

To: Melissa Foley, RMP Manager
Jay Davis, RMP Lead Scientist
From: Don Yee, Quality Assurance Officer
Date: September 16, 2019
Re: 2018 RMP Sediment Data Quality Assurance Report

Introduction

In 2018, sediment samples were collected from 27 stations (7 historical sites, with the rest from the GRTS random draw panels) 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 Quality Assurance Program Plan, cruise plans, cruise reports, and field sampling reports. These documents are available from the SFEI website (<http://www.sfei.org/content/status-and-trends-monitoring-documents>).

The samples were analyzed for the following parameters by the laboratories indicated:

- *ALS – grain size, total organic carbon, total nitrogen, total solids*
- *BAL – Arsenic, Mercury, Methylmercury, Selenium*
- *CCSF - Aluminum, Cadmium, Copper, Gadolinium, Iron, Lead, Manganese, Nickel, Silver, and Zinc*
- *SGS-AXYS – PCBs, PAHs, PBDEs, and 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, 100% of the ALS field sample results, 98% of the BAL samples, 99% of CCSF, and 98% of SGS-Axys results were determined to be acceptable for use in RMP reports and calculations, with the main cause of data rejection usually being blank contamination at concentrations close to (>33% of) concentrations found in field samples.

This memo provides a high-level summary of the quality assurance assessment for each dataset. Non-conformances with the QAPP and possible indicators of variability and uncertainty in reported values, with 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.

Quality Assurance Summary for 2018 RMP Sediment Samples

ALS – grain size, total organic carbon, total nitrogen, total solids

Overall the ALS sediment ancillary data appear reasonable, with 100% of the results reportable. Non-detects were found for over half (55%) of TN samples, as well as 1 sample for TOC, and 3 for granule/pebble (large particles that are sparse/absent in some fine grained samples). TOC and TN were not found in the method blanks at concentrations above the method detection limits, and grain size and total solids typically do not have blanks analyzed. TOC and TN recovery control samples were within ~1% of their target values, so no qualifiers were needed. Precision on chemical analysis lab replicates was also good, with average RSD for TOC and TN of ~1%. For grain size, the precision was evaluated on the percent results of the sand/silt/clay fractions having <20% nominal difference (rather than relative difference, e.g. 20% RPD on a fraction at 1% of total mass would only allow 0.2% variation, practically impossible, given the heterogeneity of grain size typically seen in the Bay). All variations in grain size fractions were less than 20%. *The main issue of potential concern was that the mean TN concentration was also about half of the prior averages (2009-2014 RMP), likely exacerbated by the extensive non-detects. In future rounds we should investigate using a different analytical or prep methods or another lab to get fewer non-detect data.* All other ancillary analytes had averages within ~30% of their means in prior RMP rounds, so did not suggest any net bias of sites or change in analytical methods.

BAL – Arsenic, Mercury, Methylmercury, Selenium

Data for trace elements analyzed by BAL, for the most part appear reasonable. With 98% of the results reportable; only 3 selenium results were rejected for the basic field samples, and 1 selenium result was rejected among all analytes in the 3 archived samples reanalyzed. Method detection limits were acceptable with a non-detect (ND) reported for only 1 methyl mercury result. Only total Solids and selenium were found in the method blanks at concentrations above the method detection limits. Thus 11% (4 out of 36 analyses for field and archive samples) of selenium results were flagged with the censoring qualifier of “VRIP”. The rest of the selenium results and all of total solids results were flagged with the non-censoring qualifier “VIP”, due to likely smaller to no impacts on reported results. Recoveries of methyl mercury in CRM samples, and arsenic, mercury, and selenium in matrix spike samples were acceptable, averaging well within 35% of target values (21% for MeHg, and <10% for the rest). Average RSDs for the reported analytes were 11% or better, well below the 35% MQO target, so no added precision flags were needed. Some analytes were similar in reported concentration ranges to prior years; arsenic averaged 85% of 2009-2014 results, and mercury 107%. However, methyl mercury averaged 150%, and selenium 160% of the 2009-2014 data. Generally lower concentrations of these latter analytes with sporadic non-detects may in part explain the larger variation. *Results on reanalyzed archive samples (from CB100s, LSB046s, and SB110s stations in 2014) were also more variable than desired/expected for some analytes. Concentrations were 92%, 31%, and 210% of 2014 results at the same stations for As, 351%, 81%, and 302% for Hg, 138%, 121% and 1340% for MeHg, and 157%, 176%, and 330% for Se. Although these samples were separate subsamples from those analyzed in 2014, variations among sediment field or lab replicates within one year analyzed at the same time are generally less than 2-fold lower or higher. The high bias for MeHg and Se on both all the reanalyzed individual archive samples and on annual*

averages are suggestive of a shift, but the variation among archives makes it hard to verify the significance of differences for any given analyte. Reanalysis of more archives for all these analytes may be warranted for the next round given the variability, to better establish whether the causes are primarily subsampling variability, or shifts or variability in the analytical method.

CCSF - Aluminum, Cadmium, Copper, Gadolinium, Iron, Lead, Manganese, Nickel, Silver, and Zinc

CCSF analyzed the remaining trace elements historically reported by the RMP, with gadolinium added as a possible trace element chemical of emerging concern. The gadolinium analyses do not include the usual recovery sample types, so are reported only for exploratory screening purposes. Overall 99% of the results for target analytes are reportable; only 3 silver results were rejected. Method detection limits were acceptable with no non-detects (NDs) reported for any target analytes. Iron and silver were detected in some blanks, with 3 silver results censored for those field samples being <3x the blank.

Recoveries for lead measured in certified reference material samples and for the remaining historical metals (excluding gadolinium) measured in matrix spikes averaged <10% error, well within the target 25%. Gadolinium recovery was measured in blank spikes, averaging 3% error, also less than the 25% target MQO. Average relative standard deviations (RSDs) on lab replicates were <10% for all metals aside from cadmium (17% RSD), but all met the 25% target. Baywide averages were similar to prior years, within ~10% of 2009-2014 averages for all metals. Pairwise comparisons of the reanalyzed 2014 archives showed consistency with their prior results, with only 3 results for analytes more than 10% different (but all <20%).

SGS-AXYS – PCBs, PAHs, PBDEs, and Fipronils

SGS-Axys analyzed the trace organic compounds in sediment samples, with the vast majority of results (>99% of PCBs, 96% of PAHs, 92% of PBDEs, and 100% of fipronils) reportable. There were some results for compounds reported as non-detects, similar to prior years: 30% of PBDEs, 54% of PAHs, and all fipronils. One-third (33%) of the 209 PCB congeners were detected (>MDL) in at least one blank, and 9 PCBs had one or more field sample results censored for being <3x the batch average blank result. About 15% of the PAH analytes, and 12% of PBDEs were detected in at least one blank, with no blank detects of fipronil compounds. Recoveries of PCBs were within 35% of certified values in CRMs except for two congeners (PCB 087 and 151), both less than 5% higher, and qualified. Remaining PCB congeners analyzed in blank spike samples had recovery errors averaging <20% and required no qualifiers. PBDEs with certified values in CRMs averaged within 35% of targets, needing no flags, but one PAH, Dibenz(a,h)anthracene, averaged 60% higher than its target and was flagged but not censored. The remaining PBDEs and fipronils in blank or matrix spikes similarly had recoveries within 35% of targets, but two PAHs were outside of those limits in blank spikes; Acenaphthene, averaging more than double its spiked value was censored and no concentrations reported, and Tetramethylnaphthalene, 1,4,6,7-, averaging 46% higher than its target was qualified but concentrations still reported. Precision on PCBs, PAHs, and PBDEs were determined from lab replicates, with about 20% of PCBs with relative standard deviations (RSDs) averaging over the 35% target and flagged, but none >70% which would require censoring. Only one PBDE (BDE 208, average RSD 36%) and one PAH Methylanthracene, 2-, (RSD averaging 35.2%), were just over the target 35%, so both

were flagged but not censored. Precision for fipronils was calculated in replicate matrix spikes due to extensive non-detects in field samples. Fipronil matrix spike RSDs averaged <35% so needed no qualifiers. For PCBs, PAHs, and PBDEs, field replicate RSDs were in similar ranges as for lab replicates, so the process of compositing and subsampling appears to add not much more variability.

