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To: Philip Trowbridge, RMP Manager
Jay Davis, RMP Lead Scientist
From: Don Yee, Quality Assurance Officer
Date: December 31, 2017
Re: 2016 RMP Bivalve Samples Quality Assurance Report

Introduction

In 2016, bivalve samples were collected from 8 stations (including a reference control/ bivalve source site) for the Regional Monitoring Program for Water Quality in San Francisco Bay. The details of the cruise and sample collection methods are described in the RMP Quality Assurance Program Plan, cruise plans, cruise reports, and field sampling reports. These documents are available from the SFEI website (http://www.sfei.org/programs/sf-bay-regional-monitoring-program).

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

- *AMS – Ancillary Measurements*
- *SGS-AXYS – PAHs, PBDEs*
- *BAL - Selenium*

The SFEI Data Services Team checked the laboratory results using the methods and data quality objectives in the RMP Quality Assurance Project Plan (QAPP). Overall, 83% of the field sample results (301 of 326 PBDE values, 226 of 320 PAH, and 8 of 8 selenium) 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 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 not rejected have been uploaded to the San Francisco Regional Data Center and CEDEN.

Quality Assurance Summary for 2014 RMP Bivalve Samples

AMS – Bivalve Ancillary Measurements
2016 bivalve growth measures reported by AMS looked to be within the typical ranges for mean mass (~1g for transplant Mytilus, ~0.05g for resident Corbicula), standard error

similarly 5-10% of mean for both, and survival >95% for two transplant stations (but 0% at BC10 due to sedimentation). Overall 80% of the data were reportable as one station had no surviving bivalves to report. The CTD cast data during the bivalve deployments and collections were also generally as expected, with some of the results censored due to the boat/CTD bobbing in the chop and exposing the probe to the air, and results at depth <1m were all flagged for insufficient depth.

SGS-AXYS – Bivalve PAHs
2016 bivalve PAH samples analyzed by SGS-AXYS had some blank contamination issues, with 72% of the data usable (not rejected). Naphthalene in field samples of all species and biphenyl in all *Mytilus* was <3x the concentration in the blank samples and was censored. Many other PAHs and alkyl PAHs were also found in the blank at concentrations comparable to those in field samples (~1/3 of field sample concentration or higher), and therefore, the field results for these compounds were rejected in some samples. PAH recoveries were good, but Alkyl PAHs as usual had no recovery QC samples as there are no real standards for these combined alkyl PAH groups, only for individual (mostly C1- or methyl) alkyl PAH compounds. Precision was good, with no analytes censored for poor precision. PAHs and alkyl PAHs have been the analyte groups with which SGS-AXYS has had the most blank contamination trouble with historically (possibly because they commonly use toluene and other aromatic solvents). An inquiry has been made with SGS-AXYS to investigate alternative extraction methods.

SGS-AXYS – Bivalve PBDEs
2016 bivalve PBDEs had 93% of results reportable, with censoring of BDE 153, 197, and 207 for blank contamination, and BDE 209 for poor precision (RSD > 70%). BDE 153, 197, and 207 are often not detected, but BDE 209 generally may account for ~10% of PBDEs, which may impact interpretation somewhat, but does not cross the threshold (censored data contributing ~30% of the typical sum) where we elect not to report a sum for the analyte group.

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

Appendix: Dataset QA Summaries
RMP Bivalves, 2016

AMS-CA

Bivalves

Growth and Survival, CTD cast

QA Issues for Project Manager to Review

None

Hold time review (especially desired by stormwater programs)

Not applicable

QA Review

Dataset completeness

The dataset reported mass mean and stderr, growth, and survival at 3 transplant stations, (although one station had no survival), and the mass mean and stderr for two resident stations.

Overall acceptability

2016 bivalve mass and growth measures reported by AMS looked to be within the typical ranges for mean mass (~1g for transplant Mytilus, ~0.05g for resident Corbicula), stderr similarly 10x-20x lower than mean for both, and survival >95% for two transplant stations (but 0% at BC10 due to sedimentation).

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

A brief checklist of conditions follows:

1. Check range of individual dry weight means. Yerba Buena Island is usually the highest, and Coyote Creek one of the lowest. MCALs will usually be around 1g (dw). CFLU will be around 0.05g (dw)

o Transplants MCAL dry weights were all around 1g like in previous years. Max growth was around 0.6g gain at Yerba Buena Island, but negative at the other two transplant stations reported.

