April 17, 2014

Wildomar Autumnwood Development Project Chemical Analysis
Data Package Review

Background

On February 20, 2014, DTSC Cypress region staff contacted staff in DTSC's Environmental Chemistry Laboratory (ECL) regarding analytical testing results for samples collected at the Wildomar Autumnwood Development. Soil, water, and air samples had been collected and analyzed by commercial laboratories. ECL was requested to review Level 4 data packages from the laboratories to assess the lab data's usability for risk assessment and decision making at Wildomar. Theo and Bill requested that the review focus on water samples and air samples. Soil samples were not to be reviewed at this time.

Level 4 data packages from four laboratories were provided to ECL for review: Calscience Environmental Laboratories in Garden Grove, CA (VOC (8260) water analysis); Weck Laboratories in City of Industry, CA (Formaldehyde (8315) water analysis); Environmental Analytical Services (EAS) in San Luis Obispo, CA (Formaldehyde (TO-11) air analysis); and H&P Mobile Geochemistry Inc. (H&P) in Carlsbad, CA (TO-15 and 8260SV air analysis).

Scope of Review

At ECL, review of analytical data for its usability is an assessment of whether the data are legally defensible. Use of the data for its intended purpose must be able to withstand scrutiny if challenged by other technical experts. This is NOT an audit of a laboratory or other review of the data's quality beyond the scope of the intended assessment. A Level 4 data package generally consists of:

- Cover Sheet
- Case Narrative to discuss outliers and anomalies
- Chain of Custody Records
- Sample Results (including surrogate recoveries if applicable)

- Method Blank Summary (including surrogate recoveries if applicable)
- LCS/LCSD (if applicable) recoveries and control limits summary
- MS/MSD (if applicable) recoveries and control limits summary
- GC-MS Tune summaries (if applicable)
- Initial Calibration Summaries (response factors and %RSD)
- Continuing Calibration Verification Summaries (response factors and %D)
- Summary of Internal Standards (area response and retention time) for samples and QC (if applicable)
- Instrument injection (run) logs
- Sample extraction and preparation logs
- Sample raw data (quantitation reports, chromatograms, spectra (GC/MS))
- Method blank raw data (quantitation reports, chromatograms, spectra (GC/MS))
- Quality Control raw data (LC/LCSD and MS/MSD quantitation reports, chromatograms)
- Initial Calibration raw data (tune report, quantitation reports, chromatograms)
- Continuing Calibration raw data (tune report, quantitation reports, chromatograms)

Level 4 reports are intended to provide the information needed to carry out an assessment and reach conclusions about data usability.

The data review was carried out by an expert team consisting of ECL's Quality Assurance Officer, the Section Chiefs of the ECL Analytical Support Branch's (ASB's) Berkeley and Los Angeles Laboratories, and a Subject Matter Expert.

ECL's review consists of a series of steps:

i. The requirements of the Analytical Method are compared to the laboratory's Standard Operating Procedure (SOP) to identify modifications from the Method and determine how the modifications may affect the data.
ii. The data reports are compared to the SOP to determine if the laboratory deviated from their SOP, if these deviations were documented properly, and if these deviations have an influence on the data results.
iii. The data are reviewed to determine whether quality control (QC) requirements specified in the Method and in the SOP were carried out.

iv. Any observed outliers or missing QC parameters are checked for narration and reviewed for influence on the data results.

v. Calculations are performed on one or two of the compounds reported to validate that the final results are being calculated correctly from the raw data.

vi. Validity and usability of the data are determined from the results of this review. If the information provided for review is inadequate for ECL to make a determination, additional information is requested first. If the additional information is found inadequate for ECL to make a determination, a conclusion is reached that defensibility of the data could not be determined.

Findings

None of the laboratories involved with the sample analysis provided SOPs associated with the analytical tests performed. DTSC subsequently requested SOPs and performance evaluation results from the laboratories for review by ECL.

VOC (8260) Water Analysis:

- CalScience documented outliers in the initial calibration and continuing calibrations. ECL reviewed potential effects on the sample results and determined the outliers would not have changed the final reports submitted.
- Matrix spikes were not performed because insufficient sample was provided. We cannot determine if there was anything present in the water that could have interfered with the analysis. This should be kept in mind when using the results. Sample surrogate recoveries were within criteria. This indicates that for the surrogate compounds there was adequate recovery from the water matrix. In general, for target analytes with similar physicochemical properties, recoveries could be similar. However, surrogates do not cover all the types of compounds in the analysis. The lack of specific matrix spike results should be considered if attempting to use the data for determination of the presence of the target analytes at concentrations near the reporting limit.

