

To: Philip Trowbridge, RMP Manager
Jay Davis, RMP Lead Scientist
From: Don Yee, Quality Assurance Officer
Date: June 01, 2018
Re: 2017 RMP Water Samples Quality Assurance Report

Introduction

In 2017, grab water samples were collected from 22 sites, with samples analyzed for select trace elements (Cu, MeHg, Se), ancillary water quality parameters (DOC, POC, SSC, hardness) and weak acid dissociable cyanide. Additionally, water samples were collected for toxicity tests from 7 sites, and one site (Golden Gate) sampled for nutrients (nitrogen species, silica). The sampling and analysis was conducted by the Regional Monitoring Program for Water Quality in San Francisco Bay. The details of the cruise and sample collection methods are described in the RMP Quality Assurance Program Plan, cruise plans, cruise reports, and field sampling reports. These documents are available from the SFEI website (<http://www.sfei.org/programs/sf-bay-regional-monitoring-program#tab-1-2>).

The water samples were analyzed for the following compounds by the laboratories indicated:

- *ALS – Conventional WQ Parameters, silica*
- *Brooks Applied Lab - Trace Elements*
- *CCCSD - Nutrients*
- *Pacific EcoRisk – Water Toxicity*

The SFEI Data Services Team checked the laboratory results using the methods and data quality objectives in the RMP Quality Assurance Project Plan (QAPP). For trace elements, 90% or more of the results for analyte groups were determined to be acceptable for use in RMP reports and calculations, but given low DOC recovery in matrix spikes, investigation of another lab for ancillary parameters should begin.

This memo provides a high-level summary of the quality assurance assessment for each dataset. Non-conformances with the QAPP and corrective actions needed for the next round of monitoring are highlighted in gray shading. The details of the quality assurance assessment of each dataset are provided in Appendix A.

The data have been approved by the RMP Manager and Lead Scientist, and all results have been uploaded to the San Francisco Regional Data Center and CEDEN; rejected results are uploaded but can only be downloaded by special request rather than through standard queries.

Quality Assurance Summary for 2017 RMP Water Samples

ALS - Conventional Water Quality Parameters and (Total) Cyanide

2017 conventional water quality parameter analyses by ALS had 71% of samples reportable, due to very low (~60%) DOC recovery in matrix spike samples, and cyanide blank contamination comparable to or greater than ambient concentrations in nearly half the samples. Although ~60% of cyanide results were non-detects, the cyanide MDL, around 0.8 ug/L, was about 3x below the cyanide SSO for the Bay, so the analytical method may suffice for characterizing risk in the Bay unless the criterion is changed. There was again some field blank contamination running DI water through the DOC filtering apparatus, so some modifications of the field procedures for cleaning of filter units between samples may be needed. The DI water used for the field blank was provided by the trace metals lab, which may not necessarily be totally absent organics (DI preparation machines typically monitor conductivity, not uncharged organics). Given the low MS recoveries for DOC (usually is a fairly routine analysis) we recommend investigating a different laboratory for DOC analysis (and thus likely POC as well) for the future.

Brooks Applied Lab -Trace Metals

2017 water trace metals were collected as particulate and dissolved fractions, rather than measurement of unfiltered (total) samples previously used to estimate particulate concentrations in prior RMP S&T efforts. Samples were filtered while on board the research vessel, and frozen for storage. Trace elements were analyzed by BAL, with results to be reported by column separation analysis for all analytes. Given increased interest in selenium, an intercomparison with the previous reductive precipitation (RP) separation method was conducted, so all dissolved samples were analyzed for selenium by two methods. The Se MDL for the RP method is about 5x higher, so many results detected by the column method were non-detects by RP. At sites where Se could be detected by both methods, results by RP averaged about 35% lower. Given most results were less than 3x the MDL of the RP method, that magnitude of difference appears reasonable.

