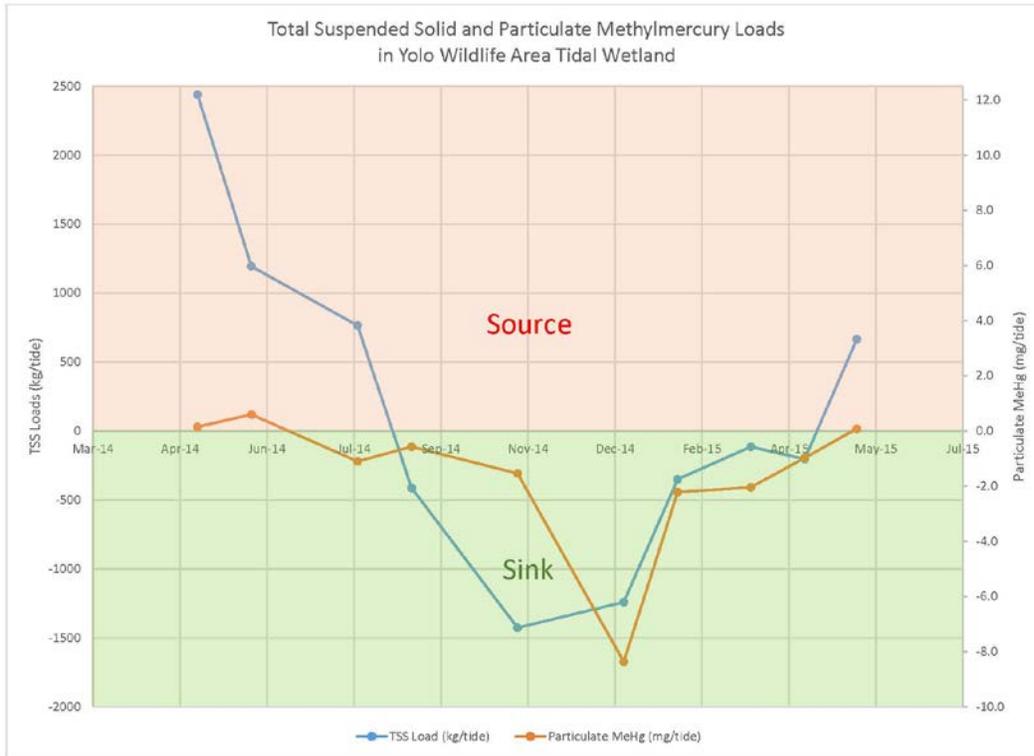


Figure 20 – Scatterplot of Total Suspended Solids versus Particulate Methylmercury Loads

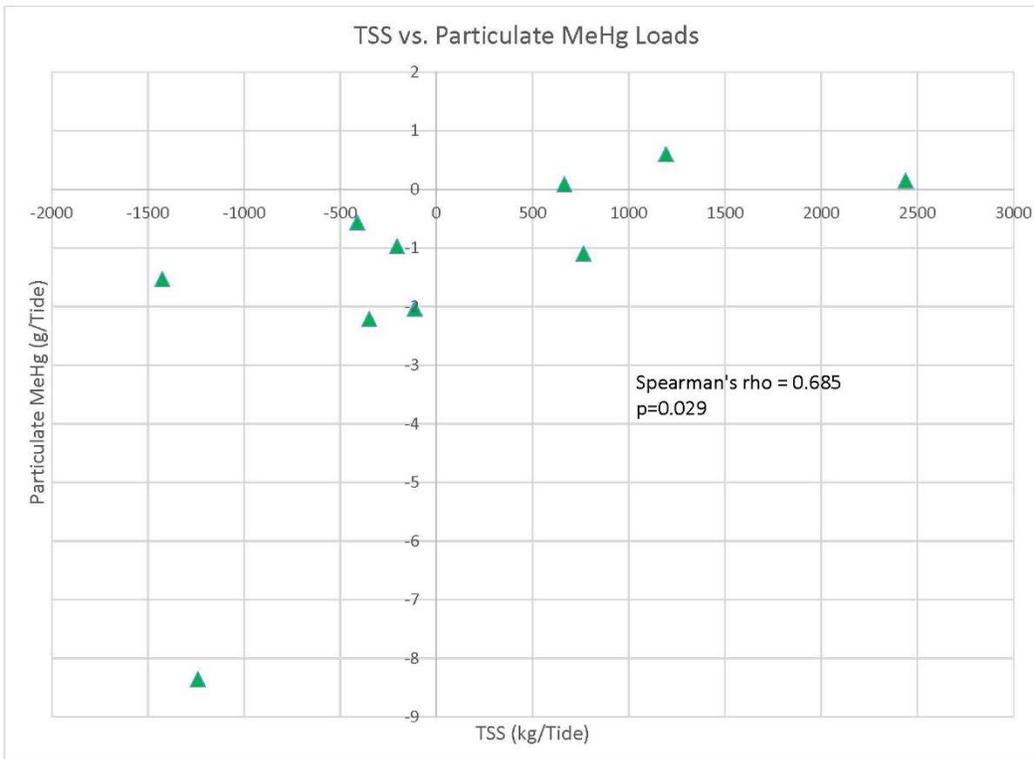


Figure 21 – Dissolved Organic Carbon and Dissolved Methylmercury Loads in the Yolo Wildlife Area Tidal Wetland

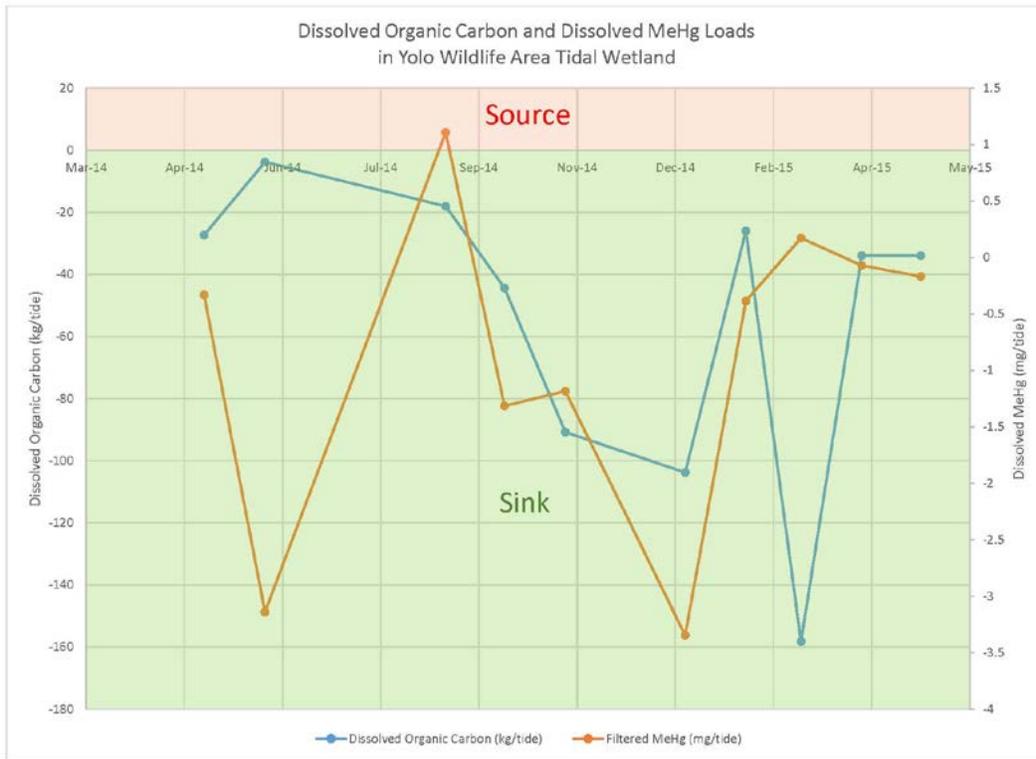


Figure 22 – Scatterplot of Dissolved Organic Carbon versus Dissolved Methylmercury Loads

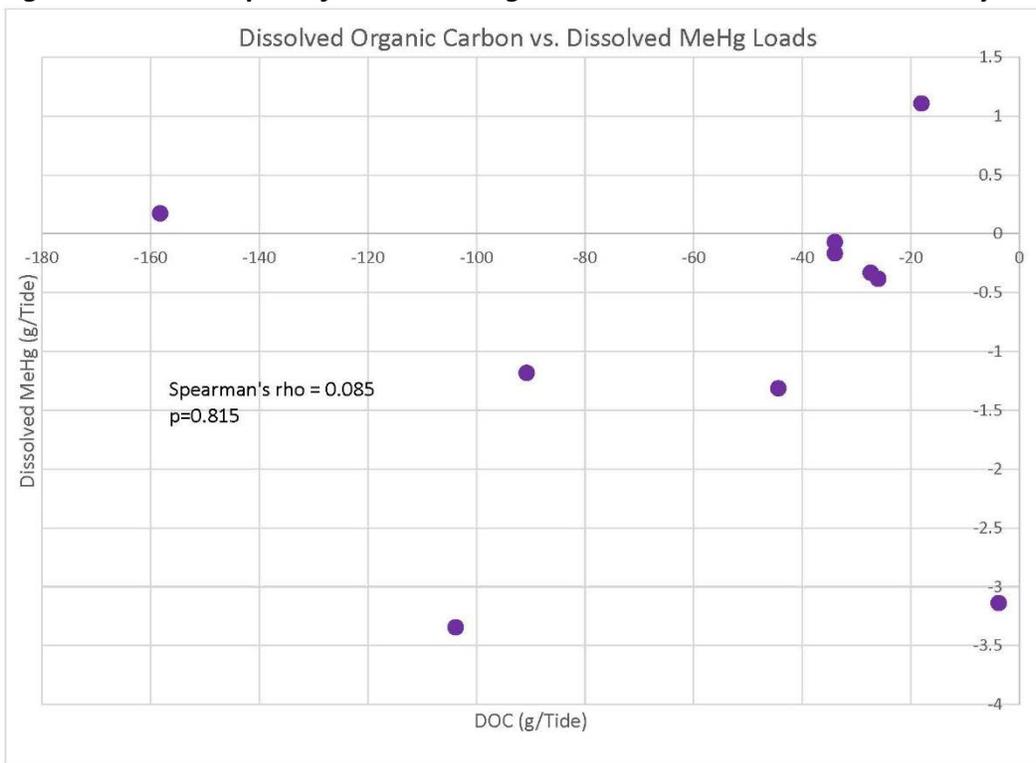


Table 5 – Spearman’s rho correlation coefficients

Relationship	n	Spearman’s	
		rho	p-value
TSS vs. particulate THg	10	0.855	0.002
TSS vs. particulate MeHg	10	0.685	0.029
DOC vs. dissolved MeHg	10	0.085	0.815

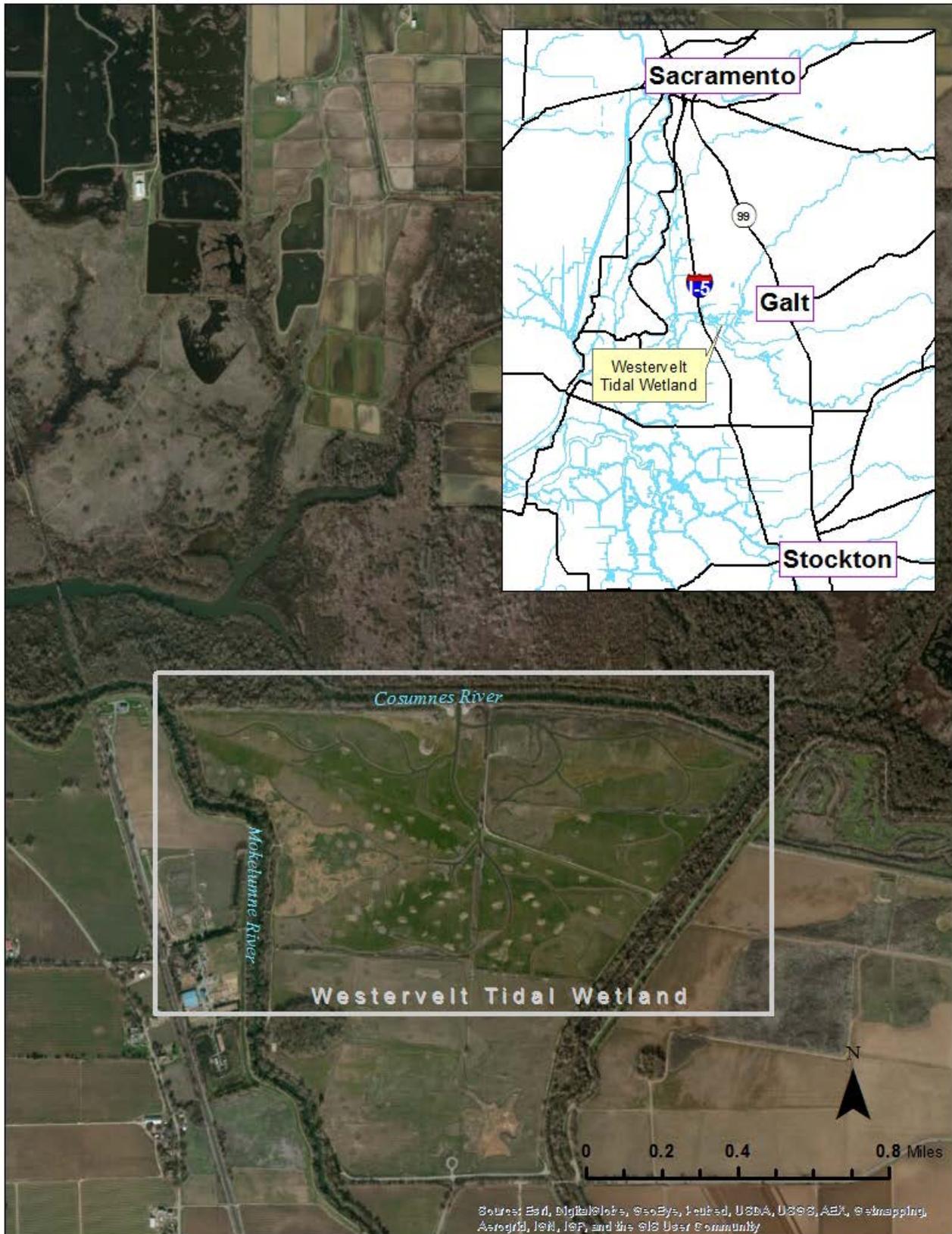
Blacklock Tidal Wetland

In June 2015, DWR started collecting data at the Blacklock Tidal Wetland. As of this report, we had completed three sampling events in June, July, and September 2015. Data analysis will be slightly more complicated for Blacklock than for the YWA Tidal Wetland, because it has two breaches and we are collecting twice as much data. We have data from the first event only, June 2015, and on one of the breaches, we were only able to collect half of a tidal cycle. That data will be included in the final report in 2018.

