Methylmercury Field Sampling Report

Sacramento and Stockton Deep Water Ship Channels

Operation and Maintenance Dredging

Prepared by

US Army Corps of Engineers ®

Sacramento District

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1.0 Introduction

The U.S. Army Corps of Engineers has prepared this field sampling report to document and present the results from the methylmercury (MeHg) control study activities conducted in November 2014. The MeHg field activities were part of the annual maintenance dredging at the Sacramento and Stockton Deep Water Ship Channels (DWSCs) as regulated by the Central Valley Regional Water Quality Control Board (CVRWQCB) under two Waste Discharge Orders: General Order (GO) No. 05-01-116 for the Sacramento DWSC and GO No. R5-2004-0061-001 for the Stockton DWSC. The objective of this MeHg study was to determine whether water discharged from the dredge material placement sites (DMPSs) has elevated MeHg levels compared to the river background and also to assess the total flux of mercury into and out of the DWSCs.

1.1 Deep Water Ship Channels

The US Army Corps of Engineers (USACE), Sacramento District, performs maintenance dredging to a depth of 30 ft along the Sacramento DWSC between Sta. 0+00 to Sta. 1850+00, and to a depth of 35 ft from Sta. 1850+00 to the Port of West Sacramento turning basin at Sta. 2290+00. About half of this area is considered part of the Yolo Bypass Subarea, which was identified in the Delta MeHg Total Maximum Daily Load (TMDL) Report (Table 8.2) as needing 78% aqueous reduction in MeHg concentrations, with the remainder of the DWSC being in the Sacramento River and West Delta Subarea, with reductions of 44% and 0% needed respectively.

The USACE, Sacramento District, also performs maintenance dredging along the Stockton DWSC between Sta. 230+00 to the Port of Stockton turning basin at Sta. 2165+00 to a depth of 35 ft. This area is in the Central Delta Subarea and West Delta Subareas, which were both identified as needing no reduction in aqueous MeHg concentrations in the Delta TMDL Report. The dredging extents, DMPSs, and delta subareas are shown in Figures 1 and 2.

1.2 Dredging Process

Maintenance dredging in the Sacramento and San Joaquin Rivers is done with a hydraulic suction pipeline dredge, which pumps the dredged slurry via pipeline to the DMPS. The dredged slurry is approximately 10-20% sediment solids from the bottom of the river and 80-90% liquid river water. At the DMPS, the slurry is discharged from the pipeline, and solids are allowed to settle out. Depending on the amount of material being dredged and the capacity of

the DMPS, effluent of decant water may or may not need to occur from the DMPS back into to the river. If the DMPS is large enough, no water is discharged back into the river, and the site will dry via percolation and evaporation. If there is more dredged slurry than capacity, then the dredged slurry is typically allowed to settle to reduce turbidity, and then is discharged back to the river in accordance with the WDRs. For a typical maintenance dredging year, discharge back to the river usually only occurs into the West and Central Delta Subareas, which were both identified in the Delta MeHg TMDL Report (Table 8.2) as needing 0% reduction of aqueous MeHg. Maintenance dredging along the Sacramento and Stockton DWSCs may be performed between August 1 and November 30 to comply with the endangered species fisheries window.

1.3 Previous DMPS MeHg Studies

Field scale studies of MeHg best management practices have been conducted as part of the Sacramento and Stockton DWSC maintenance dredging projects in the years 2009-2011. Field reports from these studies, that detail all the findings, can be found in the Methylmercury Control Study Workplan (USACE, 2014). These studies were designed to explore the following:

- Is MeHg being produced at the DMPSs?
- Do MeHg concentrations decrease over time?
- Does removing vegetation from a DMPS result in lower MeHg concentrations in the pond water after dredged material placement?
- How do co-variations of suspended sediment concentration (SSC) and MeHg in DMPS pond water differ between vegetated and cleared sites during the first two weeks after dredged material placement?
- Do pre-dredge soil concentrations of MeHg, Total Hg or Total Organic Carbon (TOC) affect concentrations of MeHg in pond water after placement of dredged material?

Results of the studies suggested that the concentration of MeHg within DMPS ponds increased rapidly within the first two weeks after placement began. There was typically a slight decrease in MeHg after reaching a maximum concentration, but MeHg concentrations in the ponds did not return to the initial concentrations measured at the start of pumping. The 2010 study showed some promising results that removing vegetation did result in significantly lower MeHg in pond water, but an additional study was needed to confirm the results. The 2011 study confirmed that vegetation removal in the test cell prior to placement of dredged slurries resulted in lower MeHg concentrations in the water column. These studies also found that the optimum holding time for water was 1-3 days, as turbidity had decreased, but before rapid

increases in MeHg concentrations. The studies also found that pre-dredge soil concentrations of MeHg, Total Hg or TOC did not significantly affect post-dredge pond water quality. During all of these studies it was unknown what the incoming source water MeHg concentrations were.

2.0 Study Design

The focus of this year's methyl mercury study was to determine whether water discharge from the dredge material placement sites (DMPSs) impacts water quality in the channels. Roberts I DMPS was selected for 2014 MeHg study based on its historical discharges and the 2014 dredging schedule. Roberts I is located on Roberts Island along the Stockton DWSC River Mile (RM) 36.5.

Approximately 220,000 cy of dredged slurry were dredged from Station 1865+00 to 2110+00 and were placed on Roberts I between October 28, 2014 and November 20, 2014. Due to the limited capacity of the DMPS, discharge from Roberts I began on November 10, 2014 and lasted for 12 days.

