Audit of Data Quality Report
July 19, 2012
Data Associated with Data Associated with Pavillion Ground Water Investigation
Phase V April 2012 Sampling Event

ADQ performed by Neptune and Company, Inc.

1. INTRODUCTION:

This Audit of Data Quality (ADQ) was performed per the NRMRL SOP, *Performing Audits of Data Quality (ADQs)*, to verify that requirements of the Quality Assurance Project Plan (QAPP) were properly implemented for the analysis of samples submitted to laboratories identified in the QAPP associated with this project. The associated QAPP for this case study was entitled *Ground-Water Investigation in Pavillion, Wyoming (QA ID G-14478, Revision 6, February 17, 2012).*

2. ADQ APPROACH:

Complete data packages were provided to the auditors for the Pavillion Wyoming April 2012 sampling event. A complete data package consists of the following: sample information, method information, data summary, laboratory reports, raw data including QC results, and data qualifiers. The QAPP was used to identify data quality indicator requirements and goals, and a checklist was prepared based on the types of data collected. Metals data were reviewed using revised acceptance criteria dated May 22, 2012.

The data packages were reviewed against the checklist by tracing a representative set of the data in detail from raw data and instrument readouts through data transcription or transference through data manipulation (either manually or electronically by commercial or customized software) through data reduction to summary data, data calculations, and final reported data. All calibration and QA/QC data were reviewed for all data packages identified in Table 1. Auditors also reviewed the final data summary (Excel Spreadsheets, " *Pavillion Apr2012 QA Summary v0.xlsx*" and "*Pavillion Apr2012 QA Summary v1.xlsx*") to determine if data had been accurately transcribed from lab summary reports and appropriately qualified based on lab and field QC results.

The critical analytes, as identified in the QAPP (Table 9), are Gasoline Range Organics (GRO); Diesel Range Organics (DRO); Semivolatile Organic Compounds (SVOCs); Volatile Organic Compounds (VOCs, also known as VOAs) of ethanol, isopropyl alcohol, tert-butyl alcohol, naphthalene, benzene, toluene, ethylbenzene, and xylene; major cation potassium, major anion chloride. Note, the VOC analysis performed by Region 8 does not include ethanol, isopropyl alcohol, or tert-butyl alcohol.

Also included in this ADQ are the following analytes: dissolved inorganic and organic carbon; dissolved gases by GC; stable oxygen and hydrogen isotopes of water; low molecular weight

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acids by HPLC; stable carbon isotope ratio of dissolved inorganic carbon, stable carbon and hydrogen isotope ratios of dissolved methane; tritium; MBAS (methylene blue active substance), glycols; ethoxylated alcohols and alklyphenols; acrylamide; methanol, ethylene glycol, and propylene glycol.

Table 1 below summarizes the samples and laboratory analyses reviewed as part of this ADQ Report.

Sample Identification	Laboratory	Analyses (all samples)
PGDW05-0412 PGDW20-0412 PGDW20d-0412 PGDW23-0412 PGDW30-0412 PGDW50-0412 PGPW02-0412 EPAMW02-0412-1 EPAMW02-0412-2	EPA, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center Shaw Lab at Ada, OK	Metals and major cations (calcium, magnesium, potassium, sodium, arsenic, selenium, uranium), headspace analysis of VOC (critical), stable oxygen and hydrogen isotopes of water, low molecular weight acids by HPLC, dissolved gases of methane, ethane, propane and n-butane.
EPAMW01-0412 EPAMW01d-0412	TestAmerica Inc, Savannah Georgia	Methylene Blue Active Substances (MBAS)
EPAMW01-0412-2 EPAMW01-0412-3 EPAMW01-0412-4 EPAMW01-0412-5	Isotech Laboratories, Champaign Illinois	Stable carbon isotope ratio of DIC, stable carbon and hydrogen isotope ratios of dissolved methane, tritium
EPAMW01-0412-6 EPAMW01-0412-7 EPAMW01-0412-8 EPAMW01-0412-9	EPA, Region VIII Golden Colorado	VOCs, SVOCs, GRO, DRO

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EPAMW01-0412-10 Associated Field Blanks, Equipment Blanks, and Trip Blanks	EPA, Region III, Environmental Science Center at Ft. Meade, MD	Glycols
	EPA, NERL, Las Vegas, Nevada	Ethoxylated alcohols and ethoxylated alkylphenols; Alkylphenols; Acrylamide
	RSKERC General Parameters Lab, Ada, OK	DOC, DIC, anions of chloride and sulfate
	ALS Laboratories	methanol, ethylene glycol, propylene glycol

Table 1. Samples and associated laboratories under this ADQ Report.

3. ADQ REPORT CONTENT:

This ADQ report includes the audit approach, the audit results, and the completed ADQ checklist.

4. ADQ RESULTS:

ADQ Definitions

To assist in the interpretation of this ADQ report, the following definitions are provided:

Deficiency – an identified deviation from project QA/QC requirements.

Finding – a deficiency that has or may have a significant effect on the quality of the reported

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results. A corrective action response is required.

Observation – a deficiency that does not have a significant effect on the quality of the reported results. A corrective action response is required.

Additional Comment – an issue that is not a deficiency but may need to be considered to improve or clarify current processes. A corrective action response is not required.

ADQ Summary

The QA/QC requirements specified in the associated QAPP have been met or the data appropriately qualified, with the following exceptions. The completion of appropriate corrective actions will minimize any significant impact to the data summarized for reporting.

