**Audit of Data Quality**
**March 2009 Sampling Event**
**Data associated with "Ground-Water Investigation in Pavillion, Wyoming," QA ID #G-14478**
**analyzed at US EPA Region VIII Laboratory**
**ADQ performed by Neptune and Company, Inc.**

**Audit of Data Quality (ADQ) Report:** December 21, 2011

Five validation Excel spreadsheets are included in this ADQ report and are provided as separate files: TO61 WO05 Semivolatiles EPA Method 8270D Validation Worksheets, TO61 WO5 Alkalinity Validation Worksheets, TO61 WO5 Anion Validation Worksheets, TO61 WO5 Headspace Methane Validation Worksheets and TO61 WO05 TPH DRO EPA Method 8015D Validation Worksheets. These worksheets include documentation of the validation process, along with sample and batch information, and recalculations.

**NOTE: Headspace methane audit is incomplete. Waiting for response to questions from Region 8 laboratory.**

1. **Laboratory Data Audited:**

**Laboratory (Organization):**
US EPA Region VIII Laboratory.

**Sample Type(s)/Methods/Analyte(s):** Five analytical methods were to be included in this task for the samples identified below: 1) 8015D TPH/DRO, 2) 8270 semivolatiles, 3) 524.2 Headspace (methane), 4) 300.0 Anions and 5) 310.1 Alkalinity.

**Sample Identification:** PGDW5, PGDW20, PGDW30 and PGDW32.
WOs associated with these samples are identified in the support Excel Spreadsheets provided with this Audit of Data Quality Report.

**QA Reviewers:** Rebecca Shircliff and David Gratson, Neptune and Company, Inc.

**Method Information (all four methods provided as separate pdf files):**
1) TPH/DRO: EPA Method 8015D (modified), Region VIII Operating Procedure (OP) ORGM-508 r1.0. Note, this method was still under development, the OTP surrogate was not yet used, samples were spiked with surrogates from the 8270 SVOC method.
2) 8270 semivolatiles: EPA Method 8270D (modified), Region VIII OP ORGM-515 r1.1
3) Headspace (methane only analyte of interest): EPA Method 524.2, Region VIII OP ORGM-004 Methane by HS _DRAFT
4) Anions: EPA Method 300.0, Region VIII OP INORM-310v12_Anions
5) Alkalinity: EPA Method 310.1, Region VIII OP INORM-302v11_Alk

**File Information:** Final Report included in file 8903002 final 16 jun 09.pdf.

TPH/DRO: Associated Files: 8903002 final 16 jun 09.pdf, 85621 - LSR, Report, Alkalinity, Anions, DRO.pdf

Semivolatiles via EPA Method 8270: Associated Files: 8903002 final 16 jun 09.pdf, 85622 - Headspace, 8270.pdf

Headspace (methane): Associated Files: 8903002 final 16 jun 09.pdf, 85622 - Headspace, 8270.pdf

Anions: Associated Files: 8903002 final 16 jun 09.pdf, 85621 - LSR, Report, Alkalinity, Anions, DRO.pdf

Alkalinity: Associated Files: 8903002 final 16 jun 09.pdf, 85621 - LSR, Report, Alkalinity, Anions, DRO.pdf

**QA/QC Criteria for Analytical Methods:** QAPP specified and Laboratory specific QA/QC criteria and limits were used as the basis of this ADQ. Note however, the Pavillion QAPP did not provide specific QA/QC criteria associated with the EPA Region VIII Laboratory methods. The laboratory did provide a QA/QC Summary table (attached to this report as a pdf file entitled R8 Lab Summary QA_QC.pdf). The DoD LCS study refers to a study used to derive statistical control limits for Semivolatile and Volatile analytes in laboratory control samples (spiked blank matrix). The QA/QC Summary table, DoD statistical limits, and information gathered during the TSA at Region VIII were used to evaluate the laboratory against data quality indicators and to assess the usability during this ADQ. Table 1 below is a summary of these QA/QC criteria for the SVOCs and DRO, quality control specifications for anions, headspace methane, and alkalinity were derived from the associated SOPs. Note in all cases (anions, headspace methane, alkalinity) the SOP was not finalized until after these data were analyzed.