An intercomparison with other labs that have measured Se in SF Bay was also conducted for a subset of water sites. Included in the interlab intercomparison were Greg Cutter's group at Old Dominion University, Robin Stewart's group at USGS Menlo Park, and the SFPUC Southeast Treatment Plant laboratory. The results of that intercomparison (with BAL column results used) showed good comparability among labs dissolved fraction samples, <25% relative standard deviation (RSD) for 5 of 6 sites (30% RSD for the last one). Particulate concentrations were more variable among labs; concentrations were about 10 times lower than in dissolved phase, with non-detects reported by BAL for 2 of the 6 intercomparison sites, with only 1 site <25% RSD (29-36% for the remaining 3). Nonetheless, given very low particulate concentrations, estimates of particulate by difference between total and dissolved would easily vary by that amount or more; given variation among replicates often around 10%, a difference between total and dissolved of 10% can occasionally disappear or even be reversed (e.g., if a given pair is 10% low for total and

10% high for dissolved). Given the strong dependence of current Se bioaccumulation models on particulate Se, repeating this intercomp exercise with the aim of getting more quantitative results and better agreement among labs is desired, at the least, in 2019 RMP S&T water sampling, but possibly tagging on other studies if results are needed earlier to begin implementing long term Se “leading” change indicators monitoring proposed by the Se workgroup.

After copper results were reported, a high bias relative to past years for nearly all segments (but especially in LSB) was observed, so BAL was requested to analyze all the RP separated samples (originally prepared for Se) for Cu as well, which was possible for all but one sample. The RP sample results confirmed the suspected high bias using the new column separation for Cu. The lab has indicated that a titanium interference was found for Zn and Cu, and are testing a change to a triple-quad MS instrument for use with their column method. We recommend reporting the RP sample results for Cu for now, or not reporting any Cu until results for the triple-quad are available and show no bias relative to previous RP method.

QC sample results for Cu are reported for the older RP method, and for the column method for Se, the methods being used for the reported data. Over 99% of the field sample results were reportable, with only one RP result for Cu not reportable (all other sites with sufficient material to analyze by the RP prep method). All samples were analyzed within method recommended hold times. Methods were sufficient to get detects for most analytes aside from dissolved phase MeHg, with ~70% non-detects. Results were blank corrected for MeHg but not other trace elements, and none required qualifiers for lab blank contamination. However, MeHg was found in the particulate field blank (at 41% of the average field concentration), and Cu in the dissolved field blank (analyzed by RP, at 14% of the average field result) so those results may be biased high. Recoveries on CRMs and matrix spikes averaged within 25% of target values for all analytes, so no recovery flags needed to be added. Similarly, deviations in precision averaged <25% for all analytes, so no precision qualifiers were added.

CCCSD - Nutrients

Only samples from Golden Gate site were collected and reported for nutrients. About 80% of the field sample results for nutrients were reportable, with three organic nitrogen and 1 nitrate result rejected. One nitrate result (analyzed after 6 days) was flagged for hold time past the recommended 48 hours. The MDLs were sufficient to get detection for all analytes aside from organic nitrogen, and nitrate as N (which were 100% ND). Recoveries on matrix spikes or lab control samples averaged within 10% of expected values for most analytes (meeting targets, which were either 10% of 15%), with only ammonium as N averaging 13.5%, which did not require a flag because the target limit was 15%. Similarly, precision was acceptable for all analytes, with average RSDs <10%, meeting targets of 10% of 15%, so no precision qualifiers were added. If organic nitrogen (all results rejected), and nitrate as N (no results detected) are critical analytes to report, further method refinement or selection of another lab is recommended before the next round of sampling and analysis.

Pacific EcoRisk – Water Toxicity

Water toxicity results were reported for 9 sites and controls as expected. Mean control survival met the 80% threshold, and the mean weight requirement (0.2mg/surviving mysid) was met. Reference toxicant test responses were within the typical response range in prior tox batches. The only deviations noted and flagged in the data were drifts in pH over the course of tests, exceeding the target ± 0.3 pH drift recommended, but EPA documentation of the method notes pH drifts of <1 full unit seldom cause observable effects in tests.

Appendix: Dataset QA Summaries

RMP Water, 2017

ALS – Water Conventionals

QA Issues for Project Manager to Review

Matrix spike recovery on DOC was poor (average 60% usually pretty easily +/- 10 to 20% (i.e. 80-120%)), recommend investigating another laboratory for the future.

Reporting Issues for Lab to Review

None

Formatting Issues for Data Manager to Review

None

Hold time review

Hold time met RMP QAPP targets other than for SSC, with hold times for most samples of 13 days versus a target of 7 days. Results were flagged for hold time exceedance, but in chilled and dark storage, with POC usually <5% of SSC, SSC results are not likely to have changed much.