Observations

1. **Field and Equipment Blanks, all analyses.** Section 4.1.d of the QAPP indicates that a Field Blank and Equipment blank will be collected on every day of sampling. For all of the analyses reviewed in this ADQ, this requirement was not met. In most cases samples were collected on seven different days, but only 3-4 Field and Equipment (where applicable) Blanks were collected. In addition, the following qualification issues associated with blanks are identified.

    a. The DOC result for samplePGDW05-0412 should be flagged FB due to the associated Field Blank that is not less than ten times the concentration of this sample. It is noted that the associated Equipment Blank was a non-detect.

    b. The total selenium values for several samples (PGDW05-0412, PGDW20-0412, PGDW20d-0412) are less than ten times the associated Field Blanks. These samples should be flagged FB. Also, samples, EPAMW01-0412-10, and EPAMW01-0412, and EPAMW01d-0412 are less than ten times the associated Equipment Blank concentration and should be qualified EB.

    c. The Field Blank and Trip Blanks for dissolved gases. The final summary spreadsheet includes the FB and EB flags for two samples collected on 4/19 and 4/20. It is unclear why these flags have been added since there are no Field or Equipment Blanks for these days.

    Recommended Correction Action. (a) In the summary spreadsheet, qualify all results above MDL for which there is not a corresponding FB and or/ EB. Existing qualifiers do not cover this issue, so a new one may be created. The field crews need to be sure that all field QC samples are collected. Each day of sampling a Field Blank and Equipment Blank are to be collected. How this impacts sample data interpretation needs to be addressed in the Pavillion report QAQC write-up (Appendix B). (b) Flag the samples identified above (for DOC and total Se) with "FB" or "EB" to indicate their values are less than ten times the associated Field Blank value. (c) Remove the FB and EB flags for samples PGDW50-0412

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and PGPW02-0412 for dissolved gases unless these samples are associated with Field Blank and Equipment Blank collected on 4/18/2012 based upon field notes.

Corrective Action Performed.

Groundwater samples were collected on 7 different days. Blank samples were not collected on each of the sampling days. This would have required that an unreasonable number of blank samples be collected. Collecting blanks on each sampling day would have amounted to almost one field and equipment blank per location where a complete sample set was collected (7 field/equipment blank samples to 10 complete field sample sets). It is important to document here the specific factors that controlled our sampling activities, and this deviation from the QAPP. It was originally planned for EPA to begin sampling on 4/16/2012 with the USGS. It turned out that the USGS Sampling and Analysis Plan (SAP) was not ready in time for this coordinated sampling effort, so combined EPA/USGS activities were delayed until the following week on 4/24/2012. Consequently, EPA's activities for sampling of the deep monitoring wells and selected domestic wells stretched over time further than had been originally planned – and this was out of the PI's control. Had we been able to follow the original plan, blanks (equipment and field) would have been collected on each day of sampling where appropriate (over four days).

This deviation from the QAPP will be addressed in the following way. A section in the QA/QC Appendix (Appendix B) will be prepared titled "QAPP Additions and Deviations". In this section, the deviation from collecting overly redundant Field Blanks will be noted. In terms of data flagging, samples collected on days in which no blanks were collected will use the previous blank sample for blank contamination evaluation. For example, samples collected on the 17th (PGDW23 and PGDW30) use the Field and Equipment Blanks collected on the 16th. Samples collected on the 19th and 20th (PGDW50 and PGPW02) use Field and Equipment Blanks collected on the 18th. Field Blanks and Equipments Blanks were collected on all days that the deep monitoring wells were sampled. All sample shipments included appropriate Trip Blanks (see Draft of Appendix B). There is no impact to data quality based on this QAPP Deviation.

In terms of corrective actions for the future, such a deviation from the QAPP should have been confirmed with the QAM and this will be done in any future field trip where this becomes necessary.

A QAPP addition will also be added to Appendix B that describes the time series sampling of MW01. This analysis was not included in the QAPP due to late changes in sampling adopted by the USGS. The plan for time series analysis was developed and documented in an email to QA Manager Steve Vandegrift on 4/12/2012.
Text from Appendix B is included here:

QAPP Additions and Deviations – An important addition was made to the sampling approach for MW01 following the preparation and approval of version 6 of the QAPP. This addition was documented in an email

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(4/12/2012) from a co-PI to the QA Manger overseeing this project. The email text is provided below.

The following is a change to the sampling strategy for MW01. The sampling methodology below supersedes the presentation in the QAPP titled "Ground-Water Investigation in Pavillion, Wyoming" (v6, 2/17/2012, QA ID NO. G-14478).

The USGS-EPA technical workgroup, upon consensus agreement, determined that samples were to be collected at MW01 after attainment of stabilization parameters and after purging one borehole volume. Subsequently, a letter from WYDEQ to USGS provided direction for USGS to additionally remove three casing (now borehole, based on current USGS Sampling and Analysis Plan) volumes prior to sampling at MW01. Thus, two sample collection events, at 1 and 3 borehole volumes, respectively, are currently planned. There should be no expectation that the exact same concentration of various analytes will be observed at both sampling points due to laboratory variability and oscillatory behavior frequently observed in published studies on time series testing during purging. When there is oscillatory behavior, two samples cannot define a trend. Also purge volume may impact observed sample concentrations. Consequently, it is necessary for EPA to conduct a time-series analysis at MW01 to fully characterize expected variability in concentration during purging. Time-series analysis typically involves collection of at least 10 samples over time.

The following approach will be followed by EPA during the April 2012 sampling of MW01.