Next Steps***Next Potential Wetlands***

DWR will continue to collect data from the Blacklock Tidal Wetland through May 2016. Around that time, we plan to begin studying our third tidal wetland, likely the Westervelt Cosumnes Tidal Wetland (see Figure 23 for location), which we are planning to study from June 2016 through May 2017. This schedule would leave us little time to study a fourth wetland and write up the large amount of data before the October 2018 deadline. However, ongoing discussions with Regional Board staff will continue so that, if feasible, we will study four or more wetlands in total. Other tidal wetland options for study may include Decker Island, Prospect Island (if it is built within the time period), Wildlands Liberty Island Conservation Bank, or any other tidal wetland in the Delta that meets our requirements.

Figure 23 – Location of Westervelt Cosumnes Tidal Wetland



Future Data Analyses

We want to acknowledge that DWR did not do a full data analysis in this interim report. We did not look at correlations between nor did we calculate loads for all constituents. We also did not calculate estimated loads for all constituents on a yearly basis. In the final report, we will be doing a more complete analysis, which will include data from more than the one wetland analyzed in this report.

This study is the largest and most comprehensive import/export study of freshwater tidal wetlands ever attempted. Despite being the largest study, we are collecting data from 8-12 tidal cycles throughout the year to estimate an entire year, so any monthly or yearly loads are estimations. To estimate loads, we will be taking a similar approach to analysis as Mitchell and others (2012), and we will attempt to estimate yearly loads with the collected data.

DWR will continue calculating loads of mercury, organic carbon, TSS, and chlorophyll of tidal wetlands in the Delta, Yolo Bypass, and Suisun Marsh. We will continue looking at correlations between constituents for the YWA Tidal Wetland and other wetlands to determine if any patterns exist among tidal wetlands in the region. Future data analysis will be discussed with Regional Board staff as we continue to provide study updates.

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APPENDIX A

DRAFT

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

***Draft Environmental Monitoring Plan
California Department of Water Resources***

***By Petra Lee, Senior Environmental Scientist - Specialist
Updated October 20, 2015***

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1. Introductions and Overview

To address Hg contamination in the Delta and Yolo Bypass, the Central Valley Regional Water Quality Control Board (Regional Board) adopted the Methylmercury Total Maximum Daily Load and Basin Plan Amendment that established a Delta Mercury Control Program (DMCP) (Wood and others 2010a, Wood and others 2010b). 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 MeHg and total mercury (THg) imports and exports of tidal wetlands (Mitchell and others 2012, Bergamaschi and others 2011, Langer and others 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 MeHg imports and exports of tidal wetlands 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 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 may be used to adjust TMDL allocations accordingly and plan for future tidal wetlands.

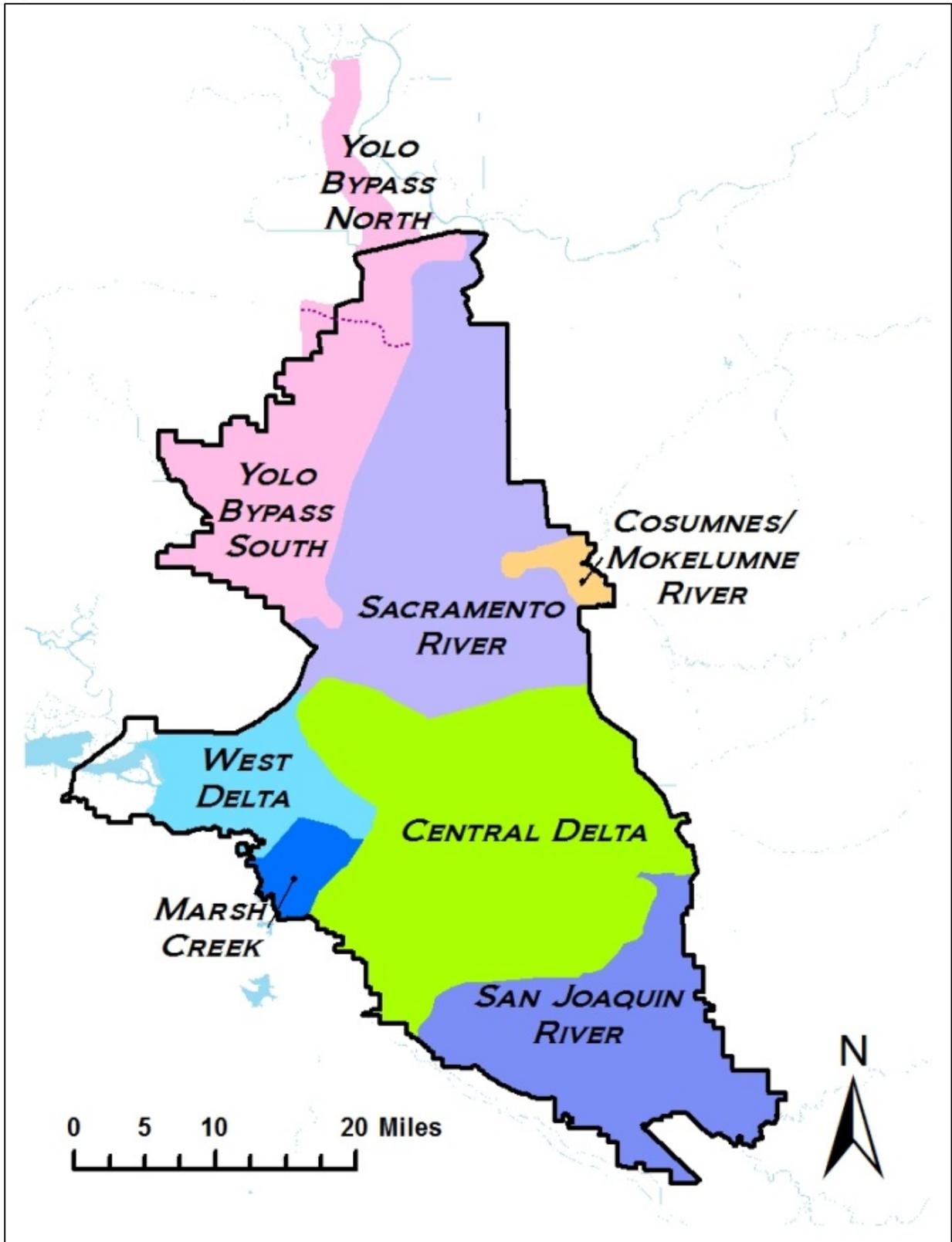
In this monitoring plan, the sampling plan details will be outlined for staff from DWR's Mercury Monitoring and Evaluation Section (MME) as well as other relevant parties.

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 and others 2010a, Wood and others 2010b) (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. As such, we 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.

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 be in contact with the Project Manager to arrange sample analysis and provide sample supplies. He will also be a point of contact for the MLML contract with DWR.

Allan Wong is the Bryte Laboratory Liaison 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.

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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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
Autumn Bonnema	MLML	MLML QA Officer	831-771-4175	bonnema@mlml.calstate.edu
Allan Wong	DWR	Bryte Laboratory QA Officer	916-375-6008	Allan.W.Wong@water.ca.gov

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 is the Regional Board Liaison for Delta Methylmercury TMDL implementation. She guides 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 2 – Other Roles

Name	Affiliation	Phone	Email
Janis Cooke	Regional Board	916-464-4672	Janis.Cooke@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 12-15 month period. A status and final report to the Regional Board are due in 2015 and 2018, respectively, unless an extension of up to two years is granted by the Regional Board Executive Officer (CVRWQCB 2011).

Table 3 – Approximate Study Schedule

Task	Anticipated Schedule
Initial Project Planning*	June 2013 – May 2014
Data Collection	April 2014 – December 2017
Data Analysis	March 2015 – March 2018
Status Report for Regional Board	May – October 2015
Final Report for Regional Board	January – October 2018

*Project planning will continue throughout the project life

5. Monitoring Strategy and Design

5.1 Ebb and Flood Tide Characterization

DWR will do in-depth studies of 3-8 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 as well as THg for 8-12 25-hour periods to estimate MeHg and THg loads over a one year period. As much as possible, sampling events will occur during spring and neap tides; however, because of staff schedules, work weekdays, site access, and other restrictions, we may not always be able to sample during spring and neap tides. 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 or mouths 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, generally 12-15 months. 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 stage 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 water quality sonde will be placed at the mouth or mouths of the wetland, near the ADCP(s), but not close enough to affect flow around the ADCP. The sonde will collect water quality continuous 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 Total Mercury and Methylmercury Sampling Events

At each wetland studied, DWR will collect THg and MeHg samples during a minimum of 8 sampling events over approximately a year period. Each event will happen over a 25-hour period in order to capture an entire tide cycle. These samples will be collected hourly, using an autosampler, 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 α .

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. Using glass bottle sets of four or eight bottles per autosampler, sample capacity of each autosampler is between 14 and 15 L, which will be a factor in how often we must change out the bottles during a tidal cycle. See Figures 2 and 3.

August 2015 Update

In April of 2014, DWR did a proof of concept to determine if the autosamplers were biasing the samples. We did a "Mini-Study" comparing the samples collected by grab sample vs. those collected via autosampler, specifically the ISCO 6712. The study was run and using a 1-Sample Wilcoxon, results indicated that MeHg and THg samples were not being biased due to collection by autosampler. More information about the proof of concept can be found in Appendix I.

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, within 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 sucks the water into the autosampler) will be attached to a cleaned strainer 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 the Yolo Wildlife Area tidal wetland, the PTFE suction line will be attached to a stake in the wetland that will keep the line from floating away, and also to a float so that the intake was sampling water (and not sucking up sediment from the bottom of the channel. See Figure 4 for a photo of the deployment.

Figure 4 – Autosamplers deployed of the Yolo Wildlife Area tidal wetland with PTFE suction lines attached to stakes and a float in the water



In the Blacklock tidal wetland, the three autosampler PTFE suction lines at each breach will be cable tied together with a plastic covered stainless steel cable. 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. The cable tied PTFE suction lines, stainless steel cable, and strainers are pictured in Figure 5. Figure 6 shows the weight and float set that the suction line will be attached to. Figure 7 shows the float, weight and suction line set up in approximately 4-5 feet of water. At Blacklock, the range of depths that the strainers will be in is 4.5-12.5 feet.

