Quality Assurance Summary
Delta RMP Mercury Monitoring FY19-20 (Year 4)

This appendix summarizes the quality assurance (QA) review of the Delta Regional Monitoring Program (Delta RMP) 2019-2020 data for laboratory analyses of mercury and ancillary measurements in water and fish.

This review was conducted by ASC scientists and technical staff under the supervision of QA officer Dr. Donald Yee. Samples were collected and analyzed by scientists and technicians from the Marine Pollution Studies Laboratory (MPSL) in Moss Landing, California.

Of the 847 total lab results for field samples, all were reportable, with none censored. All requirements of the Delta RMP Quality Assurance Program Plan (QAPP) were met for 68% of samples (no qualifiers needed to indicate deviations), with minor or moderate deviations from the QAPP for the rest. In addition to field samples not collected due to pandemic closures, one set of chlorophyll-a samples exceeded holding time due to lab closure during the pandemic. TSS and VSS results had only one field blank, less than the 4 required to achieve the 1 per 20 frequency in the QAPP, as collection of that had been scheduled for a later sampling event that was canceled. Other deviations such as analytes detected in blanks, or lab or field replicate RPDs outside of QAPP targets, also led to flagging of other samples.

One thing to note however is that variation was occasionally quite high for individual field replicate pairs (up to 47% RPD), not likely only due to lab analytical variation (maximum around 20% RPD for the same analytes). The PIs should reexamine and possibly modify the field replicate collection procedures as needed, if the goal is to get a consistent integrated representative sample from a given site and event. If instead the goal is to evaluate intra-event or intra-site gradients or variation, continuation of existing procedures may be sufficient.

Table 1 provides a high-level summary of the quality assurance review of the chemical analytical results. Each of these analyses is described in greater detail below.

Table 1. QA Summary for chemical analytical results (RPD = relative percent difference)

Analyte	**Hold Time:** Percent of Results Exceeding hold time	**Sensitivity:** Percent of Results that are non-detects	**Contamination:** Percent of Results < 3x Lab Blank result	**Precision:** Average Duplicate RPD	**Accuracy:** Average % Recovery for sample of known conc.
Water					
Total Mercury	0%	0%	0%	6%	98.38%

Methylmercury	0%	1%	3%	10%	91.47%
Chlorophyll-a	16%	0%	0%	1%	106.13%
Dissolved Organic Carbon	0%	0%	0%	3% *FR	88.45%
Total Suspended Solids	0%	8%	0%	6%	102.43%
Volatile Suspended Solids	0%	35%	0%	17%	NR
Fish					
Total Mercury	0%	0%	0%	10%	103%
Total Mercury[RS]	0%	0%	0%	9%	104%

FR - from field RPDs RS - from restoration project studies NA - not recorded

In the first four columns of Table 1, the "ideal" result is 0%, and lower numbers are considered better. In the fifth, or right-most column, the ideal is 100% recovery. The relative percent difference (RPD) among duplicate samples is calculated based on lab replicates. The accuracy is reported for CRM (with externally certified concentrations) or for MS (lab spiked) samples . ASC's data review procedures are described in our Data Management and Quality Assurance (SOP).

Approach

About 15% of all samples were analyzed for quality assurance and quality control purposes.

For our QA review, we used the data electronically submitted by the laboratory and compiled it into a local database to verify that the correct number of field samples and required number of QC samples are reported for the requested analyses, as specified in the project Quality Assurance Project Plan, or QAPP, version 5.

We compared the results for QC samples to the acceptance criteria, or measurement quality objectives (MQOs) listed in the QAPP Table 14.2. We did this by independently recalculating reported precision (as relative percent difference, RPD, or relative standard deviation, RSD) for lab replicates, and percent recovery for samples of a known concentration. In order to verify that contamination of samples had not occurred in sampling or lab analysis, we compared the results for blank samples (both field and lab blanks) to method detection limits. In cases where an analyte is detected in a blank, we compare the measured concentration in the blank sample to concentrations measured in field samples to determine the proportion of the signal that originates from lab contamination.

Where deviations from the project's measurement quality objectives were found, we attached a flag or qualifier to the record. In some cases, records may have already been flagged by the reporting lab. Qualifiers added by ASC or the lab indicates that there has been a deviation from

the project's quality criteria, and are meant to warn data users that certain records may be inaccurate or imprecise.

In the most severe cases, data potentially may be rejected and not reported. However, for this project, all data were reportable, as we did not find serious violations of the quality objectives that would lead to rejection of data. The sections below describe the detailed findings of our QA review of the reported datasets.

