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To: Philip Trowbridge, RMP Manager
Jay Davis, RMP Lead Scientist
From: Don Yee, Quality Assurance Officer
Date: 1 December, 2015
Re: 2013 RMP Water Samples Quality Assurance Report

Introduction

In 2013, water samples were collected from 22 stations for the Regional Monitoring Program for Water Quality in San Francisco Bay. The details of the cruise and sample collection methods are described in the RMP Annual Monitoring Results report (http://www.sfei.org/sites/default/files/biblio_files/2013-2014_AMR_Final.pdf). The water samples were analyzed for the following compounds by the laboratories indicated:

- *ALS - Nutrients And DOC*
- *BR - Trace Metals*
- *CCCSD - WAD CN*
- *CSJ - Copper & Nickel*
- *DFW-WPCL Fipronil*
- *EBMUD - Nutrients & Water Quality Parameters*

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, 96% of the results were determined to be acceptable for use in RMP reports and calculations.

This memo provides a high-level summary of the quality assurance assessment for each dataset. Non-conformances with the QAPP and corrective actions needed for the next round of monitoring are highlighted in gray shading. The details of the quality assurance assessment of each dataset are provided in Appendix A.

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

Quality Assurance Summary for 2013 RMP Water Samples

ALS - Nutrients and Dissolved Organic Carbon

2013 water nutrients and DOC by ALS had 87% usable data, with some nitrite blank contamination slightly over MDL, but all nitrite field sample results were also slightly over MDL so all nitrite results were censored/not reported as real signals and cannot be differentiated from lab blank contamination in such cases.

A once every 2 years snapshot of nutrient concentrations is also less useful than seasonal readings coordinated to specific events or tide phases so these measurements have been dropped (especially given ongoing nutrient strategy efforts at more relevant temporal and spatial scales). The need for periodic snapshots can be re-evaluated if/when these more localized/intensive efforts are ceased or scaled back.

2013 water DOC measurements by ALS had matrix spike recovery deviations of >10% (~18%). The prior RMP QAPP target had been <5% error, based on the SOPs of an academic lab (UCSC) that had been used by the RMP long-term. RMP had switched from the academic lab many years prior, but although recovery errors >5% had previously occurred, few/none were greatly over 10% prior, and so would be reported as flagged but not censored values. An evaluation of SWAMP and other program targets suggests that acceptance of 10% recovery errors is more typical. These results were therefore flagged but not censored, and so the 2015 RMP QAPP has been adjusted to reflect these more typical target recoveries available from contract/commercial labs. Recovery errors <10% will not be flagged in the future, and errors <20% will be flagged and not censored, but the lab will be notified that the results were flagged and attempts should be undertaken to improve performance.

Brooks Rand Laboratory -Trace Metals

2013 water trace metals were analyzed by BR with few notable deviations (99% usable), with only one very low lead concentration sample result censored due to blank noise being nearly of the same magnitude. One result each for As, Se, and MeHg had dissolved concentrations higher than total concentrations by more than typical measurement precision error, so for those individual samples the total results were also censored, given that the dissolved samples are expected to be less subject to analytical interferences (incomplete digestion, co-precipitation, etc.) as well as being more environmentally protective/conservative (being higher than total concentrations in those specific samples).

CCCSD - Weak Acid Dissociable Cyanide

2013 water WAD cyanide was reported by CCCSD with sporadic blank contamination, rendering about one-quarter of the samples unreportable (censored, 75% reported). Recovery and precision were generally acceptable, but there are many (over 50%) NDs and most results are <2x MDL (MDL ~0.5 ug/L), which has been a significant challenge in the past (and here in one-quarter of samples) as pretty much any blank detection would

render all results in a batch unreportable. The San Francisco Bay site specific objective for cyanide (for 4-day chronic exposure) is 2.9 ug/L, and all detections to date have been below that, but it would be preferable to have MDLs and blank levels at least a factor of 3 lower to ensure sufficient sensitivity. Commercial labs typically indicate MDLs ~1 ug/L or even 2 ug/L, with no blank detections as a result, but also no sample detections as well. 2015 RMP cyanide samples are being done by a different commercial lab so we can verify after those results come in whether that outcome is preferable or any more useful (likely no blank contamination detected, but also no sample detects). In discussions with the commercial lab they showed no interest in method modifications to try and get lower quantitation.