QA Review

Dataset completeness

Data were reported for 22 water cruise stations for DOC, POC, SSC, hardness, CN. Silica was reported only for the Golden Gate station in replicate. All the DOC results were reported in quadruplicate, with 2 lab reps each for POC and hardness, 1 for CN, and none for SSC. Lab blanks and LCSs were reported for all analytes. A field blank and a field duplicate was reported for all analytes but silica. MSs were reported for DOC and CN.

Percent usable (non-reject) field data

About half the individual were rejected, driven by poor DOC recovery in MS samples rendering the reported results suspect. All the DOC field samples were analyzed in quadruplicate, which makes the statistic look particularly bad, but even on the basis of collected samples rather than number of analyses, 20% are rejected (80% usable), less than the desired 90%+ usable.

Overall acceptability

The data are mostly acceptable except for DOC, which was censored for all results due to low MS recovery, and CN, censored due to some samples being near the blank contamination level.

MDLs sensitivity

MDLs were sufficient to get quantitative results for most analytes, except CN, with ~60% NDs (expected given the MDL around 1ug/L). DOC was also ND for about 1/4 of samples and POC for about 1/6th.

QB averages (procedural, field blank)

Lab blank contamination was found in one batch each for DOC and CN. Given all the CN results are at most barely above MDL, all results in that batch (43% of the samples) were <3x the blank so

censored and not reported. The DOC blank was at ~0.1 mg/L, so about 6% of samples were <3x the blank and censored. In the field blank, DOC was detected at 0.4 mg/L and hardness at 1.8 mg/L, so results may occasionally also be affected by field contamination.

Average precision from replicate field sample

Precision on lab replicates for POC averaged <5% RSD, and 12% for DOC, respectively below and above a target of 10% so flagged (VIL) for marginal DOC precision but not censored. Hardness averaged 2% RSD, below its 5% target. Average RSD on SSC was 15%, above its 10% target, so also flagged (VIL) but not censored.

Accuracy (using a variety of SRMs or Matrix spike QRECs)

Recovery on DOC MS samples was low, averaging 60% recovery, well outside the target $\pm 10\%$ sought for that, so all those results were censored (VRIU flag) for poor recovery. The CN MS recovery was 107.5%, so within its $\pm 25\%$ target. Recoveries on blank spikes were all within target ranges ($\pm 25\%$ on CN, 10% on DOC, POC, SSC, and silica, and 5% on hardness).

Comparison of dissolved and total phases

Only POC and DOC were similar analytes in different fractions, with concentrations of about the same order of magnitude for both.

Comparison to previous years

POC and DOC were similar to past years, averaging somewhere around 1mg/L (max <10mg/L), SSC around 20m/L (max <100mg/L), CN around 1 ug/L or ND, and hardness around 4000-5000mg/L, so no results look particularly out of place.

Ratio Checking Summary

Not applicable

Sums Summary

Not applicable

BAL – Water Metals

QA Issues for Project Manager to Review

None

Reporting Issues for Lab to Review

None

Formatting Issues for Data Manager to Review

None

Hold time review

Method EPA 1640M Samples were analyzed between 21 and 30 days after collection; this is in within the holding requirement specified in the 2017 RMP QAPP for Copper of 6 months after lab acidified with nitric acid pH <2.

Method EPA 1630M Samples were analyzed between 15 and 46 days after collection; this is in within the holding requirement specified in the 2017 RMP QAPP for Methyl Mercury of 6 months.

Method EPA 1638M Samples were analyzed between 47 and 57 days after collection; this is in within the holding requirement specified in the 2017 RMP QAPP for Copper and Selenium of 6 months after lab acidified with nitric acid pH <2.

EPA 1640M IC Column Separation Samples were analyzed between 43 and 52 days after collection; this is in within the holding requirement specified in the 2017 RMP QAPP for Selenium of 6 months after lab acidified with nitric acid pH <2.

EPA 1640M RP separation (BA-5020 Rev 001a) Samples were analyzed between 29 and 158 days after collection; this is in within the holding requirement specified in the 2017 RMP QAPP for selenium of 6 months after lab acidified with nitric acid pH <2.

Method BAL-5020-001a (RP Copper)

Samples were analyzed between 166 and 176 days after collection; this is in within the holding requirement specified in the 2017 RMP QAPP for Copper of 6 months after lab acidified with nitric acid pH <2.