Review details for individual datasets

Mercury in Fish Tissue (Restoration Projects)

Reviewed by Don Yee, October 2020.

The following section describes the quality assurance review for mercury and related analytes in fish tissue. Field crews from the Marine Pollution Studies Laboratory (MPSL) conducted sampling in Sept-Oct 2019. Samples were analyzed in the laboratory at Moss Landing, California in April and July 2020. The following analytes were reported:

1. Total mercury
2. Age
3. Moisture

This QA review focuses on mercury, but also describes the moisture results.

Overall Acceptability

Overall the dataset is acceptable. 100% of the results are reportable.

Hold Time

Storage and hold time requirements are listed in QAPP Table 12.1. Fish tissue samples may be analyzed up to one year after they are processed, provided that they are stored at or below a temperature of –20°C. All fish tissue samples were analyzed within 286 days or less.

Dataset Completeness

Mercury results were reported for 80 fish composite tissue samples analyzed in 4 lab batches. One lab replicate, as well as 1 MS, and 3 blanks were reported per batch, meeting the minimum requirement in the 2019-20 Delta RMP QAPP of 1 per batch of up to 20 field samples, for these QC sample types. 4 certified reference material samples (NRC DORM-4: Fish protein certified reference material for trace metals) were also analyzed. Data were reported not blank corrected.

Mercury samples were analyzed within 286 days after collection or less, within the 1-year holding time specified in the Delta RMP QAPP.

Moisture results were also reported for all the samples. The only QC samples for moisture were lab replicates (one per batch).

Accuracy

We assessed the accuracy of mercury analysis by inspecting the results for samples of a known concentration. As an indicator of measurement accuracy, we calculate the recovery, the ratio between the analytical result and the known or expected concentration. SFEI's convention is to

focus primarily on the results for certified material samples (CRMs), when present, over matrix spike or matrix spike replicates, as the CRMs are externally validated values.

Analyses of certified reference material were run at a minimum frequency of one per analytical batch (for analytical batches consisting of up to 20 field samples) or per 20 (field) samples for larger analytical batches. Matrix spikes, where an environmental sample is "spiked" with a known amount of mercury, provide secondary determination of method accuracy that can help assess matrix interferences or other analytical problems.

The average recovery for the certified reference material samples for mercury of 104% (ranging 101-106%) was well within a target MQO of between 75-125%. No qualifiers were added. The mercury matrix spikes recoveries were similar, (98-113%, averaging 108%), also within the target <25% error. The lab measurements are sufficiently accurate and no flags are required.

The accuracy of moisture could not be evaluated as the certificate for the CRM analyzed, NRC DORM-4, does not list a certified value for moisture, but the percentage was <5%, as would be expected for the material (provided pre-dried).

Precision

We analyzed the precision of analysis (ability to consistently obtain the same result) by comparing the results for replicate or duplicate samples. The analysis of lab replicates assess the repeatability of lab measurements. No field replicates were included or planned in this data submission, as fish caught at a given site may feed in different locations and differ in chemical exposure.

Lab replicates were used to assess and flag precision. The average RPD for the mercury lab replicates was 9%, and the maximum 15%, both well within the MQO target of 25%. Based on these results, measurements of total mercury in fish appear sufficiently precise, and no qualifiers were added.

Precision of matrix spike replicates and CRM replicates were examined, but not used for flagging field samples. The average RPD for the mercury matrix spike replicates was 7% (max 11%), within the MQO target of 25%. For the CRM replicates (across batches) RSD was 2%, so the mercury measurement is very consistent between batches.

The precision of the moisture results was very good, with lab replicate RPD always <2% (averaging ~1%)

Sensitivity

To review sensitivity, we calculated the percentage of field samples that are non-detects. This allows us to evaluate whether the analytical methods employed were sensitive enough to detect environmental concentrations of the targeted parameters.

The lab reported results above the method detection limit (MDL) for all field composite tissue samples for total mercury (100% detected). This indicates that the analysis methods used were of sufficient sensitivity to detect concentrations found in the fish composites.

Blank Contamination Check

The blank contamination review evaluates whether there may have been contamination in the field or laboratory during any stage of sample preparation and analysis. This review allows us to determine whether any contamination occurred that may affect the results, and if so, the magnitude of contamination.

Mercury was not measured in the method blanks at concentrations equal to, or above the reporting limits (RL), meeting the method objective of the 2019 Delta RMP QAPP of being "<RL". We found no evidence of sample contamination, and no qualifiers were added.