Most of the PCBs averaged 50% to 150% of their previous 2009-2014 RMP Status and Trends averages, although some were as low as 0% (all ND unlike prior years) or as high as 189% (nearly double prior averages). Similarly, most of the PCB congeners averaged in the same range (50-150%) of 2009-2014 averages, but some were ~0% (all ND) or as high as 4x higher. For reanalyzed archive samples, sum of PCB concentrations were around 140%, 90%, and 65% of their prior reported concentrations in 2014 for Central Bay (CB100S), Lower South Bay (LSB046S), and South Bay (SB110S) stations, respectively. Although ratios of minor congeners varied more, e.g. up to ~2x higher and 10x lower in 2018 reanalyses, this is due to higher relative analytical uncertainty at their low concentrations. The major congeners such as 138 and 153 typically had similar ratios as sums of PCBs (e.g. around 140%, 90%, and 50% for CB100S, LSB046S, and SB110S respectively).

Fipronils like in prior years had low concentrations with many NDs, so are similar (at least qualitatively, in being near or below detection limits). Due to the prevalence of NDs and concentrations near MDLs in both past and current analyses, calculations of relative concentrations between years for fipronils are inappropriate.

A number of alkylated PAHs had average concentrations orders of magnitude (e.g. nearly 300x) higher than previously reported averages for the period of 2009-2014. The difference may be largely due to the change in lab (now AXYS, previously it was EBMUD), using different digestion and analytical methods. For reanalyzed archive samples, the results were more similar, with 2018 reanalyses between ~30-230% of their prior results in 2014, averaging 88%, 92%, and 102% of 2014 results for CB100s, LSB046s, and SB110s respectively.

For PBDEs, results for congeners quantified in 2018 for archive samples were generally fairly similar to their prior results, ranging 40-200% of their 2014 results for individual congeners quantified in both periods for the specific sites. Average ratios were 91%, 101%, and 105% for CB100s, LSB046s, and SB110s respectively. This range of variation was very similar to what was seen for PCBs and PAHs. However, sums of PBDEs differed somewhat more (and were biased lower), due to more non-detects in 2018, with ratios of sum PBDEs for the 3 stations at 42%, 87%, and 64% of their 2014 sums respectively.

Overall the degree of variation between the current and prior results in the reanalyses of archives for each given site and compound was higher than typically seen for within year lab replicates, but showed no strong consistent bias suggesting a major shift in recovery or other problems.

Appendix: Dataset QA Summaries

QA Summaries

Bay RMP 2018 Sediment

BA

Sediment

As, Hg, MeHg, Se and Total Solids

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 (especially desired by stormwater programs)

Samples were analyzed between 21 and 38 days after collection. A holding time of 1 year is specified in the 2017 RMP QAPP. No 2018 samples had holding time violations. A 2014 RMP archive sample was used as a non-project sample and was flagged by the lab with the holding time flag "H".

All 2014 results were flagged with the QA code of "H" to indicate a holding time violation. The holding time specified in the 2017 RMP QAPP is 1 year.

QA Review

QA/QC Summary:

QA Issues for Project Manager to Review

Dataset completeness

Total arsenic results were reported for 27 sediment samples analyzed in one lab batch. Two blind field replicates, 4 lab replicates, 4 matrix spike/matrix spike replicates, 4 method blanks, 2 laboratory control material samples (LCMs), and 2 laboratory control samples (LCSs) were also analyzed for the 27 sediment samples which meets the minimum requirement in the 2017 RMP QAPP of 1 per 20 samples. Data were reported not blank corrected.

Total mercury results were reported for 27 sediment samples analyzed in one lab batch. Two blind field replicates, 3 lab replicates, 3 matrix spike/matrix spike replicates, 4 method blanks, 2 certified reference material samples (CRMs), and non-project samples were also analyzed for the 27 sediment samples which meets the minimum requirement in the 2017 RMP QAPP of 1 per 20 samples. Data were blank corrected.

Total methyl mercury results were reported for 27 sediment samples analyzed in two lab batches. Two blind field replicates, 3 lab replicates, 3 matrix spike/matrix spike replicates, 8 method blanks, 3 certified reference material samples (CRMs), 2 laboratory control samples (LCSs), and non-project samples were also analyzed for the 27 sediment samples which meets the minimum requirement in the 2017 RMP QAPP of 1 per 20 samples. Data were blank corrected.

Total selenium results were reported for 27 sediment samples analyzed in one lab batch. Two blind field replicates, 4 lab replicates, 4 matrix spike/matrix spike replicates, 4 method blanks, 2 laboratory control material samples (LCMs), and 2 laboratory control samples (LCSs) were also analyzed for the 27 sediment samples which meets the minimum requirement in the 2017 RMP QAPP of 1 per 20 samples. Data were reported not blank corrected.

Total solids results were reported for 27 sediment samples analyzed in one lab batch. Two blind field replicates, 4 lab replicates, and 2 method blanks were also analyzed for the 27 sediment samples which meets the minimum requirement in the 2017 RMP QAPP of 1 per 20 samples. Data were reported not blank corrected.

Three archive samples from 2014 were analyzed for total arsenic, mercury, methyl mercury, selenium, and total solids in four lab batches (arsenic and selenium in one batch, mercury in one lab batch, methyl mercury in one batch, and total solids in one lab batch). Arsenic, selenium, and total solids results were not blank corrected. Mercury and methyl mercury results were blank corrected.

The same QA for the 2018 RMP samples was extended to the 2014 archived samples.

Overall acceptability

Overall the data submission is acceptable. 98% of the results are reportable; only 3 selenium results were rejected and are non-reportable.

Overall the archived samples are acceptable. 93% of the archived results are reportable; 1 selenium result was rejected.

MDLs sensitivity

Method detection limits were acceptable with non-detects (NDs) reported for only 1 methyl mercury result.

No non-detects were reported for the archived samples.

QB averages (procedural, field blank)

Total Solids and selenium were found in the method blanks at concentrations above the method detection limits. 9% (3 out of 33) selenium results were flagged with the censoring qualifier of "VRIP". The rest of the selenium results and all of total solids results were flagged with the non-censoring qualifier "VIP".

One selenium result for the archived samples was flagged with the censoring qualifier of "VRIP". The rest of the selenium results, and all of the total solids results were assigned the non-censoring qualifier "VIP".

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

Accuracy of methyl mercury was evaluated using the certified reference material samples. The average %error for methyl mercury was 21% (average recovery 121%) which is less than the 35% target MQO. Arsenic, mercury, and selenium accuracy was evaluated using the matrix spike samples. The average %error was 2% (average recovery 98%), 10% (average recovery 104%), and 2% (average recovery 99%), respectively, well below the target MQO of 35%.