During this first year of the MethylMercury Control Study Workplan, due to logistical and contractual constraints, sampling followed the sampling plan laid out in the 2014 Methyl Mercury Field Sampling Plan (USACE, 2014) with a few minor field variances.

3.0 Field Event and Methods

3.1 Sample Locations

To evaluate the MeHg impacts to the rivers, samples were collected from three selected locations: A, B, and C (Figure 3). Location C is the discharge point of the DMPS. Samples at Location C were collected immediately before the discharge point of the DMPS, within the DMPS. Locations A and B were both in the river, within approximately 300 feet of the discharge point, near the shore. Location A was east of Location C (towards Stockton) while Location B was west of Location C (towards San Francisco). Due to tidal influence, Locations A and B switched being "upstream" and "downstream" during the course of the study. During the study, "upstream" samples were taken from Location A during Days 0 through 2 since the tide was outgoing. "Upstream" samples were collected from Location B from Days 3 to 6 since the tide was incoming.

To sample at Locations A and B in the river, the field crew collected water samples near the shoreline at approximately 0.5 foot below the water surface. Since the discharge point of Roberts I in the DWSC was inaccessible due to steep slope and heavy vegetation, Location C samples were collected within the DMPS just before the discharge pipe to the river, also approximately 0.5 foot below the water surface. Samples from Locations A, B and C were taken six times between November 10, 2014 and November 21, 2014, and one additional in-river sample was taken prior to discharge occurring.

Inaccessible river side of Discharge pipe from Roberts I

Intake at Discharge pipe at Roberts I, prior to having water on site

All samples were analyzed for MeHg and total mercury using EPA 1630 and EPA 1631E, respectively. Table 1 shows the analyte list, analytical method, and Limit of Quantitation.

Table 1: Analyte List

Analytes	Analytical Method	Limit of Quantitation (ng/L)
Total Mercury	EPA 1631E	0.5
Methylmercury	EPA 1630	0.05

3.2 Sample Procedures, Handling, and Documentation

Sampling personnel followed "clean-hands, dirty-hands" protocol according to Surface Water Ambient Monitoring Program (SWAMP) Quality Assurance Program Plan (SWAMP, 2008), Method 1669 – Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels (USEPA, 1996) and Standard Operating Procedures for Conducting Field Measurements and Field Collections of Water and Bed Sediment Samples in SWAMP (MPSL-DFG, 2007). Water samples were collected using a non-metal sampling rod with FLPE bottles, following the guidance in 1669 during all sampling activities. All sample bottles and gloves were prepared and acid-cleaned in a trace metal clean environment by Brooks Rand laboratories, LLC, and kept in sealed double bags until they were used in the field.

Water samples were collected using a non-metal sampling rod with FLPE bottles by two sampling members. One of the sampling members was designated as "clean-hands," who only handled the samples, inner Ziploc bags, and sampling bottles while the other member, designated as "dirty-hands," was assigned to handle the sampling rod, outer Ziploc bags, labels, and coolers. Any working surfaces were covered by plastic sheets to avoid contamination. When sampling for total mercury and MeHg, one 1-liter FLPE bottle was secured using an alligator clip or zip-tie at the end of the sampling rod by the "clean-hands". The "dirty-hands" then collected the water from the sample location using the sampling rod and avoiding touching the sample bottle. The sample bottle was rinsed several times at the sampling locations by dipping and pouring out the river or DMPS water before a sample was collected. The "clean-hands" sampler then took the sample bottle from the sampling rod and divided the water into a 250-ml glass bottle with BrCl as preservative for total mercury analysis and a 250-ml FLPE bottle with HCl as preservative for MeHg analysis. The "clean-hands" sampler then placed the sample bottles in the inner Ziploc bags and the "dirty-hands" sampler closed the outer Ziploc bags. All sample bottles were then placed in the coolers for shipping. All MeHg samples were also kept on ice as required by the analytical method. Total mercury samples were kept at ambient temperature.

3.2.1 Decontamination Procedures

Before collecting each sample, the sampling rod, alligator clip and/or zip-ties, and hands of sampling members were decontaminated using Formula 409 and Alconox, distilled water, and laboratory provided reagent water, and new plastic sheets were placed to cover the working surfaces. New laboratory cleaned gloves were used for each each sample collected. During each sampling day, any field blanks were collected first, the "upstream" sample next, then "downstream," and lastly the discharge sample.

3.3 Sample Quality Control

For quality control, two field duplicates, trip blanks and MS/MSD samples were analyzed. Two field blanks were also collected during this study. On selected days, field blanks were taken first after equipment decontamination. Field blanks were taken by pouring laboratory provided reagent water on the sampling rod and alligator clip/zip-tie and collected with a 1-liter sample bottle. The field blank water sample was then divided and poured into a glass bottle for total mercury analysis and a FLPE bottle for MeHg analysis.

3.4 Laboratory Analysis

Eurofins Frontier Global Sciences, Bothell, WA, performed the total mercury analysis and Brooks Rand Laboratories, Seattle, WA, performed the methylmercury analysis. Both laboratories selected to perform analyses for this investigation were accredited under the National Environmental Laboratory Accreditation Program (NELAP), and certified by the State of California. All samples collected including QC samples were analyzed for total mercury and MeHg. MeHg samples were analyzed as unfiltered using USEPA method 1630 with a limit of quantitation (LOQ) of 0.05 ng/L. For total mercury, water samples were analyzed by USEPA method 1631 revision E with a LOQ of 0.5 ng/L.