**Table 1. Region VIII Laboratory QA/QC Requirements.**

| QC Type | Semivolatiles (Method 8270D) | DRO (Method 8015D) | Frequency |
|---|---|---|---|
| Method Blanks | Preparation Blanks (same as method blank), one with each set of extraction groups within the lab, calibration blanks, <RL | Preparation Blanks (same as method blank), <RL | One per sample set |
| Surrogate Spikes | 50-150% range was used in the laboratory reports. | 60-140% of expected value, o-terphenyl | Every field and QC sample |
| Internal Standards Verification. | Every sample, EICP area within ±50% of last ICV or first CCV. Add additional IS if needed for dilutions. (SOP Sections 9.4 and 11.4.6) | NA | Every field and QC sample for applicable methods |
| Initial multilevel calibration | ICAL: minimum of 6 levels (.25 -12.5 ug/L) , one is at the MRL (0.50 ug/L), prior to sample analysis (not daily) RSD≤20%, r^2 ≥0.990 | ICAL: 10-500 ug/L RSD<=20% pr r^2>=0.990 | As required (not daily if pass ICV) |
| Initial and Continuing Calibration Checks | CCV (same source as ICAL): daily and every 12 hours, | Daily with each sequence. ICV1 =DRO, ICV2 = surrogate only check | CCV At beginning of sample set, every tenth sample, and end of sample set |

| | | | |
|---|---|---|---|
| | 80-120% of expected value | 80-120% of expected value | |
| Second Source Standards | ICV1 is from a second source (includes 7 special compounds) Once after each ICAL, 70-130% of expected value | ICV1 is from a second source, 80-120% of expected value | Each time calibration performed |
| Standard Reference Material (SRM) | Once per batch, limits based on SRM certification | See below | |
| Laboratory Control Samples (LCS) | Blank Spike, one per extraction group included once per sequence or every 20 samples. 1mL into 1 L of sample at mid level.<br><br>Statistical Limits from DoD LCS Study (rounded to 0 or 5) | Often use SRM as LCS, if so limits based on certification information, otherwise 70-130% of expected value | One per analytical batch or every 20 samples, whichever is greater |
| Matrix Spikes (MS) | Same as LCS | Same as LCS (70-130%, may develop statistical based in future) | One per sample set or every 20 samples, whichever is more frequent |
| MS/MSD | Once per batch or every 20 samples. RPD $\leq$ 20% Note, the limits in the Reg VIII lab files is $\leq$ 30% | RPD $\leq$ 25 | One per sample set or every 20 samples, whichever is more frequent |
| Detection Limit Standard (CRL) | run MDL study approximately annually | DL= RL, ICAL run down to 10 ug/L | CRLs not routinely analyzed, only report to RL (lowest |

| | | MDL study approximately annually | standard of cal model) |
|---|---|---|---|
| Reporting Limits* | 0.1 µg/L (generally)[1] | 20 µg/L[1] | NA (part of ICAL) |
| Other Method Specific | GC/MS tuning (DFTPP) : prior to ICAL and at beginning of each 12-hour period. | | |

[1]Based on 1000 mL sample to 1 mL extract
*these limits are compound dependent.

2. **Summary of Assessment**

**Findings**

1. **QC Frequency Requirements Not Met for DRO.** For the DRO method, only a method blank was ran with this batch. There was no evidence that a standard reference material (SRM), lab control spike (LCS), matrix spike/matrix spike duplicate (MS/MSD) or field sample duplicate were performed. Additionally, no surrogate was added to any of the samples; however, this was likely due to the fact that EPA Method 8270 extracts were used for DRO analysis.