1) A sample will be collected after purging 1 borehole volume (approx. 410 gallons) and after stabilization of field parameters. This is similar to the approach used during the Phase IV sampling event and the approach was agreed on by the USGS-EPA technical workgroup. This sample will be collected in duplicate (labeled EPAMW01-0412 and EPAMW01d-0412).

2) Samples will be collected after approx. every 90 gallons of continuous purging for dissolved metals (filtered), anions (filtered), water isotopes (filtered), RSKSOP259 (alcohols and volatile organics), and GRO. An identical sampling approach will be utilized as described in the QAPPv6 (same bottles, preservation, storage). Sequential samples will be labeled with -x, e.g., EPAMW01-0412-2 or EPAMW01-0412-5, for the second and fifth sample collected in series, respectively. This series of samples is intended to provide reasonable time-dependent data for major and minor elements as well as organic compounds of interest (e.g., GRO and isopropanol). The water isotope data will useful in evaluating whether significantly different water sources are pulled into the screened during interval during the prolonged purging.

3) After approximately every 270 gallons, in addition to the samples noted in 2) above, samples for glycols, MBAS, ethoxylated compounds, DRO, and SVOCs will be collected for analysis. Again see QAPPv6 for sample collection details. These samples are needed to track time-dependent (volume-dependent) behavior of critical organic analytes.

4) Finally after approx. 3 borehole volumes and stabilization of parameters, a final complete sample set will be collected. This sample will be labeled EPAMW01-0412-10.

After each sample is collected, the time will noted and water volume pumped will be noted in order to correlate the sampling point with geochemical parameters recorded in the purge log and recorded water levels in the well.

Overall this approach was followed in the field, except the order of samples had to be changed in order to deal with unexpected delays in collecting the first sample. See Table C for details about the time series sampling at MW01.

During the course of the field sampling, a deviation occurred from the guidelines discussed in the QAPP. The QAPP stated that field and equipment blanks would be collected on each day of sampling (Table B2). Sampling occurred on seven days from April 16 to April 24. Collecting blanks on each sampling day would have resulted in an unnecessarily large number of blank samples submitted for analysis, and would have amounted to almost one field and equipment blank per location where a complete sample set was collected (7 field/equipment blank samples to 10 field samples). Consequently, field blanks were collected on the 16th, 18th, 22nd, and 24th of

April. Samples collected on April 17th (PGDW23 and PGDW30) are evaluated for blank contamination using blank samples from April 16th. Samples collected on April 19 and April 20 (PGDW20 and PGPW02) are evaluated for blank contamination using blank samples from April 18th. Importantly, field blanks were collected on each occasion that MW01 and MW02 were sampled. Also, Trip Blanks were included in every sample shipment back to the analytical laboratories in accordance with the QAPP guidelines (Table B2). There is no expected impact on data quality stemming from this QAPP deviation.

FB qualifier added to PGDW05-0412 for DOC.

FB qualifier added to PGDW05-0412, PGDW20-0412, PGDW20d-0412. EB qualifier added to EPAMW01-0412-10, EPAMW01d-0412, and EPAMW01-0412. EB qualifier added.

The FB and EB for dissolved gas samples PGDW50 and PGPW02 was added following the approach explained above.

2. **Metals/major cations via ICP-OES.** As outlined in the table below (checklist item 10), not every element that is reported was included in a continuing calibration check (CCC) standard to bracket all samples. It is noted that the second source standard analyzed prior to the samples did contain all reported elements and was within the acceptance criteria, and when the CCC was analyzed it did meet the acceptance criteria. Therefore there are calibration checks that bracket the samples, but in several instances the beginning check is from the second source, not the CC check standards. These checks indicate the instrument was under control, but that the exact SOP requirements were not met with respect to continuing calibration checks.

   The matrix spike samples analyzed by ICP-OES for both the total and the filtered samples for sodium could not be evaluated due to the high sodium concentrations in the samples relative to the spike concentration. For matrix spike samples for filtered samples, one matrix spike for silicon and sulfur could not be evaluated due to the high silicon and sulfur concentrations in the samples relative to the spike concentration. The pre-digestion matrix spike for silver had low recovery, likely due to the lack of HCl acid in the digestion procedure. The post-digestion matrix spike recovery for silver was acceptable.

   Recommended Correction Action. (a) The laboratory needs to be instructed to ensure that the analytical runs include CCCs that brackets all samples with all elements that are reported and the matrix spike combinations needs to include all elements. The laboratory should also be instructed to include a LCS that is spiked at the same level as the matrix spike to allow for evaluations of recovery in instances where sample concentrations are high relative to the spiking concentration. (b) All reported samples need to be flagged J2 due to incomplete CCC frequency for Al, Ag, B, Ba, K, Na, S, Si, and P. (c) Silver needs to be flagged with K2 due to low matrix spike recovery.

   Corrective Action Performed.

   Per email from Steve Vandegrift to Shaw on 7/16/2012, the lab has been instructed to

ensure use of CCCs that bracket all samples for all elements reported. Instructions were also provided to ensure LCS samples.

The following elements (total and dissolved) were flagged as J2: Al, Ag, B, Ba, K, Na, S, Si, and P. Ag (total and dissolved) flagged with K2.