3.5 Field Variances and Non-Routine Field Conditions Encounters

The alligator clips were lost during the sample collection on Day 2 and plastic garbage ties were used to secure the sample bottles for the reminder of Day 2. Plastic reusable zip-ties were used for Days 3 through 6. The garbage ties and zip-ties were decontaminated as mentioned above.

Throughout the sampling period, a diesel pump was operating approximately 50 feet from the discharge point, location C. This pump is utilized by the dredging contractor to pump the discharge water from the DMPS to the river. Although the diesel pump was not immediately next to the sampling location, measures were implemented to prevent sample contamination. The sample team minimized contacts between the samples and the atmosphere by tightly capping the sample bottles and walking away from the pumps immediately after sample collection.

Throughout the study period, the river was generally covered with large amounts of water hyacinth. While collecting samples from locations A and B, the sample team tried to minimize contact between the sampling equipment and water hyacinth as much as possible.

Dredge and speed signs in Stockton DWSC next to Roberts Island, with water hyacinth

4.0 Sample Results

As mentioned above, MeHg and total mercury samples were collected and sent to the laboratories for analysis. Total mercury sample results were compared to the maximum soluble concentration criterion of 50 ng/L for modified elutriate test (MET) from the General Order. This is the same criteria as in the USEPA CA Toxics Rule.

For MeHg, the Water Board recommends 0.06 ng/L in unfiltered water to be used as an implementation goal in the Staff Report for Sacramento – San Joaquin Delta Estuary TMDL for Methylmercury (Water Board, 2010). For this study, the implementation goal will be used to compare the MeHg sample results.

During this study, six primary samples were collected at the downstream and discharge locations, and 7 were collected at the upstream location. Sample results are shown in Table 2. Data validation was conducted and concluded all data are usable. A detailed data validation summary is described in Section 4.1 and data validation reports are attached in Appendix A.

All total mercury sample results were below the criterion of 50 ng/L from the General Order. The highest concentration overall was actually from day 5 "upstream" sample RIB-5U, at 31.8 ng/L. The highest concentration from the discharge point was 25.9 ng/L (Day 5) and the highest concentration from 'downstream' was 9.93 ng/L (Day 4). The results show that the discharges had minimal impacts on the 'downstream' total mercury concentration and complied with the General Order.

All discharge MeHg sample results were above the implementation goal of 0.06 ng/L. Three of the six 'downstream' and two of the seven 'upstream' MeHg results were also above the goal. The highest concentration from the discharge point was 1.43 ng/L (Day 3) and the highest concentration from "downstream" was 0.132 ng/L (Day 3). The highest 'upstream' concentration was 0.135 ng/L (Day 2).

Table 2: Sample Results

Sample	Methylmercury (ng/L)	Qualifier	Total Mercury (ng/L)	Qualifier
Upstream				
RIA-0U[1]	0.02	U	5.7	J+
RIA-1U	0.072		5.76	J+
RIA-2U	0.135		7.58	J+
RIB-3U-MS/MSD	0.038	J	7.49	J+
RIB-4U	0.049	J	10.6	
RIB-5U	0.028	J	31.8	
RIB-6U	0.044	J	3.66	J+
Discharge Point				
RIC-1	1.02		13.3	J+
RIC-2	1.23		24.3	J+
RIC-3	1.43		17.7	J+
RIC-4	0.837		22.5	
RIC-5	1.05		25.9	J
RIC-7[2]	1.06		49	
RIC-6	0.995		20.1	
Downstream				
RIB-1D	0.037	J	5.87	J+
RIB-7D[2]	0.243		5.44	J+
RIB-2D	0.072		5.65	J+
RIA-3D	0.132		8.48	J+
RIA-4D	0.058		9.93	
RIA-5D	0.055		7.15	
RIA-6D	0.093		5.77	J+
Field Blank				
RIF-2	0.02	U	3.27	
RIF-6	0.02	U	0.6	

1 No discharge on day 0

2 Duplicate

U: Not detected

J+: Estimated (quantitatively) with high bias

4.1 Data Quality

The laboratory data was validated per guidelines presented by the EPA and the USACE for assessing data quality in National Functional Guidelines and Guidance for Evaluating Performance Based Chemical Data. Included in the assessment is an evaluation of holding times, QC samples, calibrations and blanks along with a quantitation check back to the supplied raw data. Detailed reports can be found in Appendix A.

