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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 Sediment Samples Quality Assurance Report

Introduction

In 2014, sediment samples were collected from 27 stations 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:

- *ALS - TOC, CHN, grain size, total solids*
- *Axys - PFCs and precursors*
- *BR - Arsenic, Mercury, Methyl Mercury, Selenium, and Total Solids*
- *CCSF – Trace Elements*
- *EBMUD – PAHs, PCBs, PBDEs, Legacy Pesticides, Fipronils*

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, 99% 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 Sediment Samples

ALS - TOC, CHN, grain size, total solids

2014 sediment ancillary parameters by ALS were generally without problems (100% reported). Total C, H, and N measurements generally met targets for recovery samples (within 10% of expected values). Reference materials for these tend to be mostly organic matter and thus have much higher percentages of total CHN mass than Bay sediments, so even if there are no good sediment references the lab should attempt to keep total mass of organic material about the same (e.g. 1g of sediment with ~2% C = 0.02g C, equivalent to 0.04 g of reference material with 50% C). If the RMP subsamples analyzed are very small, then there may be practical limits to this approach, where the mass measurement of the reference material becomes the limiting factor and primary source of error.

We have been reporting relative percent differences (RPDs) of grain size fractions following CEDEN conventions (difference divided by average result), although flagging is being done on the basis of total mass rather than as a percentage of a given fraction in recognition that small fractions will have larger relative error (RPD) inevitably, e.g. to get 20% RPD on a fraction accounting for 1% of total mass, we would need <0.2% variation in percent of that fraction, which is nearly impossible given typical sample heterogeneity even after manual attempts at homogenization. The next revision of the QAPP will be changed to reflect this adjusted evaluation basis of the targets.

Axys - PFCs and precursors

2014 sediment PFCs were largely without issue (100% reported) although there were extensive (near 100%) NDs for about half the PFCs and almost all the precursors. Only PFOS was reliably detected in over half the samples, which would be expected, and the next most abundant were detected in 25% of samples or less.

BR - Arsenic, Mercury, Methyl Mercury, Selenium, and Total Solids

2014 sediment elements (As, Hg, MeHg, Se) analyzed by Brooks Rand had no major problems (100% reported). One selenium low concentration blank spike (expected concentration about half the average RMP field sample) had very low recovery, but certified reference material (CRM) and matrix spike (MS) samples, which are more realistic indicators of sample matrix, had no issues, so field sample results were not flagged.

CCSF - Trace Elements

2014 sediment elements analyzed by CCSF had no notable issues (100% reported). There were blank detects, but well below ambient concentrations, no NDs for field samples, and good recoveries and precision on other QC samples.

EBMUD – PAHs, PCBs, PBDEs, Legacy Pesticides, Fipronils

2014 sediment PAHs by EBMUD were generally good (96% reported), although there were issues commonly and previously seen with alkylated PAHs. Extensive NDs (100% ND for half the alkyl PAHs) were seen, and also some blank contamination or variable precision was seen on a handful of the alkyl PAHs.

2014 sediment PCBs by EBMUD were generally good (99% reported), with some of the same commonly and previously seen issues as previous years. Many of the minor congeners were ND in many samples, which is to be expected, and there was some detection of PCBs in blanks, with censoring of some of the less abundant congeners since both the blank contamination and field sample concentrations would be of similar magnitude for those. There were individual congeners with variable precision, and recovery somewhat outside of the target (ideally <35% error), but these deviations were not extensive enough to impact total PCBs reported.

2014 sediment PBDEs by EBMUD were also generally good (98% reported). Only a few minor congeners (degradation/by products of deca), BDE 205 and 206, had some censored results for poor matrix spike recovery (>70% error) and blank contamination (>30% of field sample concentration), respectively. These congeners account for a small percentage of total PBDEs, however.

2014 sediment legacy pesticides had generally good results similar to previous years (near 100% reported, only one result censored for blank contamination). There were many NDs for individual pesticides (100% ND for half the analytes). Recoveries on CRMs were generally within target (<35% error), and precision on field sample replicates was good (<35% relative standard deviation (RSD)). Results on secondary indicators such as MSs and laboratory control samples (LCSs) for recovery, and precision on replicate CRM or LCS samples were sometimes a bit worse than the primary indicators (in part because some of the LCSs are spiked at low levels near the MDL) , but nothing atypical or notably bad.

2014 sediment fipronil pesticides reported by EMBUD were generally good (100% reported). The parent fipronil had the most (~30%) NDs. Replicate precision was good (<35% RSD), and recoveries biased high but not too badly (~65% high at most), so no results were censored. EBMUD will not be doing RMP sediment organics in 2018, so the Program will need to look into labs that will give at least comparable performance, and these newer pesticides may be the hardest to find suitable labs for.

