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To: Philip Trowbridge, RMP Manager
Jay Davis, RMP Lead Scientist
From: Don Yee, Quality Assurance Officer
Date: 1 December, 2015
Re: 2014 RMP Bivalve Samples Quality Assurance Report

Introduction

In 2014, bivalve samples were collected from 8 stations (including a reference control/ bivalve source site) for 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 Annual Monitoring Results report (http://www.sfei.org/sites/default/files/biblio_files/2013-2014_AMR_Final.pdf). The samples were analyzed for the following compounds by the laboratories indicated:

- *AMS – Ancillary Measurements*
- *Axys – PAHs, PBDEs, and PCBs*
- *BR – Selenium*

The SFEI Data Services Team checked the laboratory results using the methods and data quality objectives in the RMP Quality Assurance Project Plan (QAPP). Overall, 95% of the results were determined to be acceptable for use in RMP reports and calculations.

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.

Once approved by the RMP Manager and Lead Scientist, all uncensored results will be uploaded to the San Francisco Regional Data Center and CEDEN.

Quality Assurance Summary for 2014 RMP Bivalve Samples

AMS – Ancillary Measurements

2014 bivalve growth measures reported by AMS looked to be within the typical ranges for growth and mean mass and survival. The CTD cast data during the bivalve deployments and collections were also generally as expected, with some of the results censored due to the boat/CTD bobbing in the chop and exposing the probe to the air.

Axys – PAHs

2014 bivalve PAHs had insufficient material at BG20, and the rest of the samples analyzed by AXYS had some blank contamination issues, with 80% of data usable. Napthalene in all the field samples was < 3x the concentration in the blank samples and was censored. Many other PAHs and alkyl PAHs were also found in the blank at concentrations comparable to those in field samples (~1/3 of field sample concentration or higher), and therefore, the field results for these compounds were censored. PAH recoveries were good, but alkyl PAHs as usual had no recovery QC samples as there are no real standards for these combined alkyl PAH groups, only for individual (mostly C1- or methyl) alkyl PAH compounds. Precision was a bit variable, likely due in part to the blank contamination, but was bad (>70% RSD) for only one PAH (benzo(a)pyrene) and one alkyl PAH (C1 dibenzothiopenes).

PAHs and alkyl PAHs have been the analyte groups that AXYS has had the most trouble with historically (possibly because they commonly use toluene and other aromatic solvents). The Program should consider other methods or laboratories for the 2016 Bivalve Monitoring. However, it is not clear if a change in lab would improve things, or only lead to more NDs (which is not particularly useful either).

Axys –PBDEs and PCBs

2014 bivalve PBDEs had some blank contamination (95% reportable), with censoring of BDEs 37, 197, and 203, which generally account for only a small portion of PBDEs.

2014 bivalve PCBs by AXYS had only minor issues (99% reported) – mainly blank contamination of some minor congeners accounting for very little of total PCBs.

BR – Selenium

2014 bivalve selenium analyzed by BR had no issues at all (100% reported).

Appendix A: Dataset QA Summaries
RMP 2014 Bivalve Sampling

Bivalve Growth – AMS

Growth in bivalves collected by AMS was analyzed by AMS. Samples were collected between September 16 and September 18, 2014 (T-0 reference site collected June 11, 2014; T-1 reference site collected September 23, 2014).

As discussed in the cruise report, the deployment cages at site BA10 (Coyote Creek) were covered by three to four feet of sediment over the duration of deployment causing complete mortality; this site was replaced by BA30 (Dumbarton Bridge) for both chemical analyses and growth. Results included mean dry weight, dry weight standard error, growth, growth standard error, and survival for 4 transplant stations, with T-0 (reference site) values for dry weight and dry weight standard error, and T-1 (reference site) values reported for mean dry weight, dry weight standard error, growth, and growth standard error. Insufficient residents were collected from the 2 river stations [Sacramento River (BG20) and San Joaquin River (BG30)] so no bivalves were apportioned for dry flesh weight and growth analyses at either site.

Bivalve growth doesn't have the usual QC samples like other analyses, so the QC check is mainly a count of the samples and a range check of their reasonableness. Overall the data are acceptable, meeting the expectations for size range of bivalves. Reproducibility of size could not be evaluated as no replicates were reported.

A brief checklist of conditions follows:

1. Check range of individual dry weight means. Yerba Buena Island is usually the highest, and Coyote Creek one of the lowest. MCALs will usually be around 1g (dw). CFLU will be around 0.05g (dw)
    - Transplants MCAL dry weights were all around 1g like in previous years. Growth ranged from a 2% (around 0.02g) gain at Redwood Creek, half as much as in 2012, to a near 2x greater (around 0.81g) gain at (Yerba Buena Island) about 2.7 times the gain in 2012. No CFLU data to evaluate.
2. Calculate % std err = (dry wt std error / dry wt) – 5-10% is pretty typical
    - Standard error of weights was around 4-7% of total weight.
3. Survival is preferably above 50%.
    - Slowest survival reported was 61% at Yerba Buena Island.
4. Growth should look like the T-0 weight subtracted from the final dry weight.
    - Checked and okay.
5. The T-0 duplicate should be the same weight as the T-0 sample give or take 2x the standard error of the dry weight
    - No replicates reported.