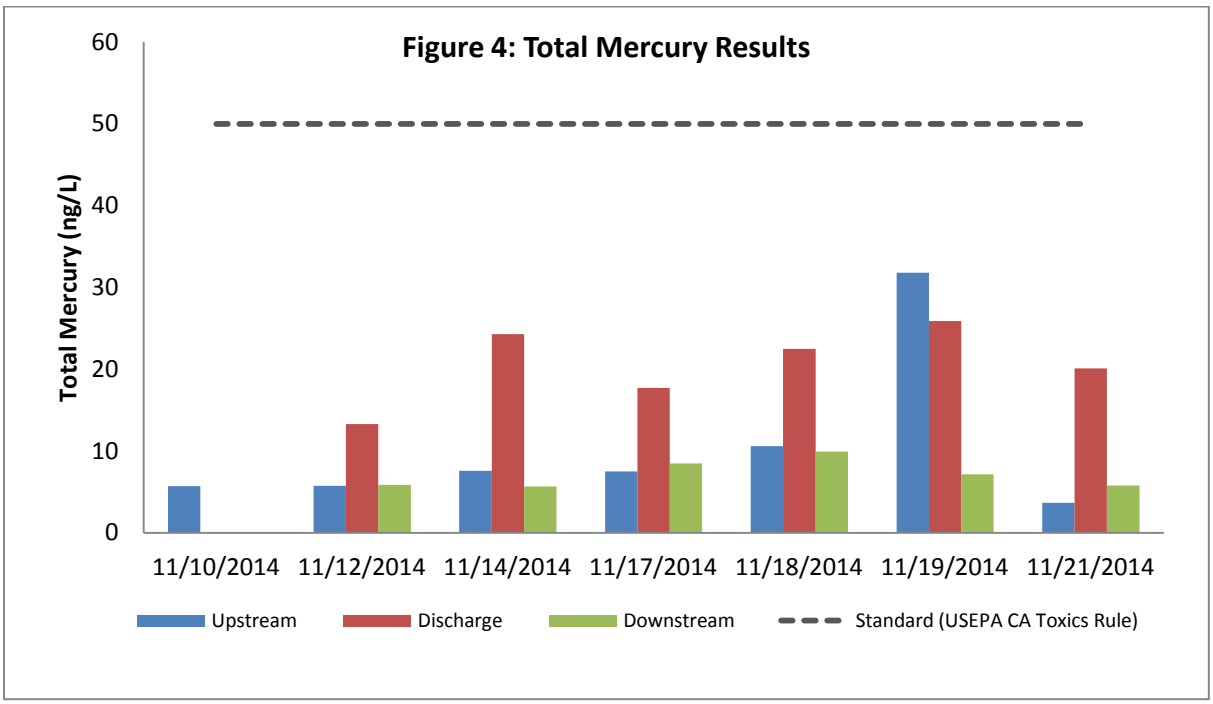
For total mercury, field duplicates, trip blanks, equipment blanks and matrix spike/matrix spike duplicate (MS/MSD) samples were analyzed along with the normal laboratory control samples. The field duplicate precision was good for RID-1D and slightly high for RIC-6. Data was flagged appropriately. Matrix spike and spike duplicate recoveries were acceptable. Trip blanks and field blanks varied in levels of contamination causing qualification of several results as estimated with a high bias. While the levels in RIF-6 were low at 0.6 ng/L, the field blank RIF-2 from November 14 (Day 2) had 3.27 ng/L of total mercury detected. All other QC samples and calibrations were acceptable. All holding times were met.

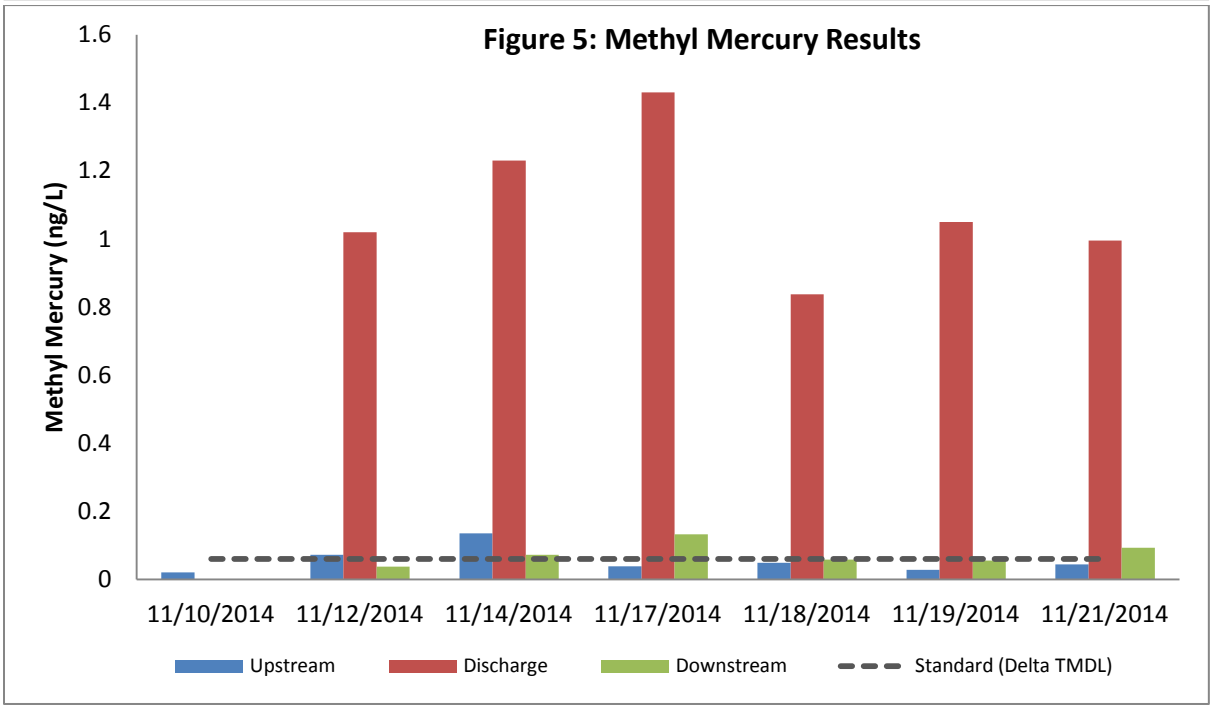
For methyl mercury, field duplicates, equipment blanks and MS/MSD samples were analyzed along with the normal laboratory control samples. No trip blanks are needed because methyl mercury is not volatile. Field duplicate precision was excellent (when calculated). Matrix spike and spike duplicate recoveries were acceptable. Samples required no qualification for blank contamination. All other QC samples and calibrations were acceptable. All holding times were met.