Laboratory control spikes and laboratory control materials were examined, but not used for the evaluation with the average %errors all less than 26%. No qualifiers were needed.

Average precision from replicate field sample

Precision was evaluated using the lab replicates. The average RSD for arsenic, mercury, methyl mercury, selenium, and total solids was 2%, 11%, 7%, 9%, and 1%, respectively, well below the 35% MQO target. Precision of the lab replicates and field replicates combined were all less than the target MQO of 35%. Certified reference material and matrix spike replicates were examined, but not used for the evaluation, and the average RSD's ranged from 1% to 11%. The RSD of the arsenic and selenium laboratory control spikes were examined, but not used for the evaluation, and were both less than 2%; the RSD for the methyl mercury laboratory control spikes was 39%. No qualifiers were added.

Comparison of dissolved and total phases

Not Applicable

Comparison to previous years

Average concentrations for arsenic were 85% (~0.9x greater), mercury 107% (~1.1x greater), methyl mercury 150% (1.5x greater), and selenium 160% (1.6x greater) than previous average

RMP sediment results (2009-2014).

Average concentrations for arsenic in the 2014 archive sample were 92% (~0.9x greater), mercury 351% (~3.5x greater), methyl mercury 138% (~1.4x greater), and selenium 157% (~1.6x greater) than the average concentrations of the 2014 RMP sediment sample for station CB100S.

Average concentrations for arsenic in the 2014 archive sample were 31% (~0.3x greater), mercury 81% (~0.8x greater), methyl mercury 121% (~1.2x greater), and selenium 176% (~1.8x greater) than the average concentrations of the 2014 RMP sediment sample for station LSB046S.

Average concentrations for arsenic in the 2014 archive sample were 207% (~2.1x greater), mercury 302% (~3x greater), methyl mercury 1340% (~13.4x greater), and selenium 330% (~3.3x greater) than the average concentrations of the 2014 RMP sediment sample for station SB110S.

Ratio checking summary (if applicable)

Not applicable.

Ratio Checking Summary

Not applicable

Sums Summary

Not applicable

CCSF

Sediment

Trace Metals and Total Solids

QA Issues for Project Manager to Review

Reporting Issues for Lab to Review

Formatting Issues for Data Manager to Review

Hold time review (especially desired by stormwater programs)

A holding time of 1 year at < -15C is specified in the 2018 RMP QAPP. Samples were analyzed between 19 and 55 days after collection except for the 2014 archive samples. No 2018 samples had holding time issues. All 2014 archive sample results were flagged with the QA code of "H" to indicate a holding time violation.

QA Review

QA/QC Summary:

QA Issues for Project Manager to Review

Dataset completeness

Total Aluminum, Copper, Gadolinium, Iron, Manganese, Nickel, and Zinc results were reported for 27 sediment samples and three 2014 sediment archive samples analyzed in 2 lab batches. Two blind field replicates, 2 lab replicates, 2 matrix spike/matrix spike replicates, 4 method blanks, 2 laboratory control material samples (LCMs), 18 laboratory control samples (LCSs), 10 CCB, and 10 CCV samples were also analyzed for the 27 sediment samples which meets the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples. Data were reported not blank corrected.

Total Cadmium and Silver results were reported for 27 sediment samples and three 2014 sediment archive samples analyzed in 2 lab batches. Two blind field replicates, 2 lab replicates, 2 matrix spike/matrix spike replicates, 4 method blanks, 2 laboratory control material samples (LCMs), 22 laboratory control samples (LCSs), 10 CCB, and 10 CCV samples were also analyzed for the 27 sediment samples which meets the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples. Data were reported not blank corrected.

Total Lead results were reported for 27 sediment samples and three 2014 sediment archive samples analyzed in 2 lab batches. Two blind field replicates, 2 lab replicates, 2 matrix spike/matrix spike replicates, 4 method blanks, 2 certified reference material samples (CRMs), 18 laboratory control samples (LCSs), 10 CCB, and 10 CCV samples were also analyzed for the 27 sediment samples which meets the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples. Data were reported not blank corrected.

Total Solids results were reported for 27 sediment samples and three 2014 sediment archive samples analyzed in 2 lab batches. Two blind field replicates, and 2 lab replicates were also analyzed for the 27 sediment samples which meets the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples. Data were reported not blank corrected.

Gadolinium results were assigned a compliance code of "Est".

Overall acceptability

Overall the data submission is acceptable. 99% of the results are reportable; only 3 silver results were rejected and are non-reportable.

MDLs sensitivity

Method detection limits were acceptable with no non-detects (NDs) reported.

QB averages (procedural, field blank)

Total iron and silver were found in the method blanks at concentrations above the method detection limits. 9% (3 out of 33) silver results were flagged with the censoring qualifier of "VRIP". The rest of the silver and all of the iron results were flagged with the non-censoring qualifier "VIP".

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

Accuracy of the lead results was evaluated using the certified reference material samples. The average %error for lead was 2% (average recovery 102%) which is less than the 25% target MQO. Aluminum, Cadmium, Copper, Iron, Manganese, Nickel, Silver, and Zinc accuracy was evaluated using the matrix spike samples. The average %error was 4% (average recovery 104%), 5% (average recovery 99%), 9% (average recovery 91%), 7% (average recovery 107%), 5% (average recovery 95%), 9% (average recovery 91%), 4% (average recovery 104%), and 6% (average recovery 94%), respectively, well below the target MQO of 25%. Accuracy of the Gadolinium results was evaluated using the laboratory control samples (LCS's). The average %error for Gadolinium was 3% (average recovery 103%) again less than the 25% target MQO.

The other matrix spike, laboratory control spike, and laboratory control material samples were examined, but not used for the flagging with the average %errors all less than 12%. No qualifiers were needed.

Average precision from replicate field sample

Precision was evaluated using the lab replicates. The average RSD for Aluminum, Cadmium, Copper, Gadolinium, Iron, Lead, Manganese, Nickel, Silver, and Zinc was 5%, 17%, 4%, 7%, 4%, 3%, 3%, 5%, 3%, and 6%, respectively, well below the 25% MQO target. Precision of the lab replicates and field replicates combined were all less than the target MQO of 25%.

Certified reference material, matrix spike, laboratory control spike, and laboratory control material replicates were examined, but not used for the evaluation, and the average RSD's

ranged from 1% to 13%. No qualifiers were added.

Comparison of dissolved and total phases

Not Applicable

Comparison to previous years

Average concentrations, excluding the 2014 archive samples results, for Aluminum were 96% (~1x greater), Cadmium were 107% (~1.1x greater), Copper were 101% (~1x greater), Iron were 102% (~1x greater), Lead were 95% (~1x greater), Manganese were 92% (~0.9x greater), Nickel were 99% (~1x greater), Silver were 98% (~1x greater), and Zinc were 96% (~1x greater) than previous average RMP sediment results (2009-2014).

Gadolinium has not been measured previously in RMP status and trends sediment samples.

Results were very similar to prior results on the archive samples reanalyzed (LSB046s, SB110s), paired against the same samples from 2014. Most reanalyses were within 10% of their prior results, except one Al (12% low), one Cd (19% high), and one silver (11% high).