Bivalve CTD Cast Data - AMS

CTD cast data for the 2014 bivalve deployment and retrieval cruises collected by AMS were reviewed by SFEI. Deployment casts for 7 bivalve stations were collected between June 10 and June 12, 2014, and retrieval casts for 9 bivalve stations were collected between September 16 and September 19, 2014; all were reviewed on April 20, 2015 with no major problems found.

Temperature, salinity, electrical conductivity, optical back scatter, dissolved oxygen, density, and pressure results were reported for a water column profile at each bivalve station. Two sites during the bivalve retrieval cruise, Dumbarton Bridge (BA30) and Redwood Creek (BA40), had no data due to operator error (forgetting to remove the syringe from the unit before deploying) and were reported and qualified as such by AMS.

14 records with times outside of reasonable ranges were flagged with the qualifier FIT (Invalid time. Likely instrument error or failure) by AMS.

119 records with no measurements in depth bin, or where the unit was initiated incorrectly and no measurements were collected, were flagged with the qualifiers FIT,FIV,Q (Invalid time. Likely instrument error or failure, Invalid velocity. Likely instrument error or failure, Questionable result) by AMS.

204 records with questionable results were flagged with the qualifier Q (Questionable result) by AMS.

287 records with depths <1m were flagged with the qualifier FS (Too Shallow for probe measurement) as appropriate.

Bivalve Selenium – BR

Selenium in bivalves collected by AMS were analyzed by BR. Samples were collected between September 16 and September 19, 2014 (reference site collected June 11, 2014), and analyzed on November 26, 2014.

Selenium and Total Solids were reported in 7 composite samples (including reference site), lab replicate, matrix spike/matrix spike replicate (MS/MSD), certified reference material (CRM), method blank, and laboratory control samples (LCS).

Review was conducted on the wet weight reported data, and selenium results were then converted to a dry weight basis. Note: there was insufficient mass to determine total solids for Sacramento

River (BG20), so dry weight selenium was estimated using total solids percentage from the organics aliquot, and the result flagged with the qualifier VJ to indicate it is an estimated value.

Sensitivity

Sensitivity was sufficient with no non-detects (NDs) reported in the field samples for either selenium or total solids.

Blanks

Selenium and total solids were not found in the method blanks at concentrations above the method detection limit.

Recovery

Recovery for selenium in the certified reference material was good with the error of 9.83% being well below the 35% target MQO. Matrix spikes and the laboratory control sample were also examined, and the recoveries were likewise good, with average errors of 13.8% and 1.7%, respectively.

Precision

Precision for selenium in the single lab replicate was good, with an RSD of 2.24%, well below the 35% target MQO. The RSD for Total Solids was 0.98%. Matrix spike replicates were also examined and the average RSD was 7.53%.

Bivalve PAHs – AXYS

PAHs and alkylated PAHs in bivalves collected by AMS were analyzed by AXYS. Samples were collected between September 16 and September 19, 2014 (reference site collected June 11, 2014), and analyzed on November 27, 2014.

PAHs and alkylated PAHs (25 PAHs, 15 alkylated PAHs), lipid, and moisture were reported for 6 composite samples (including the reference site), lab replicate, method blank, and laboratory control samples (LCS). Insufficient numbers of bivalves were collected from the Sacramento River station (BG20) so no PAH analysis was conducted.

Sensitivity

Sensitivity was sufficient with <50% non-detects (NDs) for 92% of PAHs, and 93% of alkylated PAHS (with most ≤ 29% NDs). Extensive non-detects (>50% NDs) were reported for Benz(a)anthracene, Benzo(j/k)fluoranthene, and C1-Dibenzothiophenes.

Blanks

The PAHs (Biphenyl, Chrysene, Dibenzothiophene, 2,6-Dimethylnaphthalene, Fluoranthene, Fluorene, 1-Methylnaphthalene, 2-Methylnaphthalene, 1-Methylphenanthrene, Naphthalene,

Phenanthrene and Pyrene), and the alkylated PAHS (C1-Dibenzothiophenes, C2-Dibenzothiophenes, C3-Dibenzothiophenes, C1-Fluoranthene/Pyrenes, C1-Fluorenes, C2-Fluorenes, C1-Naphthalenes, C2-Naphthalenes, C3-Naphthalenes, C1-Phenanthrene/Anthracene, C2-Phenanthrene/Anthracene, C3-Phenanthrene/Anthracene, and C4-Phenanthrene/Anthracene) were found in the single method blank.