QA Review

Dataset completeness

Method EPA 1640M

Dissolved Copper results were reported for 22 water samples analyzed in 1 lab batch. Field replicates, lab replicates, matrix spike/matrix spike replicates, field blank, method blanks, certified reference materials (CRM), laboratory control samples (LCS) and non-project samples were also analyzed. All data was reported not blank corrected.

Two field replicates, 2 laboratory replicate, 2 MS/MSD pairs, 1 field blank, 4 method blanks, 2 certified reference materials, 2 laboratory control samples, and 1 non-project field samples, 1 non-project lab replicate, and one non-project MS/MSD pair were reported for the 22 samples which meets the minimum requirement in the 2017 RMP QAPP of 1 per 20 samples.

Method EPA 1630M

Dissolved and particulate Methyl Mercury results were reported for 22 water samples analyzed in 4 lab batches.

Field replicates, lab replicates, matrix spike/matrix spike replicates, field blanks, method blanks, laboratory control materials (LCM), laboratory control samples (LCS) and non-project samples were also analyzed. All data was reported blank corrected.

Two field replicates, 2 MS/MSD pairs, 1 field blank, 12 method blanks, 6 laboratory control samples, and 2 non-project field samples, and two non-project MS/MSD pairs were reported for the 22 dissolved samples which meets the minimum requirement in the 2017 RMP QAPP of 1 per 20 samples, except for lab replicates of which none were analyzed.

Two field replicates, 1 laboratory replicate, 1 matrix spike, 1 field blank, 4 method blanks, 2 laboratory control materials, and 2 laboratory control samples were reported for the 22 particulate samples which meets the minimum requirement in the 2017 RMP QAPP of 1 per 20 samples, except for matrix spike replicates of which none were reported.

Method EPA 1638M

Particulate copper and particulate selenium results were reported for 22 water samples analyzed in 1 lab batch.

Field replicates, lab replicates, matrix spikes, field blank, method blanks, post-digestion spikes (PDS), laboratory control materials (LCM), and laboratory control samples (LCS) were also analyzed. All data was reported not blank corrected.

Two field replicates, 3 laboratory replicate, 1 matrix spike, 1 field blank, 4 method blanks, 6 post-digestion spikes, 2 laboratory control materials, and 2 laboratory control samples were reported for the 22 particulate samples which meets the minimum requirement in the 2017 RMP QAPP of 1 per 20 samples, except for matrix spike replicates of which none were reported.

EPA 1640M IC Column Separation

Dissolved selenium results were reported for 23 water samples analyzed in 1 lab batch.

Field replicates, lab replicates, matrix spike/matrix spike replicates, field blanks, method blanks, certified reference materials (CRM), and laboratory control samples (LCS) were also analyzed. All data was reported not blank corrected.

Two field replicates, 3 laboratory replicate, 3 MS/MSD pairs, 1 field blank, 4 method blanks, 2 certified reference materials, and 2 laboratory control samples were reported for the 23 samples which meets the minimum requirement in the 2017 RMP QAPP of 1 per 20 samples.

EPA 1640M RP separation (BA-5020 Rev 001a)

Dissolved selenium results were reported for 21 water samples analyzed in 3 lab batches.

Field replicates, lab replicates, matrix spike/matrix spike replicates, field blanks, method blanks, laboratory control samples (LCS), an unknown accuracy sample (UnkAcc), and one non-project sample were also analyzed. All data was reported not blank corrected.

Two field replicates, 2 laboratory replicate, 3 MS/MSD pairs, 2 field blanks, 4 method blanks, 2 laboratory control samples, 1 unknown accuracy, and 1 non-project sample were

reported for the 21 samples which meets the minimum requirement in the 2017 RMP QAPP of 1 per 20 samples.

Method BAL-5020-001a (RP Copper)

Total Copper results were reported for 20 water samples analyzed in 1 lab batch.

Blind field replicates, lab replicates, field blanks, method blanks, and certified reference material (CRM) samples were also analyzed. Data was reported blank corrected, except for the method blanks.

Two field replicates, 2 laboratory replicate, 2 field blanks, 4 method blanks, and 2 certified reference materials were reported for the 20 samples which meets the minimum requirement in the 2017 RMP QAPP of 1 per 20 samples.