Comparison to Historical Data

As a final check, we compare new analytical results to existing data to check for major changes, which can be a sign of errors, for instance due to units or incorrect calculations. We compared the average mercury concentrations in fish collected to those collected earlier for Delta RMP mercury monitoring. The average spotted bass (*Micropterus punctulatus*) mercury concentration was 1.2 ug/g ww, and for largemouth (*M. salmoides*) it was 0.6 ug/g ww. This range is very similar to prior years, where average largemouth bass mercury was between 0.3 and 0.6. Spotted bass averages were previously around 0.4 ug/g ww for 2016 and 2018. Concentrations vary among individual fish and sites, so this magnitude of differences in averages appear reasonable given interannual variability and the mix of individual samples collected each period. Age and size are recorded, and may be useful in interpretation of differences among individuals.

Mercury in Fish Tissue

Reviewed by John Ross, September, 2019,

Summarized by Don Yee, October 2020

The following section describes the quality assurance review for mercury and related analytes in fish tissue. Field crews from the Marine Pollution Studies Laboratory (MPSL) conducted sampling in August 2019. Samples were analyzed in the laboratory at Moss Landing, California in August 2019. The following analytes were reported:

1. Total mercury
2. Moisture

This QA review focuses on mercury, but also describes the moisture results.

Overall Acceptability

Overall the dataset is acceptable. 100% of the results are reportable.

Hold Time

Storage and hold time requirements are listed in QAPP Table 12.1. Fish tissue samples may be analyzed up to one year after they are processed, provided that they are stored at or below a temperature of –20°C. All fish tissue samples were analyzed within about a month.

Dataset Completeness

Fish composite tissue mercury results were reported for 112 samples analyzed in 6 lab batches. One lab replicate, as well as 2 MS, and 3 blanks were reported per batch, meeting the minimum requirement in the 2019-20 Delta RMP QAPP of 1 per batch of up to 20 field samples, for these QC sample types. 6 certified reference material samples (NRC DORM-4: Fish protein certified reference material for trace metals) were also analyzed. Data were reported not blank corrected.

Mercury samples were analyzed within about a month after collection, well within the 1-year holding time specified in the Delta RMP QAPP.

Moisture results were also reported for all the samples (allowing conversion of mercury concentrations between wet and dry weight equivalents).

Accuracy

We assessed the accuracy of mercury analysis by inspecting the results for samples of a known concentration. As an indicator of measurement accuracy, we calculate the recovery, the ratio between the analytical result and the known or expected concentration. SFEI's convention is to focus primarily on the results for certified material samples (CRMs), when present, over matrix spike or matrix spike replicates, as the CRMs are externally validated values.

Analyses of certified reference material were run at a minimum frequency of one per analytical batch (for analytical batches consisting of up to 20 field samples) or per 20 (field) samples for larger analytical batches. Matrix spikes, where an environmental sample is "spiked" with a known amount of mercury, provide secondary determination of method accuracy that can help assess matrix interferences or other analytical problems.

The average recovery for the certified reference material samples for mercury of 94% (ranging 90-98%) was well within a target MQO of between 75-125%. No qualifiers were added. The mercury matrix spikes recoveries were similar, (98-109%, averaging 103%), also within the target <25% error. The lab measurements are sufficiently accurate and no flags are required.

The accuracy of moisture could not be evaluated as the certificate for the CRM analyzed, NRC DORM-4, does not list a certified value for moisture, but the percentage was ~5%, as would be expected for the material (provided pre-dried).

Precision

We analyzed the precision of analysis (ability to consistently obtain the same result) by comparing the results for replicate or duplicate samples. The analysis of lab replicates assesses the repeatability of lab measurements. No field replicates were included or planned in this data submission, as fish caught at a given site may feed in different locations and differ in chemical exposure.

Lab replicates were used to assess and flag precision. The RPD for the mercury lab replicates averaged 10%, and the maximum 16%, both well below the MQO target of 25%. Based on these results, measurements of total mercury in fish appear sufficiently precise, and no qualifiers were added.

Precision of matrix spike replicates and CRM replicates were examined, but not used for flagging field samples. The average RPD for the mercury matrix spike replicates was 4% (max 9%), within the MQO target of 25%. For the CRM replicates (across batches) RSD was 2%, so the mercury measurement is very consistent between batches.

Sensitivity

To review sensitivity, we calculated the percentage of field samples that are non-detects. This allows us to evaluate whether the analytical methods employed were sensitive enough to detect environmental concentrations of the targeted parameters.

The lab reported results above the method detection limit (MDL) for all field composite tissue samples for total mercury (100% detected). This indicates that the analysis methods used were of sufficient sensitivity to detect concentrations found in the fish composites.