3. **Region 3 Glycols: Quality Controls.** Analyte recoveries for continuing calibration verification (CCV) / blank spikes (BS), MRL samples, fell below the percent recovery limits for low BS 5 ppb analyzed on 4-20-21/2012, low BS 5 ppb analyzed on 5/1-2/2012, low BS 10 ppb analyzed on 5/2-3/2012 and low BS 5 ppb analyzed on 5/2-3/2012. For details about the percent recoveries for the affected analytes, please see #11 below in the ADQ checklist table. Note the quantification limit was raised from 5 to 10 ppb for tetraethylene glycol and trietheylene glycol based on the low blank spike recoveries at the 5 ppb level.

   Matrix Spike 1 and its duplicate (MS1/MSD1) were below the 70-130% limits for all 4 analytes and the RPD was above 25% for 2-butoxy ethanol and triethylene glycol. The laboratory noted these issues and flagged sample results with an "A" in the final report.

   Recommended Correction Action. With respect to the CCV/BS issues, non-detect results for all 4 analytes in samples analyzed on 5/2/2012 and 5/3/12 should be qualified as K2 because of the low recoveries in the BSs (10 and 5 ppb), which are equal to the quantification limit. Therefore, all analytes in the following samples should be qualified as K2 in the final summary spreadsheet: EPAMW01-0412-7 (excluding diethylene glycol due to high detect), EPAMW01-0412-10 (excluding diethylene glycol due to high detect), EPAMW01-0412-4 (excluding diethylene glycol due to high detect) and EPAMW01d-0412 (excluding diethylene glycol due to high detect). The Case Narrative of the lab report recognizes these QC issues and in some cases analytes are J flagged.

   MS1/MSD1 were made from source sample PGDW30-0412. All samples analyzed on the same dates as this MS1/MSD1 (4/20-21/2012) should be qualified as K2 (this includes all 4 analytes) due to the low MS recoveries. Affected samples are: Field Blank 1, Equipment Blank 2, PGDW20-0412, PGDW20d-0412, EPAMW02-0412-1, PGDW23-0412, PGDW30-0412, Field Blank 2, Equipment Blank 2, and PGDW05-0412.

   Corrective Action Performed.

   K2 flags were added as recommended.

4. **DOC MDL Value and qualifiers in the Final Summary Spreadsheet.** The Field Blanks and Equipment blanks in the final summary spreadsheet for DOC use a <0.044 value when the analyte was not detected, this is the MDL for DIC not DOC. The DOC result for sample PGDW05-0412 should be flagged FB due to the associated Field Blank that is not less than ten times the concentration of this sample.

   Recommended Correction Action. Confirm the correct MDL for DOC and incorporate this

in the final data as a <value. Add the FB qualifier to sample PGDW05-0412 in the final summary spreadsheet.

Corrective Action Performed.

MDL for DOC was confirmed and the data sheet was revised with the correct MDL. The FB qualifier was added to samples PGDW05-0412 for DOC.

5. **Stable oxygen and hydrogen isotope ratios of water.** For the stable hydrogen and oxygen isotopes of water: The replicate injections of the oxygen isotopes for sample PGDW20d-0412 just exceeded the limits. The difference was 0.11 ‰ for δ18O, above the criteria of ≤0.1‰. The laboratory report identified this issue and it is believed that rounding is part of the cause to this failure. However, this sample should be qualified in the final summary spreadsheet with a J6.

   Recommended Correction Action. Sample PGDW20d-0412 should be qualified in the final summary spreadsheet with a J6.

   Corrective Action Performed.

   J6 qualifier added to PGDW20d-0412 $\delta^{18}O$ data as recommended.

6. **Stable carbon and hydrogen isotope ratios of dissolved methane.** One laboratory duplicate analysis in Job 17997 of sample EPAMW02-0412-1 exceeded the QAPP Table 10 precision limits of < 3‰ for **δ**DC1 (hydrogen isotopes of methane). The original and duplicate results were -204.6‰ and -208.3‰ respectively with a difference of 3.7‰. During the course of this ADQ, a report on the re-analysis of this sample was received from IsoTech on July 17, 2012. The sample was analyzed twice with a reported value of -209.1‰ and duplicate results of -208.3 and -209.3, well within the precision limits.

   Recommended Correction Action. The reported value in the summary spreadsheet should be updated with this re-analysis value of -209.1‰ .

   Corrective Action Performed.

   A re-issued data report was received from Isotech on 7/17/2012. The revised data for EPAMW02-0412-1 was added to the data summary.

7. **MBAS: Chain-of-Custody, Initial Calibration Information, Second Source Standard.**

   a. For Job Number 680-78755-1, that included only sample PGDW50-0412, the chain-of-

custody (COC) date and time was not completed. The COC does include the name of receiver, their signature, and affiliation as TestAmerica. The case narrative in the report indicates the sample was received on 4/20/2012.

b. The laboratory reports received do not contain initial calibration (ICAL) information. Continuing calibration checks bracket all samples as required. However, there is no information on the ICAL.

c. The QAPP indicates that a second source standard is to be included with the MBAS analysis, with each new calibration (ICAL), and have recovery of 90-110%. No information on a second source standard was provided by the laboratory. In each set of samples a laboratory control sample (LCS) was analyzed and the recovery of that sample was within these limits (90-110%). Also note the recovery of MBAS in the continuing calibration verification standard that was run prior to and bracketing all samples was not reported.

Recommended Correction Action. (a) It should be noted in the Pavillion report QA section, Appendix B that the receiving laboratory did not document date or time received on the COC, but that the data received as noted in their case narrative. (b) Because no second source standard was provided, all results should be qualified J2.

Corrective Action Performed.

The COC section of Appendix B was revised to provide this additional information about sample PGDW50-0412. MBAS data are all flagged as J2 following the recommendation.