Overall acceptability

Overall the data is acceptable.

MDLs sensitivity

Method EPA 1640M

Method detection limits were acceptable as no non-detects (NDs) were reported for dissolved Copper.

Method EPA 1630M

Method detection limits were acceptable for particulate methyl mercury as no non-detects (NDs) were reported. However, dissolved methyl mercury had extensive non-detects (>50% NDs).

Method EPA 1638M

Method detection limits were acceptable for particulate copper as no non-detects (NDs) were reported, while a few non-detects (7.41%) were reported for particulate selenium.

EPA 1640M IC Column Separation

Method detection limits were acceptable as no non-detects (NDs) were reported for dissolved Selenium.

EPA 1640M RP separation (BA-5020 Rev 001a)

Dissolved selenium had extensive non-detects (>50% NDs).

Method BAL-5020-001a (RP Copper)

Method detection limits were acceptable as no non-detects (NDs) were reported for Total Copper.

QB averages (procedural, field blank)

Method EPA 1640M

Dissolved copper was not found in the method blanks at concentrations above the method detection limits. All method blank results were NDs.

Dissolved copper was measured in the field blank at a concentration of 0.0507 ug/L (~1.8% of the average concentration in the field samples).

Method EPA 1630M

Dissolved and particulate methyl mercury were found in at least one method blank, but as the standard deviation of the method blank concentrations were below the average method blank MDLs no blank contamination flags were applied.

Particulate methyl mercury was found in the field blank at a concentration of 0.1104 ng/L (~41% of the average concentration in the field samples).

Method EPA 1638M

Particulate copper and selenium were not found in the method blanks at concentrations above the method detection limits. All method blank results were NDs

EPA 1640M IC Column Separation

Dissolved selenium was not found in the method blanks at concentrations above the method detection limits. All method blank results were NDs.

EPA 1640M RP separation (BA-5020 Rev 001a)

Dissolved selenium was not found in the method blanks at concentrations above the method detection limits. All method blank results were NDs.

Method BAL-5020-001a (RP Copper)

Total copper was found in the method blanks at concentrations above the method detection limits (average concentration 0.14 ug/L; ~7% of the average concentration in the field samples). However, the standard deviation of the blank results was less than the average of the method blank method detection limits so were not qualified.

Total copper was measured in the field blanks at an average concentration of 0.265 ug/L (~14% of the average concentration in the field samples).

Accuracy (using a variety of SRMs or Matrix spike QRECs)

Method EPA 1640M

Accuracy was evaluated using the certified reference materials. The average %error for dissolved copper was 7.6% (average recovery 107.6%) below the target MQO of 25%. The average % error for dissolved copper in the laboratory control samples was 3.6% (average recovery 103.6%). No qualifiers were needed.

Method EPA 1630M

Accuracy was evaluated for particulate methyl mercury using the certified reference materials, while the dissolved methyl mercury was evaluated using the matrix spikes. The

average %error for particulate methyl mercury was 18.54% (average recovery 81.46%) and the average %error for dissolved methyl mercury was 11.96% (average recovery 92.54%); both below the target MQO of 35%. Particulate matrix spikes and laboratory control samples (dissolved and particulate) were examined, but not used for the evaluation, ranging from 9.55% to 18.68%, below the MQO target. No qualifiers were needed.

Method EPA 1638M

Accuracy was evaluated using the certified reference materials. The average %error for particulate copper was 16.06% (average recovery 83.94%) and for particulate selenium it was 0.5% (average recovery 100.05%); below their respective target MQOs of 25% and 35%. Matrix spikes and laboratory control samples were examined, but not used for the evaluation, with the average %error ranging from 5.6% to 15.33%. No qualifiers were needed.

EPA 1640M IC Column Separation

Accuracy was evaluated using the certified reference materials. The average %error for dissolved selenium was 4.16% (average recovery 95.84%) below the target MQO of 35%. Matrix spikes and laboratory control samples were examined, but not used for the evaluation, with the average %error ranging from 1.25% to 3.06%. No qualifiers were needed.

EPA 1640M RP separation (BA-5020 Rev 001a)

Accuracy was evaluated using the matrix spikes. The average %error for dissolved selenium was 8.05% (average recovery 95.45%) below the MQO target of 35%. Laboratory control samples were examined, but not used for the evaluation, with the average % error of 15.08% being well below the 35% target MQO. No qualifiers were needed.