The variation in the equipment blanks for total mercury shows the difficulty in sampling and shipping this low level volatile test. The data for methyl mercury is excellent with little variation and no contamination seen in the field/analytical process. All the data is usable for project decisions, no data was rejected.

5.0 Discussion

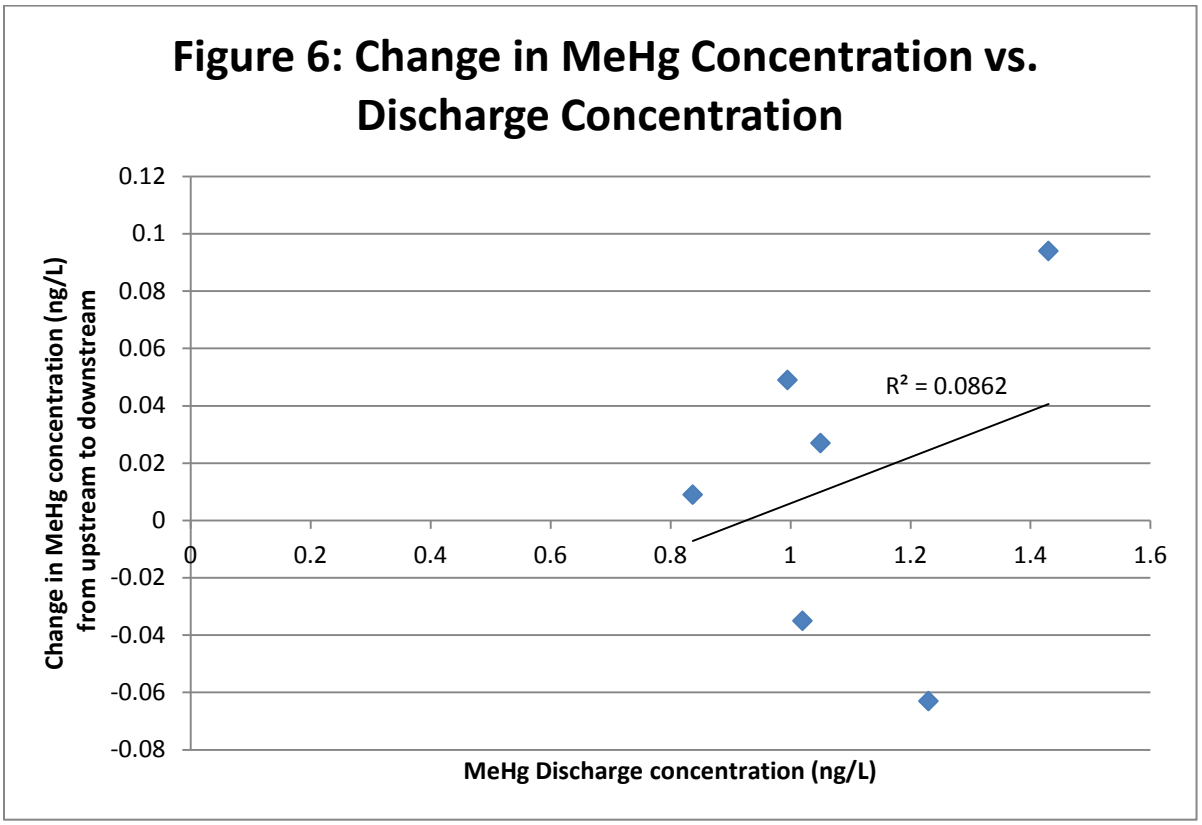
For all samples, total mercury was in compliance with the general order criterion of 50 ng/L. However, all of the discharge samples, as well as some of the upstream and downstream samples, were above the TMDL implementation goal for methyl mercury of 0.06 ng/L (see Figures 4 and 5).