8. **Reg 8 VOCs: Second Source Standard Checks.** (a) The initial calibrations were not immediately verified by a second source calibration verification (ICV) standard containing all analytes. Instead, a mixture of SRMs was analyzed after the initial calibrations. Because of the lack of complete ICVs, all sample results are qualified as estimated and are suitable for screening purposes only. The final summary spreadsheet does include the J2 qualifier for these results. Based upon the language in the Region 8 laboratory report it would appear that the J8 qualifier should be applied to all VOC values in the final summary spreadsheet, to indicate these are suitable for screening purposes only. (b) Also, sample EPAMW02-0412-2 was diluted 20x but the QLs were not adjusted to account for this factor.

Recommended Correction Action. (a) It is recommended that the final summary spreadsheet include the J8 qualifier for all VOC analytes, all samples. (b) For sample EPAMW02-0412-2 adjust the QLs for the 20x dilution.

Corrective Action Performed.

The J8 qualifier was applied globally to the Region 8 VOC data as suggested. The suggestion about sample dilution and adjustment of QLs reinforces the need to make

use of the D(value) data flag. The QLs for sample EPAMW02-0412-2 have been adjusted to account for the 20x dilution.

9. **SVOC Qualifiers.** (a) For compound 2,4-dimethylphenol, all flags associated with the samples that did not detect this compound should be U1 (to match all other analytes) in the final summary spreadsheet. (b). The final summary spreadsheet also needs to use the K qualifier for matrix spike related flags, in place of the current J flags for the compounds and samples noted below.

   Recommended Correction Action. (a) Apply the U1 flag in place of the U flag for 2,4-dimethylphenol.

   (b) The following revisions to the final summary spreadsheet are necessary:

   For sample EPAMW02-0412-1, apply the K2 for analytes bis (2-ethylhexyl) phthalate, chrysene, and terpinol, remove the J2 flags.
   For sample EPAMW01-0412, apply the K2 for adamantane and the K1 for phenol, remove the J2 flags.

   Corrective Action Performed.

   All data qualifiers revised as noted. I appreciate the effort here of tracking down these issues and correcting the flags.

10. **GRO.** (a) Two samples were found to be above the pH value of 2 when they arrived at the laboratory: PGDW50-0412 (1204003-18) at pH of 7, and Equipment Blank 4 (1204003-23) at a pH of 5. Sample PGDW50-0412 has been properly qualified in the laboratory report and final summary spreadsheet. However, the final summary spreadsheet needs to include the J9 flag for the Equipment Blank 4. Equipment Blank 4 was analyzed within seven days of collection, meeting the holding time requirement for an unpreserved sample. (b). Sample EPAMW02-0412-2 was analyzed at a 10X dilution for gasoline TPH. The "D(10)" flag should be added to the final summary spreadsheet.

    Recommended Correction Action. (a) Qualify Equipment Blank 4 with the J9 flag. Remind the sampling crew to double check the pH value of the samples in the field after they have been acidified to ensure they reach the proper preservation range. (b) Add the "D(10)" flag to the GRO value for sample EPAMW02-0412-2.

    Corrective Action Performed.

    The J9 flag was added to sample EquipBlk04 for GRO. The D(10) flag was added to sample EPAMW02-0412-2 for GRO. We will continue to strive for 100% efficiency in acidifying samples.

11. **Low MW Organic Acids.** (a) The lab IDs appear to be wrong in the lab report for PGDW05-0412 (lab ID should be 6511-04, not 6507-4) and EPAMW01-0412-10 (lab ID should be 6521-14, not 6125-4). (b) The field duplicate pair for EPAMW01-0412 was above the 30% RPD limits for acetate and formate, note that the lab dup for this same sample was below 15% so this may be a associated with true variation in the field samples. (c) The value for formate in sample PGDW20-0412 in the final summary spreadsheet should be 1.69 (not 1.63). (d) EPAMW02-0412-2 arrived broken. A sample designated for VOA analysis was used as a substitute as directed by the PI, Dr. Wilkin. VOA samples were preserved with TSP, low molecular weight acid samples with NaOH. This sample should flagged J3 and J9. EPAMW02-0412-2 chromatogram appears questionable due to baseline issues.

Recommended Correction Action. (a) The lab IDs should be corrected as mentioned above in the final lab reports (note this does not affect final summary spreadsheet). (b) The J7 qualifiers on samples EPAMW02-0412-1, EPAMW02-0412-2 and EPAMW01-0412-10 should be removed from final summary spreadsheet, since these samples were not part of a field duplicate pair that exceeded the QAPP requirements. (c) Correct the final summary spreadsheet value for formate in sample PGDW20-0412 to read 1.69. (d) EPAMW02-0412-2 should be flagged with J3 and J9 as the original sample arrived broken and the VOA sample that was substituted wasn't preserved for low molecular weight acids per QAPP requirements. This same sample exhibited baseline problems during analysis. There is not an appropriate flag for baseline problems with a sample analysis. This should be addressed in the Pavillion report QA section (Appendix B).

Corrective Action Performed.

An email was sent on 7/20/2012 from the QAM to Shaw requesting the specific lab IDs to be corrected as pointed out in (a). The J7 qualifiers were removed on the identified samples as suggested. The formate value for PGDW20-0412 was corrected to 1.69 mg/L. J3 and J9 flags were added to EPAMW02-0412-2. The need for additional data qualifiers is noted in Appendix B in the section discussing data qualifiers and their use.