2. **Data Not Properly Qualified.** The QC performed for the DRO method did not meet the frequency requirements set in the SOP. Due to lack of QC data to verify the quality of the data, all DRO samples should be qualified as estimated.

   For the anions method, there were no qualifications of samples due to QC criteria exceedance described in question 12 below. Sulfate sample analysis associated with the matrix spike should be qualified as estimated. Additionally, samples with Chloride values close to the MDL should be qualified as estimated.

**Observations**

1. **QC Frequency Requirements Not Met for Anions.** For the anions method, a matrix spike was not ran every 10 samples for the run sequence, e.g. the first matrix spike (MS1) was ran after over 20 field samples were analyzed. MS1 and

the second matrix spike (MS2) were separated by less than 10 samples, but MS2 and the third matrix spike (MS3) were separated by over 20 samples. This same type of pattern (a couple of matrix spikes separated by 10 or less and then a couple spikes separated by 20 or more) continues for MS4, MS5 and MS6. There six total matrix spikes. Method blank spikes were also not ran every 20 samples for the run sequence, for example blank spike 1 (BS1) and blank spike 2 (BS2) were separated by nearly 30 samples and BS2 and the third blank spike (BS3) were separated by 23 or more samples. Additionally there is no blank spike ran after BS3, but close to 35 samples are analyzed after BS3.

2. **Holding Time Exceedance for Nitrates/Nitrites.** The associated samples (PGDW5, PGDW20, PGDW30, and PGDW32) all met the holding times for nitrates and nitrites. However, there are a large number of samples within the entire batch that did not meet the 48 h holding time for nitrates and nitrites. The results for these samples were qualified based on holding time exceedance. For more detail, see method worksheet, specifically the associated **Case Narrative** and **Samples** spreadsheets.

3. **Potential Holding Time Exceedance for Semivolatiles.** There are two extraction logs for the semivolatile samples. The first has a start date of 03/10/2009, within the 7 day holding time limit. The start date for the second it 03/13/2009, this would be beyond the 7 day limit. See raw data pages 141 and 142 of 573. However the laboratory report – Organic Data Review Checklist Sample Quality Control (page 3 of 573) indicates the holding times were met.

4. **Recalculations Do Not Agree with Reported.** Recalculations for the anions method gave different values for Chloride and Sulfate for sample PGDW20 with a RPD between Neptune & Co., Inc. and reported values of ~22 and 23%, respectively. See the TO61 WO5 Anion Validation Worksheets for more details.

5. **QC Results Requirements Not Met for Anions.** For the anions method, the MS recovery for Sulfate in sample 0900054-MS3 was 59.3% and does not meet the %R criteria. Additionally, MDL check #1 (page 140 of 85621 LSR report), the Chloride was out of the acceptable range with a value of 0.764. For MDL check #2 (page 147 of 85621 LSR report), the Chloride was out of the acceptable range with a value of 0.799. For MDL Check #3 (page 190 of 85621 LSR report), the Chloride was out of the acceptable range with a value of 0.803 and Phosphate was out of the range with a value of 0.302. The acceptable range for Chloride is 0.25 to 0.75 (i.e. $\pm$ 50% of 0.5 CRA value) and the acceptable range for Phosphate is 0.1 to 0.3 (i.c. $\pm$ 50% of 0.2 CRA valuc).

   Additionally, there appears to be a discrepancy in the actual RPD values between MS and MSD. For example, MS1 has a result of 142 mg/L for Chloride and MSD1 also has this same result, yet the RPD is listed as 0.0598. This should be 0 RPD. Calculating the RPD for Fluoride for the same two samples (MS1 and MSD1), gave a value of 0.9569 but 1.1 is listed as the

RPD for these two samples.

