North Bay Selenium 2019-20 QA Summaries

Brooks Applied

Bay Water

Selenium

QA Issues for Project Manager to Review

We should standardize within project whether to assign field blanks to specific locations. It is probably best to always assign field blanks to a specific site and event, even if in aggregate (field blanks over time) the contamination is common and not limited to a given

site/event/crew/equipment combination. The State likes (perhaps requires) that field blanks only be associated with specific sites and events with which they are collected. Although that makes for the best correlation, it is impractical to collect field blanks for all stations and events, and it should be reasonable to consider that field blanks might be detected if they were taken at other sites. If it is rare/infrequent, then field blank contamination might be specific to only a given site/event/crew.

Reporting Issues for Lab to Review
None

Formatting Issues for Data Manager to Review
No Station Code was listed for one field blank, 12am collection time (placeholder). SWAMP/State only likes field blanks to be associated with field samples from the same site. Could not find a water collection time or site in the cruise report PDF.
Not a major problem but the other field blank had a site code; we should try at least to be internally consistent, probably best to always assign a site/time.

Hold time review (especially desired by stormwater programs)
All samples were analyzed within the half year hold time for dissolved samples (92 days or less). Particulate samples were analyzed within 99 (well with 1 year hold time).

QA Review
Dataset completeness
The dataset includes 34 dissolved and 38 particulate field samples, analyzed in 8 batches, with 4 or more method blanks per batch, and a lab rep, LCS, CRM, and MS/MSD pair in each batch.

Percent usable (non-reject) field data
All (100% of) the data are usable with added qualifiers needed only on a few samples due to lab or field blank contamination.

Overall acceptability
 Overall the data is acceptable

MDLs sensitivity
The method is sufficiently sensitive with no NDs reported in field samples..

QB averages (procedural, field blank)
Results are reported not blank corrected. Selenium was detected in a few lab and field blanks but at low concentrations. In the lab blanks, although individual detected blanks were flagged, none had batch averages over MDL, so field samples were not flagged.
One detected field blank was flagged, and had a field sample from the same site and event that was flagged (VIPF for field blank contamination).

One of the detected field blanks had no station code provided (12am default collection time), so though the blank itself was flagged, no field samples were flagged as that field blank had not been assigned any specific site.

Average precision from replicate field sample
Lab replicate RPDs for 2019 were all <10% for dissolved phase and <35% for particulate for samples at least 3xMDL, meeting the target 35%. Lab RPDs for 2020 were all <20% for both dissolved and particulate, meeting the target 35% RPD. No added precision flags were needed.

Accuracy (using a variety of SRMs or Matrix spike QRECs)
Recovery on CRMs ranged 87-107% of target, averaging 96%. MS recoveries ranged 84-124%, and LCS 92-112%, also well within the target ±35% MQO, so no recovery flags were needed.

Comparison of dissolved and total phases
Dissolved to particulate ratios are in line with many observations for the Bay, with dissolved accounting for around 90% or more of total water column Selenium.

Comparison to previous years
Dissolved Se concentrations ranging around 0.1-0.2 ug/L are within the range typically seen for the region (Suisun Bay averaged 0.09ug/L in RMP S&T 2010-present).

Caltest

Bay Water

Ancillary

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)
All samples were processed/preserved within ~1 day, meeting the 14day hold limit for chlorophyll a and TOC specified in the project. Analysis times on SSC were all within 7 days, well within the project 1 year maximum. Chlorophyll a and TOC were analyzed within 20 days, also within the project 6 month limit.

Dataset completeness

The dataset includes 10 batches each with 2 field samples, with a lab replicate, blank, and 2 LCS each batch for SSC. Chlorophyll a batches include a blank and lab replicate. TOC batches included a blank, lab replicate, and LCS/Ds and MS/Ds

Percent usable (non-reject) field data

All (100% of) the data are usable with added qualifiers needed only on a few field samples due to matrix spike recoveries and replicate precision.

Overall acceptability

Overall the data is acceptable

MDLs sensitivity

About 20% of the Chlorophyll a results were ND in both years, with average MDLs of ~1.7 and 0.8 mg/m3 for 2019 and 2020 respectively. All other analytes had no NDs.

QB averages (procedural, field blank)

Results were reported not blank corrected. All blanks were NDs, so no added qualifiers were needed.

Average precision from replicate field sample

Ancillary parameters were occasionally quite variable in the few lab and field replicates reported in each year. chlorophyll a was analyzed in one duplicate in each year that were in a quantitative range, with the 2020 RPD 42%, over the target 25%, so that pair and other samples in that lab batch were flagged (VIL).