CSJ - Copper and Nickel

Intercomparisons between City of San Jose-analyzed samples for copper and nickel and results from BR were generally good, with <5% difference between labs for these metals in dissolved phase. For total phase, there were slightly different biases: San Jose was ~10% higher on Cu, and 6% lower on Ni. Those differences are still within typical analytical accuracy and precision limits though. Given the low cost of the intercomparison it would be a good cross check to continue to have for an analyte of high concern written into the basin plan, even if the level of alarm is lower with the site specific objective. However, the TRC recommended that the comparison be discontinued; for now this may be a reasonable choice given ambient levels are currently below the SSO by more than the amount of variation sometimes seen in inter-lab comparison exercises (up to ~25%), but any upward shift in ambient results may warrant resumed intercomparison (either continually or as a periodic re-check) to increase certainty in the results.

DFW-WPCL - Fipronil

Results for 2013 water fipronil and its degradates were 100% reportable but ND in all samples. Recovery errors were somewhat outside of the 35% target for the parent compound and the sulfone (both low biased), but results were not censored. Given the extensive NDs, analysis of these compounds are probably better sought in a sediment matrix.

EBMUD - Nutrient and Water Quality Parameters

2013 water nutrients and other conventional ancillary parameters reported by EBMUD had no notable issues and were 100% reportable.

Similar to the previous discussion on other nutrients, the utility of snapshot values every other year for chla, phaeophytin, and ammonia is questionable given other higher

frequency or more spatially intensive monitoring. The only advantage of S&T water random sites is the breadth of their spatial distribution, which over time may flesh out questions not addressed by higher frequency routine monitoring (e.g. Polaris, only in the spine of the Bay) or more spatially intensive efforts (e.g. channel to mudflat transects, but only done usually in single subsegments of the bay at a time, e.g. south bay, or lower south bay).

Appendix A: Dataset QA Summaries
RMP 2013 Water Sampling

Water Nitrate, Nitrite, Phosphorous, Silica, and POC - ALS

Nitrate, Nitrite, Phosphorous, Silica and Particulate Organic Carbon (POC) in water samples collected by AMS were analyzed by ALS. Samples were collected between July 30, 2013 and August 8, 2013, and analyzed between August 14, 2013 and August 30, 2013.

Nitrate, Nitrite, Phosphorous, Silica and POC results were reported for up to 26 samples (including lab replicates and blind field replicates), blank spike/laboratory control samples (LCS), and matrix spike/matrix spike duplicates (MS/MSD). Instead of "Phosphorous", orthophsphate was actually reported (similar to other recent years). Also, nitrate+nitrite was actually analyzed and reported, with nitrate calculated by subtraction of nitrite (also directly analyzed).

Sensitivity

Sensitivity was sufficient with no non-detects (NDs) reported for nitrate, nitrite, phosphorous, silica and POC.

Blanks

Only nitrite was found in the method blanks, at concentrations slightly above the method detection limit (MDL). However, nearly all the nitrite field samples were also only slightly over the MDL, with none >3x the blank, so all nitrite results were censored with the flag VRIP (Data rejected - Analyte detected in field or lab generated blank, flagged by the Quality Assurance Officer (QAO)).

Recovery

Recovery errors were <10% for all analytes (most <5%, and measurement quality objectives (MQOs) of 10-15%) so no added flags for poor recovery were needed.