Method BAL-5020-001a (RP Copper)

Accuracy was evaluated using the certified reference materials. The average %error for Total Copper was 10.65% (average recovery 110.65%) below the target MQO of 25%. No qualifiers were needed.

Average precision from replicate field sample

Method EPA 1640M

Precision was evaluated using the laboratory replicates. The average RSD for dissolved copper was 0.85%, well below the 25% target MQO. Lab replicates combined with field replicates, certified reference material replicates, matrix spike replicates, and laboratory control samples were examined, but not used for the evaluation, with the average RSD ranging between 0.46% and 14.83%; all well below the 25% target MQO. No qualifiers were added.

Method EPA 1630M

Precision was evaluated for particulate methyl mercury using the laboratory replicates, while the dissolved methyl mercury results were evaluated using the matrix spike replicates. The average RSD for particulate methyl mercury was 0.87% and the average

RSD for dissolved methyl mercury was 9.37%; both below the MQO target of 35%. Particulate lab replicates combined with field replicates, particulate certified reference materials, and laboratory control samples (dissolved and particulate) were examined, but not used for the evaluation, ranging from 2.28% to 14.08%, all below the target MQO.

Method EPA 1638M

Precision was evaluated using the laboratory replicates. The average RSD for particulate copper was 2.02% and the average RSD for particulate selenium was 3.64%; both well below their respective MQO targets of 25% and 35%. Lab replicates combined with field replicates, certified reference materials, and laboratory control samples were examined, but not used for the evaluation, ranging from 0.71% to 24.79%, all below the target MQOs.

EPA 1640M IC Column Separation

Precision was evaluated using the laboratory replicates. The average RSD for dissolved selenium was 7.83%, well below the 35% target MQO. Lab replicates combined with field replicates, certified reference material replicates, matrix spike replicates, and laboratory control samples were examined, but not used for the evaluation, with the average RSD ranging between 1.67% and 15.08%; all well below the target MQO of 35%. No qualifiers were added.

EPA 1640M RP separation (BA-5020 Rev 001a)

Precision was evaluated using the matrix spike replicates. The average RSD for dissolved selenium was 0.91%, well below the 35% target MQO. Laboratory control samples were examined, but not used for the evaluation, with the average RSD of 2.02% also being well below the 35% MQO target. No qualifiers were added.

Method BAL-5020-001a (RP Copper)

Precision was evaluated using the laboratory replicates. The average RSD for Total Copper was 5.48%, well below the 25% target MQO. Lab replicates combined with field replicates, and certified reference material replicate samples were examined, but not used for the evaluation, with average RSD's of 10.06% and 11.13%, respectively; all below the 25% target MQO of 25%. No qualifiers were added.

Comparison of dissolved and total phases

Not applicable.

Comparison to previous years

Average concentrations for dissolved Copper, Methyl Mercury, and Selenium were compared to the dissolved average concentrations for the 1993-2015 RMP Status and Trends water samples with Copper being 144% (1.4x greater), Methyl Mercury 42% (~0.4x greater), and Selenium 40% (0.4x greater).

Average concentrations for Total Copper were compared to the average concentrations for Total Copper in the 1993-2015 RMP Status and Trends water samples with Total Copper being 47% (~0.5x greater).

No comparison could be performed for particulate results.

Ratio Checking Summary

Not Applicable

Sums Summary

Not applicable

CCCSD – Water Nutrients

QA Issues for Project Manager to Review

The laboratory rejected all of the Organic Nitrogen sample results with the QA code of LRM - A matrix effect is present, flagged by laboratory. In addition all Nitrate as N results were reported as being non-detects (NDs) with a method detection limit of 0.046 mg/L which compares to a historical average MDL of 0.008 and a highest historical MDL of 0.02 mg/L in 2013.

Reporting Issues for Lab to Review

None

Formatting Issues for Data Manager to Review

None

Hold time review

All Ammonium as N, Nitrite as N, Orthophosphate as P, and Phosphorus as P results were analyzed within 2 days of collection less than the holding times specified in the RMP QAPP (28 day, 48 hours, 48 hours, and 28 days respectively). Nitrate as N was analyzed between 1 and 6 days after collection; the single result analyzed 6 days after collection exceeds the 48 hours hold time specified in the QAPP and was flagged with the QACode “H” for a holding time violation.

