



Date: August 1, 2016

From: Donald Yee, ASC QA Officer

To: Philip Trowbridge, Delta RMP Project Manager

Re: Review of 2015-2016 Current Use Pesticide Study QC Data

General summary

A review of the first year QC data for laboratory analyses of pesticides, ancillary measurements, and toxicity tests conducted for the Delta RMP by three labs found some issues, most often in the transcription and coding of data for upload to CEDEN. There were some deviations from the Delta RMP QAPP, mostly already flagged by the reporting labs in their electronic submissions, but some were either missed or may have been incorrectly applied by the labs (e.g., perhaps by rounding before comparison to criteria for some toxicity test water quality parameters).

Approach

In the review, we (the Project data management team (PDMT) and Project QA Officer (PQAO)) use the data electronically submitted by the laboratories and compile it into a local database to verify that the correct number of field samples and required number of QC samples are reported for the requested analyses. The reported QC samples are compared to the project QAPP, by independently recalculating reported precision (RPD or RSD) and percent recovery. Blank samples are compared to reported detection limits; if the analyte is detected, the concentration in the blank sample is also compared to the concentration in the associated environmental sample. Where deviations from the project measurement quality objectives are found, if the data have not already been flagged by the reporting lab, associated field samples are qualified by ASC to indicate the deviations as a warning to possible users that the data reported may be inaccurate or imprecise. In the most severe cases (e.g., where blank concentrations could account for more than a third of the reported concentration in a field sample, or QC sample results average more than two-fold outside the acceptance range for a given analysis (e.g., $\pm 50\%$ for an analyte with a $\pm 25\%$ target) data may be censored (flagged as rejected, data downloadable but not plotted or used in sums or other statistics). If data not meeting MQOs were not flagged by the laboratory, the PDMT and PQAO communicate with the

laboratory to verify the reported data contain no transcription errors, missed conversions or similar errors. If necessary, corrections are made to the data during this process. Otherwise, the data are flagged by the PQAO (QA Codes in the database that start with letter "V" are applied by PQAO rather than the lab). Systematic problems with the analysis or reporting of data are discussed with the lab to identify appropriate corrective actions for either re-reporting the samples or for future analyses.

USGS - Current Use Pesticides

General findings and recommended actions

There were issues with precision for several pesticides, possibly due in part to their low concentrations, and some minor to moderate deviations from QAPP recovery targets for others, but not serious enough to warrant censoring of any data. The variable precision in replicates for some analytes despite being well above their respective MDLs suggests that those MDLs may need to be reviewed and possibly revised.

Completeness

Results were reported for 150 current use pesticides, with 63 or more sample results (12 months collected at 5 stations (=60 samples) plus field replicates (5% frequency = 3 samples)) per pesticide for 2015, so 100% of expected samples were reported. Blanks, matrix spikes (MSs), and replicates were also reported.

Hold times

All of the samples were prepared/preserved within the 48 hr hold time limit (all <1 day). However, a number of the samples in the March, May, and June 2016 sampling were analyzed more than 30 days after the prep, up to 44 days, and were given a hold time flag (VH) for the relevant analytes, but not censored.

Sensitivity

Around 65% of reported analytes (~96 of 150 pesticides) were all non-detect in 2015-2016. Even pesticides detected were found in less than half the samples. Many pesticides if present at all would likely only be at very low concentrations, so this result is expected.

Blank contamination

Samples were reported without blank correction for the pesticides, with none detected in all of the lab and field blank samples, so no blank qualifiers were needed.



Precision

Precision was primarily evaluated on MS replicates, as most of the pesticides were ND in nearly all samples. RPDs on MS replicates averaged 15% or better for all analytes, well within the target 25%. Some analytes were detected in field replicate samples, but some pairs had field replicate RPDs of 200% (despite one result being well over 3x the MDL, e.g., Azoxystrobin at 32x MDL and Boscalid at 10x). Those analytes were flagged with VIL (but not censored) for marginal precision despite good RPDs on matrix spikes, since concentrations of ambient samples at most other stations (without field replicates) are more likely to be similar to the unspiked samples with field replicates rather than spiked MS samples. For those analytes well over MDL in one result but ND in an unspiked field -replicate, MDLs should be reassessed as the variable results would suggest that these pesticides cannot be quantified reliably at the level of the estimated MDL. Sufficient sample volume to analyze lab replicates of split samples were not planned or collected at any stations.

Accuracy

Recoveries were evaluated from matrix spike samples, with average deviation greater than 25% error from the target value (but none over 37%) on only a handful of analytes: Cymoxanil, Clothianidin, Flonicamid, Novaluron, and total Cyfluthrin. Those analytes were flagged VIU for marginal precision, but not censored.

USGS - DOC/POC, TSS, and Copper

General findings and recommendations

All of the data were reportable for the target analytes (none censored), despite some minor deviations from the QAPP target ranges. Total nitrogen was not a target analyte, but also reported, so available QC results for those analyses are also reported despite not being required. The largest issue appears to be unusual recoveries on some lab control samples, which may be an artifact of transcription or substitution errors, and is being investigated with the reporting lab. Another issue requiring further examination is the variability of TSS results, which may reflect natural variability, or suggest a need to refine/revise lab and field methods for collection and analyses of these samples.