Ratio Checking Summary

Not applicable

Sums Summary

Not applicable

ALS

Sediment

Grain Size, TOC, and Total Solids

QA Issues for Project Manager to Review

Reporting Issues for Lab to Review

Formatting Issues for Data Manager to Review

Hold time review (especially desired by stormwater programs)

Grain size samples were analyzed between 9 and 16 days after collection. A holding time of 6 months is specified in the 2018 RMP QAPP. No holding time issues were flagged.

Total Organic Carbon samples were analyzed between 16 and 22 days after collection. A holding time of 28 days is specified in the 2018 RMP QAPP. No holding time issues were flagged.

Total Solids samples were analyzed between 6 and 13 days after collection. No holding time is specified in the 2018 RMP QAPP. No holding time issues were flagged.

QA Review

QA/QC Summary:

Dataset completeness

Grain size results were reported for 27 sediment samples analyzed in 1 lab batch (Silt/0.0039 to <0.0625 mm, Clay/<0.0039 mm, Silt/<0.0625 mm, Sand/0.0625 to <2.0 mm, Sand/V. Fine 0.0625 to <0.125 mm, Sand/Fine 0.125 to <0.25 mm, Sand/Medium 0.25 to <0.5 mm, Sand/Coarse 0.5 to <1.0 mm, Sand/V. Coarse 1.0 to <2.0 mm, and Granule + Pebble/2.0 to <64 mm). Two blind field replicates, and 2 lab replicates were also analyzed for the 27 sediment samples which meets the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples. No spiked samples were analyzed. Data were reported not blank corrected.

Grain size fractions were re-scaled so that they added to 100%.

Total Organic Carbon (TOC) results were reported for 27 sediment samples analyzed in 2 lab batches. Two blind field replicates, 3 lab replicates, 2 method blanks, and 2 laboratory control samples (LCS) were also analyzed for the 27 sediment samples which meets the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples. Data were reported not blank corrected.

ALS_TOC_TS - Total Solids results were reported for 27 sediment samples analyzed in 1 lab batch. Two blind field replicates, and 3 lab replicates were also analyzed for the 27 sediment samples which meets the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples. No spiked samples were analyzed. Data were reported not blank corrected.

ALS_PCMS - Total Solids results were reported for 27 sediment samples analyzed in 2 lab batches. Three blind field replicates, and 3 lab replicates were also analyzed for the 27 sediment samples which meets the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples. No spiked samples were analyzed. Data were reported not blank corrected.

Overall acceptability

Overall the data submission is acceptable. 100% of the results are reportable.

MDLs sensitivity

Method detection limits were acceptable with only a few non-detects (NDs) reported; 1 for TOC and 3 for Granule + Pebble/2.0 to <64 mm.

QB averages (procedural, field blank)

TOC was not found in the method blanks at concentrations above the method detection limits. No method blanks were reported/analyzed for grain size analysis.

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

Accuracy of the TOC results was evaluated using the laboratory control samples. The average %error of ~1% (average recovery 98.8%) was well below the 10% target MQO.

No spiked samples were reported/analyzed, for grain size or Total Solids analysis. No qualifiers were needed.

Average precision from replicate field sample

Precision was evaluated using the lab replicates. The average RSD for TOC was ~1% once again well below the MQO target of 10%. Precision of the TOC lab replicates and field replicates combined were also less than the target MQO. Laboratory control spike replicates were examined, but not used for the evaluation, and had an average RSD of ~2%.

The average RSD for the Total Solids lab replicates, and for the lab replicates and field replicates combined was ~1%. No RSD method quality objective listed in the QAPP.

Precision for the grain size analysis was made on the absolute differences between the replicate results when only two replicates were analyzed, or the standard deviation of the results when there were more than 3 replicates. All absolute differences and standard deviations were <20% so no qualifiers were needed.

Comparison of dissolved and total phases

Not Applicable

Comparison to previous years

Sediment samples were dominated by Fines (71% dw) as were the 2009-2014 RMP Status and Trends sediment samples (average 66% dw). Likewise, sand concentrations were similar (26% dw compared to 29% dw).

Average concentration for TOC was 129% (~1.3x greater) than the 2009-2014 RMP Status and Trends sediment samples, and for Total Solids 94% (~0.9x greater).

Ratio Checking Summary

Not applicable

Sums Summary

Not applicable

ALS

Sediment

Total Nitrogen

QA Issues for Project Manager to Review

Reporting Issues for Lab to Review

Formatting Issues for Data Manager to Review

Hold time review (especially desired by stormwater programs)

Total Nitrogen samples were analyzed between 38 and 45 days after collection. A holding time of 100 days is specified in the 2018 RMP QAPP. No holding time issues were flagged.

QA Review

QA Issues for Project Manager to Review

Dataset completeness

Total Nitrogen (TN) results were reported for 27 sediment samples analyzed in 1 lab batch. Two blind field replicates, 2 lab replicates, 1 method blank, and 2 laboratory control samples (LCS) were also analyzed for the 27 sediment samples which meets the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples for those sample types. No matrix spike samples were reported/analyzed. Data were reported not blank corrected.

Overall acceptability

Overall the data submission is acceptable. 100% of the results are reportable.

MDLs sensitivity

Non-detects (NDs) were extensive for Total Nitrogen (~55% of results were NDs).

QB averages (procedural, field blank)

TN was not found in the method blank at a concentration above the method detection limit.

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

Accuracy of the TN results was evaluated using the laboratory control samples. The average %error of ~1% (average recovery 99.48%) was well below the 15% target MQO. No qualifiers were needed.

Average precision from replicate field sample

Precision was evaluated using the laboratory control sample replicates. The average RSD for TN was ~1% once again well below the MQO target of 15%. Laboratory and field replicates were examined, but not used for the evaluation because of extensive NDs. No qualifiers were added.

Comparison of dissolved and total phases

Not Applicable

Comparison to previous years

Average concentration for TN was 54% (~0.5x) the 2009-2014 RMP Status and Trends sediment sample average.

Ratio Checking Summary

Not applicable

Sums Summary

Not applicable

SGS AXYS

Sediment

PCB

QA Issues for Project Manager to Review

Overall acceptability

Overall the dataset is acceptable. 99.7% of the results are reportable.

Accuracy

The accuracy for sediment PCBs was flagged following the SFEI RMP Status and Trends convention of using the average percent error of the certified material samples (CRMs), when present, in preference to the percent error of the matrix spike/matrix spike replicates or the percent error of the laboratory control sample, as the CRMs are externally validated values.

The majority of PCB certified reference material (CRM) results met the method quality objective listed in the 2018 RMP QAPP of “expected value \pm 35%”, except for PCB 087 and PCB 151. The average percent errors were generally less than a RPD of 35%, except for PCB 087 and PCB 151 with average percent errors of 37.12% and 38.51%, respectively. All PCB 087 and PCB 151 results were flagged with the non-censoring qualifier “VIU”.

No matrix spike/matrix spike duplicates were analyzed/reported.

The PCB laboratory control sample results meet the method quality objective of “expected value \pm 35%, and the average percent error ranged from 0.73% to 16.73% all < 35%.

The accuracy of the total solids data could not be determined.

Precision

The precision of field samples in the database is flagged following the SFEI RMP Status and Trends convention of using lab replicates in preference to using field replicates, although both are reviewed and described narratively when provided.

The average RSD for the subset of PCB congeners in the lab replicates ranged from 0.31% to 66.46%, and 24 out of 133 (18%) were above the 35% MQO target. All the results for PCB congeners with average RSDs greater than 35%, but less than 70% were flagged with the non-censoring qualifier “VIL”.