Precision

Precision on lab replicates were within the target MQOs (15% for nitrogen analytes, and 10% for the rest), except for the ones evaluated using the field replicates, where variability was higher, i.e. POC and nitrate, with average relative standard deviations (RSDs) of 12% and 24%, respectively. Although lab replicates are preferred for evaluation of precision, results for POC and nitrate were flagged with the non-censoring qualifier of VIL (relative percent difference (RPD) exceeds control limit, flagged by QAO) for variable precision on the basis of field replicates for lack of alternative measures.

Water Dissolved Organic Carbon - ALS

Dissolved Organic Carbon (DOC) in water samples collected by AMS was analyzed by ALS. Samples were collected between July 30, 2013 and August 8, 2013, and analyzed on August 22, 2013.

Dissolved Organic Carbon results were reported for 47 field samples; blind field replicates, lab replicates, matrix spike/matrix spike replicates (MS/MSD), method blanks, and laboratory control spikes (LCSs) were also analyzed in one batch. Data were reported not blank corrected.

Sensitivity

Sensitivity was sufficient with no non-detects (NDs) reported for DOC in the field samples, blind field replicates, and lab replicates.

Blanks

DOC was not found in the method blanks at concentrations above the method detection limit.

Recovery

Matrix spike samples were used to evaluate the accuracy of DOC. Recoveries were good, with an average error of 18.45%; greater than the target MQO of 10%, but less than 20%. Matrix spike recovery errors were outside of then current QAPP limit of 5%, but a review of other programs' MQOs for DOC suggests a 10% limit is more routinely achievable. These data were therefore flagged for falling moderately outside those limits, but not severely enough to be censored, with the non-censoring qualifier of VIU (Percent Recovery exceeds laboratory control limit, flagged by QAO).

Precision

Precision on lab replicates with an average RSD of 6.58% was less than the 10% target MQO; including the field replicates the average RSD was 6.75%. MS/MSD replicates were examined and the average RSD of 11.53% was just above the MQO of 10%. LCS replicates were also examined and the average RSD was less than the 10% MQO (0.90%).

Water CTD Cast Data - AMS

CTD cast data for the 2013 water cruise collected by AMS was reviewed by SFEI. CTD casts were collected between July 30, 2013 and August 8, 2013, and reviewed on February 10, 2014 with no major problems found.

CTD cast results were reported for 21 water stations. No information is available for station CB037W as AMS was unable to download the data; also the full extent of the downcast was not captured at BC10 and BG30. At site SB066W, the syringe was not removed from the CTD prior to deploying. Upon retrieval the syringe was removed and a very short cast captured before moving off station.

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

Water Trace Element Suite (Ag, As, Cd, Co, Cu, Fe low and high level, Hg, MeHg, Mg, Ni, Pb, Se, and Zn) - BR

Ag, As, Cd, Co, Cu, and Fe low and high level, Hg, MeHg, Mg, Ni, Pb, Se, and Zn in water samples collected by AMS were analyzed by BR. Samples were collected between July 30, 2013 and August 8, 2013, and analyzed between August 8, 2013 and March 11, 2014.

Ag, As, Cd, Co, Cu, and Fe low and high level, Hg, MeHg, Mg, Ni, Pb, Se, and Zn were reported for 22 water samples, blind field replicates, lab replicates, matrix spike/matrix spike replicates (MS/MSDs), certified reference materials (CRM), laboratory control material (LCM), laboratory control samples (LCS), method blanks, and a field blank. "Other client samples" were also analyzed. Results were reported blank corrected.

Sensitivity

Sensitivity was sufficient for most of the analytes, with <50% non-detects (NDs) for most, except dissolved and total Silver (dissolved 96% NDs, total 82% NDs). Dissolved methyl mercury had 29% NDs.

Blanks

Results were reported blank corrected. The standard deviation of the blanks were <MDL in all cases, except for lead in one batch (B131302; 0.0035 versus 0.003 ug/L). The lead results were flagged with the non-censoring qualifier of VIP (Analyte detected in field or lab generated blank, flagged by QAO). One dissolved lead result was flagged with the censoring qualifier VRIP (Data rejected - Analyte detected in field or lab generated blank, flagged by QAO). Only one field blank was analyzed so no standard deviation could be calculated, but mercury and nickel were measured in the field blank.