Hold time

Hold time was met for most analyses aside from 5 of the DOC samples, analyzed up to 43 days after collection, past the 30 day hold time. These results were flagged for hold time violations (VH flag applied by the PQAO, for the few where the lab had not previously applied an H flag for hold time), but not censored.



Completeness

The dataset includes 60 site event combinations (12 months, 5 sites) for 2015, and 15 (3 months for the same sites), reported for DOC, POC, copper, and TSS. Filter blanks, and LCSs were reported for all analytes, and MS/MSD results were also reported for DOC and copper. Field replicates were reported for DOC, copper, and TSS, and lab replicates (of field grab samples) were reported for copper and DOC.

Sensitivity

Methods were generally sufficient to report the target analytes in nearly all the samples; only 3 copper analyses and 1 DOC were reported as non-detect. Total nitrogen, a non-target analyte, was ND in 13% of samples.

Blank contamination

Only DOC was found in one of the filter blanks at a low concentration, <30% of even the lowest concentration grab sample, so samples from that batch were flagged but not censored.

Precision

Variation among TSS field replicates was greater than sought in the QAPP, averaging RPD ~32%, over the 25% target. The PM should work in conjunction with field crews and labs to consider alternative sampling and subsampling methods and strategies to minimize variation in TSS. Otherwise, the variation in TSS may make it of limited use for interpreting site characteristics and processes. RPDs on replicates averaged better than 10% for DOC, and better than 25% for copper field samples. Precision on MS and LCS replicates was similar or even better, averaging <10% RPD for both DOC and copper.

Accuracy

Recovery in a number of DOC (dissolved organic carbon) and TN (total nitrogen) lab control samples was unusually low, and very constant across replicates (exactly 5% and 10% respectively), suggesting some kind of rounding, substitution, or transcription artifact or error. For the time being we have censored (flagging as rejected and not used in summary statistics) these LCS results (as there are sufficient other LCS samples for these analytes) and are investigating with the USGS lab to identify their cause.

Excluding those anomalous results, recoveries on LCS and MS samples were generally good, with average errors <10% on all the target analytes, well within the targets specified in the QAPP. There were no LCS or recovery samples for POC, but TPC (total



particulate carbon) recoveries would be most analogous, and also averaged <10% error. No added flags were required for recovery deviations.

Dissolved and particulate phases

Only organic carbon was analyzed in more than one fraction (dissolved and particulate). DOC was generally > POC, with a median ratio of around 3:1. However, a few samples had POC > DOC, which might be needed to interpret if anomalies are found in field data for pesticides and other pollutant chemicals at those sites.

UCD APHL - Toxicity

General findings and recommended actions

Issues were found with the toxicity data submitted, mostly with water quality parameters (e.g. temperature and pH) slightly outside the recommended test range. There were also samples analyzed beyond hold time (on follow-up re-tests), failures of test acceptability criteria for some controls (with alternative controls used for those tests), and significant effects for some blanks, which were already flagged by the lab and noted in their narrative report.

The QAPP currently lists target ranges for various water quality parameters, but many of the deviations not flagged by the lab were less than one full pH unit or degree C for example. If the desire is for the limits to be rounded to the nearest whole unit before being flagged (e.g. TW flag for water quality deviations), the QAPP should be adjusted to reflect that, and the acceptance ranges modified as needed to accommodate (e.g. pH 5.5 to 9.5 as the limits rather than 6(.0) to 9(.0))

Hold time

The Delta RMP QAPP has hold time for toxicity of either 36 or 48 hours depending on the test organism. ToxBatch start times are only given in whole date increments in the CEDEN database so anything less than 2 day hold time is interpreted as meeting hold time. A number of samples were tested up to 11 days after collection and were flagged for hold time.

Completeness

The data reported included 5 stations for 15 months with negative controls, salinity controls, field blanks, and bottle blanks, reported for 3 species in tox tests.



Overall 3% (43 of 1,290) of the WQ measurements were not reported, with ammonia and unionized ammonia most often missing (in 8 of 86 reported initial results for LABQA samples). A handful of initial or final measurements for other WQ measurements were also missing, for a mix of LABQA and field samples, and a request has been made for the lab to make better effort at complete recording of these parameters.

Blank contamination

The blanks on occasion showed significant toxicity, but not consistently enough for the lab to identify causes and appropriate corrective actions to take.

Precision

Although there were replicates of 4 field samples (12 replicate pairs for the 3 species together) for toxicity tests, and there were sometimes differences in degrees of the effect, there was generally no significant difference between replicate field samples. The lab appropriately flagged (IL, for precision outside of targets) for the one case when the difference exceeded 20%.

There were also some deviations among field replicates in initial water quality conditions, in excess of the QAPP listed 20% RPD target. These differences could reflect collection of slightly different parcels of water in the field, some variation in laboratory measurement, or a combination of both. There were no water quality results identified in the database as lab replicates, so the lab versus field causes of the differences could not be isolated. Flags (VIL, for precision deviations) were added to the water quality results for these replicates. The validity of the associated toxicity tests are not changed, since the initial water quality conditions are recorded separately for the different field samples, but the differences in water quality between replicates suggest a need for continued attention to sampling and subsampling methods to minimize future variation.

Accuracy

Reference toxicant tests are the primary means of assessing toxicity test accuracy. Reference toxicant test results were not included in the electronic database received, but were presented in control charts in the UC Davis lab report (p.28f), with a few deviations noted (outside the accepted variation of two standard deviations from the running mean).