The average RSD for the subset of PCB congeners in the field replicates ranged from 0.65% to 94.23%, the majority (61%) were below the target MQO of 35%.

The average RSD for the total solids results in the lab replicates was 3.91% and for the field

replicates it was 3.42%. No method quality objective is specified in the 2018 RMP QAPP.

Reporting Issues for Lab to Review

Formatting Issues for Data Manager to Review

Hold time review (especially desired by stormwater programs)

The 2018 PCB sediment samples were analyzed between 207 and 226 days after collection well within the 1 year holding time specified in the 2018 RMP QAPP. The 2014 archived sediment samples were analyzed 1688 days after collection.

No holding time requirement specified for total solids.

QA Review

Dataset completeness

PCBs (209 congeners) were reported for 30 (27 collected in 2018 and 3 archived samples from 2014) sediment samples analyzed in 3 lab batches.

Two blind field replicates and two lab replicates were analyzed for the 27 sediment samples meeting the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples, but not the requirement of 1 per batch for those sample types.

Three method blanks were analyzed meeting the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples, or 1 per batch for those sample types.

Two certified reference material samples (NIST 1944: New York/New Jersey Waterway Sediment) were analyzed for a subset of the analytes meeting the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples, but not the requirement of 1 per batch for those sample types.

No matrix spike/spike replicates were analyzed/reported failing to meet the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples, but not the requirement of 1 per batch for those sample types.

Three laboratory control samples were also analyzed meeting the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples, or 1 per batch for those sample types. Data were reported not blank corrected.

Total solids were reported for 27 sediment samples analyzed in 3 lab batches. Total solids results were also reported for two blind field replicates and two lab replicates meeting the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples, but not the requirement of 1 per batch for those sample types. Total solids were not reported for the certified reference material, and laboratory control samples, but no requirements are listed in the 2018 RMP QAPP for those sample types. No matrix spike samples were analyzed/reported.

Overall acceptability

Overall the data submission is acceptable. 99.7% of the results are reportable.

MDLs sensitivity

The lab reported results above the detection limit in the sediment samples for 44% (92 out of 209) of the PCB congeners. Extensive non-detects (> 50% NDs) were reported for 12% (25 out of 209) of the PCBs (PCB 005, PCB 023, PCB 038, PCB 055, PCB 073, PCB 078, PCB 079, PCB 080, PCB 081, PCB 104, PCB 106, PCB 111, PCB 112, PCB 121, PCB 123, PCB 126, PCB 127, PCB 142, PCB 145, PCB 159, PCB 161, PCB 169, PCB 186, PCB 192, and PCB 204).

QB averages (procedural, field blank)

One-third (33%) of the 209 PCB congeners were measured in the method blank at concentrations equal to, or above the method detection limit (MDL), failing to meet the method objective of the 2018 RMP QAPP of being "<MDL".

Results for 77 of the PCB congeners were flagged for some degree of blank contamination; some of the results for 9 PCBs were qualified with the censoring "VRIP" flag (Data rejected - Analyte detected in field or lab generated blank, flagged by QAO).

Total Solids were not reported/analyzed in the method blank.

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

For samples with a known concentration, consisting of certified reference material (CRM), 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. Analysis of CRMs allows us to evaluate measurement accuracy, or how close our measurement comes to a consensus/expected value. Matrix spikes, where an environmental sample is "spiked" with a known amount of mercury, provide an alternative determination of method accuracy that can account for matrix interferences or other analytical problems. Laboratory control samples are an aliquot of a reference matrix fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure to determine the accuracy of the method by measuring recovery; they are not externally validated values.

Only a subset of the 209 PCB congeners were analyzed in the certified reference material (NIST 1944). The percent errors for the analytes in the CRM with certified values were generally below the target MQO of 35%, the exceptions were PCB 087 and PCB 151, with average percent errors of 37.12% (average recovery 137.12%) and 38.51% (average recovery 138.51%), respectively. All the PCB 087 and PCB 151 results were flagged with the non-censoring qualifier "VIU" (Percent Recovery exceeds laboratory control limit, flagged by QAO).

No matrix spike/matrix spike duplicates were analyzed/reported. The average percent error examined for the subset of the PCB congeners in the laboratory control sample ranged from 0.73% (average recovery 99.27%) to 16.73% (average recovery 99.27%) within the target 35% error.

The accuracy of the total solids data could not be determined.

Average precision from replicate field sample

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

Lab replicates were used to decide whether precision flags were needed. The average RSD for the subset of PCB congeners in the lab replicates ranged from 0.31% to 66.46%, and 24 out of 133 (18%) were above the 35% MQO target. All the results for PCB congeners with average RSDs greater than 35%, but less than 70% were flagged with the non-censoring qualifier "VIL" (RPD exceeds control limit, flagged by QAO).

The average RSD for the subset of PCB congeners in the field replicates ranged from 0.65% to 94.23%, the majority (61%) were below the target MQO of 35%.

The average RSD for the total solids results in the lab replicates was 3.91% and for the field replicates it was 3.42%. No method quality objective is specified in the 2018 RMP QAPP.

Comparison of dissolved and total phases

Not Applicable

Comparison to previous years

Average concentration for the sediment PCBs ranged from 0% to 189% of the previous average of the 2009-2014 RMP Status and Trends samples (in units of ug/kg dw), where they could be compared.

Ratio Checking Summary

Thanks for the answer on PCB 11.

The data are OK to go.

Jay

On Mon, Jun 17, 2019 at 9:27 AM John Ross <johnr@sfei.org> wrote:

Jay,

PCB 11 was qualified for blank contamination. Is the data alright to sum and report?

John

On Mon, Jun 17, 2019 at 8:50 AM Jay Davis <jay@sfei.org> wrote:

Hi John;

This dataset looks good - I don't see anything suspicious.

The only thing that stands out a little in terms of Aroclor composition is a relatively high contribution from 1254 in CB011S.

Why are the PCB 11 data censored (I'm not conversant in qualifiers)?

Thanks,

Jay

Sums Summary

Not applicable

SGS AXYS

Sediment

Fipronils, PBDEs, and PAHs

QA Issues for Project Manager to Review

There were 8 PAHs (Dibenzothiophenes, C1-, Dibenzothiophenes, C2-, Dibenzothiophenes, C3-, Fluorenes, C1-, Fluorenes, C2-, Fluorenes, C3-, Naphthalenes, C4-, and Phenanthrene/Anthracene, C4-) with concentrations which were orders of magnitude higher than previously reported for the period of 2009-2014. I checked the results and units in the hardcopy report with those in the electronic data submission and they were in agreement, so I do not believe any transcription error is the cause. Instead it seems more likely it is due to the fact that AXYS is now performing the analysis (previously it was EBMUD) using different digestion and analytical methods (AXYS MLA-021 compared to EPA 3545_3640A_3611B and EPA 8270M).

Overall acceptability

Overall the dataset is acceptable. 100% of the fipronil results are reportable. 91.8% of the PBDE results are reportable. 96.5% of the PAH results are reportable.

Accuracy

Fipronil:

The accuracy for fipronil was flagged following the SFEI RMP Status and Trends convention of using the average percent error of the matrix spike/matrix spike replicates when certified material samples (CRMs), where not present, in preference to the percent error of the laboratory control sample.

The fipronil matrix spike results meet the method quality objective listed in the 2018 RMP QAPP of “expected value \pm 35%, and the average percent error were all < 35%.