Recovery

Certified reference material samples were used to evaluate the accuracy for Arsenic, Cadmium, Copper, Iron, Manganese, Mercury, and Nickel. The other trace elements were evaluated using the matrix spikes. Recoveries in all cases were good, with <25% average error (MQO of 25% error for all analytes except for Arsenic, Methyl Mercury, Mercury, and Selenium where the MQO is 35% error).

Precision

Precision on lab replicates was good, with average RSDs <25% for all analytes (MQO of 25% for all analytes except for Arsenic, Methyl Mercury, Mercury, and Selenium where the MQO is 35%).

Comparison of dissolved and total phases

Dissolved to total ratios of the analytes were generally good within sites, except for a few specific samples, where dissolved fractions were over 35% higher than the total: BA30 Arsenic, CB038W Methyl Mercury, and BA30 Selenium. For these it is assumed that the problem is more likely to be

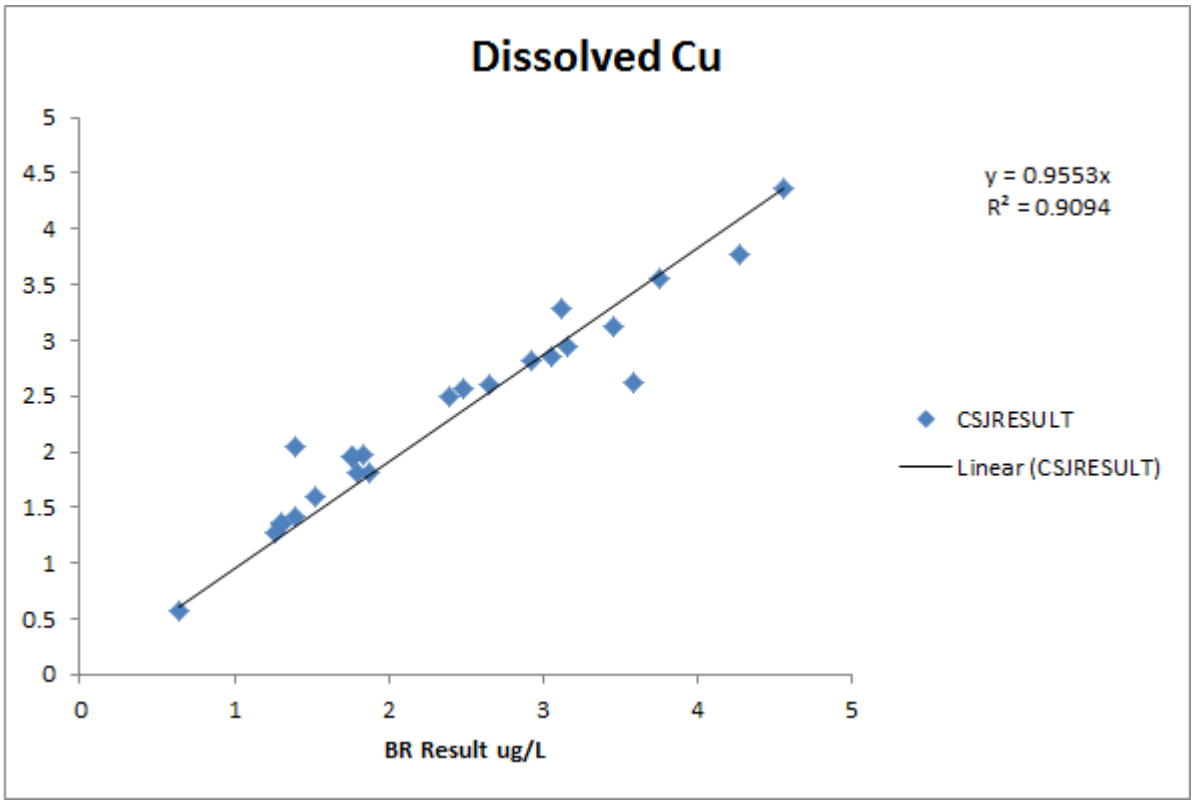
with the total fraction sample, so those results were flagged with the censoring qualifier VRVQ (Data rejected - Based on professional judgement QA/QC protocols were not met, flagged by QAO).