Appendix A: Dataset QA Summaries

RMP 2014 Sediment Sampling

Sediment Carbon, Hydrogen, Nitrogen, Total Organic Carbon, Total Solids, and Grain size – ALS

Carbon, Hydrogen, Nitrogen, Total Organic Carbon (TOC), Total Solids, and Grain size in sediment samples collected by AMS were analyzed by ALS. Samples were collected between August 5, 2014 and August 13, 2014, and analyzed between August 25, 2014 and September 22, 2014.

Carbon, Hydrogen, Nitrogen, and TOC were reported for 29 sediment samples, Total Solids for 30 sediment samples, and Grainsize for 31 sediment samples, including lab replicates. Samples were collected from 27 sediment stations. Lab blanks and laboratory control samples (LCSs) were also reported for Carbon, Hydrogen, Nitrogen, and TOC.

Holding times were 45 days or better for Carbon, Hydrogen, and Nitrogen (frozen), 31 days or better for Grain size and 28 days or better for TOC (not frozen). Frozen samples should show negligible Carbon, Hydrogen, and Nitrogen loss. Grain size should not degrade, and at least the ASTM D422 method has no indicated hold time. Water TOC typically has 28 day hold time when refrigerated; sediment TOC would likely be less affected given an overall higher C content.

Sensitivity

Sensitivity was sufficient for all analytes with no non-detects (NDs) reported in the field samples.

Blanks

Only total Hydrogen was detected in blanks, at levels about 2x the MDL but still >3x lower than all field samples. All samples were flagged with the non-censoring qualifier VIP (Analyte detected in field or lab generated blank, flagged by QAO) for total Hydrogen contamination.

Recovery

Recovery on Carbon, Hydrogen, Nitrogen, and TOC laboratory control samples (LCSs) was very good, averaging <10% error in all cases. The LCS for Carbon, Hydrogen, and Nitrogen were on the high side: ~40% total C, 2-10% total N, and 6-7% total H, so the recoveries may be better than typical for RMP samples. Ideal RMP target values would be <20% dry weight for C and <2% for N, given that in bay sediments seldom have >10% C and 1% N mass, respectively. The lab narrative has them as EDTA and birch leaf, so it's unlikely that the composition of the LCS can be adjusted. However, if the per analysis total C and total N quantities are similar (by analyzing less total mass for these LCSs than for our typical sediment samples), then the noise in the signal may be more reasonably typical for RMP samples.

Precision

Precision on replicates was good for Carbon, Hydrogen, Nitrogen, and TOC, with average RSDs within the 10% target values. Total solids had RSDs <1%. Grain size fractions were more variable, although the absolute standard deviation (stdev) of the results (= RSD x Avg for each grain size) typically averaged <10% of total mass. Samples may be somewhat heterogeneous, so precision especially on grainsize fractions amounting to <10% of total mass may be highly variable. (e.g., granule with 3% of total mass had RSD of 93%, medium sand 13% of mass had 31% RSD. Other fractions were 25% RSD or better, and had average stdev <5% of total mass).

Sediment CTD Cast Data - AMS

CTD cast data for the 2014 sediment cruise collected by AMS was reviewed by SFEI. CTD casts were collected between August 5, 2014 and August 13, 2014, and reviewed on April 15, 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 of 27 sediment stations.

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

154 records with no measurements in depth bin 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.

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

Sediment Perfluorinated Compounds and Precursors – AXYS

Perfluorinated compounds (PFCs) and precursors in sediment samples collected by AMS were analyzed by Axys. Samples were collected between August 5, 2014 and August 13, 2014, and analyzed between September 3, 2014 and September 19, 2014.

Thirteen PFCs were reported for 27 sediment samples, and 19 precursors for 11 sediment samples. Lab replicates, method blanks, and laboratory control spikes (LCSs) were also analyzed.

Sensitivity

Results were 100% non-detects (NDs) for 6 of the PFCs, but the usual most abundant, PFOS, was detected in nearly 60% of the sediment samples. The remaining PFCs were found in 25% or less of the samples. The precursors were ND in nearly all samples, with only N-Ethyl Perfluorooctane Sulfonamido Acetic Acid, and Bis(1H,1H,2H,2H-perfluorodecyl)phosphate detected in 2 and 1 of the samples, respectively.

Blanks

Perfluorinated compounds (PFCs) or the precursors were not found in the method blanks at concentrations above the method detection limit.