No hold time is specified in the QAPP for Chlorophyll a and Organic Nitrogen which were analyzed within 5 days, and 2 days of collection, respectively (there is a holding time listed of 28 days for the analyte Total Kjeldahl Nitrogen). No additional qualifiers were added.

QA Review

Dataset completeness

Ammonium as N, Chlorophyll a, Nitrate as N, Nitrite as N, Organic Nitrogen, Orthophosphate as P, and Phosphorus as P results were reported for 1 water sample, blind field replicates, laboratory replicates, matrix spike/matrix spike replicates (MS/MSD), lab blanks, and laboratory control samples (LCS's) analyzed in eight lab batches. Other client samples were provided for Nitrate as N. All data was reported not blank corrected.

Overall acceptability

Method detection limits were sufficient to have no non-detects (NDs) reported for the analytes Ammonium as N, Chlorophyll a, Nitrite as N, Orthophosphate as P, and Phosphorus as P. Extensive non-detects (NDs > 50%) were reported for Nitrate as N (100%) and Organic Nitrogen (100%).

None of the nutrients were found in the method blanks at concentrations as great than the method detection limits. No blank contamination qualifiers were added.

Accuracy was evaluated using the matrix spikes, except for Chlorophyll a and Organic Nitrogen which were evaluated using the laboratory control samples. The average %error for Ammonium as N, Chlorophyll a, Nitrate as N, Nitrite as N, Organic Nitrogen, OrthoPhosphate as P, and Phosphorus as P were 13.49%, 8.78%, 9.08%, 9.53%, 6.25%, 3.50%, and 3.99% respectively; all below the respective target MQO's for Ammonium as N (15%), Chlorophyll a (10%), Nitrate as N (15%), Nitrite as N (15%), Organic Nitrogen (used the target MQO of 15% for Total Nitrogen), OrthoPhosphate as P (10%), and Phosphorus as P (10%). No qualifiers were needed.

Precision was evaluated using the lab replicates, except for Organic Nitrogen which could not be evaluated because all of the results were non-detects (batch was rejected data LRM by lab). The average RSDs for Ammonium as N, Chlorophyll a, Nitrate as N, Nitrite as N, OrthoPhosphate as P, and Phosphorus as P were 6.89%, 1.92%, 3.97%, 0.48%, 5.93%, and 1.46% respectively; all below the respective target MQO's for Ammonium as N (15%), Chlorophyll a (10%), Nitrate as N (15%), Nitrite as N (15%), OrthoPhosphate as P (10%), and Phosphorus as P (10%). The precision of matrix spikes and laboratory control samples were examined where available and all were below their respective MQO targets. No flags were added.

Results were compared as possible to the historic average RMP Status and Trends water sample results collected at the same station (Golden Gate). Ammonium as N results were 37% (~0.4x as great), Chlorophyll a results were 111% (~1.1x as great), Nitrate as N results were 0% (all NDs compared to historic average of 0.15 mg/L), Nitrite as N results were 82% (~0.8x as great), and OrthoPhosphate as P results were 95% (~1.0X as great) of the historical averages.

Organic Nitrogen and Phosphorus as P could not be compared as they have not been measured before in RMP Status and Trends water samples.

MDLs sensitivity

Method detection limits were sufficient to have no non-detects (NDs) reported for the analytes Ammonium as N, Chlorophyll a, Nitrite as N, Orthophosphate as P, and Phosphorus as P. Extensive non-detects (NDs > 50%) were reported for Nitrate as N (100%) and Organic Nitrogen (100%).

QB averages (procedural, field blank)

None of the nutrients were found in the method blanks at concentrations as great than the method detection limits. No blank contamination qualifiers were added.

Accuracy (using a variety of SRMs or Matrix spike QRECs)

Accuracy was evaluated using the matrix spikes, except for Chlorophyll a and Organic Nitrogen which were evaluated using the laboratory control samples. The average %error for Ammonium as N, Chlorophyll a, Nitrate as N, Nitrite as N, Organic Nitrogen, OrthoPhosphate as P, and Phosphorus as P were 13.49%, 8.78%, 9.08%, 9.53%, 6.25%, 3.50%, and 3.99% respectively; all below the respective target MQO's for Ammonium as N (15%), Chlorophyll a (10%), Nitrate as N (15%), Nitrite as N (15%), Organic Nitrogen (used the target MQO of 15% for Total Nitrogen), OrthoPhosphate as P (10%), and Phosphorus as P (10%). No qualifiers were needed.