- The compounds reported were not detected in any of the samples.
- Unidentified peaks or peak patterns were not observed in the sample chromatograms.

- **Formaldehyde (8315) Water Analysis:** When attempting to repeat the calculations using the raw data provided, ECL observed an error in Weck laboratory's calibration factors. It was not obvious why the calibration factors were off by 1000x. To save time, ECL contacted the manufacturer of the instrument software directly to resolve the problem. It was determined that Weck had changed the parameters on the chromatogram graphing settings by a factor of 1000 which changed the absorbance unit value by a factor of 1000. This factor change was not adjusted in the equation used to determine the calibration factors and thus was not incorporated in those results. Once this error was identified by the manufacturer, ECL was able to properly check the calculations and was able to confirm the values reported by Weck in their final reports. The lack of documentation or understanding by Weck associated with their change in chromatogram graphing settings necessitated ECL to perform a more detailed review of their data package to ensure data usability.
- ECL noted that the laboratory deviated from their SOP by using a final extract volume of 10 ml rather than the 5 ml specified in their SOP. Weck did not provide narration to explain the SOP deviation. ECL carried out further review and was able to determine that this deviation did not affect the reporting limit of 30 ppb specified in their SOP. All samples were able to meet this reporting limit.
- ECL's review of the raw chromatograms identified that the formaldehyde-adduct peak was integrated as a shoulder on a much larger 2,4-dinitrophenylhydrazine (DNPH) peak. DNPH was not included in the calibration standards so we cannot determine the effect of the DNPH interference with the low standard of the calibration. Non-detects may be false negatives. ECL did not attempt to determine why Weck failed to obtain good peak separation in their analysis. A review of the EPA 8315 method indicates that good separation of the DNPH and formaldehyde peaks is obtainable.

- The Blank Spike (BS) and Matrix Spike (MS) samples were prepared the same way as the samples and spiked at a concentration of 100 µg/L. The peak observed on the chromatogram was of significant size to identify it from the shoulder of the DNPH peak. ECL is confident those calculated values at or above 100 µg/L are usable.
- One of the matrix spike sets reported had poor precision results. There was no indication through narration or results that the matrix spike set was reanalyzed or re-extracted. It was beyond the scope of our review to determine if this is a laboratory problem or an isolated incident.

Formaldehyde (TO-11) Air Analysis:

- The initial report submitted by EAS was reviewed and found to be confusing and missing documents. In response to questions that were raised, EAS submitted a completely new Level 4 report.
- EAS provided a list of modifications they followed compared to the TO-11 method. These modifications allowed for wider (less precise) quality control criteria for the initial calibration, continuing calibration, and precision (sample duplicate) compared to the TO-11 method.
- ECL reviewed the chromatograms and observed that DNPH present in the cartridges used in the analysis provided a large peak that overlapped with the much smaller formaldehyde peak. The calibration standards used in the analysis do not include DNPH, so ECL was unable to determine if DNPH would have interfered with the low standard of the calibration. Non-detects may be false negatives. ECL did not attempt to determine why EAS failed to obtain good peak separation in their analysis. A review of the TO-11 method indicates that good separation of the DNPH and formaldehyde peaks is obtainable.
- The TO-11 method does not discuss the analysis of a laboratory control sample (LCS) or blank spike sample. The laboratory analyzed LCS samples but they did not extract them through a cartridge. The DNPH interfering peak is not present in the chromatogram indicating they prepared them like continuing calibration standards. There is no quality control requirement in TO-11 that the lab must

show they can recover what is trapped on the DNPH cartridge for each batch of samples. The method does mention spiking a blank cartridge with a solution of the derivatized standard compounds to be used in round-robin studies to intercompare laboratories performing the analysis. The method also requires that before initial use of the method the lab is to demonstrate the ability to obtain adequate recovery of spiked samples. ECL was not provided information on internal studies or round-robin studies. Performance Evaluation (PE) Samples have not been available for this analysis until just recently. The laboratory informed ECL that they will be participating in future PE sample studies but had not started this process. In response to ECL's questions, the laboratory performed a cartridge spike study where they spiked two separate cartridges and eluted with solvent. Each cartridge was analyzed in duplicate and the results were reported to ECL. The results showed that the laboratory could recover formaldehyde from the cartridges.