Blank Contamination Check

The blank contamination review evaluates whether there may have been contamination in the field or laboratory during any stage of sample preparation and analysis. This review allows us to determine whether any contamination occurred that may affect the results, and if so, the magnitude of contamination.

Mercury was not measured in the method blanks at concentrations equal to, or above the reporting limits (RL), meeting the method objective of the 2019 Delta RMP QAPP of being "<RL". We found no evidence of sample contamination, and no qualifiers were added.

Comparison to Historical Data

As a final check, we compare new analytical results to existing data to check for major changes, which can be a sign of errors, for instance due to units or incorrect calculations. We compared the average mercury concentrations in fish collected to those collected earlier for Delta RMP mercury monitoring. The average smallmouth bass (*Micropterus dolomieu*) mercury concentration was 0.5 ug/g ww, and for largemouth (*M. salmoides*) it was 0.6 ug/g ww. This range is very similar to prior years, where average largemouth bass mercury was between 0.3

and 0.6. Prior years did not include smallmouth, but spotted bass averages were previously around 0.4 ug/g ww for 2016 and 2018. Concentrations vary among individual fish and sites, so this magnitude of differences in averages appear reasonable given interannual variability and the mix of individual samples collected each period. Age and size are recorded, and may be useful in interpretation of differences among individuals.

Mercury and Ancillary Parameters in Water Samples

In this section, we describe the analysis of water samples for mercury (Hg), methylmercury (MeHg), and ancillary water quality parameters chlorophyll-a (Chl-a), dissolved organic carbon (DOC), total suspended solids (TSS), and volatile suspended solids (VSS). The QA for these analyses is summarized above in **Table 1**.

Overall Acceptability

Overall the dataset is acceptable. 100% of the results are reportable. The main issue that was encountered was a hold time exceedance for chl-a analyses due to lab closure for COVID-19. Variation in field replicates exceeded QAPP targets (up to ~45% RPD), PIs should reexamine collection procedures to evaluate whether this is to be expected or should/could be reduced.

Hold Time

The lab analyzed water samples for mercury and methylmercury within their hold time limits of 90 and 180 days respectively (see QAPP Table 12.1 for hold times and sample storage requirements). The lab analyzed samples within required hold times were also met for DOC (30 day), Total Suspended Solids and Volatile Suspended Solids (7 day).

However, chlorophyll a samples from March 2020 were analyzed past their 28 day hold, due to lab closure for COVID-19. The maximum hold time was 125 days. ASC's QA Officer flagged these results "VH" for a hold time exceedance, but the results are still reported. Samples were stored frozen during the closure, so the degradation was minimized as much as was possible.

Dataset Completeness

Results were reported for 38 environmental samples (5 sampling events at 6 sites, and 4 events at 2 sites), less than the originally planned number (see QAPP Table 6.2(b)) due to COVID-19 closures precluding collection of April 2020 samples.

In addition, the lab reported results for various QC samples of the required type and frequency, as summarized in Table 2 below. The minimum frequency for QC samples is stated in QAPP Table 14.2. Dissolved and total fraction Hg and MeHg samples are processed in the same way for lab analyses, so total fraction QC samples apply to both fractions. QAPP listed frequencies for QC samples were met, except for field blanks for TSS and VSS. After FY18-19, the QAPP was amended to indicate that neither TSS nor VSS field blanks are required.

For ancillary analytes, some QC sample types like CRMs are not available or typically run for analyses. However, there was always at least one type of QC sample analyzed in replicate for precision (at least field replicates, usually also lab replicates, sometimes MS/MSDs), one or more types for recovery (LCS or MS or CRM), and lab blanks to evaluate contamination.

Table 2. Number of sample results submitted by lab for water samples, by sample type

Analyte	Environ-mental samples	Field duplicates	Lab duplicates	Field blanks	Lab blanks	CRM	LCS	MS	MSD
Target Analytes									
Dissolved Hg	38	5	1	5					
Total Hg	38	5	4	5	15	5		10	10
Dissolved MeHg	38	5		5					
Total MeHg	38	5	5	5	15			10	10
Ancillary analytes									
chlorophyll-a	38	5			15		5		
TSS	38	5	5		10	5			
VSS	38	5	5						
DOC	38	5		5	7		18	6	6

Accuracy

We assessed the accuracy of lab analyses by inspecting the results for samples of a known concentration. As an indicator of measurement accuracy, we calculate the average percent error between the analytical result and the known concentration in the standard. SFEI's convention is to give preference to the results for certified material samples (CRMs), when present, over matrix spike or matrix spike replicates, as the CRMs are externally validated values.