Recovery

Recovery on LCS samples was good, with recovery errors of <35%, except 40% (low bias) for Perfluorohexylperfluorooctylphosphinate, and Bis(perfluorooctyl)phosphinate, both precursors. Results for both these precursors were slightly outside of the target maximum 35% error, so were flagged with the non-censoring qualifier VIU (Percent Recovery exceeds laboratory control limit, flagged by QAO).

Precision

Only PFOS was detected in lab replicates, with RPD <30%, but results averaged <3xMDL, so would not have been flagged even if the precision was worse since results were not in a highly quantitative range.

Sediment Arsenic, Mercury, Methylmercury, Selenium, and Total Solids – BR

Arsenic, mercury, methylmercury, selenium, and Total Solids in sediment samples collected by AMS were analyzed by BR. Samples were collected between August 5, 2014 and August 13, 2014, and analyzed between September 5, 2014 and October 31, 2014.

Arsenic, mercury, methylmercury, selenium, and Total Solids were reported in 27 sediment samples, lab replicates, matrix spike/matrix spike replicates (MS/MSDs), certified reference materials (CRMs), method blanks, laboratory control samples (LCS), and other client samples. All data were reported blank corrected.

Sensitivity

Sensitivity was sufficient for all analytes with no non-detects (NDs) reported in the field samples.

Blanks

Arsenic, mercury, methylmercury, selenium, and Total Solids were not found in the method blanks at concentrations above the method detection limit.

Recovery

Recoveries on the certified reference materials were generally good with the average error ranging from 0.26% for mercury to 20.69% for selenium, all well below the target MQO of 35% for arsenic, mercury, methylmercury, and selenium. Matrix spike and LCS samples were examined, but not used for evaluation of the data, with the average error below the 35% target for all of the analytes except selenium, which had an average LCS error of 73%.

Precision

Precision on lab replicates was good, with the average RSD ranging from 1.27% for Total Solids to 9.67% for selenium, all well below the 35% target MQO for arsenic, mercury, methylmercury, and selenium. Certified reference material and matrix spike replicates were also examined, but not used for the evaluation, with all of the average RSDs being less than the target MQO of 35% (ranging from 0.32% to 20.72%).

Sediment Trace Elements – CCSF

Trace elements in sediment samples collected by AMS were analyzed by CCSF. Samples were collected between August 5, 2014 and August 13, 2014, and analyzed between October 9, 2014 and October 16, 2014.

Trace elements were reported in 27 sediment samples, lab replicates, matrix spike/matrix spike replicates (MS/MSDs), certified reference materials (CRMs), laboratory control materials (LCMs), method blanks, laboratory control samples (LCS) samples, and other accuracy samples (CCVs) were also reported.

Sensitivity

Sensitivity was sufficient for all the target trace elements with no non-detects (NDs) reported in the field samples.

Blanks

Of the target trace elements, only nickel, silver, and zinc were found in the method blanks, but their concentrations were always >3x lower than in field samples so no results were censored.

Recovery

Recoveries on the certified reference materials were good, with the average errors for trace elements in samples with certified values always <25%; errors for trace elements in samples with uncertified values were also <25%, other than antimony (26%). However, recovery errors for antimony in samples with certified values were <1%, so no added recovery flags were needed.

Precision

Precision on lab replicates was good, with average RSDs <25% for all trace elements.

Sediment PAHs – EBMUD

PAHs and alkylated PAHs in sediment samples collected by AMS were analyzed by EBMUD. Samples were collected between August 5, 2014 and August 13, 2014, and analyzed between October 2, 2014 and December 16, 2014.

PAHs and alkylated PAHs were reported in 27 sediment samples, lab replicates, and matrix spikes (MSs), certified reference materials (CRMs), method blanks, and laboratory control samples (LCS).

Sensitivity

Sensitivity was sufficient with <50% NDs for all target PAHs (all < 42% (2,6-Dimethylnaphthalene 41.38% and 2,3,5-Trimethylnaphthalene, 37.93%) with most <4%). More than half the alkylated PAHs (10 out of 19) were ND in 100% of the samples, especially C4 forms (all 100% ND), with the MDLs the same for all the alkylated PAHs (average 1.44 ug/Kg dw).

Blanks

2-Methylnaphthalene, C1-Naphthalenes, and C3-Naphthalenes were found in one method blank at levels of 13%, 15%, and 51% of the average field sample concentrations, respectively. Ten C3-Naphthalenes 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; 1 C1-Naphthalene result in the same batch was also flagged VRIP.