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

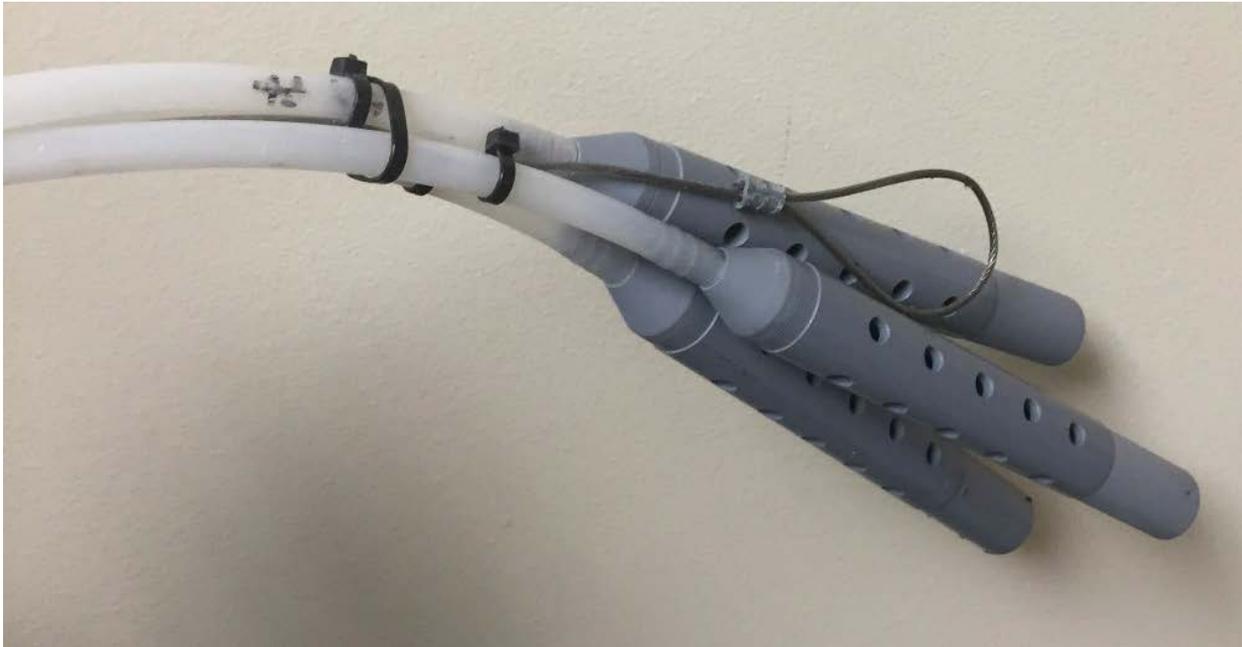
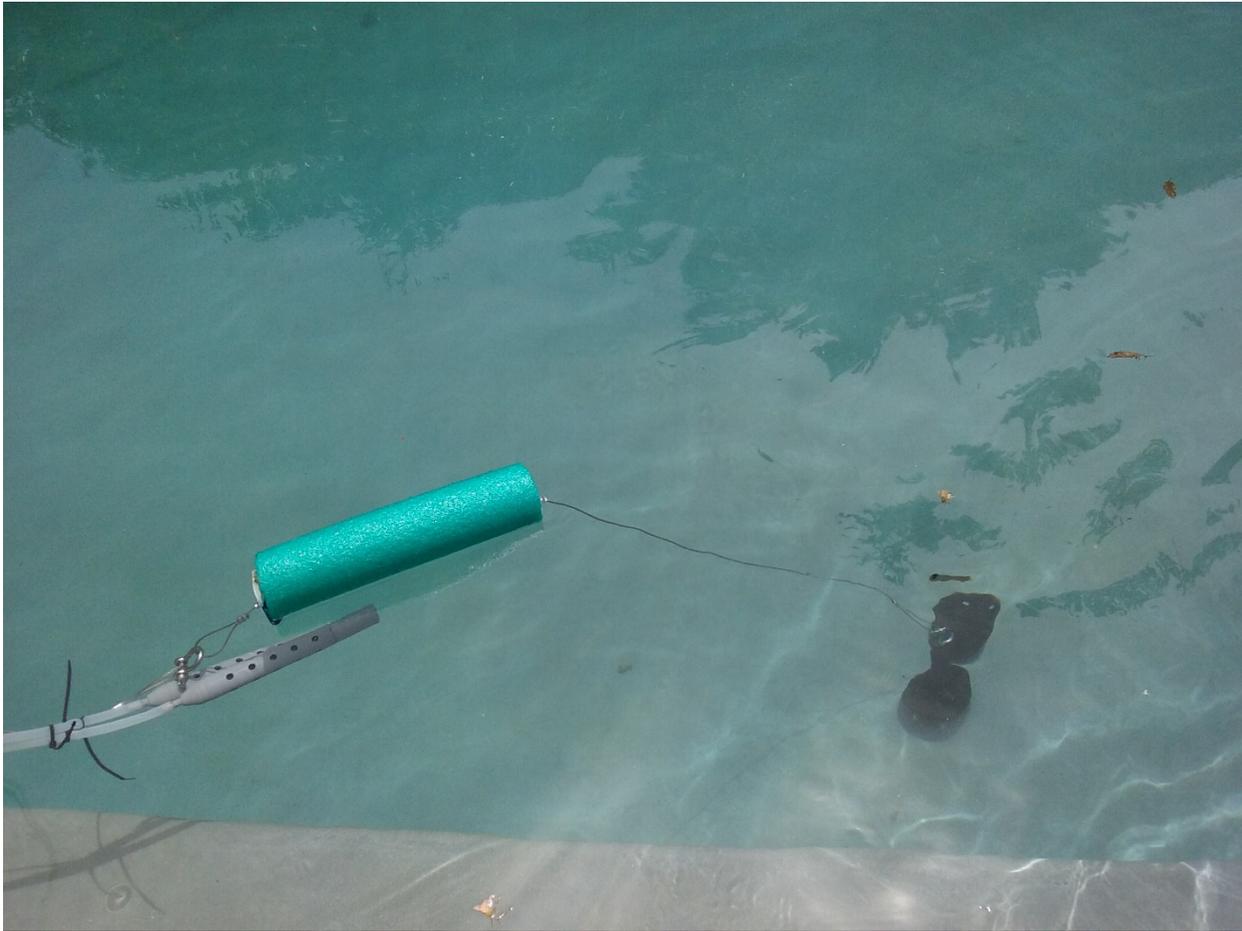


Figure 6 – Float and weight set up



Figure 7 – Autosampler suction line set up for Blacklock tidal wetland

5.1.1.4 Comparing Hourly Calculated Compositing and Manually Compositing Flow-Weighted Samples

To reduce the number of THg and MeHg samples that DWR is paying for to be analyzed, we will be manually compositing samples using flow data, tides, and a flow-weighting technique. Initially, DWR will do a proof of concept that the manually compositing samples provide the same loads as hourly data. We will collect and analyze hourly samples, analyze manually compositing samples, and calculate composites from hourly data. We will do this two times and compare the results using a 1-Sample Wilcoxon. If the manually compositing samples and calculated hourly composites are not different, we will switch to solely collecting water to do manually compositing samples. If the samples are different, we will continue to work with our methods until we get two sets of samples that are not significantly different using the 1-Sample Wilcoxon.

September 2015 Update

DWR staff collected and analyzed samples for two 25-hour tidal cycles at the YWA Tidal Wetland. We analyzed the hourly samples and calculated a composite value using flow data.

We compared the calculated composite value (calculated composites) to the composites that we manually composited in the lab (manual composites).

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 8 shows bar graphs of the loads, which shows that while there were some visual differences, but that on the whole, the values tracked fairly well. Additionally, we graphed the data using box plots and visually, they appeared to be similar. See Figure **Error! Reference source not found.**9 for the associated boxplots.

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Figure 8 – Calculated versus Manually Composited Loads

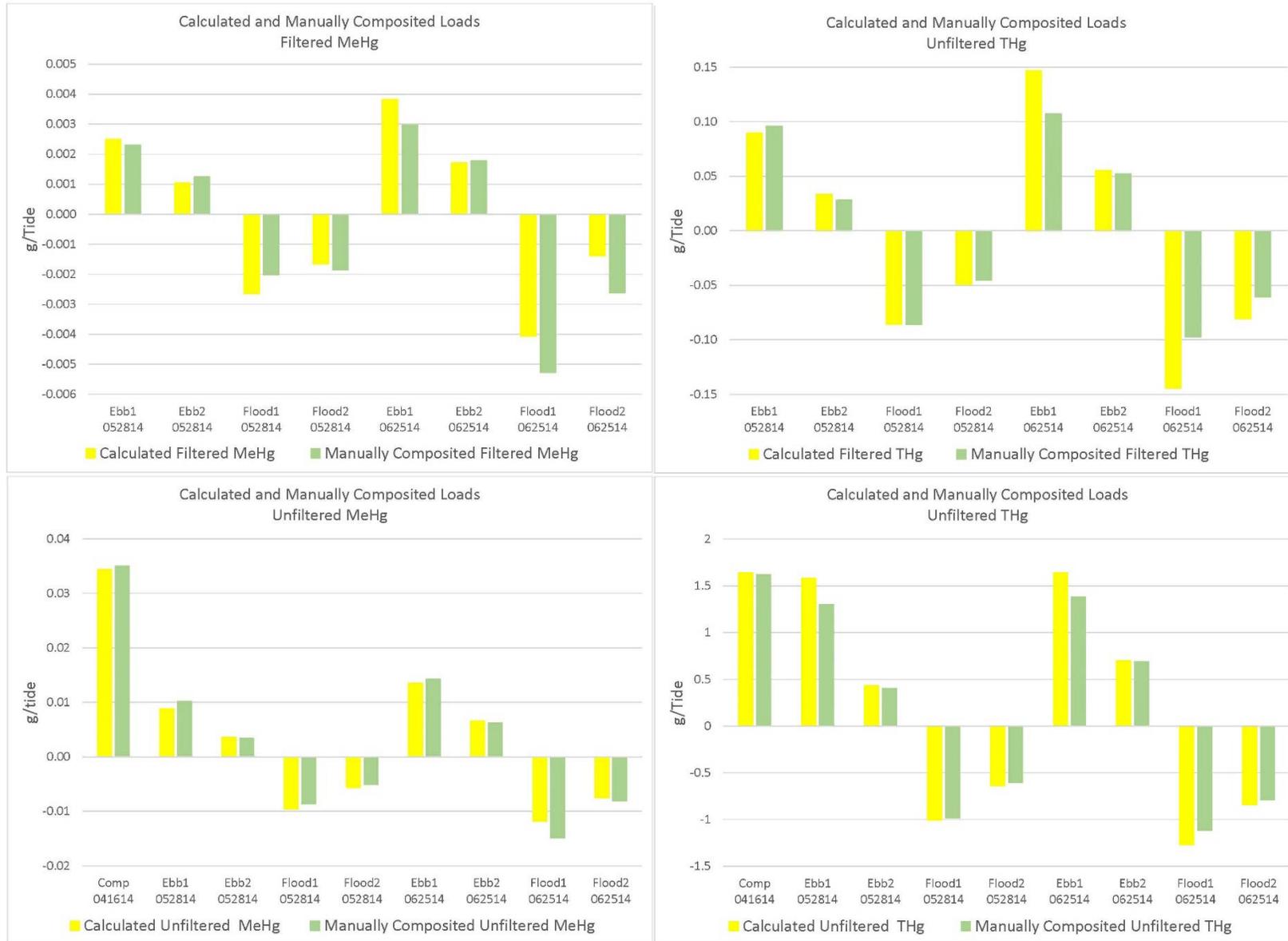
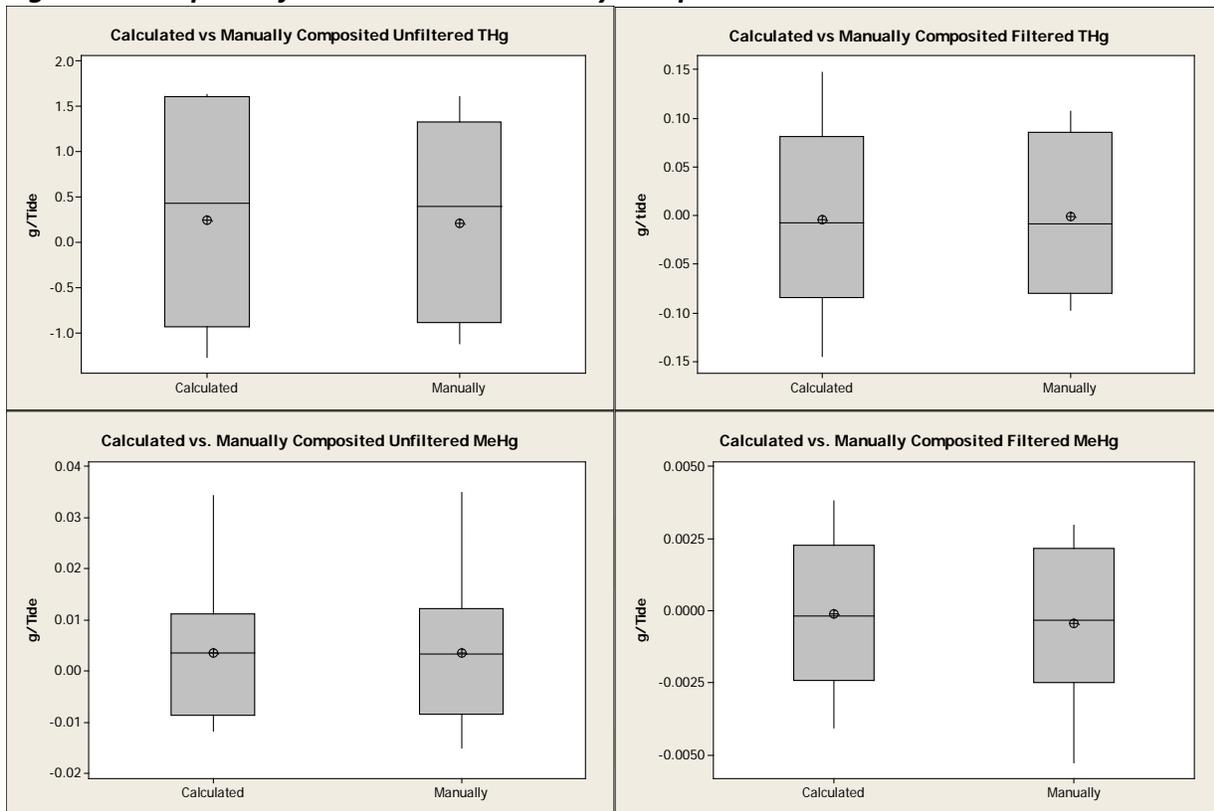