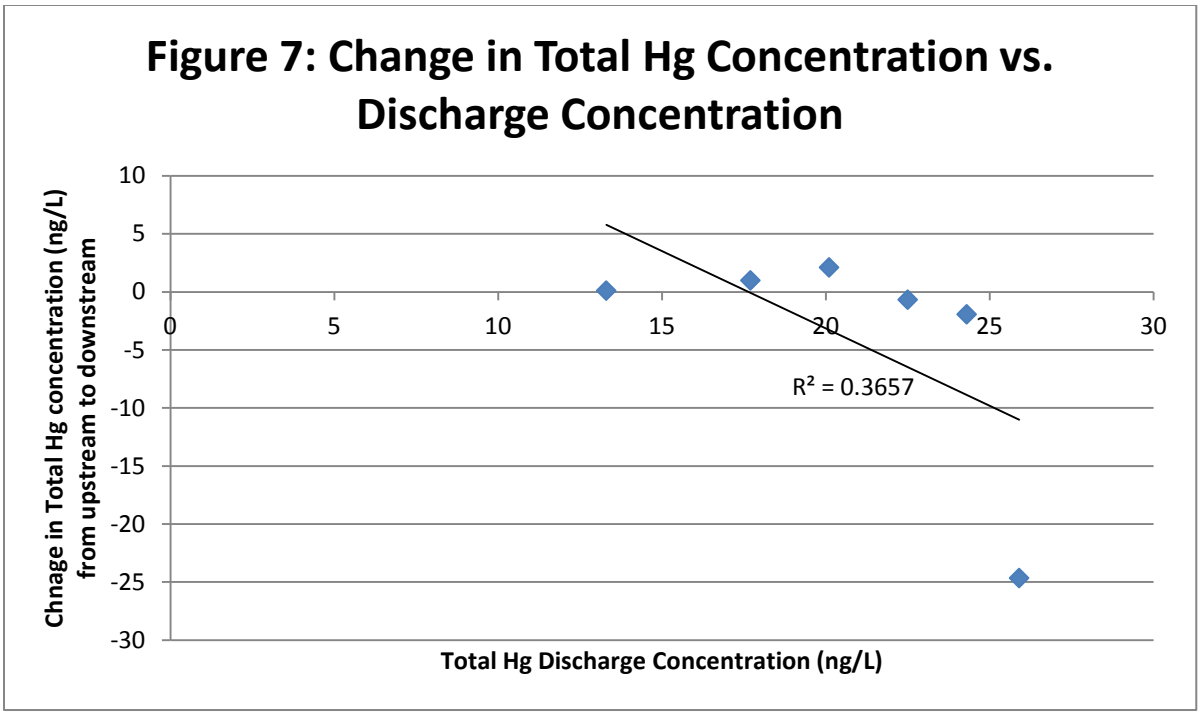




There is not an obvious impact on the downstream methyl or total mercury concentrations from the DMPS discharge. As can be seen in Table 3, the average MeHg concentration was higher in the downstream than upstream, but the average Mercury concentration was actually lower in the downstream water, despite the discharge results being higher. As can be seen in Figures 6-7, there is not a significant correlation between the discharge concentrations and the change in concentrations from the 'upstream' to 'downstream' points. These discrepancies may be due to the relatively small number of samples, and also to the sensitivity of the extremely low level analytical tests. Several of the Total Mercury results (13 of 19 total), from all three sample collection points, were flagged as estimated or estimated with a high bias. Six of the 19 MeHg results were also flagged as estimates or non-detect, although 5 of those were for the upstream samples, and none from the discharge point.

Table 3: Average MeHg and Hg Concentrations		
	MethylMercury (ng/L)	Total Mercury (ng/L)
Upstream	0.06	10.37
Downstream	0.07	7.14
Discharge	1.09	20.63





An analysis of the flux of total mercury and methyl mercury into and out of Roberts I during the maintenance dredging in 2014 shows that there is a net removal of both mercury and methyl mercury from the channel. While the discharge water from the site contains increased concentrations of MeHg and Hg on average, the amount moved in the water is very small compared with the amount removed with the dredged sediment that remains on the DMPS.

Table 4: Estimated Total Hg and MeHg Removed from Channel into Roberts I in 2014

Analyte	Matrix	Net mass removal from DWSC (g)
Methyl Mercury	Water – influx to DMPS	0.01[1]
	Water – outflux to River	-0.27[1]
	Sediment	77.52[2]
	Total	77.26 g
Total Mercury	Water – influx to DMPS	2.59[3]
	Water – outflux to River	-6.16[3]
	Sediment	12,920[4]
	Total	12,916 g

1. Uses average upstream and discharge MeHg concentrations measured during this study, assumes dredge slurry is 90% water, surveyed sediment volumes (2014), and for the Stockton channel uses estimated volumes of the DMPS, and assumes 0.5 inch per day percolation/evaporation for 14 days
2. Uses ratio of MeHg:TotHg of 0.006 (from Delta MeHg TMDL Staff Report pg 120), and TotHg soil amounts calculated in 4.
3. Uses average upstream and discharge TotHg water concentration measured during this study
4. Uses surveyed sediment volumes, and pre-dredge sediment mercury concentrations from 2014 predredge sediment sampling for this reach, and average measured specific gravity of soil of 2.53, based on historical results for the Stockton DWSC predredge sampling.

The methyl mercury results from the discharge point seen during the 2014 sampling event were higher than 'effluent discharge' samples collected in 2010 and 2011 at similar timing during discharge at Roberts I. The average MeHg discharge concentration measured in 2014 was 1.09 ng/L, while the average past effluent concentration was 0.14 ng/L (87% lower). Total Mercury concentrations were closer on average, with the 2014 average being 20.6 ng/L, and the 2010-2011 average being 28.6 ng/L (39% higher). The cause of these differences is unknown; possible reasons could include differences in sampling location, weather conditions, effluent timing, and influent concentrations, or just small numbers of samples and random variability, among others. The 'effluent discharge' samples from 2010 and 2011 were not taken specifically near the Roberts I discharge pipe and pump, just in the DMPS, outside of the test cells created to test BMPs.

Table 5:
2014 Discharge Point and 2010 & 2011 Effluent Discharge Sample Results

Date	Methylmercury (ng/L)	Total Mercury (ng/L)
11/12/2014	1.02	13.3
11/14/2014	1.23	24.3
11/17/2014	1.43	17.7
11/18/2014	0.837	22.5
11/19/2014	1.05	25.9
11/21/2014	0.995	20.1
11/5/2011	0.14	44.5
11/11/2011	0.141	22.3
12/2/2010	0.138	18.9

6.0 Conclusion

The sampling event at the Roberts I DMPS occurred as expected during the 2014 dredge season, following the "clean-hands, dirty-hands" sampling protocol. Results from the sampling are seen in Table 2 and Figures 4 and 5. All Total Mercury results were below the criteria set in the GO. All of the discharge results for MeHg were above the 0.06 ng/L criteria proposed in the Delta TMDL, however there was not an identifiable correlation showing an increase in either Total or Methyl Mercury from upstream to downstream of the discharge point in the river.