TO-15 Air Analysis:

- A leak check compound was used during the sampling event. H&P reported the presence of the leak check compound above the reporting limit in all the samples ranging from 7.5 to 1000 µg/m^3. The presence of this compound in the samples indicates leakage occurred during sampling. It is beyond the scope of ECL's review to determine the impact of leakage on the sample results.
- How H&P calibrated the instrument was not clearly presented in their report. This made a check of H&P's calculations more difficult and necessitated follow-up inquiries for clarification and additional details. After a review it was determined that the instrument was calibrated with a larger sample volume then indicated in the SOP. There was no clear narrative information in the report on why this was done.
- The sample volumes listed on the preparation logs indicate that a larger volume of sample was analyzed yet the dilution factor used in the calculation matched that used for the method blank which used a smaller sample volume. ECL was

able to contact the laboratory directly and was provided a clear explanation of the calculation of the final dilution factor.

- Sample 10L-SV had an internal standard response high outside criteria. The laboratory did not narrate this nor did they reanalyze the sample. The high response would cause a low bias to the associated sample results.
- Methanol was a last minute addition to the list of compounds of interest. The laboratory was unable to perform a standard 5-point calibration curve and thus used a single point calibration for quantitation. The laboratory did not perform any quality control analysis for methanol. These results should be used as estimated values.
- The laboratory did not provide the correct explanation of a flag on the initial calibration report.
- The chromatograms showed unidentified peaks and peak patterns. In response to DTSC's request, the laboratory provided Total Petroleum Hydrocarbon (TPH) estimations for all samples and Tentatively Identified Compound (TIC) reports for three of the samples (approximately 10 percent of the total samples collected).

8260SV Air Analysis:

- A leak check compound was used during the sampling event. H&P reported the presence of the leak check compound above the reporting limit in seven of the samples analyzed over a three day period. The presence of this compound in the samples indicates leakage occurred during sampling. It is beyond the scope of ECL's review to determine the impact of leakage on the sample results.
- The reference spectra provided for many of the compounds were incorrect. ECL was able to determine, through additional review, that the results were properly identified by the lab. ECL reviewed all reported detected results for spectra matching.
- ECL observed that field duplicate (co-located) samples submitted to H&P were analyzed on two of the three sampling days. H&P did not report precision results for these samples. ECL requested additional information about this practice. H&P responded that field duplicates are not determined for precision criteria by the

laboratory. ECL noted that the laboratory SOP mentions that field duplicates should be analyzed daily and provides control criteria for precision. The SOP also gives corrective action if the precision criteria are not met. The laboratory did not follow their SOP. ECL did not attempt to do precision determination for the duplicates.

- A review of the chromatograms showed unidentified peaks and peak patterns. In response to DTSC's request, the laboratory provided TPH estimations for all samples the TIC reports for three of the samples.

Usability Determination

VOC (8260) Water Analysis:

ECL has determined that the data submitted is usable for risk assessment.

Formaldehyde (8315) Water Analysis:

ECL has determined that the data are usable with restrictions. The actual calculated values have an uncertainty based on the chromatography interference by DNPH that was observed in the samples but not in the calibration standards. Quantitative use of the data for values near the reporting limit is not recommended. However, none of the samples had observed chromatographic peaks that were greater than the laboratory spike samples. Therefore a conclusion could be made that none of the samples contained formaldehyde above 100 µg/L, the amount spiked in the laboratory spike samples.

Formaldehyde (TO-11) Air Analysis:

ECL has determined that the data are usable with restrictions. The actual calculated values have an uncertainty based on the chromatography interference by DNPH that was observed in the samples but not in the calibration standards. Quantitative use of the data for values near the reporting limit is not recommended. None of the samples had observed chromatographic peaks that were greater that the

laboratory cartridge spike study samples. Using the concentration of spike used in the study, a conclusion could be made that none of the samples contained formaldehyde above 75 µg/m^3.

TO-15 Air Analysis:

ECL is unable to determine the impact of leakage on the usability of the sample results. The methanol results reported should be used as estimated values, based on the single point calibration curve used to quantitate the values and the lack of additional quality control results. Unidentified peaks and peak patterns are present in the chromatograms. The laboratory provided Total Petroleum Hydrocarbon (TPH) estimations for all samples and Tentatively Identified Compound (TIC) reports for three of the samples. ECL has determined that the data are otherwise usable for risk assessment.

8260SV Air Analysis:

ECL is unable to determine the impact of leakage on the usability of the sample results. Unidentified peaks and peak patterns are present in the chromatograms. The laboratory provided TPH estimations for all samples and TIC reports for three of the samples. ECL has determined that the data are otherwise usable for risk assessment.