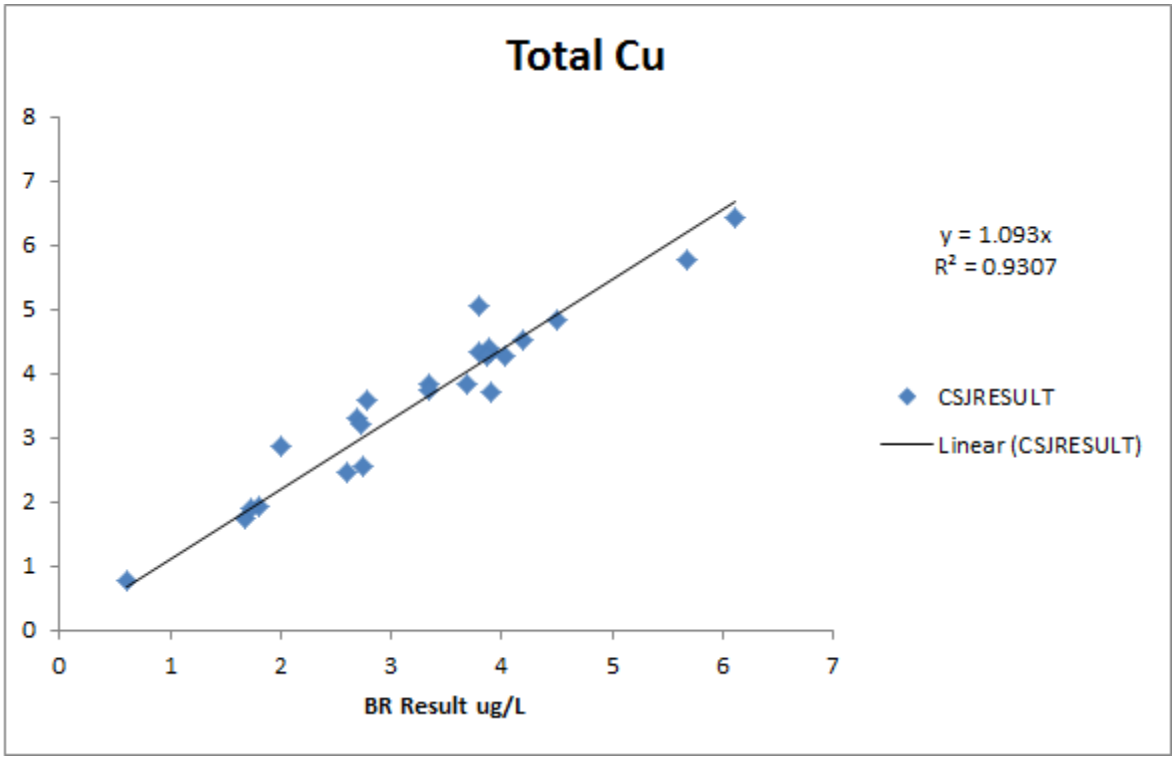
City of San Jose Inter-comparison Study

Copper and nickel concentrations from BR were compared with those reported by the City of San Jose, with more weight given to the dissolved comparison, since there might be subsampling issues with totals that may not necessarily be a problem with the analytical lab.

Dissolved copper and nickel concentrations reported by BR tended overall to be higher than those from the City of San Jose, but only by a few percent (2.6-4.5%). Two individual station dissolved copper comparisons and four individual station dissolved nickel comparisons differed by more than 20% (only 1 copper and 2 nickel differed by more than 35%).