The fipronil laboratory control sample results meet the method quality objective listed in the 2018 RMP QAPP of “expected value \pm 35%, and the average percent errors were all < 35%.

PBDEs:

The accuracy for PBDEs was flagged following the SFEI RMP Status and Trends convention of using the average percent error of the laboratory control samples matrix spikes when certified material samples (CRMs) and matrix spike/matrix spike replicates were not present, or when the CRMs if present did not have externally validated values (only reference vales).

The PBDE laboratory control sample results meet the method quality objective listed in the 2018 RMP QAPP of “expected value \pm 35%, and the average percent errors were all < 35%.

PAHs:

The accuracy of the PAHs was flagged following the SFEI RMP Status and Trends convention of using the certified reference material (CRM) results, when present, and the laboratory control samples when the PAH analytes did not have externally validated results in the CRM.

The percent errors for the analytes in the CRM with certified values were below the target MQO of 35%, except for Dibenz(a,h)anthracene with an average percent errors of 61.2% (average recovery 161.2%). All the Dibenz(a,h)anthracene results were flagged with the non-censoring qualifier "VIU" (Percent Recovery exceeds laboratory control limit, flagged by QAO).

The average percent error examined for the subset of PAHs in the laboratory control samples were generally below the target MQO of 35%, the exceptions were Acenaphthene and Tetramethylnaphthalene, 1,4,6,7-, with percent errors of 114.93% (average recovery 214.93%), and 46.33% (average recovery 146.33%), respectively. All the Acenaphthene results were flagged with the censoring qualifier "VRIU" (Data rejected - Percent Recovery exceeds laboratory control limit, flagged by QAO). All the Tetramethylnaphthalene, 1,4,6,7- results were flagged with the non-censoring qualifier "VIU" (Percent Recovery exceeds laboratory control limit, flagged by QAO).

Precision

The precision of field samples in the database is flagged following the SFEI RMP Status and Trends convention of using lab replicates in preference to using field replicates, although both are reviewed and described narratively when provided.

Fipronil:

The fipronil results could not be evaluated using the lab replicates due to the large number of non-detects (almost all results were NDs) instead the matrix spike replicates were used. The average RSDs were all below the target MQO of 35%. No qualifiers were added.

PBDEs:

Lab replicates were used to decide whether precision flags were needed for the PBDEs. The average RSD for the subset of PBDEs in the lab replicates were generally below the MQO target of 35%, the exception was PBDE 208 with an RSD of 35.98%. All the PBDE 208 results were flagged with the non-censoring qualifier "VIL" (RPD exceeds control limit, flagged by QAO).

Average field replicate RSDs for the PBDEs were generally below the MQO target of 35%, the single exception was PBDE 138 with an RSD of 49%. No additional qualifiers were added.

PAHs:

Lab replicates were used to decide whether precision flags were needed for the PAHs. The average RSD for the subset of PAHs in the lab replicates were generally below the MQO target of 35%, the exception was Methylantracene, 2- with an RSD of 35.21%. All the Methylantracene, 2- results were flagged with the non-censoring qualifier "VIL" (RPD exceeds control limit, flagged by QAO).

The average RSDs for the certified reference material and laboratory control samples were generally below the target MQO of 35%. The only exception was PBDE 206 with an average RSD of 63.09%. No additional qualifiers were added as the lab replicate RSD for PBDE 206 was below the target MQO of 35% (26.14%).

Average field replicate RSDs for the PAHs were below the MQO target of 35%, except for Acenaphthene (36%) and Biphenyls, C2- (37.2%). No additional qualifiers were added.

Reporting Issues for Lab to Review

Formatting Issues for Data Manager to Review

Hold time review (especially desired by stormwater programs)

The 2018 fipronil sediment samples were analyzed between 222 and 230 days after collection well within the 1 year holding time specified in the 2018 RMP QAPP for pesticides. The 2014 fipronil archived sediment samples were analyzed between 1698 and 1700 days after original collection.

The 2018 PBDE sediment samples were analyzed between 213 and 232 days after collection well within the 1 year holding time specified in the 2018 RMP QAPP. The 2014 PBDE archived sediment samples were analyzed between 1696 and 1698 days after original collection.

The 2018 PAH sediment samples were analyzed between 248 and 259 days after collection well within the 1 year holding time specified in the 2018 RMP QAPP. The 2014 PBDE archived sediment samples were analyzed between 1724 and 1730 days after original collection.

QA Review

Dataset completeness

Fipronil:

Fipronils (5) were reported for 30 sediment samples (27 samples collected in 2018 and 3 archived samples from 2014) analyzed in 2 lab batches. Two blind field replicates were analyzed for the 30 sediment samples meeting the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples, but not the requirement of 1 per batch for those sample types. Two lab replicates were analyzed for the 30 sediment samples meeting the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples, or 1 per batch. Two method blanks were analyzed meeting the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples, or 1 per batch for those sample types. Two matrix spike/spike replicates were analyzed meeting the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples, or 1 per batch for those sample types. Two laboratory control samples were also analyzed meeting the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples, or 1 per batch for those sample types. No certified reference materials were analyzed/reported. Data were reported not blank corrected.

PBDEs:

PBDEs (50) were reported for 30 sediment samples (27 samples collected in 2018 and 3 archived samples from 2014) analyzed in 3 lab batches. Two blind field replicates and two lab replicates were analyzed for the 30 sediment samples meeting the minimum requirement in the

2018 RMP QAPP of 1 per 20 samples, but not the requirement of 1 per batch for those sample types. Three method blanks were analyzed meeting the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples, or 1 per batch for those sample types. Two certified reference materials (NIST 1944) were analyzed meeting the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples for those sample types, but not the requirement of 1 per batch. Three laboratory control samples were also analyzed meeting the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples, or 1 per batch for those sample types. No matrix spike/matrix spike replicates were analyzed/reported. Data were reported not blank corrected.

PAHs:

PAHs (84) were reported for 30 sediment samples (27 samples collected in 2018 and 3 archived samples from 2014) analyzed in 3 lab batches. Two blind field replicates and two lab replicates were analyzed for the 30 sediment samples meeting the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples, but not the requirement of 1 per batch for those sample types. Three method blanks were analyzed meeting the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples, or 1 per batch for those sample types. Two certified reference materials (NIST 1944: New York/New Jersey Waterway Sediment) were analyzed meeting the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples for those sample types, but not the requirement of 1 per batch. Three laboratory control samples were also analyzed meeting the minimum requirement in the 2018 RMP QAPP of 1 per 20 samples, or 1 per batch for those sample types. No matrix spike/matrix spike replicates were analyzed/reported. Data were reported not blank corrected.

Total Solids:

Total solids were reported for the 30 sediment samples analyzed for fipronil, PBDEs, and PAHs.

Overall acceptability

Overall the dataset is acceptable. 100% of the fipronil results are reportable. 91.8% of the PBDE results are reportable. 96.5% of the PAH results are reportable.

MDLs sensitivity

Fipronil:

The lab reported results above the detection limit in the sediment samples for 80% (4 out of 5) of the fipronil analytes. Extensive non-detects (> 50% NDs) were reported for 100% (5 out of 5) of the fipronil analytes (Fipronil, Fipronil Desulfinyl, Fipronil detrifluoromethylsulfinyl, Fipronil Sulfide, and Fipronil Sulfone).