12. **Total Metals by ICP-MS.** (a) Total lead and thorium were above the quantitation limits (QL) in the digestion blank. Lead was 0.274 µg/L and thorium was 0.076 µg/L. Samples with detected amounts that are less than 10x the blank concentration should be flagged LB. (b) Samples analyzed initially with a report date of 5/14/12 were not analyzed using the CCT-KED, ICS (Interference Check Standards), LLICV (Low Level Initial Calibration Verification), or LCS (Laboratory Control Sample). But, the samples were re-analyzed for As, Cr, Cu, Ni, and Se (report date 6/11/12) as directed by the PI, to include method revisions which incorporate corrective actions from recent ADQs that address implementation of these QC checks.

Recommended Correction Action. (a) Samples with detected amounts of lead and thorium concentrations that are less than 10x the concentrations in the digestion blanks should be flagged with LB. (b) Sample results for Cd should be flagged with K3 as they were not included in the re-analysis. Sample results for Cd, Hg, Pb, Sb, Th, Tl, and U should be flagged with J2 as these were not re-analyzed using the QC checks described above.

Corrective Action Performed.

Recommended qualifiers added.

13. **Microwave Digestion, Parameters for Total Metals.** The temperature ramp and hold conditions of the microwave digestion plots for a sample was compared to the Standard Operating Procedure RSKSOP-179 Revision 3, September 2011. Section 9.5 of the SOP provides the quality assurance metrics: maximum allowable deviation of the temperature by no more than 15% after ramp up, and before the end of digestion. Appendix A of this SOP provides the parameters (AQ9XPRESS): ramp for 10 minutes, to 170 Celsius, 100 psi, hold for 30 minutes at that temperature. The time versus temperature ramp that was reviewed indicates the temperature of 170 Celsius takes approximately 15 minutes but that once achieved the temperature stays within approximately 10 degrees Celsius (6%). While the digestion met the SOP requirement of +/-15%, EPA Method 3015A requires a maximum allowable deviation of +/-5 degrees C. EPA Method 3015A also requires preparation of an LCS, spiked at the same level as the pre-digestion matrix spike. Section 6.1.2 of this EPA Method also requires that the accuracy of the temperature measurement system should be periodically validated at an elevated temperature, and it describes a procedure for doing so. The laboratory has not incorporated these elements of 3015A into their SOP.

    Recommended Correction Action. (a) The EPA should instruct the laboratory to incorporate all QC and operational requirements of EPA Method 3015A into the laboratory SOP. (b) It is recommended that the total metals results be flagged with J2.

    Corrective Action Performed.

    Shaw's metals lab will be instructed to revise RSKSOP179v3, in particular, to insure that LCS samples are included with every batch of samples run through digestion.

    Several points are made about the digestion of this sample set: (1) ramp time took approximately 15 minutes, (2) once at 170°C the temperature stayed within approximately 10°C as opposed to ±5°C, (3) the requirement of a LCS, and (4) periodic system checks of temperature and pressure controls. These points are addressed here. It is important to note that these comments are in reference to Method 3015A. Method 3015A, like all SW-846 methods, is intended to provide guidance, by providing general methodology and information on how to conduct an analytical procedure or technique. Method 3015A should serve as a starting point for the development of lab-specific SOPs, like RSKSOP179.

    Method 3015A states that the "temperature of each sample should rise to 170°C ±5°C in *approximately* (ital added) 10 minutes and remain at 170°C for 10 min, or for the remainder of the 20-min digestion period" (section 11.3.5). So it is clear that the 10 min ramp time is not fixed, nor should it be, as this variable has little to do with method performance. I do not believe that this was being singled out as a critical issue in this

Observation. Note that RSKSOP-179 maintains temperature for a longer period than the 10 min recommendation in 3015A. This is desirable in order to maximize the acid digestion of any particulate materials in the samples, which is the primary goal of the digestion.

It is difficult to quantitatively evaluate temperature trends from the printout of T versus time for this run. So the evaluation presented in the Observation comments above may be reasonable. I constructed 5°C intervals around the 170°C isotherm. Analysis indicates that after about 15 minutes, temperature stayed within the 170°±5°C envelope approximately 90% of the time between 15 and 40 minutes of digestion, or temperature was out of the envelope (and just barely) for 2.5 minutes. So for about 22.5 minutes the recommended temperature envelope was attained. This exceeds extraction guidance provided in 3015A.

The issue about the LCS is significant and the laboratory has been instructed to run LCS samples with each digestion batch. Method 3015A states in section 9.3.2 "laboratory control sample (LCS) should be included with each analytical batch....When the results of the matrix spike analysis indicate a potential problem due to the matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix." So it is clear that the guidance provided in 3015A requires the LCS (or some other control) in situations where matrix spike problems are encountered. Matrix spike problems are noted for Na and S in this data set. Spiking concentrations were too low, relative to sample concentrations, to provide meaningful results for these elements.

In section 6.1.2, Method 3015A states that "The accuracy of the temperature measurement system should be periodically validated at an elevated temperature". A method is provided that can be used for this purpose. The Shaw instrument is serviced on an annual basis. It is our understanding that this annual service verifies temperature and pressure accuracy and control. The QAM is working to establish that this is in fact the case, and that function performance was verified during the last service date.

In summary, RSKSOP179 will be revised, for example, to address LCS samples and to provide critical documentation about annual services. Because, Na and S were not adequately evaluated with the matrix spike, these elements require the J2 qualifier (in addition to the qualifier noted in Observation 2 above). This issue will be presented in the QA/QC Appendix as an additional factor affecting total Na and total S concentrations. Note additional data qualifiers may be necessary pending information that is anticipated from the outfit that provides annual service on the instrument.