1. Calculate mass %std err = (dry wt std error / dry wt) – 5-10% is pretty typical

o Standard error of weights was around 5-10% of total weight.

1. Survival is preferably above 50%.

- Lowest survival reported was at Yerba Buena Island with no result reported. There was also insufficient usable backup station material.

1. Growth should look like the T-0 weight subtracted from the final dry weight.

- Checked and okay.

1. The T-0 duplicate should be the same weight as the T-0 sample give or take 2x the standard error of the dry weight.

- No replicates were reported.

The CTD cast data during the bivalve deployments and collections were also generally as expected, with some of the results censored due to the boat/CTD bobbing in the chop and exposing the probe to the air, and results at depth <1m were all flagged for insufficient depth.

SGS-AXYS

Bivalves

PAHs

QA Issues for Project Manager to Review

An inquiry is being made with the lab if naphthalene blanks, a recurrent problem, can be improved any.

Hold time review (especially desired by stormwater programs)

Samples stored frozen were all analyzed in under 200 days of collection, well within RMP desired <1year hold time.

QA Review

Dataset completeness

The dataset included bivalve PAHs from 2 stations for Corbicula, and 6 results (5 stations + lab replicate) for Mytilus, reported for all the PAHs listed in the contract. Moisture and lipid were also reported.

Overall acceptability

Overall the data are acceptable, although all napthalene (and related methyl forms) field sample results are less than 3x higher than in blanks,

MDLs sensitivity

Methods were sufficiently sensitive that a handful of analytes were non detect in more than half the samples. Benz(a)anthracene, Acenaphthene, and Dibenzothiophene were all ND in Corbicula. Benz(a)anthracene, Dibenz(a,h)anthracene, and Dibenzothiophene were ND in over

half the Mytilus.

Blank averages (procedural, field blank)
Many of the alkylated PAHs were found in the blanks. 9 of the other PAHs were as well, with Naphthalene and its methyl forms especially so, where the blanks were >⅓ of the field sample values for 100% of both species, and all those results rejected (VRIP flag) and not reported. Biphenyl was also censored in all Mytilus samples.

Accuracy (using a variety of SRMs or Matrix spike QRECs)
Recovery was good for most PAHs with certified values in the SRM (NIST 1974) with recovery errors averaging below the 35% target. The exceptions were Perylene (38%) and Fluorene (49%), flagged (VIU) but not censored. Recoveries on LCS samples were even better, with average error always <25%.

Average precision from replicate field sample
Precision on the lab replicate was good, with RSD always 25% or better, well within the target 35%, so no flags were needed for precision.

Comparison of dissolved and total phases
Not Applicable

Comparison to previous years
Concentrations were generally similar to those from 2014, ranging ±3x of 2014 results for most analytes. Two exceptions were Benz(a)anthracene, and Benzo(j/k)fluoranthene, which were well over 200x the 2014 results.. The problem appears to be mainly with low 2014 results.

Ratio Checking Summary

5/11/2017 email from Rebecca Sutton

> 2016 bivalve PAH and alkyl PAH data appear reasonable overall. No changes suggested.
>
> PAH Detailed Narrative:
> There are a fairly typical number of data rejections due to blank contamination.
>
> Replicate samples (T-0) showed excellent agreement. This sample was an unfortunate choice for replication.
>
> There were unusually high detection limits for benz(a)anthracene (avg MDL 7). The highest average ratio observed in previous datasets is 6%, suggesting this should not invalidate ratios or sums significantly. Of note, the most contaminated sample (BC10) had detectable levels associated with almost 12% of the signal (the only detection). Means and standard deviations of ratios were calculated excluding T-0 (reference site, patterns not typical of Bay). Apart from expected ratio deviations in T-0, the only value

that (just) exceeded two standard deviations above the mean (aside from benz(a)anthracene/BC10) was phenanthrene in BD30.

HPAHs were proportionally higher in BA10 and BA40 (Lower South and South Bay). This may suggest a difference in PAH sources. Higher proportions of LPAHs, along with higher proportions of alkyl relative to parent compounds, is indicative of a petrogenic PAH source; higher proportions of HPAHs is indicative of a pyrogenic source.
Sample BC10 showed unusually high levels of contamination, even higher than noted in 2014 data. Ratio patterns did not indicate the measurements were in error. The T-0 reference site showed very low levels of contamination, as expected.

Alkyl PAH Detailed Narrative:
There are a fairly typical number of data rejections due to blank contamination. We do have more measurements than were available in 2014.