Calculations based on pre-dredge sediment testing and this sampling event show that there is a large net removal of both Total and methyl Mercury from the river with maintenance dredging. The majority of mercury removed from the river during dredging is in the sediment, and very little of it returns to the river via discharge of decant water.

A Methyl Mercury study during the 2015 dredging season is planned. This study will follow the 2014 Methyl Mercury Control Study Work plan of February 2014, prepared by USACE for the Waterboard. The 2015 study is set to be performed by Applied Marine Sciences, as a subcontractor to Ross Island Sand & Gravel Co, the maintenance dredging contractor USACE has on contract to perform the 2015 maintenance dredging. This field study will look further at the issue of impacts to Mercury and Methyl Mercury concentrations in the river from maintenance dredging.

7.0 References

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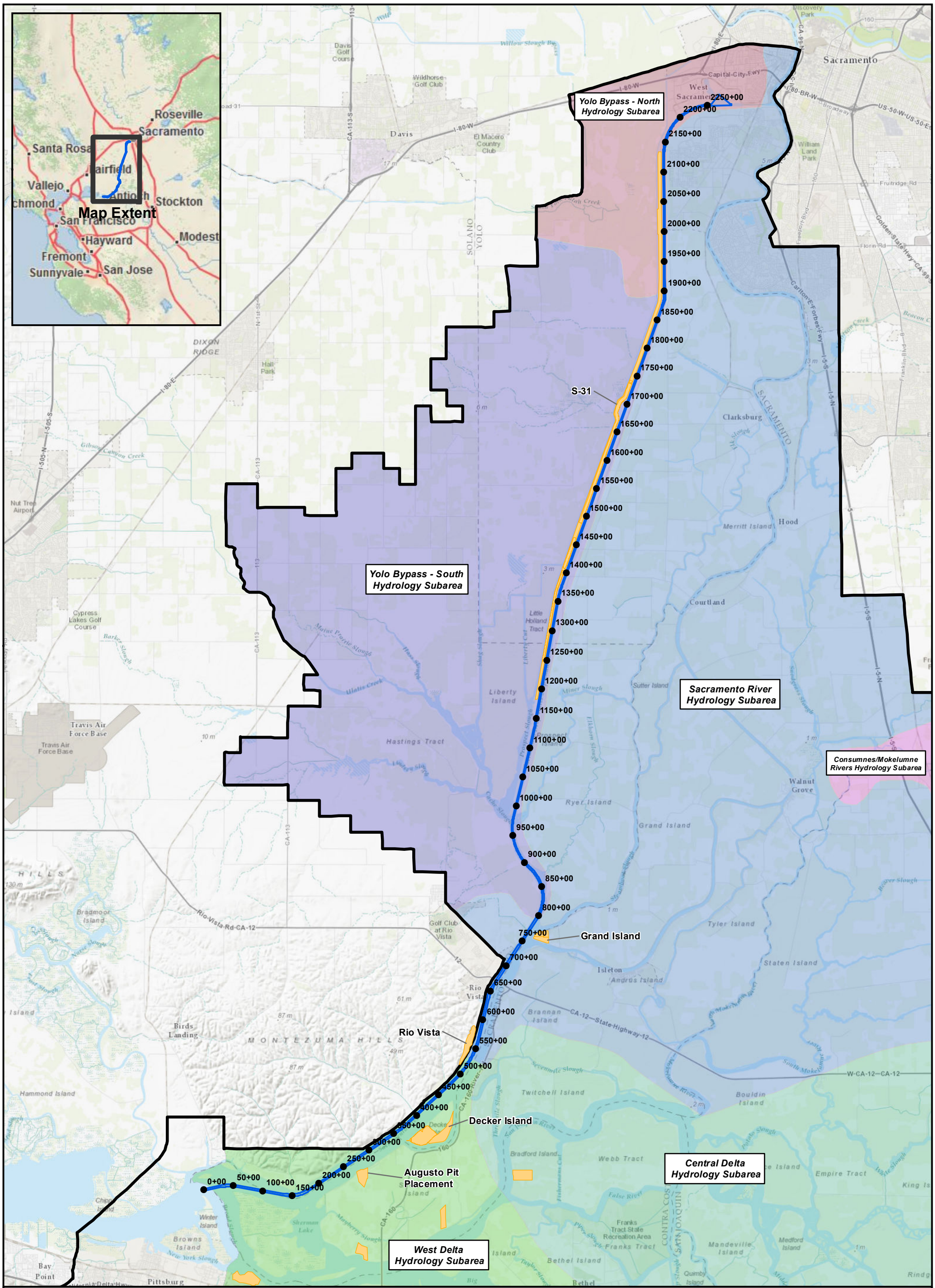

Figure 1

Sacramento Deep Water Ship Channel (DWSC) Dredged Material Placement Sites with Delta Hydrology-Based Delineation of Subareas