6. **ICV for TPH-DRO Ran Before ICAL and May be from Another Sequence.** The ICV for the associated sample sequence was performed before the ICAL (according to the sequence) instead of after. It is also possible that this ICV was analyzed for a sequence different from the associated samples. Although the sequence on page 300 of file 85621 - LSR, Report, Alkalinity, Anions, DRO.pdf shows this ICV1 ran with the above sample PGDW20, it is possible that is ICV1 ran not ran in the same sequence as the sample. The reason this might be apparent is that the name for ICV1 (9C13001-ICV1) indicates that it was sequence 9C13001 while the sequence for PGDW20 is 9C30003. The fact that ICV1 sample record indicates that it was calculated from the QLast update/calibration curve on Mon Mar 02 10:15:56 2009 (instead of the Fri Mar 13 13:59:26 2009 as the associated samples) also indicates that it might not be the correct ICV1 for this sample.

7. **Calibration Curve for Associated Samples Not in Raw Data File.** The sample record for sample PGDW20 on page 316 of file 85621 - LSR, Report, Alkalinity, Anions, DRO.pdf indicates that the calibration curve used for calculation of this sample was created on Fri Mar 13 13:59:26 2009; since that curve is not in the raw data, the curve that is in the raw data (and may not be the correct calibration curve to be using) is dated Mon Mar 02 10:15:56 2009. The data validators were instructed by William Batschelet of EPA to use this calibration curve since the calculated and reported numbers match and because the lab was in a transition period during this analysis making it difficult to find the correct calibration curve (see email at the end of this document).

8. **SRM Calibration Check Low for 2, 4 Dinitrophenol in Method 8270.** The SRM analyses (CCV2) for 2,4 Dinitrophenol had a recovery of 17.4%, below the limit of 70%. The initial CCV met the recovery limits. This analyte was not detected in the samples but there is a slight potential for false negative due to this low recovery.

9. **Internal Standard Area for Perylene-d12 in sample PGDW30.** The internal standard area for Perylene-d12 in sample PGDW30 was below the 50% value of the associated ICV and CCV. However, all surrogates for this sample were within the QC limits, including a recover of 117% for Terphenyl-d14 the surrogate associated with Perylene-d12. The CCV that was analyzed in the run sequence just prior to this sample was acceptable as was the CCV analyzed after this sample. Raw electronic data should be reviewed for likely interference with the internal standard.

**Editorial Comments**

1. **DRO Method Listed in Final Report.** Final report (file 8903002 final 16 jun 09.pdf) lists 8015**B** as the method used for DRO samples (pages 5-7). Page 3 (DRO organics summary) of the same document says that 8015D is used for analysis of

TPH/DRO.

2. **Trap Sample.** On page 7 of the final report (file 8903002 final 16 jun 09.pdf) there is a "trap_sample" listed for lab number 8903002-41D. Should this be a trip_sample instead?

**Outstanding Issues:**

1. **Headspace Gas – Methane Analysis.** During the validation of the headspace methane data several general and data specific questions were generated. These issues are outlined below. These questions were posed to William Batschelet of the Region 8 Laboratory, a response is still waiting.

General Questions:
Should each set of samples have a complete ICAL associated with them that was analyzed during the same time period (batch)? Section 9.3 of SOP ORGM-004 says ICAL required before any samples are analyzed, I am not sure if that means each batch or in general. If a complete ICAL is not required with each batch, do you have separate ICALs depending upon the sample containers so that the ICAL aqueous and headspace volumes are identical to the samples?

Does the ICAL use a 1 mole % of methane standard? If so, there needs to be a factor of 100 applied, correct? For example in the SOP, page 5 of 14, CALCULATIONS for 5 mL headspace: 5.714*5/5 = 5.71 ug/L. The 5.71 ug/mL is a for 1 mole % standard, correct? I don't see where the factor of 100, for a 1 mole % calibration standard, is included.

Specific Questions (Batch 900045)
The report I have for LSR R08090001 does not include the March 10, 2009 calibration model, with individual and average response factor so I am not exactly sure how to evaluate your ICAL and I don't believe I have enough information to calculate the concentration from the raw response.