Average precision from replicate field sample

Precision was evaluated using the lab replicates, except for Organic Nitrogen which could not be evaluated because all of the results were non-detects (batch was rejected data LRM by lab). The average RSDs for Ammonium as N, Chlorophyll a, Nitrate as N, Nitrite as N, OrthoPhosphate as P, and Phosphorus as P were 6.89%, 1.92%, 3.97%, 0.48%, 5.93%, and 1.46% respectively; all below the respective target MQO's for Ammonium as N (15%), Chlorophyll a (10%), Nitrate as N (15%), Nitrite as N (15%), OrthoPhosphate as P (10%), and Phosphorus as P (10%). The precision of matrix spikes and laboratory control samples were examined where available and all were below their respective MQO targets. No flags were added.

Comparison of dissolved and total phases

Not applicable.

Comparison to previous years

Results were compared as possible to the historic average RMP Status and Trends water sample results collected at the same station (Golden Gate). Ammonium as N results were 37% (~0.4x as great), Chlorophyll a results were 111% (~1.1x as great), Nitrate as N results were 0% (all NDs compared to historic average of 0.15 mg/L), Nitrite as N results were 82% (~0.8x as great), and OrthoPhosphate as P results were 95% (~1.0X as great) of the historical averages.

Organic Nitrogen and Phosphorus as P could not be compared as they have not been measured before in RMP Status and Trends water samples.

Ratio Checking Summary

Not Applicable

Sums Summary

Not Applicable

PER – Water Toxicity

QA Issues for Project Manager to Review

None

Reporting Issues for Lab to Review

None

Formatting Issues for Data Manager to Review

None

Hold time review

Hold time was approximately 1 day for all samples.

QA Review

Dataset completeness

Dataset includes water toxicity results for 9 sites and controls. Water Quality measurements reported included Ammonia as NH₃, Unionized Ammonia as NH₃, Dissolved Oxygen, pH, and Salinity. Similar to previous years the case narrative states the tests were conducted in a temperature controlled room [at 26°C with temperature being monitored daily under a 16L:8D photoperiod], but no actual temperature data were submitted, except in a table in the report showing the initial water quality characteristics of the samples.

Overall acceptability

Overall, the data are acceptable.

Mean control survival met the test acceptability threshold of 80%. The minimum requirement for an acceptable test of an average weight of at least 0.20 mg/surviving mysid in the controls was satisfied. No significant toxicity or reduction in growth was found in the collected samples.

A reference toxicant test was performed using the first batch of mysids in order to assess the sensitivity of the *Americamysis bahia* test organism to toxic stress. The EC50 and IC50 for this test were consistent with the typical response ranges established by the reference toxicant test database for this species, indicating that these test organisms were responding to toxic stress in a typical fashion.

In order to perform the tests at salinities appropriate for the test organism, the SU051W, BG20, and BG30 ambient water samples were adjusted to a salinity of 25 ppt using a commercial artificial sea salt (Crystal Sea Salt®-bioassay grade); this treatment was recorded in the ToxResults and ToxSummary tables. The remaining ambient waters were tested at their respective ambient salinities.

Ammonia as NH₃ and Unionized Ammonia as NH₃ results were all non-detects. The salinity of the test waters were in the range of 20‰ to 30‰. Dissolved oxygen concentrations were greater than 5.0 mg/L.

There were many samples with $> \pm 0.3$ pH drift over the duration of the toxicity tests, flagged as VTW (for minor WQ deviances) in ToxTestQAcode of ToxSummary table, and ToxResultQAcode of ToxResults table (explanation comment also added to both tables), although the EPA method notes problems don't usually appear unless the shift is >1 pH unit.

The ToxBatch table was updated with "Some WQ deviances" in ToxBatchComments, and flagged with the BatchVerification codes of VLC,VMD (Cursory Verificaton/Validation, Minor Deviations, Flagged by QAO).

Ratio Checking Summary

Not Applicable

Sums Summary

Not Applicable