Replicate samples (T-0) showed good agreement. There is one exception, for C3-fluorenes, where one of the sample values was rejected due to blank contamination. (The other value was 6.9 ng/g.) This sample was an unfortunate choice for replication.

BC10 alkyl PAH values, where available, were high, consistent with high PAH values mentioned above. T-0 values were low, as would be expected for this reference site. Medians (and full data comparisons) show C3-fluorenes values are somewhat comparable with values observed in 2014 and significantly lower than observed in 2012 and prior. I noted this observation first in my 2014 data review, and don't think any corrective action was needed.

Patterns in alkyl vs parent compound proportions suggest a primarily petrogenic signal.

SGS-AXYS

Bivalves

PBDEs

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)
All samples were analyzed for PBDEs between 99 and 206 days after collection, well within the 1 year hold time recommended in EPA 1614 for PBDEs in tissue.

QA Review

Dataset completeness

Results were reported for PBDEs, moisture and lipid in 7 bivalve composites (Total) analyzed in 1 lab batch. A Lab replicate, CRM, and LCS were analyzed for for a suite of PBDEs, with a total of 49 congeners (including coeluters) reported. The QA review was conducted on LABQA and field sample results expressed on a ng/g dw basis..

Overall acceptability

Overall the data were acceptable.

MDLs sensitivity

MDLs were generally sufficient for major congeners, but with extensive non-detects reported for the less abundant congeners in many of the composites, with up to 100% NDs (not found in any samples) for about a third to a quarter of the congeners.

QB averages (procedural, field blank)

Results were reported not blank subtracted, and PBDEs were detected in the method blanks at levels above the method detection limits, so some congeners were flagged for blank contamination, with some BDE 153, 197, and 207 results <3x the blank result censored (VRIP flag).

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

Recoveries were within 23% of target or better for CRMs and within 11% or better for LCSs, well within the target 35% or less, so no qualifiers were needed for recovery.

Average precision from replicate field sample

Precision was adequate for lab replicates other than for a few congeners. BDE 35 and 208 had RSDs over the target 35% and flagged but not censored, but BDE 209 had an RSD of >70% so was censored (VRIL flag) and not reported.

Comparison of dissolved and total phases

Not Applicable

Comparison to previous years

Average BDE congener concentrations were compared to 2014 results and were in a similar range for transplanted Mytilus (2016 averaged 93% of 2014 results for congeners detected in both times), and about double (180% of 2014 results) for resident Corbicula.

Ratio Checking Summary

The following email thread documents issues raised and resolved during the ratio checking step.

5/3/2017 email from Rebecca Sutton

Hi John - Here's my review:

2016 PBDE/bivalve data appear reasonable overall.
We have a number of rejected measurements for higher congeners; this is not expected to impact PBDE percentages or totals significantly. Some analytes were detected in blanks, consistent with previous years' measurements.

The lab replicate measurements for BD30 were in excellent agreement, though unfortunately this was the sample with the lowest levels of contamination. One of the BDE-153 values was rejected due to blank contamination, reflecting relatively low levels in the sample; this does not impact overall ratios significantly.

The general regional trend of river sites having the highest values is observed, consistent with past measurements. A slight surprise, the reference site (T-0) is not the most contaminated site! Measurements were not that much higher than in 2014 (sum PBDEs 7.6 vs 5.0), so this doesn't necessarily signal a problem with the sample.

Outlier ratio values exceeding two times the standard deviation were calculated including the T-0 site. T-0 had a few high congener outlier values on the high side, perhaps indicating slightly greater contribution of Deca. These congeners make up only ~5% of the total PBDEs. BC10 seems extra rich in the dominant congener, BDE-47. None of these outliers indicates problems with the data.

Comparison of site-specific PBDE totals in the Bay between 2014 and 2016 indicates increases at river sites (double for BG20, slight for BG30), and decreases at BC10, BA40, BD30. We are no longer seeing a clear and consistent decline across every region, possibly due to decreased number of sites (since 2012) and the impacts of drought on contaminant levels.

5/3/2017 email from Don Yee
Hi Becky,
"A slight surprise, the reference site (T-0) is not the most contaminated site! "
You mean not the LEAST contaminated site I assume?
7.5 vs 5.5, 5.2 for the lowest (done in replicate) feels a bit outside expected random lab analysis variance, but also not high enough for total panic. 10 vs 5 would be more concerning, raising questions of how that would happen. Some bizarro dupuration or biodilution?
Don

5/3/2017 email from Rebecca Sutton
Thanks for the QA on my text! We can always ask the lab to check their sample labels to make sure they didn't mix up samples. And ask them to review dilution calculations.