PBDEs:

Results above the detection limit were reported in the sediment samples for 70% (35 out of 50) of the PBDE analytes. Extensive non-detects (> 50% NDs) were reported for 28% (14 out of 50) of the PBDE analytes (PBDE 010, 017, 030, 035, 077, 079, 105, 116, 128, 140, 181, 184, 190, and 205).

PAHs:

The lab reported results above the detection limit in the sediment samples for 46% (39 out of

84) of the PAH analytes. Extensive non-detects (> 50% NDs) were reported for 6% (5 out of 84) of the PAH analytes (Benz(a)anthracene, Dimethyldibenzothiophene, 2,4-, Dimethylphenanthrene, 3,6-, Methylphenanthrene, 9/4- and Tetramethylnaphthalene, 1,4,6,7-).

QB averages (procedural, field blank)

Fipronil:

Fipronil analytes were not measured/reported in the method blanks at concentrations above the method detection limit (MDL) meeting the method objective of the 2018 RMP QAPP of being "<MDL".

PBDEs:

A minority of the PBDE analytes (6 out of 50) were measured in the method blank at concentrations equal to, or above the method detection limit (MDL), failing to meet the method objective of the 2018 RMP QAPP of being "<MDL". Results for 6 of the PBDE analytes were flagged for some degree of blank contamination; some of the results for 3 of the analytes (PBDE 037, 183, and 208) were qualified with the censoring "VRIP" (Data rejected - Analyte detected in field or lab generated blank, flagged by QAO).

PAHs:

PAH analytes (11 out of 84) were measured in the method blank at concentrations equal to, or above the method detection limit (MDL), failing to meet the method objective of the 2018 RMP QAPP of being "<MDL". Results for 11 of the PAH analytes were flagged for some degree of blank contamination; some of the results for 3 of the analytes (Biphenyls, C1-, Biphenyls, C2-, and Dibenzothiophenes, C3-) were qualified with the censoring "VRIP" (Data rejected - Analyte detected in field or lab generated blank, flagged by QAO).

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

For samples with a known concentration, consisting of certified reference material (CRM), 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. Analysis of CRMs allows us to evaluate measurement accuracy, or how close our measurement comes to a consensus/expected value. Matrix spikes, where an environmental sample is "spiked" with a known amount of mercury, provide an alternative determination of method accuracy that can account for matrix interferences or other analytical problems. Laboratory control samples are an aliquot of a reference matrix fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure to determine the accuracy of the method by measuring recovery; they are not externally validated values.

Fipronil:

No certified reference material was analyzed for the fipronils so they were evaluated using the matrix spike/matrix spike replicates. The percent errors for the fipronils were all below the target MQO of 35%. No qualifiers were needed.

The percent errors for the fipronils in the laboratory control samples were all below the target MQO of 35%.

PBDEs:

The certified reference material (NIST 1944: New York/New Jersey Waterway Sediment) analyzed for a subset of the PBDEs did not have certified values, but instead reference values so the PBDEs were evaluated using the laboratory control samples (LCSs). The percent errors for the PBDEs were all below the target MQO of 35%. No qualifiers were needed.

PAHs:

The certified reference material (NIST 1944: New York/New Jersey Waterway Sediment) analyzed for a subset of the PAHs did not all have certified values, so in the cases where they had only reference values the laboratory control samples (LCSs) were used instead. The percent errors for the analytes in the CRM with certified values were below the target MQO of 35%, except for Dibenz(a,h)anthracene with an average percent errors of 61.2% (average recovery 161.2%). All the Dibenz(a,h)anthracene results were flagged with the non-censoring qualifier "VIU" (Percent Recovery exceeds laboratory control limit, flagged by QAO).

The average percent error examined for the subset of PAHs in the laboratory control samples were generally below the target MQO of 35%, the exceptions were Acenaphthene and Tetramethylnaphthalene, 1,4,6,7-, with percent errors of 114.93% (average recovery 214.93%), and 46.33% (average recovery 146.33%), respectively. All the Acenaphthene results were flagged with the censoring qualifier "VRIU" (Data rejected - Percent Recovery exceeds laboratory control limit, flagged by QAO). All the Tetramethylnaphthalene, 1,4,6,7- results were flagged with the non-censoring qualifier "VIU" (Percent Recovery exceeds laboratory control limit, flagged by QAO).

Average precision from replicate field sample

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

Fipronil:

The fipronil results could not be evaluated using the lab replicates due to the large number of non-detects (almost all results were NDs) instead the matrix spike replicates were used. The average RSDs were all below the target MQO of 35%. No qualifiers were added.

PBDEs:

Lab replicates were used to decide whether precision flags were needed for the PBDEs. The average RSD for the subset of PBDEs in the lab replicates were generally below the MQO target of 35%, the exception was PBDE 208 with an RSD of 35.98%. All the PBDE 208 results were flagged with the non-censoring qualifier "VIL" (RPD exceeds control limit, flagged by QAO).

Average field replicate RSDs for the PBDEs were generally below the MQO target of 35%, the single exception was PBDE 138 with an RSD of 49%. No additional qualifiers were added.

PAHs:

Lab replicates were used to decide whether precision flags were needed for the PAHs. The average RSD for the subset of PAHs in the lab replicates were generally below the MQO target of 35%, the exception was Methylanthracene, 2- with an RSD of 35.21%. All the Methylanthracene, 2- results were flagged with the non-censoring qualifier "VIL" (RPD exceeds control limit, flagged by QAO).

The average RSDs for the certified reference material and laboratory control samples were generally below the target MQO of 35%. The only exception was PBDE 206 with an average RSD of 63.09%. No additional qualifiers were added as the lab replicate RSD for PBDE 206 was below the target MQO of 35% (26.14%).

Average field replicate RSDs for the PAHs were below the MQO target of 35%, except for Acenaphthene (36%) and Biphenyls, C2- (37.2%). No additional qualifiers were added.

Comparison of dissolved and total phases

Not Applicable

Comparison to previous years

Fipronil:

Average concentration for the fipronil analytes in the sediment samples were 0% of the previous average of the 2009-2014 RMP Status and Trends samples (in units ug/kg dw), where they could be compared, 2018 results were all non-detects.

PBDEs:

Average concentrations for PBDEs in the sediment samples ranged from 0% to 367%, but were generally less than 150% of the previous average of the 2009-2014 RMP Status and Trends samples (in units ug/kg dw), where they could be compared.

PAHs:

Average concentrations for PAHs in the sediment samples ranged from 0% to 28474%, but were generally less than 150% of the previous average of the 2009-2014 RMP Status and Trends samples (in units ug/kg dw), where they could be compared. The new analyte list contains PAH and alkylated PAH analytes not previously analyzed/reported for the RMP Status and Trends samples.

There were 8 PAHs (Dibenzothiophenes, C1-, Dibenzothiophenes, C2- Dibenzothiophenes, C3-, Fluorenes, C1-, Fluorenes, C2-, Fluorenes, C3-, Naphthalenes, C4-, and Phenanthrene/Anthracene, C4-) with concentrations which were orders of magnitude higher than previously reported for the period of 2009-2014. I checked the results and units in the hardcopy report with those in the electronic data submission and they were in agreement, so I do not believe any transcription error is the cause. Instead it seems more likely it is due to the fact that AXYS is now performing the analysis (previously it was EBMUD) using different digestion and analytical methods (AXYS MLA-021 compared to EPA 3545_3640A_3611B and EPA 8270M).

Ratio Checking Summary

Rebecca

Sutton

9:50 AM (4 minutes ago)

to me, Elizabeth,
Amy

Hi John - I'm starting with fipronil - this one is easy!