Figure 9 – Boxplots of Calculated vs. Manually Composited Loads

5.1.1.5 Manually Composited Flow-Weighted Samples

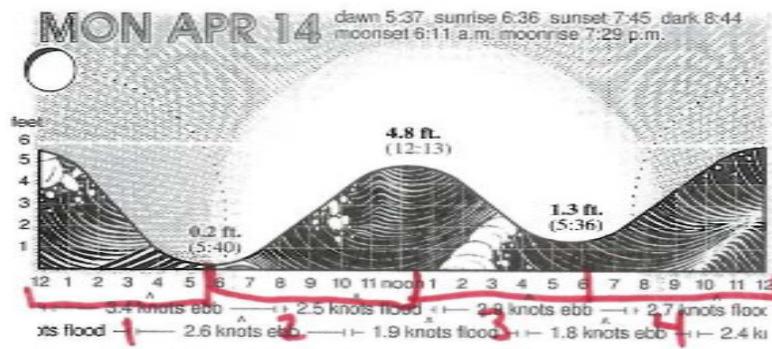
To composite the THg and MeHg samples using flow data, DWR will download flow data from the ADCP and calculate flow weighted composites using the compositing recipe worksheet. An example of the output is shown in Figure 10. The study area has a mixed semidiurnal tidal cycle, meaning there are two high and two low tides of varying heights a day. 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 11 shows an example of the four potential sample groups that could occur.

Figure 10 – Example of Flow Weighted Compositing Recipe

Tidal Cycle: Ebb Tide 1					Tidal Cycle: Flood Tide 1				
Bottle #	Collection Time	Flow (cfs)	Proportion of Total Flow during Tidal Cycle	Weight of subsample required (g)	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	2	6/25/2014 0:00	-83.5458	0.095	381
8	6/25/2014 6:00	207.541	0.235	939	3	6/25/2014 1:00	-171.478	0.196	783
9	6/25/2014 7:00	162.8851	0.184	737	4	6/25/2014 2:00	-211.594	0.241	966
10	6/25/2014 8:00	158.8693	0.180	719	5	6/25/2014 3:00	-200.361	0.229	915
11	6/25/2014 9:00	124.2403	0.141	562	6	6/25/2014 4:00	-195.474	0.223	892
12	6/25/2014 10:00	93.11139	0.105	421	7	6/25/2014 5:00	-13.7974	0.016	63
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: Ebb Tide 2					Tidal Cycle: Flood Tide 2				
Bottle #	Collection Time	Flow (cfs)	Proportion of Total Flow during Tidal Cycle	Weight of subsample required (g)	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	16	6/25/2014 14:00	-27.4708	0.051	205
22	6/25/2014 20:00	132.8415	0.305	1220	17	6/25/2014 15:00	-62.7364	0.117	469
23	6/25/2014 21:00	122.2913	0.281	1123	18	6/25/2014 16:00	-144.556	0.270	1080
24	6/25/2014 22:00	97.9128	0.225	899	19	6/25/2014 17:00	-161.499	0.302	1207
25	6/25/2014 23:00	70.1516	0.161	644	20	6/25/2014 18:00	-139.001	0.260	1039

Figure 11 – Example of Potential Sample Groups



Initially, DWR planned to target events during spring and neap tidal cycles, in order to measure the extremes of the tidal cycle. However, it is highly likely that non-spring and neap tides will be sampled due to a Monday-Friday work week, lab hours, personnel availability, and timing of spring and neap tides. Because we anticipate higher methylmercury production rates during the warmer summer months, we plan to sample more frequently during summer than during winter.

5.1.2 Sampling Locations

DWR plans to study 3-8 (several) tidal wetlands, and will choose tidal wetlands year to year and include them in this monitoring plan. Currently, we plan on studying the wetlands that are described below, but plans may change. This monitoring plan will be updated appropriately as it will be a living document.

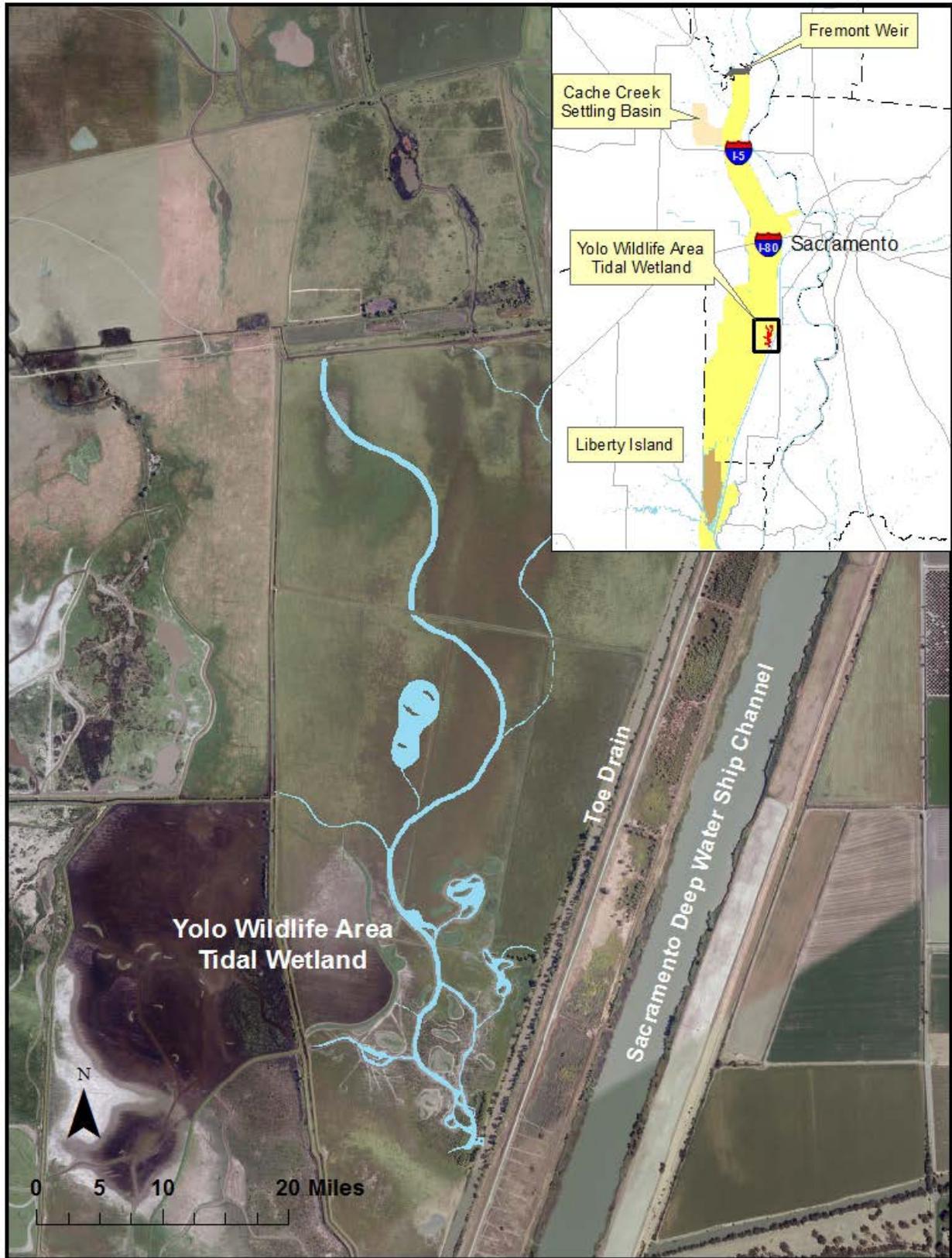
5.1.2.1 Yolo Wildlife Area Tidal Wetland

The first wetland we will be studying is the Yolo Wildlife Area tidal wetland, which is located in the southern portion of the Yolo Wildlife Area (see Figure 12). The wetland is tidal, has one opening (mouth), and contains fresh water. This tidal wetland may be altered to accommodate Putah Creek flow in the future.

The wetland is open to hunting from September 1st through the first week of February, with a week of non-hunting in early October. Because of this, sampling may be less frequent during those months. Additionally, the tidal wetland is located in the Yolo Bypass which can flood during winter months, and we will not be able to collect samples during flooding. Because this is the first wetland that we will be studying, we will determine how to and whether or not to estimate winter imports and exports after sampling begins. Additionally, this wetland is located close to the DWR office, and can be monitored more frequently in order to refine methods.

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Figure 12 – Location of Yolo Wildlife Area Tidal Wetland



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, Jeff Stoddard, before setting foot onto the land.
3. The tidal wetland is relatively new and has very little vegetation, making it not ideal for 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.

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Figure 13 – Yolo Wildlife Area Tidal Wetland Equipment Locations



5.1.2.2 Blacklock Area Tidal Wetland

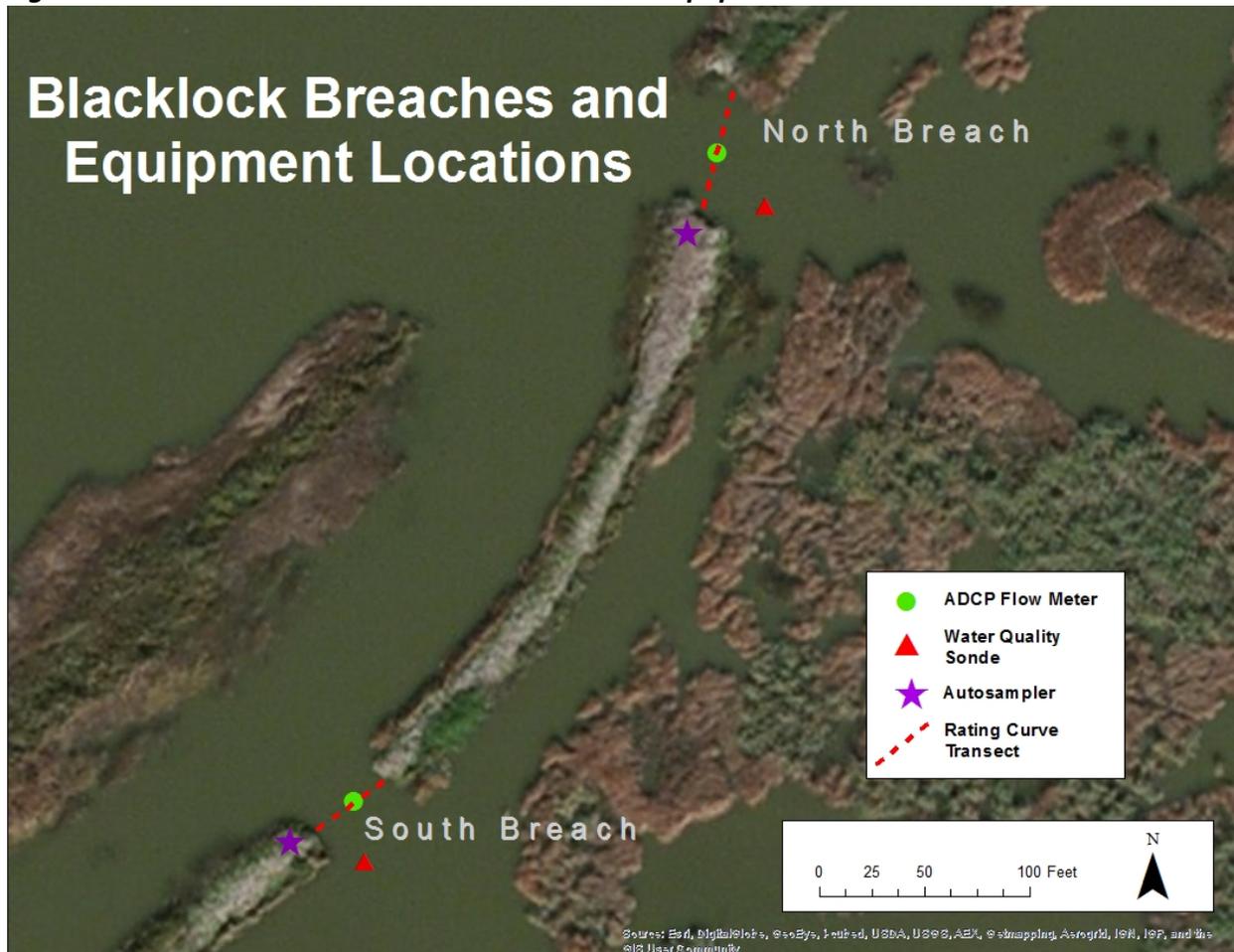
The second wetland that we will be studying is Blacklock tidal wetland which is located in the Suisun Marsh, west of the DMCP. The Blacklock property was acquired by DWR in December 2003 and is approximately 70 acres of tidal wetland. In July 2006, an unplanned breach occurred on the northwest levee, 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 during the study.