14. NERL Analyses: COC, Holding Times, QC sample results.

a. **Chain-of_Custody.** The COCs indicate that samples PGDW23-0412 and EPAMW02-0412-1 were sent to the laboratory on two different days. Review of the file labeled *1 Samples Received log.pdf* shows the first sample listed above as being collected on 4/17 and arriving at the laboratory on 4/18 and then in a separate COC

being sampled on 4/17 at the same time (11:45 am) but arriving at the laboratory on 4/24. Sample EPAMW02-0412-1 is also on this second COC where the samples arrive on 4/24. Yet this sample is also listed on the COC where the samples arrive at the laboratory on 4/18. This sample has two different sampling dates and times: 4/16 at 2:50 pm and 4/18 at 2:30 pm.

Recommended Correction Action. Review the COCs and identify if the samples are incorrectly labeled or were sent on two different occasions.

Corrective Action Performed.

Samples PGDW23-0412 and EPAMW02-0412-1 were collected on 4/17/2012 and 4/16/2012, respectfully, for analysis of ethoxylates, alkyphenol, octylphenol, and acrylamide. These samples were shipped on 4/17/2012 and arrived at the NERL/Las Vegas lab on 4/18/2012. The NERL/Las Vegas lab requested additional sample from MW02. This additional sample from MW02 was collected on 4/18 and delivered on 4/24; the sample was for other purposes not related to this study. In addition, the NERL/Las Vegas lab requested additional samples from one of the domestic wells. I selected to provide additional samples from PGDW23; these samples were sent on a different day than the primary samples for which analyses were requested (ethoxylates). Again these samples were requested by NERL/Las Vegas for other purposes not related to this study. The COCs appear to be correct.

b. **Holding Times.** The extraction logs indicate some samples extracted on 5/21 were collected on 4/16/2012 (PGDW20-0412, EquipBlk01) – past the 30 day holding time. Similarly, samples collected on 4/16/2012 (EPAMW02-0412-1), 4/18 (PGDW23-0412) and 4/24 (EPAMW01-0412-7) were extracted on 6/1/2012 – past the 30 day holding time. All three analytical methods have a 30-day holding time period. A holding time should also be established between the extraction date and the analysis date.

   Recommended Correction Action. The J5 flag should be added to the final summary spreadsheet for samples PGDW20-0412, Equipment Blank 1, EPAMW02-0412-1, PGDW23-0412, and EPAMW01-0412-7 due to the extraction past the 30-day holding time. This applies to ethoxylates, alkylphenols, and acrylamide.

   Corrective Action Performed.

   The J5 flag was not added to all the noted samples/analytes as recommended because many of these data have been rejected, R-flagged. These points, however, will be added to Appendix B as additional reasons that impact data quality. J5-qualifiers were added to data for nonylphenol, octylphenol, and acrylamide. However, based on observations noted below, data for these analytes have also been rejected. Note too that following issue (c) below,

C15EOx results are now rejected. I will follow up with QAM to see if these were re-extractions after a primary extraction, and if data from the 5/21 extraction were in fact the ones reported.

c. **Ethoxylates, QC Issues.** A number of QC samples did not meet the QAPP requirements. All data were rejected by the PI with the exception of C15EOx. Based upon the multiple instances of low recoveries of the fortified blanks and matrix spikes, the laboratory stated, "… the quantitation values for the ethoxylated alcohols should not be considered more than estimates of the actual values."

For this analyte group (C15EOx), the following QC did not meet the QAPP requirements: 63% recovery for the laboratory fortified blank extracted 4/20/2012, 144% recovery for the fortified blank extracted 5/7/2012, 12% recovery for the matrix spike of sample PGDW20-0412 extracted 4/25/2012, 28% recovery for the matrix spike of sample PGDW20d-0412 extracted 4/25/2012, 180% recovery of the matrix spike of sample EPAMW02-0412-2, negative 1.8% recovery for the matrix spike of sample EPAMW01-0412.

Also, no laboratory-fortified blank was analyzed on 4/30/2012. However multiple matrix spike samples were analyzed on this date along with the required calibration checks. The samples associated with this analytical batch include: samples PGDW30-0412, Field Blank 02, Equipment Blank 02, PGDW05-0412 and matrix spike of samples PGDW20-0412, PGDW20d-0412, PGDW23-0412. Matrix spike recoveries for these samples are shown in in the paragraph above.

Recommended Correction Action. Qualify all C15EOx results with a J2 due to the lack of the laboratory-fortified blank for some samples and due to the systematic failure of the laboratory-fortified blank in multiple occasions. Also, qualify C15EOx results with a K2 in the following samples due to low recovery of the matrix spikes: PGDW20-0412, PGDW20d-0412, EPAMW01-0412; and K1 to sample EPAMW02-0412-2 due to the high matrix spike recovery. It is recommended that the results for C15EOx be qualified J8, based upon the multiple QC issues identified in this review and by the laboratory.

Corrective Action Performed.