Overall total copper concentrations from BRL were ~10% lower than the San Jose results, while total nickel results were ~6% higher. Five individual station total copper comparisons and one individual station total nickel comparison differed by more than 20% (only 1 copper and 1 nickel differed by more than 35%).

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R² = 0.9307
CSJRESULT
Linear (CSJRESULT)
BR Result ug/L
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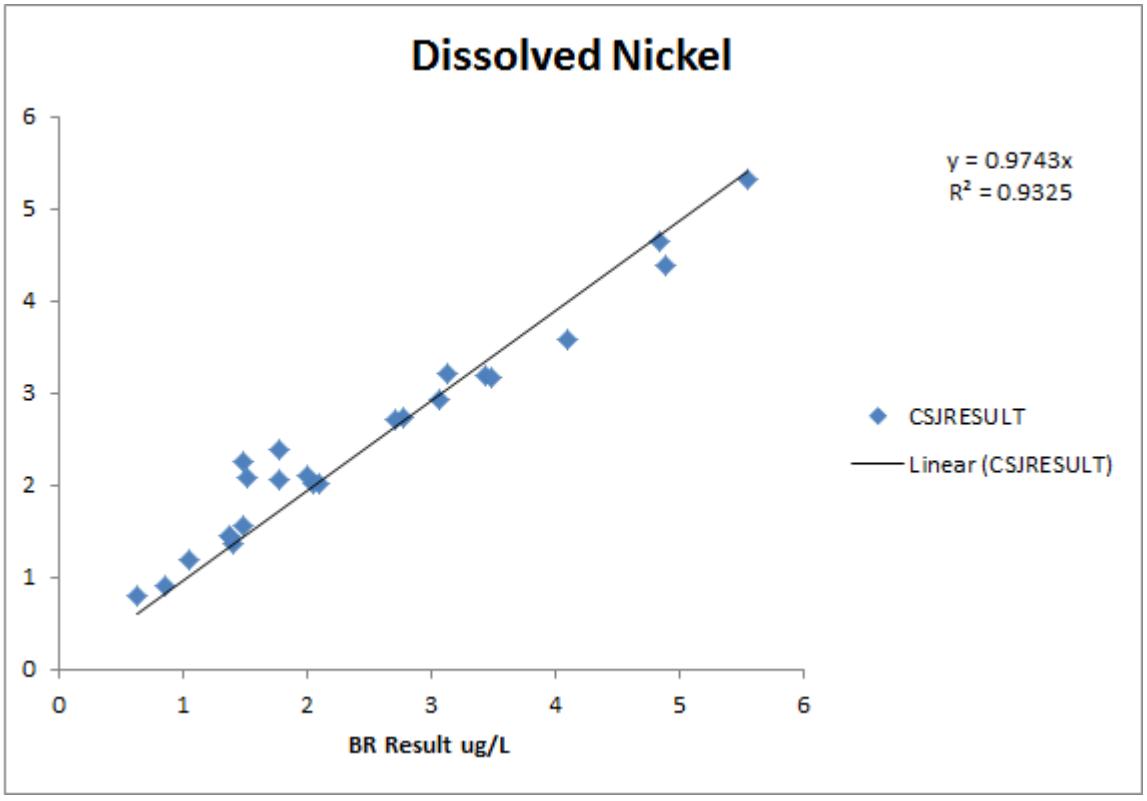
1
2
3
4
5
6
7
8