5/4/2017 email from Don Yee

Hi Becky,

Is the Deca on the T-0 high enough to be a possible blank contribution bias.

I know in past years 209 has been a blank issue wiping out results for low conc samples, so is the conc on the high-ish enough end that it might be a cause?

Blank hits are totally sporadic and we can't have really robust stats within batch so we kind of arm wave guessing that min and max blanks might be about 2x (your single blank result might be either 2x higher or lower), if you subtract 2x the blank amount on Deca would the numbers be more in line with past totals.

(Our blank rule is the result survives if it's minimum 3x the blank, but obviously cases where your blank gets lucky and has 0 or less contamination than all other samples, or the opposite, your blank is the only one that gets contaminated out of 10-20 samples). Our 3x rule sort of says we give up trying to quantify if we have direct evidence (from the average blank same batch) that the blank could account for a third or more.

Other people/groups present it as something of an expected maximum probable concentration (the real concentration is at most the result, which could be all blank contamination (real = 0), or all real sample). yet others present it as non-detect with an elevated MDL. There's no one "right" way, depends on what you want to do with it, right?

Don

5/8/2017 email from Rebecca Sutton

Hi all - I'm back from vacation.

You can ask the lab to review the T-0 findings relative to others, saying the levels overall are a bit higher than expected, given it's a reference site. Make sure the sample was correctly labeled (e.g., they didn't mix up a couple samples and mis-report which values go with each site), and that any calculations were done correctly (e.g., they didn't mix up a dilution). That sort of thing.

We don't usually see a lot of Deca in tissue, we find it in sediment. So I don't anticipate this is an issue for these samples.

5/9/2017 email from Andrew Porat

Hi John,
One of our senior data quality specialists here reviewed the results for the L26221-3 sample as requested.
No errors could be found for the labeling or identification for this sample. The raw instrument data and subsequent calculations for the analysis were reviewed carefully and confirmed to be correct. No errors were found.
Hope this proves helpful.
Best regards,
Andrew Porat
Project Manager

5/10/2017 email from Rebecca Sutton

Hey Don - What do you think? There's no indication of a real problem or error, it's just that the T-0 sample had higher PBDE values than expected. (The T-0 sample is not universally contaminated - I'm seeing "properly" low levels of PAHs.)

I have no specific reason to qualify/QA flag anything, it's just more of a puzzle...

5/10/2017 email from Don Yee

Stuff does sometimes happen, and 5 vs 7 is not super alarming. It is possible that things depurate over time, e.g. all the bivalves had PBDE like T-0 at the start, and lost it during deployment. it is possible that the lab had a bit of blank contamination, correction, had a bit of contamination that ended up in a sample, but not the blank, but you can't cover all the possibilities without a ton of samples, which you would only do if getting down to the bottom of it was critical.

And yeah, PAH and PBDE contamination wouldn't necessarily occur together.

5/11/2017 email from Rebecca Sutton

Thanks for the guidance!

John, at this point I'd say we accept the data, no extra flags. I'm getting to work on PAHs now.

Brooks Applied

Bivalve Tisse

Selenium, Total solids

QA Issues for Project Manager to Review
None

Hold time review (especially desired by stormwater programs)
Hold times were all less than one year, meeting the RMP QAPP.

QA Review
Dataset completeness
Se and total solids were reported for 6 field sites and a control site, with one lab replicate. Results for 4 blanks, 1 CRM, 1 LCS, and 2 matrix spikes were also reported.
Overall acceptability
Overall the data were very good, with no issues.

MDLs sensitivity

There were no NDs for Se in any species.

Blank averages (procedural, field blank)
Selenium was not detected in any blanks, so no qualifiers were needed.

Accuracy (using a variety of SRMs or Matrix spike QRECs)
Accuracy was good, averaging <20% error for all recovery sample types, well within the target 35% error. No recovery qualifiers were needed.

Average precision from replicate field sample
Precision on replicates was good, <10% RPD on lab and MS dupes, so no precision qualifiers were needed.

Comparison of dissolved and total phases
Not Applicable

Comparison to previous years
Concentrations were pretty similar to medians and means of 2008-2014 data for both species (~2.5 ug/g for Mytilus, 4.5 for resident Corbicula).

Ratio Checking Summary
Not applicable