If my sample (PDGW20) in this set had a response of 62895 (area count), can you provide me with the back calculation to 137 ug/L please. I also note that the ICAL that appears to be used for this data set had the highest volume at 250 uL, with a response of 54643. Thus, the sample area count provided for this example is above the ICAL, would you agree?

The final report also says the calibration was from 1.86 to 186 ug/L. How does this relate to the SOP table that shows from 5.71 to 571.4 ug/L, since I believe both apply to a 5 mL headspace?

What is the expected concentration of the CCVs in this sample data set? They are reported at circa 62 ug/L, using a 150 uL injection (I think). See 310001.D data file, and note the factor of 0.0071 ug/mL in the hand written calculation. Is the .0071 ug/mL for density at STP or what?

The raw data report does include a 2008 ICAL, with concentration values in ug/mL. This is from Sept 04 10:49:17 2008. Are the ug/mL concentrations the mass of methane in headspace or in the aquoeous phase?

**ITEMS REVIEWED**

| Number | ADQ Issue | Yes | No | NA | Comments |
|---|---|---|---|---|---|
| **File Information** | | | | | |
| 1 | Provide File names: See Section 2.0 above. | | | | |
| **Sample Information** | | | | | |
| 2 | Are samples uniquely identified and correctly transcribed throughout the data package to the summary of results? | **X** | | | Samples are uniquely labeled as PGDW5, PGDW20, PGDW30, and PGDW32 for all methods. In addition, samples are identified by unique Lab IDs throughout the final report and raw data packages for all methods. |
| 3 | Does sample collection documentation indicate that samples were collected as described in the QAPP, and the schedule and volumes in the planning documentation? | **X Partial** | | | The only sample collection documentation within the report files is: date/time sample was collected and volume (for SVOC samples only). |
| 4 | Does sample collection documentation indicate appropriate preservation? | **X** | | | Samples were shipped on iced and cooler temperature monitors upon receipt read 4°C. Could not find records of acid preservation for DRO samples. |
| 5 | If applicable, is chain-of-custody documentation complete? (Contains relinquished and received signatures, all samples identified with analyses, custody seals where appropriate) | **X** | | | COC documentation was found in files associated with specific work orders/batches. See Excel spreadsheets for further details. Scanned images of the custody seals are included in the laboratory reports. |

Email form William Batschelet dated November 7, 2011:

Dave,

I'll answer the TPH-DRO questions first and then deal with the headspace analysis. It looks like we have the same pdf page numbers, so I'll use them in referencing my answers.
As originally conceived, the analysis request for the Pavillion samples was a generic "Let us know what you see." i.e., screening. The laboratory was in a state of transition at that time, with a new director in January and QA officer in February. In addition, the TPH-DRO analyst was starting to include o-terphenyl (OTP) as a surrogate in the analysis. The TPH-DRO analysis was an afterthought and was performed using the extracts from the 8270 analysis. As such, the extracts contained the 8270 surrogates but not OTP. This had minimal effect on the results as demonstrated by the two prep blanks: data file 31309009, p 310 – 311, and data file 31309010, p 312 – 313, where the results were right at or less than the reporting level of 15 µg/L.
Regarding the calibration, the date/time stamps on the individual analysis reports do not match that in the method. As I said, this was a time of transition. However, I have recalculated the calibration from the concentrations and responses listed in the method on p 417, and I get the same average response factor (RF) listed on p 382. I used my calculated RF to determine the concentration for sample 8903002-31, data file 31309013, p 320, and got the same exact result: 19.239.
Regarding 9C13001-CAL1, CAL2, and CAL3, those were OTP standards which were used for other samples in the analytical sequence after CCV2. They were not included in this report since they were not relevant to the analysis.
I hope this answers your questions.

Regards, Bill

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