This additional review persuades me to reject C15EOx data. This will be explained in the QA/QC Appendix B. The R qualifier has been added to all samples for C15EOx.

d. **Acrylamide, laboratory-fortified blank:** No laboratory-fortified blank was analyzed with the batch on 5/1/2012, the QAPP specifies one is to be analyzed with each batch. The batch did include a full initial calibration and continuing calibration verification and a number of sample matrix spikes. The concentration of the spike solution is not clear from the run logs; therefore matrix spike

recovery values are not known for those samples. The samples associated with this analytical batch include: samples PGDW30-0412, Field Blank 02, Equipment Blank 02, and PGDW05-0412; matrix spike of samples PGDW20-0412, PGDW20d-0412, PGDW23-0412 and PGDW05-0412.

Recommended Correction Action. Qualify samples PGDW30-0412, Field Blank 02, Equipment Blank 02, and PGDW05-0412; matrix spike of samples PGDW20-0412, PGDW20d-0412, PGDW23-0412 and PGDW05-0412 with a J2 for the due to lack of the laboratory-fortified blank. Have the laboratory provide the spike concentration and matrix spike recovery values for all samples. Additional flagging may be necessary upon receipt and evaluation of the matrix spike recoveries.

Corrective Action Performed.

J2 qualifiers added. We will follow up with QAM to receive additional information from the NERL/Las Vegas lab. Note R flags have been used.

e. **Alkylphenols, spike recoveries.** The matrix spike recovery of sample PGDW20-0412, which was extracted and analyzed in triplicate, had values of 69%, 63% and 58% for nonylphenol, these are below the QAPP limits of 70%. One laboratory-fortified blank sample for nonylphenol (NP) had a recovery of 64%. This QC sample is associated with the majority of the samples. A second laboratory-fortified water sample, spiked at a higher concentration apparently, was also included. However, the spike concentration of this second laboratory-fortified water sample is not clear in the report. All samples should be qualified K2 based upon the low recovery of NP.

Also, the final text report provided with the samples results is consistent with the final summary spreadsheet. However, the intermediate values differ slightly for sample EPAMW02-0412-1 nonylphenol is reported at a value of 28 ug/L. The laboratory spreadsheet provided with the report shows values of 37.6 and 48.3. Octylphenol is reported at a value of 2.9 ug/L for this same sample but this same laboratory spreadsheet has values of 3.133 and 3.434. All other spreadsheet values match the test report and final summary spreadsheet.

Recommended Correction Action. All samples should be qualified K2 based upon the low recovery of NP in the laboratory-fortified blank. This K2 also will signify the low matrix spike recovery of NP in sample PGDW20-0412. Have the laboratory provide the spike concentration and recovery values for all samples. Have the laboratory explain the differences noted between the final report values and the raw data values for sample EPAMW02-0412-1. Additional flagging may be necessary upon receipt and evaluation of the matrix spike recoveries.

Corrective Action Performed.

EPAPAV0037027

It was my original intent to retain the alkylphenol data. However, based on these ADQ observations as well as the missed extraction holding times and blank contamination, it is my current view that these data should be rejected as well. Nonylphenol and octylphenol data are rejected. If additional information is received by the QAM that clarifies some of these issues, the data qualifier could be revisited in the future, but only with new information.

f. **Alkylphenols, calibration range.** The initial calibration range highest level was 1.00 ng/ul. The matrix spikes were in general at 1.00 ng/ul and several samples are reported at values above this for both analytes. Review of the raw data files indicates that for octylphenol, the sample area count was below the highest standard. However the internal standard areas for samples EPAMW02-0412-1 and EPAMW02-0412-2 do exceed those in the standards. Sample EPAMW02-0412-1 had nonylphenol area counts that exceed the highest calibration standard. It is not clear that the samples were diluted and re-analyzed; therefore it appears that the values for samples EPAMW02-0412-1 (both analytes) and octylphenol for sample EPAMW02-0412-2 are above the calibration range.

Recommended Correction Action. Qualify the results for NP and OP in these two samples with a J2, unless the laboratory can confirm they were diluted so that both the analyte area count and internal standard area count were within the calibration range and acceptance limits.

Corrective Action Performed.

See response to (e) above. This observation will be pointed out in the QA/QC Appendix B summary.

EPAPAV0037029

ADQ Checklist					
Number	**ADQ Issue**	**Yes**	**No**	**NA**	**Comments**
Sample Information					
1	Are samples uniquely identified and their identification correctly transcribed throughout the data package to the summary of results?	Yes*, except for low molecular weight acids.			**Low MW Organic Acids:** The lab IDs appear to be wrong in the lab report for PGDW05-0412 (lab ID should be 6511-04) and EPAMW01-0412-10 (lab ID should be 6521-14). These should be corrected in the final lab reports (does not affect final summary spreadsheet). **EPA NERL:** The COCs indicate that samples PGDW23-0412 and EPAMW02-0412-1 were sent to the laboratory on two different days. Review of the file labeled *1 Samples Received log.pdf* shows the first sample listed above as being collected on 4/17 and arriving at the laboratory on 4/18 and then in a separate COC being sampled on 4/17 at the same time (11:45 am) but arriving at the laboratory on 4/24. Sample EPAMW02-0412-1 is also on this second COC where the samples arrive on 4/24. Yet this sample is also listed on the COC where the samples arrive at the laboratory on 4/18. This sample has two different sampling dates and times: 4/16 at 2:50 pm and 4/18 at 2:30 pm.
2	Does sample collection documentation indicate that samples were collected as described in the QAPP, and the schedule and volumes in the planning documentation?	Yes, with the exception of Field and Equipment Blanks that were not collected on every day of sampling.			**All Analyses:** A Field Blank, and in some cases an Equipment Blank, was not collected each day of analysis. This applies to all analytical suites to some extent. For example, only 3 equipment blanks were