Ship Channel Extents

US Army Corps of Engineers
SACRAMENTO DISTRICT

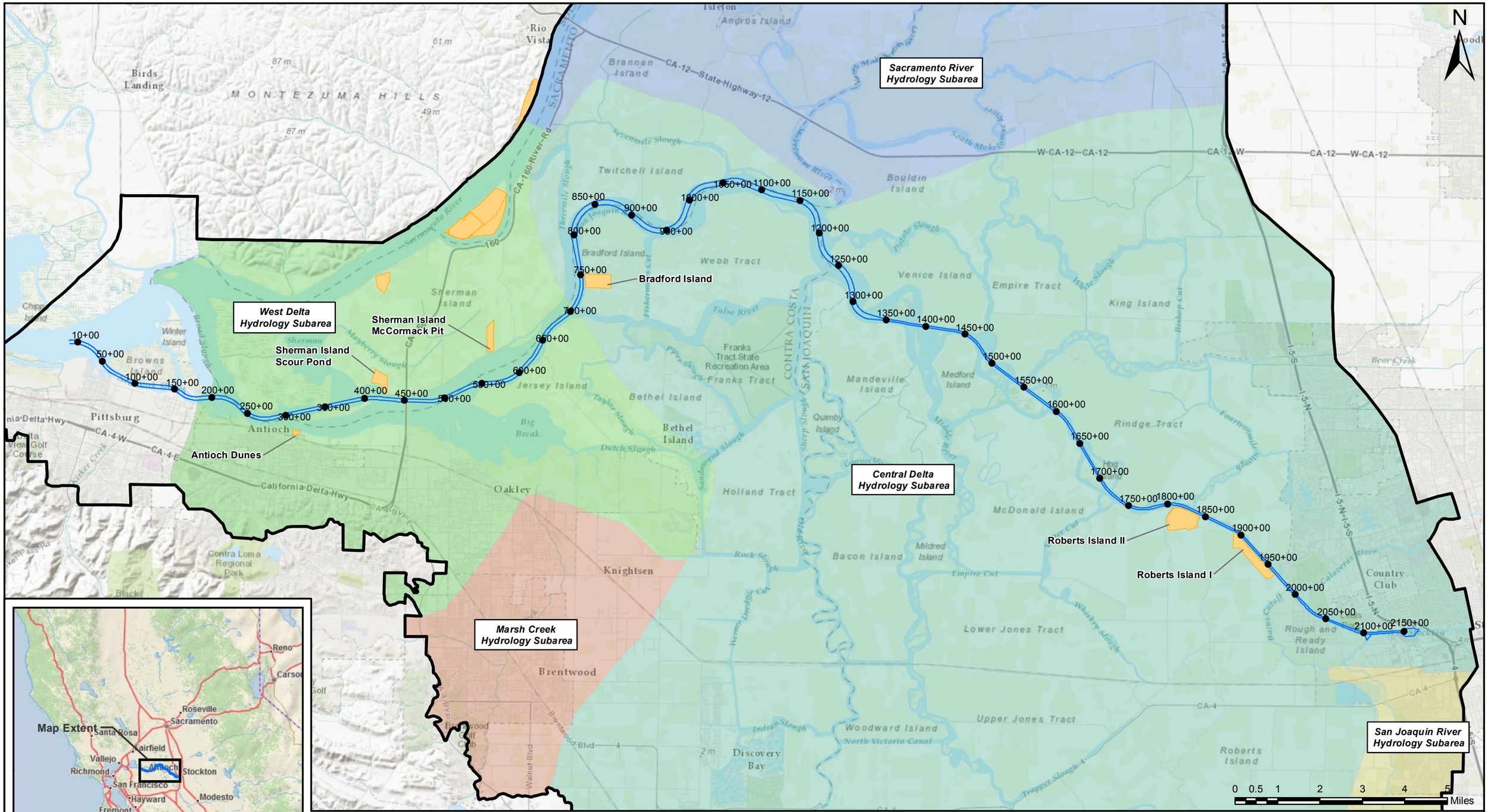

Figure 2

- DWSC Stationing
- San Joaquin DWSC
- Legal Delta
- DWSC Dredging and Landing Sites

San Joaquin Deep Water Ship Channel (DWSC)
Dredged Material Placement Sites
with Delta Hydrology-Based Delineation of Subareas

Ship Channel Extents

US Army Corps of Engineers. SACRAMENTO DISTRICT

EGIS

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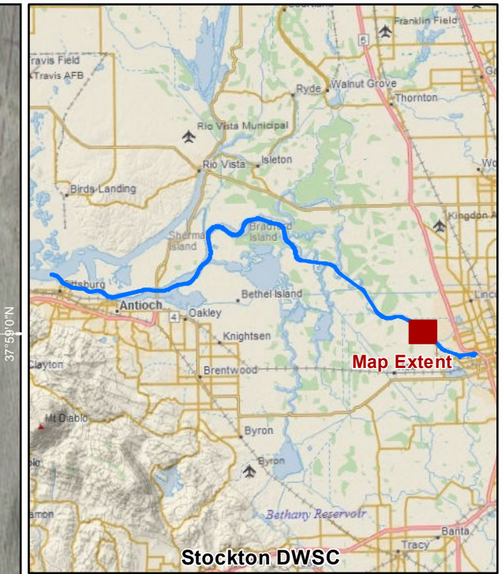

Legend

- RIA - Location A
- RIB - Location B
- RIC, Discharge Point
- Stockton DWSC Stationing
- Channel Miles
- Roberts I DMPS
- Shipping Channel

Aerial Imagery Source: June 2014, NAIP 1m

N

0 300 600 1,200 Feet

Figure 3
Methylmercury Study
Sampling Locations

STOCKTON DEEP WATER SHIP CHANNEL

US Army Corps of Engineers®
SACRAMENTO DISTRICT

February 2012 \\arcfcl\Project_data\CA\CM\Stockton_DWSC\GIS\GIS_Projects\Annual_Sampling_Locations\2012\2012_stockton_desc_sampling_fig-1.mxd