The ADCPs, which will be used to collect velocity, stage, and flow data, will be mounted on a weight 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. 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

5.1.3 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, total and dissolved
 - MeHg, total and dissolved
 - Total Organic Carbon

- Dissolved Organic Carbon
 - Total Suspended Solids (for Blacklock only)
2. The following physical parameters will be measured at the mouth of the wetland via water quality sonde (YSI EXO1 or EXO2):
- Temperature
 - Specific conductance
 - Salinity
 - Turbidity
 - Total chlorophyll
3. While sampling, field crews will collect the following field measurements with calibrated handheld meters (YSI ProPlus and Hach Turbidimeter) and will collect samples to submit to the lab:
- Temperature
 - Specific conductance
 - 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 distribution 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 autosampler, 4L, or 250mL glass bottle, 2L PETG 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 autosampler, 4L, or 250mL glass bottle, 2L PETG 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 autosampler bottle, 4L, or 250mL 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 autosampler bottle, acid-cleaned 4L or 250mL 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 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 autosampler bottle, acid-	40mL glass vial	EPA 415.1	No	H3PO4 to <pH 2, <4°C	28 days	Bryte Lab

Parameter	Sample Container	Lab Submittal Container	Analytical Method	Filtered?	Preservation	Hold Time	Analytical Lab
	cleaned 4L glass bottle, or 40mL vial						
Dissolved Organic Carbon	Acid-cleaned autosampler bottle, acid-cleaned 4L glass bottle, or 40mL vial	40mL glass vial	EPA 415.1	Yes, rinsed 0.45um capsule filter	H3PO4 to <pH 2, <4°C	28 days	Bryte Lab
Chlorophyll <i>a</i>	Acid-cleaned autosampler bottle, acid-cleaned 4L glass bottle, or 1 pint HDPE bottle	Frozen glass filter folded inside coin envelope	Standard Method 102	Yes. Water filtered through glass fiber filter, to catch chlorophyll.	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, 4 L acid-cleaned glass sample bottles, or directly into the acid-cleaned 250 mL sample containers submitted to the labs. 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 Hg. See Figure 16 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.

Figure 16 – O2Si Example Certificate of Analysis



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 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

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 mercury and methylmercury 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 composited 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. Hold time for THg samples is 90 days. See Table 4 for lab methods.

5.1.4.2 Total Suspended Solids Sample Collection Methods

Total Suspended Solids (TSS) will be collected in a 1 L 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 as 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 α 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 be 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, Tables 5 and 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
pH	pH units	±0.2	±0.2	0.01	0 to 14
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 <i>a</i>	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, pH, 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 in order 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 of 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 filter 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 dark	180 days
Methylmercury (dissolved)	Filter within 24 hours of collection with a 0.45 µm capsule filter prior to preservation	0.5% 12N HCl within 48 hours of collection Store <4°C in dark	180 days
Total Suspended Solids	Unfiltered	No preservation Store <4°C	7 days
Total Organic Carbon	Unfiltered	Vial contains H ₃ PO 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 ₃ PO ₄ to bring sample to pH <2 Store <4°C	28 days
Chlorophyll <i>a</i>	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 dark until filtered, then freeze filter at <-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 <i>a</i>	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 located in Appendix F. Examples of COC's 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 (in PST) when they were taken (if measurements were taken)
- Water sampling information including time of collection (in PST) (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 water resource engineer staff will use their method of documentation when they measure flow in the mouth(s) of the wetlands with an Acoustic Doppler Current Profiler (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 Field and Laboratory Information Management System (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 located 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 COCs 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 COC's will be kept in organized binders stored in the Project Manager's cubicle. Electronic copies of these documents will be stored on the DWR shared server in 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 and 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), and filter blanks; collect and analyze field 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 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 laboratory control standards (LCS), certified reference materials (CRM), and matrix spikes (MS) as specified in the method and SOP for the particular analyte. Following is a brief description of these laboratory quality assurance procedures:

- A laboratory control sample or a certified reference material 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, a LCS is prepared in the laboratory, and is a control matrix spiked with a known quantity of an analyte. A 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.
- A matrix spike 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
pH	adjustable	Standard buffer solution; 2 point calibration: pH 7, pH 10	Calibration before each field run; accuracy check after each field run	20% or 2 per Trip
Specific Conductivity	adjustable	Salt Standard solution (KCl), 1 point calibration: 2767 μ S/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 <i>a</i>	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 in order 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 a randomly chosen hour during the 25-hour tidal cycle collection event, or once every set of three samples collected for sonde verification. Tables 11 and 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 particular analyte, which can be found in Table 6. For a majority of the analytes, the measurement quality objective for precision is a 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. In order 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 SOP in Appendices A and H.

DWR staff will check for contamination by routinely conducting various blank checks including bottle blanks, trip blanks, sampling 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 of the bottles that we receive from MLML will be from lots with clean bottle blanks (all of the results are below the MDL).

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 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 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, since the field blank will travel in the ice chest to MLML or are transported to Bryte Lab, it will also be considered trip blanks.

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 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 quality assurance (QA) samples and information (blanks, field duplicates, method detection limits (MDL's), 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 the Field Laboratory Intake Module System (FLIMS). MeHg data from MLML will be entered into FLIMS by MME 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 answer our hypotheses or suggest trends. Additional statistical analyses may be done

Table 13 – Possible Statistical Analyses

Variable 1	Variable 2	Statistical Test 1	1 wetland	All wetlands
dTHg		Kruskell Wallace		X
dMeHg		Kruskell Wallace		X
tTHg		Kruskell Wallace		X
tMeHg		Kruskell Wallace		X
d & tMeHg	d & tTHg	Regression	X	
dMeHg	tMeHg	Regression	X	
dTHg	tHg	Regression	X	
d & tMeHg	Chlorophyll	Regression	X	X
dMeHg	DOC	Regression	X	
tMeHg	TOC	Regression	X	
TSS	Turbidity	Regression	X	
Total chlorophyll	Chlorophyll a	Regression	X	
dMeHg	Season	Kruskell Wallace	X	X

Variable 1	Variable 2	Statistical Test 1	1 wetland	All wetlands
tMeHg	Season	Kruskell Wallace	X	X
dTHg	Season	Kruskell Wallace	X	X
tTHg	Season	Kruskell Wallace	X	X
d & tMeHg	Vegetation	Regression		X
tHg	TSS	Regression	X	X
d & tMeHg	Salinity	Regression	X	X
pTHg	TSS	Ratio	X	

9.3 Status and Final Reports

The Delta Mercury Control Program (DMCP) requires a status report by October, 20 2015, and a final report by October 20, 2018 (CVRWQCB 2011). The report 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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*Draft Appendices for
Methylmercury Import and Export
Studies on Tidal Wetlands
In the Sacramento-San Joaquin
Delta, Yolo Bypass, and Suisun Marsh
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. This SOP describes the procedures used to acid-clean the autosampler tubing, bottles, and accessories, in addition to how to dilute the acid to the appropriate concentration, clean the strainers, and cleaning the autosampler itself.

2. Summary of Method

This method will be used to clean the autosampler body, bottles, strainers, tubing, and racks. The autosampler bodies and racks will be cleaned with Micro-90 and tap water to remove any dirt and debris. As they are not directly touching the samples, they do not need to be rinsed beyond with tap water.

The strainers will be cleaned and scrubbed with Micro-90 and then rinsed with tap water, then type 2 water, then placed into a clean reclosable bag until use.

The outside of the silicone and PTFE tubing will be cleaned with Micro-90, then rinsed with tap water and then type 2 water, just like the strainer. The idea is to remove debris and dirt that could potentially contain mercury. Once the outside is cleaned, DWR staff will clean the inside of the tubing using Micro-90, tap water, type 2 water, and then using a 10% hydrochloric acid (HCl) solution to remove mercury inside the tubing, then rinsing with type 1 water.

The autosampler bottles will be cleaned inside and outside with Micro-90 and tap water, then rinsed with tap water, then type 2 water. The bottles will then be bagged and taken to Bryte Lab where we will fill them with 10% HCl and they will soak for a minimum of 3 days. After the bottles have soaked, the acid will be removed and the interior of the bottles will be rinsed with type 1 water, and placed into a clean bag.

The accessories, which include, but are not limited to beakers and PTFE funnels, will be cleaned with Micro-90, then rinsed with tap water, then type 2 water, then soaked in 10% HCl for a minimum of three days, then final rinsed with type 1 water, and bagged in a clean reclosable bag.

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 problematic 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 acid, so precautions, such as protective gear, should be used. Staff should read the Bryte Laboratory Safety Manual and read and sign any relevant Job Hazard Assessments (JHAs) before working with acid.

5. Apparatus and Materials

Reagents for Equipment cleaning:

- 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

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

Equipment to Clean:

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

Equipment Used to Clean:

- Peristaltic autosampler pump, battery cable, and charged battery
- Various sizes of reclosable plastic bags
- Clean poly gloves or small bags
- Zip ties, large and small
- Large, new garbage bags
- Labels

Safety Equipment:

- Lab coat
- Eye protection
- Nitrile gloves
- PVC apron

6. Detailed Procedures:Cleaning Autosampler Body and Racks

1. Scrub the plastic parts of the auto sampler, and racks with a dilute micro-90/tap water solution.
2. Rinse with tap water and allow racks to dry in clean area that does not have excessive dirt (inside lab for example, not warehouse). After racks dry, place them into a cleaned autosampler.
3. Allow autosampler to dry in an area that doesn't have excessive dirt (inside lab, not warehouse, for example), and store in area without excessive dirt or dust.

Making Dilute Acid Solution

1. Determine amount of 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 or other appropriate container with Type 2 water from Bryte.
4. **THIS STEP SHOULD ONLY BE DONE IN AN ACID FUME HOOD.** Carefully add appropriate amount of acid into carboy, using markings on the side of the carboy. Acid needs to be only approximately 10%, so for safety, ONLY pour acid directly from original container

into carboy full of water. Either stir acid with long glass stir rod, or place the cap with a plastic bag under it to seal it fully, and gently shake until acid is mixed. Make sure that spigot is closed during mixing.

5. Make sure carboy is labeled appropriately with "10% Hydrochloric Acid", and a hydrochloric acid sticker.
6. Store acid in safe area, in a secondary container that can hold acid if carboy leaks. Make sure container is also labeled with "Hydrochloric Acid".

Autosampler Bottle Cleaning Procedure

At West Sacramento Lab Facility:

1. Scrub the outside and inside of each bottle with a dilute micro-90/tap water solution. Clean caps, including Teflon liners inside of cap (remove liner and clean underneath), with micro-90/tap water solution. Rinse caps, cap liners, and bottles with tap water, inside and out.
2. Put on new poly gloves, and rinse caps, cap liners, and bottles three times with Type 2 water.
3. Place caps (with liners) on bottles and place capped bottles into a clean plastic bag, and seal. 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 Job Hazard Assessment associated with this project. The JHA 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 a clean hood with the glass sash pulled down as far as possible and the hood turned on, fill a bottle with 10% hydrochloric acid (HCl or acid). Acid will be dispensed from carboy or carefully poured from another container.
7. To prevent acid burns, rinse the outside of the cap and bottle with Type 2 water before placing the bottle into a clean, resealable plastic bag, then into a secondary container (a plastic tub) that can contain the acid if any of the bottles break. Label the bag with how many times the acid has been used.

8. Repeat steps 6 and 7 until all bottles are filled with acid.
9. Allow bottles to soak for a minimum of three days.
10. Repeat step 5, and work in an acid hood in a clean room. After bottles have soaked for a minimum of three days, empty bottles of acid into designated carboy or another bottle, and label carboy or bottle bag with the date and number of times acid has been used, or neutralize and dilute acid and dispose after 6 uses.
11. Wearing clean gloves, rinse each empty bottle and the inside of the lid three to four times with Type 1 water.
12. Still wearing clean gloves, cap bottle, and rinse outside of cap and bottle with Type 2 water.
13. Remove caps and allow bottles to dry in a clean hood with cap. (Can skip this step if hood is not available for drying. Most of the time, a hood will not be available for drying in Bryte Lab's clean room.)
14. Place capped bottles into appropriately sized zipper-closure polyethylene bag and label outer bag with the date of completion and "acid cleaned". Cross out any other writing on bag, if it exists.

Cleaning ISCO Autosampler Tubing

At West Sacramento Lab Facility:

1. Scrub outside of both types of tubing, PTFE suction line and silicone autosampler tubing, with dilute micro-90/tap water solution.
2. Rinse outside of all tubing thoroughly with Type 2 water.
3. Inspect PTFE tubing, and if length markings have been removed or are faded, rewrite tubing lengths on both ends with a black permanent marker.
4. Place silicone tubing into a clean reclosable plastic bag and seal, and place PTFE tubing into a clean garbage bag and tie closed.