Unfortunately, MDLs were significantly higher than in previous years (avg 0.22 vs. 0.0035 in 2014, different lab). As a result, only a single detection was reported, for fipronil sulfone at site LSB002S (0.199 ug/kg dw). Fipronil sulfone and fipronil desulfinyl are typically the dominant degradates present, and the Lower South Bay is typically the most contaminated portion of the Bay, so this detection makes sense in terms of analyte and location. The value for fipronil sulfone reported in 2018 is consistent with levels reported in 2014 (max 0.253).

The 2014 data suggest that fipronil and fipronil sulfide would likely be non-detect with 2018 MDLs, consistent with observations, while fipronil desulfinyl might be detectable if found at similar levels (2014 max 0.355).

In summary, the dataset is acceptable, but the high MDLs have limited its utility. We should see what can be done to lower MDLs.

The LSB046S fipronil desulfinyl maybe should have been detected, even with the higher detection limits of SGS AXYS. Instead it's ND.

Rebecca Sutton PBDE Review:

2018 PBDE sediment data appear reasonable overall.

SUGGESTED CHANGE: Qualify "sum of PBDEs (SFEI)" for station ID BG30 as VJ,VLB. BDE-209 was ND for this sample, but given the high MDL for this congener and its typically high proportion in sediment, this suggests the PBDE sum is a low biased estimate. (Note: A similar request was made in 2014 data review for the samples taken at this site and BG20.) If reanalysis of 2014

CB100S is included in publicly available data, it should receive the same qualifier.

Interlaboratory comparison (2014 samples, n=3) suggests BDE-209 values trend lower than previous analysis, though not necessarily exceeding statistical cutoffs. Measurements of this congener are also commonly influenced by high MDLs. Since BDE-209 is the dominant portion of the PBDE total, and the congener of greatest interest with respect to trends relating to recent phase-out, the change in laboratory should be considered alongside any future calculations regarding statistical significance of declines over time.

BDE-209 is observed to make up 56% (median and average) of the total PBDE signal in 2018 samples, somewhat lower than 67% (median) or 63% (average) in 2014. Declines are expected eventually due to nation-wide phase-out in 2013, but we'll need at least one more round of sampling to see if this is happening. For BDE-47 the median is 12.7% (9% in 2014), and the average is 11.8% (10% in 2014).

A review of PBDE ratios reveals few values fall outside two standard deviations of the mean (2018 samples only). A major exception is BG30, relating to the lack of detection of BDE-209, typically the dominant congener in sediment. BG30 had an unusually high ratio of BDE-15, a congener associated with photolytic debromination, as well as BDE-47 and BDE-100, both associated with the Penta commercial mixture. (The 2014 CB100S sample with no detection of BDE-209 had deviations for a greater number of different congeners.) BD31 had an unusually high ratio of BDE-17, associated with microbial debromination, as well as BDE-49. SPB057S had an unusually high ratio of BDE-207, possibly influenced by censoring of BDE-208 (VRIP), which is often found at comparable levels in samples.

Overall, regional distribution of BDE-209 is consistent with previous measurements, with higher levels often observed at sites in the Lower South Bay. For BDE-47, higher levels are seen at sites in Lower South Bay and Suisun Bay (influenced by river discharges).

Liz Miller Review of PAHs.

Here is the PAH/alkyl PAH sediment:

2018 PAH/sediment data appear reasonable overall.

Except for site SB011S, which had consistently substantially higher detected concentrations than all other sites, median and maximum measurements per analyte line up well with previous years' data. Site SB011S was located near the South San Francisco/San Bruno area, and may therefore have high analyte concentrations compared to other sites due to its proximity to a highly impervious, industrialized area. Site CB002S was the closest site to SB011S and also had high detected concentrations, although more comparable to previous years' data.

A review of PAH ratios reveals few values fall outside two standard deviations of the mean. Despite the order of magnitude higher concentrations compared to other sites, site SB011S does not appear to have unusual PAH ratios. However, two other sites, BG30 (San Joaquin River) and SU011S (west Suisun Bay), stand out:

- Site BG30 contains low ratios of many LMWPAHs, but a high ratio of biphenyl, naphthalene, methylnaphthalenes, and retene. It also has low ratios of many HMWPAHs, except for benzo(a)pyrene, chrysene, fluoranthene, and methylfluoranthene, 3-/Benzo(a)fluorine. The analytes with high ratios are generally derived from coal tar and natural sources, so these ratios are likely due a mixture of contamination from natural and anthropogenically derived PAHs.
- Site SU011S contains high ratios of many LMWPAHs and lower ratios of several HMWPAHs. These ratios are associated with petrogenic sources. Bay area refineries are all located in North Bay, so may be contributing factors to the signal seen here.

In general, the spatial distribution of total PAH levels are consistent with previous years' data, with the exception of the high contamination along the southwestern coast of Central Bay and northwestern coast of South Bay.

Duplicate BG20 and CB011S measurements are somewhat inconsistent. Some of this may be due to low levels compared to MDLs, resulting in ND for one of the samples and a value for the other. For BG20, 16% of replicate analyte measurements are more than 30% different. For CB011S, 8% of measurements are more than 30% different.

LSB011S field replicate measurements are all within 30%. Site CB011S was used as both a field and lab replicate, and the lab replicates were somewhat inconsistent. The field replicate agrees more with lab replicate #1 for this site (10% of measurements are more than 30% different from lab replicate 1 compared to 24% from lab replicate 2). The differences between the field replicate and the two lab replicates are generally of similar magnitude, and thus lab variation alone is likely responsible for most of the observed differences.

2018 alkyl PAH/sediment data appear reasonable.

A comparison of this year's measurements with previous years' indicates similar measurements, although several analytes that were previously below detection are now quantifiable due to lower MDLs. Several analytes have also been added to the list and cannot be compared to previous years' data.

A comparison of duplicate CB011S lab replicates shows consistent values for each analyte, with the exceptions of Dibenzothiophenes C1 and Phenanthrene/Anthracene C1. These analytes were also inconsistent in duplicate BG20 lab replicates, as well as Fluorenes C2 and C3, Dibenzothiophenes C1 and C4, and Benzofluoranthenes/Benzopyrenes C2. With the exception of Phenanthrene/Anthracene C1 in CB011S samples, these inconsistencies are likely due to low levels compared to MDLs.

Comparison of duplicate field LSB011S shows consistent values for each analyte, with the exception of Fluoranthenes/Pyrenes C4 and Acenaphthenes C1 (although these analytes are at low concentrations). Field replicates of CB011S are more difficult to compare because CB011S was also used as a lab replicate, and the lab replicates were somewhat inconsistent. Lab replicate 1 is more consistent with the field sample measurements.

The distribution of alkyl PAHs is consistent across sites, but not across PAH parent compounds. Phenanthrene/Anthracene, Fluoranthene/Pyrenes, Benz(a)anthracenes/Chrysenes, Benzofluoranthenes/Benzopyrenes and Biphenyls indicate a somewhat more pyrogenic source characterized by lower contributions of alkyl relative to parent compounds. Contributions from recent wildfires in the region may account for part of the signal, but have not caused observable changes

outside of the usual interannual variations in past sampling.

Napthalenes, Fluorenes, and Dibenzothiophenes show a more petrogenic distribution of contaminants, with higher contributions of alkyl relative to parent compounds.

Liz

Sums Summary

Not applicable