SSC had multiple replicates each year, but RPDs ranged up to 64% in 2019, and 31% in 2020, exceeding the target, so those pairs and their batch field samples were flagged. However the LCS replicate RSDs were <10%, so the variation is likely primarily field sampling heterogeneity. TOC replicates were run on MS/MSD pairs, and with RPDs 7% or lower, met the 10% RPD target

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

Recoveries on chlorophyll a LCS were all within the target 75-125% (86-118%).

SSC recoveries on LCS were 89-104%, within the target 90-110% range aside from one LCS recovery at 89% slightly outside the 90-110% target so the individual LCS was flagged (VEUM), but the batch average on LCS/D passed so batch field samples did not need to be qualified.

TOC LCS recoveries ranged 97-107%, meeting the 90-110% target. Some TOC MS recoveries were outside of the target 90-110% range (80 to 123%) and flagged (VGB), but were spikes of non-project samples, so did not lead to flagging of project samples.

Comparison of dissolved and total phases
Not applicable

Comparison to previous years
The average and range of results for SSC, chlorophyll a, and TOC are similar to the means from Suisun Bay in RMP Status and Trends monitoring. chlorophyll a results using the cd3.sfei.org tool ranged 0.6-8.9 mg/m3, average 3.2, which is a little higher than the observations here averaging 1.7-1.9 mg/m3 for the two years. RMP DOC results from 1994-2015 averaged around 2.3mg/L, and POC 2004-2013 averaged 1.3mg/L, so were abou t the same order of magnitude seen in this project (2.2 and 2.6 mg/L average for the two years).

Brooks Applied

Clam Tissue

Selenium

QA Issues for Project Manager to Review
The June & July 2019 set includes some very low results. Given the mold growth problems BAL was having on drying samples at the start of the project it may be best to dump/disregard these results from the early events. Possible flags to add
VBZ   Sample preserved improperly, flagged by QAO, or
VVQ   Based on professional judgement QA/QC protocols were not met, flagged by QAO
Add to some comment field "lab noted mold growth during drying"

Reporting Issues for Lab to Review
None

Formatting Issues for Data Manager to Review
After PM notes what QACode option they like, I would suggest rejecting all of the June & July 2019 field samples. Decide if the note on mold growth should go into some composite comment field, or the Result comment field, or both.

Hold time review (especially desired by stormwater programs)
All samples Hold times were all 76 days or less, well within the project QAPP 1 year hold time.

QA Review
Dataset completeness
The dataset includes 83 tissue composites analyzed for Se in 8 batches, with 11 lab replicates (minimum one per batch), with 4 or more method blanks per batch, and an LCS, CRM, and MS/MSD pair in each batch. Total solids was also analyzed to report results in dry weight basis, with blanks as the only QC samples for those.

Percent usable (non-reject) field data
All (100% of) the data are usable with added qualifiers needed only on a few samples due to lab or field blank contamination.

Overall acceptability
 Overall the data is acceptable, aside from some June and July 2019 data which appear to be unusually low in Se, perhaps due to mold growth during lab drying.

MDLs sensitivity
The method is sufficiently sensitive with no NDs reported in field samples..

QB averages (procedural, field blank)
Selenium results are reported not blank corrected. The only detected blanks were for total solids, but were near MDL and <RL, with little impact on tissue solids measurements and consequent dry weight calculations.

Average precision from replicate field sample
Lab replicate RPDs for Se were 15% or less, averaging 3% in 2019 and 8% in 2020., well within the target 35%. One field replicate had an RPD of 8%, also within the target 35%. MS/MSDs also had RPDs all 17% or less, meeting the 35% target, for pairs where spiked results were at least double those in parent unspiked samples, so no added precision flags were needed.

Accuracy (using a variety of SRMs or Matrix spike QRECs)
CRM recoveries were between 81 - 101%, within the target 65-135% range. MS recoveries were between 71-114% (for samples where the spike was at least half of the expected value), within the target 65-135% range. LCS recoveries range 79-104% also within the target range, so no recovery flags were needed.

Comparison of dissolved and total phases
Not applicable

Comparison to previous years
Average concentrations were around 7 ug/g dw for the two years, ranging from around 0.6 up to 12 ug/g across the size ranges and years. The lowest concentrations appear to be on the low side of previous USGS results, which were seldom <4 ug/g dw (for the period 1995-2010, https://pubs.usgs.gov/of/2010/1252/pdf/ofr20101252.pdf.

Many of these low results appear to be from Jun & Jul 2019 at the start of the project, when BAL were still working out sample drying and processing, and there was some mold growth on samples. It may be best to disregard these results.