At Bryte Laboratory:

Steps 4-11 can be done at Bryte Lab or West Sacramento Lab

5. Put on clean poly gloves to remove tubing from bags.

6. Wearing clean gloves, assemble all the silicone peristaltic pump tubing and PTFE tubing into an autosampler to clean. All tubing will be cleaned at the same time, and rather than the pump tubing going into the autosampler body, all tubing will be connected in a continuous line.
7. To connect PTFE to the silicone tubing, place end of PTFE suction line tubing slightly inside silicone tubing, and secure with zip tie. To connect silicone tubing to other silicone tubing, use barbed connectors and secure with zip tie if needed. Zip ties will be needed to secure silicone tubing ends near peristaltic pump.
8. A clean 4 L beaker or other large, clean glass or HDPE container should be used to put rinsate in (dilute Micro-90 solution, Type 1 water, Type 2 water, or acid).
9. Fill container with dilute Micro-90 solution.
10. Place both ends of tubing (intake and outtake) into a container and run pump in a loop, ensuring that 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 or quadruple that amount of time for an appropriate rinse time. Make sure volume of rinsate is large enough to fill tubing entirely, so no gaps occur. Rinsate should cycle through tubing continuously.
11. After three rinses, pull intake tube out of rinsate and allow tubing to drain of detergent solution. Rinse container, keeping the ends of the tubing away from touching sources of contamination (inside sink, etc.).
12. Fill container with Type 2 water and place intake into water. Allow Type 2 water to rinse inside of tubing for a total of three entire rinses. This should be three times the volume of the tubing.
13. Remove intake from container and allow rinsate to drain from tubing.
14. *The next section concerns working with acid. Before working with acid, be sure to have read the appropriate JHA and accompanying documents. Be sure to wear protective equipment, including, but not limited to, lab coat, safety eyewear, protective gloves, PVC apron, long pants, and closed toe shoes.*
15. Staff can use the acid carboy and place intake and outtake into the carboy. Turn on pump and allow acid to circulate through the tubing at least three times, using the carboy as a reservoir containing the intake and outtake.
16. After a minimum of three rinses, pull the intake tube from the container of acid and allow acid to drain from tubing.

17. Safely dispose of the acid by neutralizing or putting it aside in a safe place until it can be dealt with properly.
18. Fill container with Type 1 water and place intake into the container. Turn on pump and allow a volume of water to rinse the tubing, for a minimum of three rinses.
19. A methylmercury and total mercury equipment blank must be collected after each set of tubing is cleaned. Using clean hands/dirty hands methods, after three rinses of type 1 water, staff will collect a total mercury and methylmercury sample, processing it as all other samples.
20. Pull intake and allow type 1 water to drain until tubing is empty.
21. Using a new set of poly gloves, touch only the outside of the tubing (not the ends), coil PTFE tubing, place clean poly gloves over ends, and cinch with a small zip tie. Place clean tubing into clean garbage bag and seal. Put label on garbage bag with "Acid Cleaned Tubing", the date, and length of tubing.
22. Place clean silicone tubing into resealable bags labeled, "Acid Cleaned Tubing", and the date

Cleaning the Strainer

1. Scrub strainer with dilute micro-90/tap water solution.
2. Put on new poly gloves and rinse strainer thoroughly with Type 2 water.
3. Place strainer into clean, appropriately sized resealable plastic bag, and close.
4. Label bag with "Micro-90 cleaned" and the date.

Cleaning Small Glass Beakers and PTFE Funnels

At West Sacramento Lab Facility:

1. Scrub the outside and inside 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 a clean plastic bag, and seal. 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 Job Hazard Assessment associated with this project. The JHA 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, long pants, and a set of arm-length poly gloves if working directly with acid.
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 4 L glass beaker, and then fill with 10% hydrochloric acid (HCl or acid). Acid will be dispensed from carboy or carefully poured from another container.
7. To prevent acid burns, cover 4 L beaker with parafilm and rinse the outside of the beaker with Type 2 water. With a permanent marker, write contents and how many times the acid has been used on the parafilm.
8. Repeat steps 6 and 7 until all small beakers and funnels are submerged in acid.
9. Allow beakers and funnels to soak for a minimum of three days, leaving the acid filled beakers in the hood with the hood turned on and the sash lowered as far as it can be.
10. Repeat step 5, and work in an acid hood in a clean room. After beakers and funnels have soaked for a minimum of three days, pour as much acid into an acid carboy as possible. Label carboy or bottle bag with the date and number of times acid has been used, or neutralize and dilute acid and dispose after 6 uses.
11. Wearing clean gloves, remove each beaker and funnel and rinse each three to four times with Type 1 water.
12. Place small beakers and funnels into appropriately sized zipper-closure polyethylene bag and label outer bag with the date of completion and "acid cleaned". Cross out any other writing on bag, if it exists.

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-Weighted Composite 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 start with the bottles for the unfiltered THg and MeHg analyses and then the bottles for all of the other unfiltered analytes (total organic carbon (TOC) and then 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 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 of the other filtered analytes (mostly dissolved organic carbon (DOC)). As a note, capsule filters must be pre-rinsed with 1 L of water so that the filter does not contaminate the DOC sample.

3. Contamination and Interferences

Preventing water samples from mercury contamination during the filtering and splitting process is a great challenge. 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.

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 hands” 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 we will be filtering and splitting the samples must be free of dirt and dust as much as possible. The filter tubing will be cleaned by Moss Landing Marine Laboratories (MLML) using the method described in their MPSL-101 SOP to ensure that the tubing will not contaminate samples.

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 well 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 when convenient to minimize slipping hazards.

5. Apparatus and Materials

- Peristaltic pump
- Polyethylene or nitrile gloves that are stored inside a sealable plastic bag
- Large plastic bag to cover lab bench where filtering is conducted
- Waste bucket or sink for rinse water

- One 1000mL graduated cylinder to measure rinse water
- Ice chest filled with wet ice or refrigerator 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 of the samples collected that day; 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 will be wet from the ice water in the ice chest, so it is necessary to place these in a dedicated spot in order to keep the rest of the plastic-covered lab bench dry and clean.

6.2 Splitting the water 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 up 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 of 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 that contains one of the hourly or composited water samples from the ice chest or refrigerator, and places it next to the sink.
- 5) The “clean hands” person opens up the inner bag, removes the 4 L bottle, and 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 7-14, 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.
- 7) After replacing his/her gloves, the “clean hands #2” person opens up 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 in order 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 the 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 of the outer bags of the filled containers. The “dirty hands” person then places the bottles into the ice chest or refrigerator.
- 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 ice chest. 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 of the bottles for the unfiltered analytes are filled, the “clean hands” person will put the capped 4 L bottle back into its inner bag and then carry the bottle to the dedicated spot next to the peristaltic pump.

6.3 Filtering the remaining water sample into the bottles for the filtered analyses

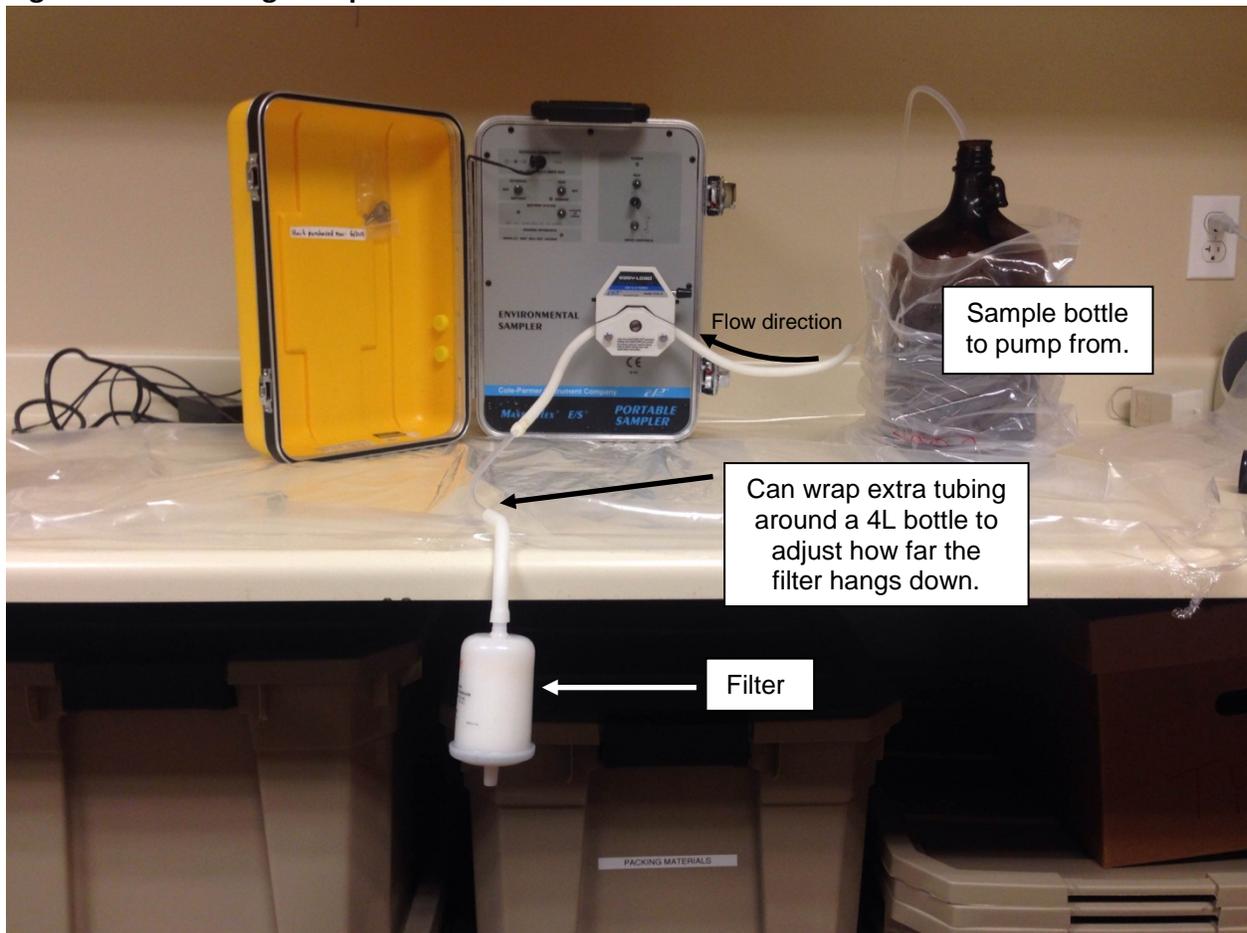
- 1) “Clean hands” and “dirty hands” personnel will put on a new set of gloves.
- 2) First, the tubing and filter will be set up on the peristaltic pump. The “dirty hands” person opens up the outer bag of the cleaned and double-bagged C-Flex and Teflon tubing set from MLML, and “clean hands” opens the 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 B.1 for an example.

Figure B.1 – 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 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.

NOTE: If tubing leaks at join points, zip ties can be placed around the join by “dirty hands” to reduce leaks.

- 7) After the filter and tubing are rinsed, filter water 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 either a fridge or an ice chest. Repeat for the filtered MeHg sample.
- 10) Once the THg and MeHg samples are filtered, all of the bottles containing samples for trace-metals analysis are complete, so the “clean hands-dirty hands” method 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 of the unfiltered and filtered bottles have been filled, processed, and stored in a fridge or ice chest, 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.

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 of the samples have been processed in this way, the individual sample bottles will be stored in a lab refrigerator or ice chest between 1-4 °C 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 upon receipt at the lab and within 28 days of collection. The MeHg samples will be shipped to MLML.

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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 semi-diurnal tidal cycle. To reduce the number of THg and MeHg samples that DWR must have analyzed, we will be manually compositing samples using flow data, tides, and a flow-weighting technique. To composite the THg and MeHg samples using flow data, DWR will download flow data from the ADCP and calculate flow weighted composites using the compositing recipe worksheet. This SOP will describe how staff will flow-weight composite water samples.

2. Summary of Method

Autosamplers will collect 25 hourly samples into 25 separate sample bottles. Using a 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 section 6.1.1.5 in the Monitoring Plan for more details.

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 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 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 hands” 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 Appendix A, Autosampler, Accessory, and Bottle Cleaning.

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 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 4 L bottle
- Polyethylene or nitrile gloves that are stored inside a sealable plastic bag
- Acid-cleaned PTFE or Teflon funnel
- Acid-cleaned 50 mL and/or 100 mL glass beaker
- Kim wipes
- Compositing recipe!

6. Detailed Procedures

Compositing Setup

1. Calculate mass of water to take from each bottle using flow data and 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 make sure scale is measuring in grams.
3. Handling of the samples should be done using the clean hands/dirty hands method.
4. Person 1 will put on a pair of poly gloves (dirty hands) and open outer bag of an acid-cleaned 4 L composite bottle. Person 2 will put on a pair of poly gloves (clean hands) and will open inner resealable bag and remove composite bottle and place it onto scale.
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 the funnel from the bag and place it into mouth of composite bottle.
7. Dirty hands will open bag with the acid-cleaned beaker (50 or 100mL) 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.