Recovery

Recoveries on the certified reference materials were used to evaluate accuracy except for Acenaphthene, Acenaphthylene, Biphenyl, Dibenzothiophene, 2,6-Dimethylnaphthalene, 1-Methylnaphthalene, 2-Methylnaphthalene, and 2,3,5-Trimethylnaphthalene, which were evaluated using matrix spikes. Recoveries were generally good with the average error ranging from 1.3% to 32.67% for all target PAHs, all below the target MQO of 35%. No spiked samples were usable for the alkylated PAHs, no expected or certified reference values being reported; therefore, as in prior years, alkylated PAH results were flagged with the flag VBS for insufficient QA procedures.

Precision

Lab replicates were used to evaluate precision except for 2,6-Dimethylnaphthalene, which was evaluated using CRMs. RSDs were generally good with the average RSD well below the 35% target MQO. Exceptions were 2,6-Dimethylnaphthalene and C1-Fluoranthene/Pyrenes with average RSDs of 36.28%, and 83.67%, respectively. C1-Fluoranthene/Pyrenes results with average RSDs >70% were flagged with the censoring qualifier VRIL (Data rejected - RPD exceeds control limit, flagged by QAO). 2,6-Dimethylnaphthalene results with an average RSD >35% but <70% were flagged with the non-censoring VIL (RPD exceeds control limit, flagged by QAO).

A comparison of duplicate samples showed consistent values for each analyte, with two exceptions: C1-Fluoranthene/Pyrenes and C1-Chrysenes. The VRIL flag was subsequently also added to the C1-Chrysenes results.

Sediment PCBs – EBMUD

PCBs in sediment samples collected by AMS were analyzed by EBMUD. Samples were collected between August 5, 2014 and August 13, 2014, and analyzed between September 23, 2014 and October 27, 2014.

PCBs (209 congeners) were reported in 27 sediment samples, lab replicates, matrix spike samples (MSs), certified reference materials (CRMs), method blanks, and laboratory control samples (LCS).

Sensitivity

Sensitivity was sufficient to have <50% NDs for 76% of the PCB congeners (159 out of 209); the remaining 23% of congeners had extensive NDs, with 23 out of those 50 congeners being 100% non-detects.

Blanks

PCB 004, PCB 006, PCB 008, PCB 011, PCB 015, PCB 016, PCB 017, and PCB 018 were found in the blank of at least one batch at levels from 8% to 41% of the average concentrations in the field samples (most less than 13%). PCB 004 was found in the two blanks at levels of 34% and 41% of the average PCB 004 field sample concentrations. Thirteen PCB 004 sample results 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; 5 PCB 011, 4 PCB 006, 3 PCB 018, 2 PCB 015, 2 PCB 017, 1 PCB 008, and 1 PCB 016 results were also flagged VRIP.

Recovery

Recoveries on the certified reference materials were used to evaluate accuracy; matrix spike samples were used to evaluate congeners without certified CRM values. Recoveries were generally good with the average error ranging from 0.69% to 60% with the majority of congeners (97%; 158 out of 163) less than the target 35% MQO. The remaining 5 PCB congeners (PCB 007, PCB 009, PCB 095, PCB 099, and PCB 170) had average errors >35% but <70% and so were flagged with the non-censoring flag VIU (Percent Recovery exceeds laboratory control limit, flagged by QAO). Average matrix spike and LCS sample errors not used in the evaluation were examined, with the average errors all below the target MQO of 35%.

Precision

Lab replicate samples were used to evaluate precision; congeners not able to be evaluated using the lab replicates were evaluated using CRM replicates in the case of PCB 045, and LCS replicates for the rest. RSDs were generally good with the average RSD ranging from 0% to 63% with the majority of congeners (96%; 156 out of 163) below the 35% target MQO. The remaining 7 PCBs (PCB 004, PCB 016, PCB 017, PCB 018, PCB 026, PCB 027, and PCB 032) had average RSDs >35% but <70% so were flagged with the non-censoring flag VIL (RPD exceeds control limit, flagged by QAO). The remaining CRM and LCS samples were also examined, but not used for the evaluation, with all of the average RSDs being less than the target MQO (ranging from 0.08% to 29.53%).

Sediment PBDEs – EBMUD

PBDEs in sediment samples collected by AMS were analyzed by EBMUD. Samples were collected between August 5, 2014 and August 13, 2014, and analyzed between October 30, 2014 and January 20, 2015.

PBDEs (50 congeners) were reported in 27 sediment samples, lab replicates, matrix spikes (MS), method blanks, and laboratory control samples (LCS).

Sensitivity

Sensitivity was sufficient to have <50% NDs for 38% of the PBDEs (19 out of 50); the remaining 62% had extensive NDs, with 19 out of those 31 PBDEs being 100% non-detects.