Dissolved Nickel
y = 0.9743x
R² = 0.9325
CSJRESULT
Linear (CSJRESULT)
BR Result ug/L
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1
2
3
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5
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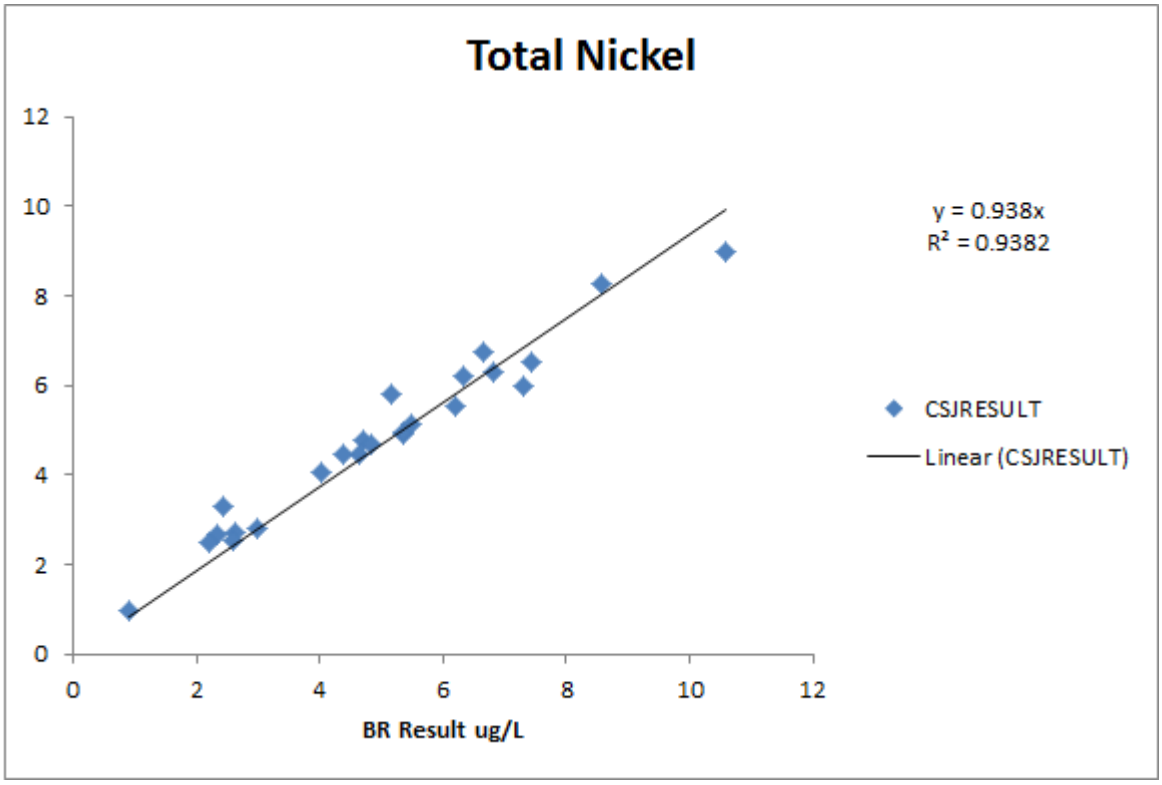

Water Weak Acid Dissociable (WAD) Cyanide - CCCSD

Weak Acid Dissociable (WAD) cyanide in water samples collected by AMS was analyzed by CCCSD. Samples were collected between July 30, 2013 and August 8, 2013, and analyzed between July 31, 2013 and August 16, 2013.

WAD cyanide was reported for 22 water samples, field replicates, lab replicates, matrix spikes, method blanks, laboratory control spikes (LCSs), and a field blank.

Sensitivity

Non-detects were extensive (<50% NDs) with eighteen (66.7%) of the 27 sample results (22 field samples, 3 lab replicates, and 2 field replicates) being NDs. The average cyanide result of 0.58 ug/L was slightly above the average MDL of 0.44 ug/L.

Blanks

Some blank contamination for WAD cyanide was measured in two of the lab batches. Twenty-two percent (6 of 27) results were flagged with the censoring qualifier VRIP (Data rejected - Analyte detected in field or lab generated blank, flagged by QAO). No blank contamination was measured in the single field blank.

Recovery

Recoveries on matrix spikes were good (average recovery was 93.89%) and the average recovery error was 17.16%, less than the target MQO of 25%. LCS recoveries were also examined and had an average recovery of 100.21% and an average recovery error of 11.93%, less than the 25% target MQO.