First Autosampler Bottle in Compositing Set

9. ***NOTE:*** Keep autosampler bottle samples well mixed before and during compositing. Particles may settle quickly, so shake capped bottle between dispersals. ***This is VERY important.***
10. 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.
11. Dirty hands will pick up autosampler bottle and pour water over beaker, while clean hands makes sure beaker gets thoroughly rinsed, inside and out.
12. Once the beaker is rinsed, dirty hands will pour water into beaker and clean hands will use that water to rinse funnel, 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).*

13. Dirty hands will cap the autosampler bottle and shake the sample for 10-20 seconds, and will continue to do so throughout procedure as much as possible, particularly before each pour.
14. 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 $\pm 0.5-1\%$ is acceptable.**
15. Dirty hands will cap the autosampler bottle between pours and shake for 10-20 seconds before each pour.
16. 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.*
17. Once the mass is reached for that autosampler bottle, clean hands will place beaker on resting spot.
18. Dirty hands will recap autosampler bottle, place back into labeled bag, then place in a cold, dark place (fridge or ice chest with wet ice).
19. Dirty hands will tare scale.

Second and Next Consecutive Autosampler Bottles in Compositing Set

20. **NOTE:** Keep autosampler bottle samples well mixed before and during compositing. Particles may settle quickly, so shake capped bottle between dispersals. **This is VERY important.**
21. Dirty hands will open bag of the next autosampler bottle and remove bottle from bag and begin shaking bottle for a minimum of 1 minute to mix contents well.
22. Clean hands will hold small beaker over sink.
23. Dirty hands will pour well mixed water from the autosampler bottle over beaker, while clean hands makes sure beaker gets thoroughly rinsed.

24. Repeat steps 14-18 until finished with each autosampler bottle in the ebb or flood composite.

After Pouring All Autosampler Bottles in Compositing Set

25. 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.
26. 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.
27. Clean hands will place composite bottle into inner bag with help from dirty hands who will be holding both sets of bags. 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 cold, dark place (fridge <4°C or in ice chest on wet ice) until sample is dispersed. Sample splitting and filtering will follow the Standard Operating Procedure outlined in Appendix B.

Appendix D

Standard Operating Procedure

Methylmercury Sample Preservation

Department of Water Resources
Originated by: Petra Lee
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 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 the staff mishandling, preservation equipment, and through dirt and dust in the air. Sample hold time 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 containers;
- 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 hands” 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 acid dispenser only handles the pipette and any acid equipment.

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 on ice at all times.

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 slippery and wet.

Before working with acid, be sure to have read the appropriate JHA and accompanying documents. Be sure to wear protective equipment, including, but not limited to, lab coat, safety eyewear, protective gloves, PVC apron, long pants, and closed toe shoes. Additionally, all preservation work should be done in a hood.

Lastly, acid should be carried to and from the hood by a person in full protective equipment in a bottle tote safety carrier.

5. Apparatus and Materials

- Hydrochloric Acid (HCl), Baker Analyzed, 12N, VWR Part #JT9535-3
- (1) Acid cleaned 50 or 100mL beaker
- (1) Pipette adjusted to 1.25mL and tips
- Baking soda for safety and acid neutralization
- (1) 2 or 4L bottle for acid neutralization
- (1) Acid disposal container, can be a ½ pint HDPE sample bottle
- Safety gear, including lab coats, long and short gloves, eyewear, and plastic aprons
- Methylmercury samples to be preserved
- Ice chest with wet ice

6. Detailed Procedures

6.1 Roles of personnel

Ideally, three people should be involved in sample preservation. One person will dispense acid, and will be referred to as acid dispenser. A second person will be “clean hands” and will handle the inner bag and bottle of the MeHg bottle to be preserved. A third person will be “dirty hands” and will handle only the outer bag of the sample and anything else that needs to be moved or used (other than what the acid dispenser is handling). All staff will wear gear identified above, except “clean hands” will also wear shoulder length poly gloves over nitrile gloves.

6.2 Set up

1. All preservation will be done in a hood.
2. Wearing all appropriate protective gear, the acid dispenser will pour an approximate amount of acid into an acid cleaned 50mL beaker.
3. The acid dispenser will then open the acid disposal container and using the pipette (set to 1.25mL), will draw up acid and dispose of it in the acid disposal container. The acid dispenser will do this three times, then cap the acid disposal container and put it aside to neutralize later.

6.3 Sample Preservation

1. Dirty hands will remove bagged sample from ice chest and open the outer bag of a sample to be preserved. Clean hands will open 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 to release any gasses, and then close cap completely to seal the bottle.
4. Clean hands will place bottle back into inner bag with dirty hands help, and will seal the inner bag.
5. Dirty hands will seal outer bag and place the preserved sample on ice, being careful not to mix the sample up with unpreserved samples.

6.4 Clean up and acid disposal

1. After all samples have been preserved, either clean hands or dirty hands will fill a 2 or 4 L glass bottle with tap water in the hood.
2. The acid preserver will draw tap water into the pipette tip to dilute it, and then expel the tip into the water. The acid preserver may need to carefully push the tip into the water.
3. Next, the acid preserver will pour the acid disposed in the acid disposal container into the water to dilute it, and then will put the entire container into the water, making sure it is submerged.

4. The acid preserver will add baking soda to the solution to neutralize the acid, then turn on the tap water to dilute the neutralized acid as it is poured down the sink.
5. After acid is neutralized and diluted and poured down the sink with plenty of tap water, the pipette tip may be thrown away, and protective gear may be removed.

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Appendix E

Standard Operating Procedure

Filtering Chlorophyll Samples

Department of Water Resources

Originated by: David Bosworth

November 27, 2013

1. Scope and Application

This SOP describes the techniques that DWR staff will use to filter water samples collected in 1 pint or ½ pint bottles from the field to then be analyzed for chlorophyll *a*. See the “Sample Collection SOP” for the field collection procedures.

2. Summary of Method

DWR staff will transport samples collected in 1 pint or ½ pint polyethylene bottles back to our lab in the Division of Environmental Services on wet ice. 100 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 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 MgCO₃ 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

All personnel that handle environmental samples known to contain or have been in contact with human waste should be immunized against known disease-causing agents.

Since these procedures involve pouring water into volumetric flasks 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 three 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 100 mL volumetric flask
- 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
- Waste bucket or sink for rinse water
- Manila envelopes pre-labeled with waterproof labels printed from the Bryte Lab FLIMS system
- Black or blue pen to write sample volume and collection time on the envelopes
- Laboratory Freezer

Reagents

A saturated magnesium carbonate solution will be made as follows:

- 1) Add MgCO_3 to Type 2 at a ratio of 1 gram of MgCO_3 to 100 mL of DI.
- 2) Mix well and let the solution sit for 48 hours in order for the excess MgCO_3 to settle.
- 3) Decant the clear solution above into a clean 500 mL squirt bottle.

6. Detailed Procedures

6.1 Lab work bench setup

- 1) Wipe down the area where you will be filtering and working with the water samples with a clean cloth.
- 2) Set out the three-port vacuum manifold and the 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.
- 3) Inspect the filter funnels, their platforms, and the volumetric flask to make sure that they are clean. If not, rinse them with Type 2 a few times.

7.2 Filtering the water sample through the filtering apparatus

- 1) Place one 1.0 μm glass-fiber filters with the rough side facing downwards on a filter funnel platform using filter forceps. Attach the filter funnel and check to see that it is seated correctly. Leave the valves on the filter manifold in the closed (horizontal) position.
- 2) Remove one of the 1 pint or $\frac{1}{2}$ pint polyethylene containers with sample water from the sample ice chest and shake the sample completely. Pour approximately 15 mL of sample water into the clean 100 mL volumetric flask, 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 three times, pour and measure 100 mL of the sample water in the flask. Make sure that the bottom of the meniscus lines up with the etched line in the flask. Pour the contents of the volumetric flask into the prepared filter funnel, and add 1-2 mL of the MgCO_3 solution from the squirt bottle to the water sample prior to filtration.
- 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 three times with deionized 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 deionized water from the squirt bottle. Continue to run the vacuum pump to allow all of 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 and the sample collection time on the envelope with a black or blue pen. Place the envelope with the filter in the laboratory freezer immediately.
- 9) The filtering process for this sample is now finished. Remove and discard the bottom filter from the filter funnel platform, discard the remaining sample water from the 1 pint or $\frac{1}{2}$ pint container, and recycle the bottle. Before using the filter funnel for a new water sample,

rinse it out with tap water and deionized water. Rinse the volumetric flask a couple times with deionized water before using it to measure another water sample.

Repeat the chlorophyll filtering procedures described above for the remainder of the water samples using new glass fiber filters for each sample. 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 1 week of collection.

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Appendix F Sampling and Processing Forms

Figure F-1 – 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: _____
<u>Autosampler Notes:</u>								
<u>Grab Sample Notes:</u>								
<u>Other Notes:</u>								

Figure F-2- Water Quality Collection Field Record



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		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

Hand-Held and Sonde Data

Field Instrument IDs: _____ Removed Probe/Sensor ID's: _____
 YSI 63: _____ Conductivity/Temperature: _____
 HACH 2100P: _____ Turbidity: _____
 YSI ProODO: _____ 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:

Figure F-3 - 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: ____/____/____ Probe/Sensor ID's: _____

Performed by: _____ Conductivity/Temperature: _____

Probe/Sensors Cleaned? Y / N 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- **Calibration and Maintenance Notes:**

Thermometer: ____ (°C)

Probe: ____ (°C)

Accuracy Verified? Y / N

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

Maintenance-

Date: ____/____/____

Performed by: _____

Sonde Body Cleaned? Y / N Batteries Changed? Y / N

Central Wiper Cleaned? Y / N Battery Voltage: _____

Central Wiper Parked Correctly? Y / N Clock Checked/Set (PST) Correctly? Y / N

Logging-

File: _____

Logging Start Date & Time: ____/____/____ ____:____ (PST) Sample Interval: 00: ____ :00

Deployment Date & Time: ____/____/____ ____:____ (PST) SDI-12 Address: _____

Logging Active? Y / N Sample & Hold? Y / N

Sonde Maintenance and Logging Notes:

Figure F-4 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 Standard	2 Sonde (pre-cleaning)	3 Total Deviation (= 2 - 1)	Ratings (Circle One for Each Constituent)			
			4 Excellent	5 Good	6 Fair	7 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)	8 Sonde (post-cleaning)	9 Drift (= 8 - 1)	10 Fouling (= 2 - 8)	11 Shift (if [9] > [4] = 3, else = 10)
Battery: _____ (V)	DO: _____	_____	_____	+ / - _____ (% sat.)
**pH probe post-cal check	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 F-5 Filtering Notes

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.				

Figure F-6 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 F-7 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	9/22/2014 11:45	22.9	0.057	229
2	9/22/2014 12:45	4.5	0.011	45
8	9/22/2014 18:45	80.9	0.202	810
9	9/22/2014 19:45	88.5	0.221	886
10	9/22/2014 20:45	76.0	0.190	760
11	9/22/2014 21:45	56.2	0.141	562
12	9/22/2014 22:45	40.0	0.100	400
13	9/22/2014 23:45	30.8	0.077	308

Tidal Cycle: Flood Tide 1				
Bottle #	Collection Time	Flow (cfs)	Proportion of Total Flow during Tidal Cycle	Weight of subsample required (g)
3	9/22/2014 13:45	-21.2	0.051	203
4	9/22/2014 14:45	-84.9	0.203	813
5	9/22/2014 15:45	-114.5	0.274	1097
6	9/22/2014 16:45	-130.2	0.312	1247
7	9/22/2014 17:45	-66.8	0.160	640

Tidal Cycle: Ebb Tide 2				
Bottle #	Collection Time	Flow (cfs)	Proportion of Total Flow during Tidal Cycle	Weight of subsample required (g)
20	9/23/2014 6:45	102.2	0.240	960
21	9/23/2014 7:45	107.2	0.252	1007
22	9/23/2014 8:45	83.3	0.196	782
23	9/23/2014 9:45	60.3	0.142	567
24	9/23/2014 10:45	41.2	0.097	387
25	9/23/2014 11:45	31.7	0.074	298

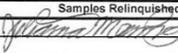
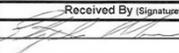
Tidal Cycle: Flood Tide 2				
Bottle #	Collection Time	Flow (cfs)	Proportion of Total Flow during Tidal Cycle	Weight of subsample required (g)
14	9/23/2014 0:45	-0.2	0.000	2
15	9/23/2014 1:45	-46.0	0.092	368
16	9/23/2014 2:45	-127.1	0.254	1017
17	9/23/2014 3:45	-153.0	0.306	1224
18	9/23/2014 4:45	-123.0	0.246	984
19	9/23/2014 5:45	-50.6	0.101	405

DRAFT

Appendix G Chain of Custody

Figure G-1 – Example of Moss Landing Marine Laboratories Chain of Custody

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

Sampler Julianna Manning_DWR Address 3500 Industrial Blvd. 2nd Floor City State Zip West Sacramento CA 95691		Send Results To same Address City State Zip Email julianna.manning@water.ca.gov																							
Date Required/Reason 60 days turn around																									
Sample Identification/Location <small>(Draw map on separate sheet if necessary)</small>		Collection		Total/Unfiltered			Dissolved/Filtered																		
		Date	Time (PST)	Salinity (ppt)	Trace Elements (Specify Below)	Total Hg	Total MMHg	Total Boron	Diss Trace Metals (Specify Below)	Diss Hg	Diss MMHg	Diss Boron	SSC	TSS	Chl-a	Pesticides (Specify Below)	Water	Soil	Tissue	Plastic	Glass	VOA Vial	Temp	Acid	
DWR Sample Code	Station Name																								
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				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				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				1			x	x
EH0814B0499	Ebb 1 Duplicate	8/11/2014	12:30														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		8-18-14				S. Manning		8/19/14 9:30am		@ S. Manning													

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

Figure G-2 – 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)

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.