Seven Naphthalene field sample results in that batch were qualified with the censoring flag of VRIP (Data rejected - Analyte detected in field or lab generated blank, flagged by QAO) for being <3x the blank contamination; six Dibenzothiophene and 2-Methylnaphthalene, five Biphenyl and C1-Dibenzothiophenes, four 2,6-Dimethylnaphthalene, 1-Methylnaphthalene, and C1-Naphthalenes, three C3-Dibenzothiophenes and C3-Phenanthrene/Anthracene, one C2-Dibenzothiophenes, Fluoranthene, C1-Fluoranthene/Pyrenes, Fluorene, C1-Fluorenes, 1-Methylphenanthrene, C2-Naphthalenes, Phenanthrene, C2-Phenanthrene/Anthracene, C4-Phenanthrene/Anthracene, and Pyrene results in the same batch were also qualified as VRIP.

Recovery

Recoveries on the single laboratory control sample were generally good with the average error ranging from 0% to 14.87% for the PAHs, all well below the target MQO of 35%. As in prior years alkylated PAH results were flagged with the flag VBS for insufficient QA procedures.

Precision

Lab replicate precision was generally good with RSDs ranging from 0.39% to 141%, with all but three RSDs below the 35% target MQO. Benzo(a)pyrene, C3-Dibenzothiophenes, and C2-Naphthalenes had RSDs of 141%, 141%, and 43.86%, respectively. C2-Naphthalenes results were flagged with the non-censoring qualifier VIL (RPD exceeds control limit, flagged by QAO), whereas the Benzo(a)pyrene and C3-Dibenzothiophenes results were flagged with the censoring flag of VRIL (Data rejected - RPD exceeds control limit, flagged by QAO).

Bivalve PCBs – AXYS

PCBs in bivalves collected by AMS were analyzed by AXYS. Samples were collected between September 16 and September 19, 2014 (reference site collected June 11, 2014), and analyzed on November 25 and November 26, 2014.

PCBs (209 congeners), lipid, and moisture were reported for 7 composite samples (including reference site), lab replicate, method blank, and laboratory control samples (LCS).

Sensitivity

Sensitivity was sufficient with ≤50% non-detects (NDs) for 91.4% (191 out of 209) of the PCB congeners (with most, 70% (144 out of 209), having no NDs). Extensive non-detects (>50% NDs) were reported for 9% (18 out of 209) of the congeners.

Blanks

About 13% (28 out of 209) PCBs were found in the single method blank at concentrations above the method detection limit. Eight PCB 003 field sample results in that batch were qualified with the censoring flag of VRIP (Data rejected - Analyte detected in field or lab generated blank, flagged by QAO) for being <3x the blank contamination; three PCB 001 and one PCB 002, PCB 015, and PCB 037 results in the same batch were also flagged VRIP.

Recovery

Recoveries for the individual congeners in the single laboratory control sample were generally good with the errors ranging from 0% to 12%, all well below the 35% target MQO.

Precision

Precision for the congeners in the single lab replicate sample was good, with RSDs ranging from 0% to 18.72%, well below the 35% target MQO.

Bivalve PBDEs – AXYS

PBDEs in bivalves collected by AMS were analyzed by AXYS. Samples were collected between September 16 and September 19, 2014 (reference site collected June 11, 2014), and analyzed between November 25 and December 6, 2014.

PBDEs (49 congeners) were reported in 7 composite samples (including reference site), lab replicate, method blank, and laboratory control samples (LCS).

Sensitivity

Sensitivity was sufficient to have <50% non-detects (NDs) for almost 70% of the PBDEs (with most ≤37.5% NDs); the remaining 30% had extensive NDs (>50% NDs).

Blanks

PBDE 028, 037, 047, 049, 085, 099, 100, 154, 197, and 203 were found in the single method blank, at levels of 1%, 54%, 0.6%, 0.2%, 3%, 1.3%, 0.4%, 1.3%, 31%, and 57% of the average field sample concentrations, respectively. Seven PBDE 037 field sample results in that batch were qualified with the censoring flag of VRIP (Data rejected - Analyte detected in field or lab generated blank, flagged by QAO) for being <3x the blank contamination; six PBDE 203 and five PBDE 197 results in the same batch were also flagged VRIP.

Recovery

Recoveries for the individual PBDEs in the single laboratory control sample were good with the errors ranging from 0.51% to 8.4%, all well below the 35% target MQO.

Precision

Precision for the PBDEs in the single lab replicate sample were generally good, with RSDs ranging from 0.28% to 35.02%, with all but one RSD well below the 35% target MQO (the rest with RSDs <17%). The exception, PBDE 126, had an RSD of 35.02%, just barely above the target MQO of 35%, so results were flagged with the non-censoring qualifier VIL (RPD exceeds control limit, flagged by QAO).