Blanks

PBDE 206 was found in the blank of one batch, at a level 19.5% of the average field sample concentration. Four PBDE 206 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 average blank contamination.

Recovery

Recoveries on the matrix spike samples were used to evaluate accuracy. Recoveries were generally good with the average error ranging from 0.97% to 76.99% with the majority of PBDEs (95%; 42 out of 44 of the useable matrix spike results) less than the 35% target MQO. Of the remaining 2 PBDEs, PBDE 196 had average errors >35% but <70% so results were flagged with the non-censoring flag VIU (Percent Recovery exceeds laboratory control limit, flagged by QAO), while PBDE 205 results with average errors >70% were flagged with the censoring qualifier VRIU (Data rejected - Percent Recovery exceeds laboratory control limit, flagged by QAO). Average LCS sample errors were examined, but not used in the evaluation, with the average errors below the target MQO of 35%, except for PBDE 196 and PBDE 205, which were 43% and 65%, respectively.

Precision

Precision was evaluated using the lab replicate samples; PBDEs not able to be evaluated using the lab replicates were evaluated using the LCS replicates. RSDs were generally good with the average RSD ranging from 0% to 24%, all below the 35% target MQO.

Sediment Pesticides – EBMUD

Pesticides in sediment samples collected by AMS were analyzed by EBMUD. Samples were collected between August 5, 2014 and August 13, 2014, and analyzed between October 20 and October 24, 2014.

Results were reported for 22 pesticides in 27 sediment samples, lab replicates, matrix spike samples (MSs), certified reference materials (CRMs), method blanks, and laboratory control samples (LCS) samples.

Sensitivity

Sensitivity was sufficient to have <50% non-detects (NDs) for 59% of the pesticides (13 out of 22); the remaining 41% of analytes had extensive NDs, with 5 out of those 9 pesticides (Endrin, delta-HCH, Heptachlor epoxide, Mirex, and Oxychlordane) being 100% NDs.

Blanks

Hexachlorobenzene was found in the method blanks at levels equal to 7.3% and 8.1% of the average concentrations in the field samples. One Hexachlorobenzene sample result was 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.

Recovery

Recoveries on the certified reference materials were used to evaluate accuracy; matrix spike samples were used to evaluate pesticides without certified values. Recoveries were fair with the average error ranging from 1.24% to 65.16%, and for .;/the majority of analytes (86.4%; 19 out of 22) were less than the target 35% MQO. The other 3 pesticides (delta-HCH, cis- and trans-Nonachlor) had average errors >35% but <70% so were flagged with the non-censoring qualifier VIU (Percent Recovery exceeds laboratory control limit, flagged by QAO). Matrix spike and LCS sample errors not used in the evaluation were examined, with the average errors below the target MQO of 35%, except for DDE(o,p'), delta-HCH, and cis-Nonachlor which had average errors >35% but <70%.

Precision

Lab replicates were used to evaluate precision; pesticides not able to be evaluated using lab replicates were evaluated using replicates of the CRMs in the case of DDT(p,p') and cis-Nonachlor, and LCS replicates for the rest. RSDs were good with the average RSD ranging from 0% to 23.49%, all below the 35% target MQO. The remaining CRM and LCS samples were also examined, but not used for the evaluation, with average RSDs ranging from 0.35% to 105.15%; pesticides with RSDs greater than the 35% target MQO were DDE(o,p') (41% and 73%), cis-Nonachlor (67%), and alpha-HCH (105.15%).

Sediment Fipronil – EBMUD

Fipronil and degradates in sediment samples collected by AMS were analyzed by EBMUD. Samples were collected between August 5, 2014 and August 13, 2014, and analyzed between October 20 and October 24, 2014. This is a resubmitted data submission, with EBMUD reverting to an older calibration fitting method.

Fipronil and 3 degradate results were reported for 27 sediment samples, lab replicates, matrix spike samples (MSs), method blanks, laboratory control samples (LCSs), and a certified reference material (even though there was no expected values for fipronils).

Sensitivity

Sensitivity was generally sufficient for all analytes, with 10% non-detects (NDs) for fipronil sulfide and 31% NDs for fipronil.

Blanks

Fipronil and degradates were not found in the method blanks at concentrations above the method detection limits.

Recovery

Recoveries were moderately outside the 35% target MQO, with average errors ranging from 43 to 65%, mostly biasing high. Fipronil and the 3 degradates were, therefore, flagged with the non-censoring qualifier VIU (Percent Recovery exceeds laboratory control limit, flagged by QAO).

Precision

Precision of the lab replicates was good, with average RSDs of 25% or better (within the 35% target MQO).