Container Summary		
Glass, Clear, 250 ml		2
Bottle Check: Lab Initials: <i>MLC</i>	Field Initials: <i>DS</i>	Total: 2

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

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

Submittal ID: EH0614B0020

DWR Sample Number **EH0614B0369** Collection Date *6/20/2014* Collection Time: *15:30* EC:
Station No.: (None) *19* 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 *6/20/2014* Collection Time: *14:30* EC:
Station No.: (None) *19* Station Name: (None) Matrix: Water, Purified
Add'l Note: Auto Sampler Pre-Sampling Tubing Blank Cost Code: VMERCURY0SWP

Total Mercury

Figure G-3 – Example of Bryte Lab Checklist Included With Chain of Custody

Submittal ID: EH0614B0020

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

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

Appendix H
Moss Landing Marine Laboratories
Method # MPLS-101
SAMPLE CONTAINER PREPARATION FOR ORGANICS AND TRACE METALS, INCLUDING MERCURY AND METHYLMERCURY

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 # z140406redline
- 4.63 Zipper-closure Polyethylene Bags, 4milx6"x8": Packaging Store Part # z140608redline
- 4.64 Zipper-closure Polyethylene Bags, 4milx9"x12": Packaging Store Part # z1400912redline
- 4.65 Zipper-closure Polyethylene Bags, 4milx12"x15": Packaging Store Part # z1401215redline
- 4.66 Zipper-closure Polyethylene Bags, 4milx13"x18": Packaging Store Part # z1401318redline

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 (HNO₃), concentrated redistilled: Seastar Chemicals Part # BA-01
- 5.14 Nitric Acid (HNO₃), BAKER INSTRA-ANALYZED*, 69.0–70.0% (15N): VWR Part # JT9598-34
- 5.15 Nitric Acid (HNO₃), 7.5N (50%): prepared by adding 1 part Baker HNO₃ to 1 part MilliQ
- 5.16 Nitric Acid (HNO₃), 6%: prepared by adding 1 part Seastar HNO₃ to 16.67 parts MilliQ
- 5.17 Nitric Acid (HNO₃), 1%: prepared by adding 1 part Seastar HNO₃ 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% HNO₃ 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 HNO₃, 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 Micro/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 HNO₃ 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% HNO₃ 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 HNO₃ 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% HNO₃ 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 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 HNO₃ 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% HNO₃ by putting a small 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 HNO₃ 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

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.

Assumptions made:

1. All of 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. In the main study, no autosampler will be collecting more than 8 consecutive samples.
3. Also 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.

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 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.

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.

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 the main study's sampling plan. 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 and bottles have been placed. 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.

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; the 250 mL bottles will be submitted to the appropriate labs. 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.

Flow-weighted 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.

Statistical Analysis

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

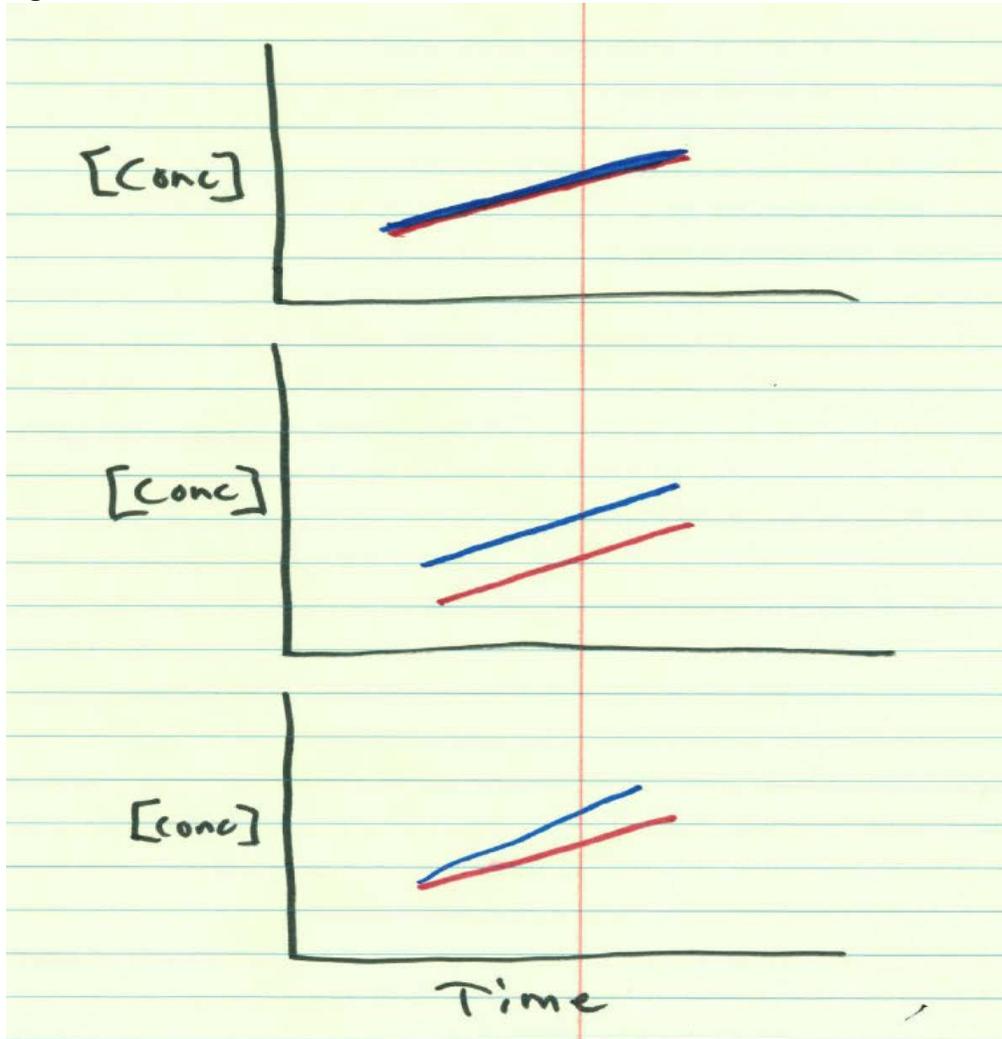
In addition, we will create time-series graphs of the MeHg or THg concentration data. The autosampler and grab samples will each be modeled separately with regression lines to examine whether concentration trends differ between the two groups. Figure 1 illustrates the possible scenarios. In these graphs, 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 1



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 2 and 3 are graphs of the grab and autosampler data over the 8-hour period.

Figure 2 shows the THg data over an 8-hour time interval

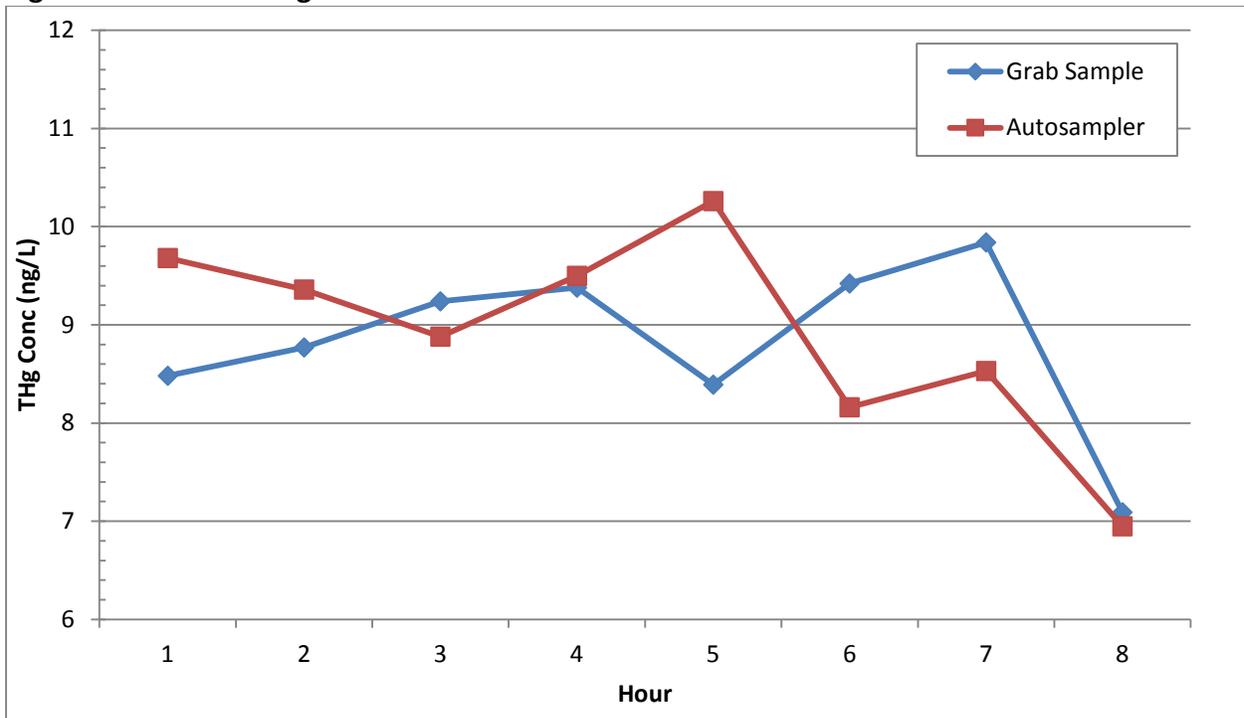
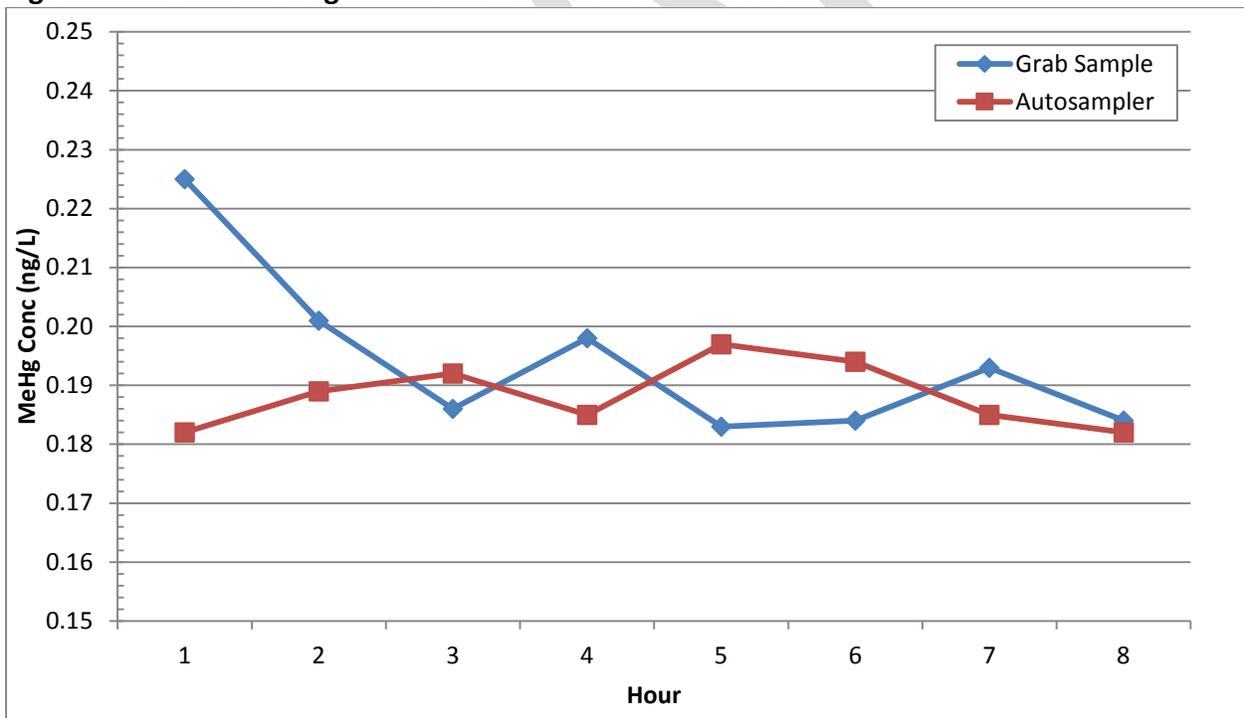


Figure 3 shows the MeHg data over an 8-hour time interval



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 out 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.