Of the reported analytes, only mercury had natural matrix CRM results, with average recovery errors of 3% (mean recovery 100.5%).

DOC and TSS CRMs were lab created materials, with recovery within targets as well (average 1% error, 100% recovery on DOC, 4% error, 99% recovery on TSS).

Chl-a recovery was evaluated using LCS samples, averaging 7% error, 96% recovery.

Recovery errors on MS samples averaged <10% for Hg, well within its target 25%, and <11% for MeHg, within its 30% target.

Recovery errors on MS samples averaged 28% for DOC, above its 20% target; however, recoveries on the CRM results were acceptable as noted previously, so results were not flagged.

Precision

We analyzed the precision of analysis methods (ability to consistently obtain the same result) by comparing the results for replicate or duplicate samples. The analysis of lab replicates (split and analyzed in the laboratory) allows us to assess the repeatability of lab measurements.

Precision averaged 10% RPD for Hg and MeHg lab replicates, for samples where concentrations were large enough to quantify reliably, i.e. results that were at least 3x the MDL. Variation in Hg and MeHg among field samples duplicates from individual sites was somewhat larger, but still averaged <15% RPD.

Lab precision averaged 12% or better, well within the 25% RPD target for ancillary analytes (DOC, TSS, VSS). Precision on chl a was determined from field replicates, as samples are collected on filters, typically not suitable for subsampling as lab replicates. Variation among field samples duplicates from individual sites was somewhat larger, but still averaged 16% RPD or better for all the ancillary analytes. One thing to note however is that variation was occasionally quite high for individual field replicate pairs (up to 47% RPD). The PIs should reexamine and possibly modify the field replicate collection procedures as needed; if the objective is to estimate the upper bound or illustrate the maximum variation occurring in the spatial scale of a site or of the temporal scale of a collection event, the variation may be acceptable. In contrast, if the goal is to illustrate relative success of getting a consistent signal, method modifications are likely needed to ensure the collected field replicates are more consistent.

Sensitivity

For the sensitivity review, we evaluated the percentage of field samples that are non-detects. This allows us to evaluate whether the analytical methods employed were sensitive enough to detect environmental concentrations of the targeted parameters.

The lab methods were sufficient to detect nearly all analytes in samples, with the exception of VSS, where 40 of 100 samples were non-detect.

There were also 2 chl-a results, 2 Hg, 1 MeHg, and 1 DOC result below detection limits.

Blank Contamination Check

The blank contamination review evaluates whether there may have been contamination in the field or laboratory during any stage of sample preparation and analysis. This review allows us to determine whether any contamination occurred that may affect the results, and if so, the magnitude of contamination.

Samples were reported NOT blank corrected for DOC and MeHg, but blank corrected for the other analytes. Lab blanks were all non-detects for the uncorrected analytes, and had variation

below detection limit for the blank subtracted analytes, so no results were qualified for blank contamination. DOC was detected in four field blanks at concentrations 0.2 to 0.4 mg/L, about 2 to 4x above the detection limit of 0.1 mg/L in samples analyzed by the contract laboratory MBAS, but still at least 6x lower than the average field sample result.

Comparison to Historical Data

As a final check, we compare new analytical results to existing data to check for major changes, which can be a sign of errors, for instance due to units or incorrect calculations. As this is the third year of monitoring for water Hg and MeHg and the various ancillary parameters in the Delta RMP, the new data, largely from the same sites with the same (or similar) collection and analytical methods, can be directly compared.

Table 3 below lists the reported ranges for the various reported parameters for this year, compared to the range for prior years combined. The data largely span the same range for all analytes, with slightly lower minimum and/or higher maximum reported values for the individual analytes. We did not see any obvious errors in the data as a result of this QA step.

Table 3. Range of Delta RMP reported concentrations 2019-20 versus prior years

Parameter	Delta RMP (prior range)	Delta RMP 2019-20
Mercury		
Dissolved Mercury	<0.12 – 7.5 ng/L	0.41 - 1.67 ng/L
Total Mercury	<0.12 – 26.3 ng/L	0.46 - 9.72 ng/L
Dissolved Methylmercury	0.01 – 0.26 ng/L	<0.01 - 0.10 ng/L
Total Methylmercury	<0.01 – 0.39 ng/L	0.03 - 0.24 ng/L
Ancillary		
TSS	1 – 183 mg/L	<2 - 72.5 mg/L
DOC	<0.18 – 8.1 mg/L	1.4 - 5.0 mg/L
VSS	<1 – 65 mg/L	<1.6 - 11.2 mg/L
chl-a	<0.28 – 47.5 ug/L	0.51 - 25.2 ug/L