Precision

Precision on matrix spike replicates (lab and field sample replicates were mostly NDs so RPDs were not calculable) was good, with an average RSD of 21.12%, less than the MQO of 25%. LCS replicates were also examined and the average RSD was also less than the 25% MQO (14.69%).

Water Fipronil, Fipronil Desulfinyl, Fipronil Sulfide, and Fipronil Sulfone – DFG-WPCL

Fipronil, Fipronil Desulfinyl, Fipronil Sulfide, and Fipronil Sulfone in water samples collected by AMS were analyzed by DFG-WPCL. Samples were collected between July 30, 2013 and August 8, 2013, and analyzed on August 13, 2013.

Fipronil, Fipronil Desulfinyl, Fipronil Sulfide, and Fipronil Sulfone were reported for 10 water samples, matrix spike/matrix spike replicates, field blank, method blanks, and laboratory control spikes (LCSs).

Sensitivity

Fipronil, Fipronil Desulfinyl, Fipronil Sulfide, and Fipronil Sulfone were 100% non-detects (NDs) in the water samples.

Blanks

Fipronil, Fipronil Desulfinyl, Fipronil Sulfide, and Fipronil Sulfone were not found in the method blanks, or the one field blank, at concentrations above the method detection limit.

Recovery

Recovery errors for Fipronil and Fipronil Sulfone in the matrix spikes averaged 56.25% and 37.5% respectively, >35% but less than 70%, so were flagged with the non-censoring qualifier of VIU (Percent Recovery exceeds laboratory control limit, flagged by QAO). Fipronil Sulfide and Fipronil Desulfinyl had recovery errors less than the target MQO of 35% so no additional qualifiers were needed.

Precision

Precision on lab replicates was good, with average RSDs <35% for all analytes (target MQO of 35%).

Water Ammonium, Chlorophyll a, Hardness as CaCO3, Pheophytin a, Salinity, and Suspended Sediment Concentration - EBMUD

Ammonium as N, Chlorophyll a, Hardness as CaCO3, Pheophytin a, Salinity, and Suspended Sediment Concentration (SSC) in water samples collected by AMS were analyzed by EBMUD. Samples were collected between July 30, 2013 and August 8, 2013, and analyzed between August 2, 2013 and August 23, 2013.

Ammonium as N, Chlorophyll a, Hardness as CaCO3, Pheophytin a, Salinity, and SSC were reported for 22 water samples, field replicates, lab replicates, method blanks, certified reference materials, matrix spikes, and laboratory control spikes (LCSs). No recovery samples were analyzed for Chlorophyll a and Pheophytin a.

Sensitivity

Sensitivity was sufficient for most analytes at all stations, except for Ammonium as N which had non-detects (NDs) at two stations.

Blanks

Ammonium as N, Chlorophyll a, Hardness as CaCO3, Pheophytin a, Salinity, and SSC were not found in the method blanks at concentrations above the method detection limit.

Recovery

Recoveries for the majority of analytes were good, with average errors <15% target for Ammonium as N, <10% target for Suspended Sediment Concentration, and <5% target for Hardness as CaCO3. Recovery errors for Salinity averaged 5.69%, greater than the target MQO of 5%, and so were flagged with the non-censoring qualifier of VIU (Percent Recovery exceeds laboratory control limit, flagged by QAO). No recovery samples were provided for Chlorophyll a and Pheophytin a, so results were flagged with the qualifier VBS for incomplete QA procedures.

Precision

Precision on lab replicates was good for most of the analytes, with average RSDs <15% target for Ammonium as N, <10% target for Pheophytin a, and Suspended Sediment Concentration, and <5% target for Hardness as CaCO3 and Salinity. The average RSD for Chlorophyll a in field and lab replicates (17.45%) was greater than the 10% target MQO, and so was flagged with the non-censoring qualifier VIL (RPD exceeds control limit, flagged by QAO) for marginal precision.