PTR-MS MOBILE LABORATORY VAPOR MONITORING MONTHLY REPORT – MONTH 11

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Acronyms and Abbreviations

ASTM	ASTM International
COPC	Chemical of Potential Concern
DEF	Diesel Exhaust Fluid
DR	Deficiency Report
EEGA	Engine Exhaust Group A
EEGB	Engine Exhaust Group B
GC/MS	Gas Chromatograph – Mass Spectrometer
GPS	Global Positioning System
HPLC	High Performance Liquid Chromatograph
MA	Methanol Group A
MDL	Method Detection Limit
ML	Mobile Laboratory
NDEA	N-Nitrosodiethylamine
NDMA	N-Nitrosodimethylamine
NIOSH	National Institute for Occupational Safety and Health
OEL	Occupational Exposure Limit
PTR-MS	Proton Transfer Reaction – Mass Spectrometer
PTR-TOF	Proton Transfer Reaction – Time of Flight
RL	Reporting Limit
SME	Subject Matter Expert
TOF-MS	Time of Flight – Mass Spectrometer
VOC	Volatile Organic Compound

Executive Summary

In support of the Hanford Vapor Monitoring, Detection, and Remediation Project, Washington River Protection Solutions, LLC has subsidized the implementation of a mobile vapor monitoring laboratory developed by TerraGraphics Environmental Engineering, Inc. (Statement of Work #306312, "Mobile Laboratory Services and Lease"). The contract secures services associated with the lease and operation of the Mobile Laboratory designed specifically for trace gas analysis based on the Proton Transfer Reaction – Mass Spectrometer and supplemental analytical instruments. Operation of the Mobile Laboratory will be at the discretion of Washington River Protection Solutions, LLC, and will be conducted to support a variety of projects including continuing background studies, fugitive emissions, waste-disturbing activities, leading indicator studies, and general area sampling. Other applications of the Mobile Laboratory will be determined as needed by Washington River Protection Solutions, LLC.

This report covers operations and testing activities from August 1, 2019, through August 30, 2019.

During Month 11, Mobile Laboratory Operators performed testing, maintenance, modifications, verifications, calibrations, and received continuous training on the Mobile Laboratory instrumentation.

For the remainder of Month 11, the Mobile Laboratory Operators performed area monitoring around the 200 East and 200 West Area in order to collect data on the concentrations of chemical vapors downwind of potential sources. This included the monitoring of AP-106 to AP-102 Waste Transfer, AP-106 Rinse and Flush, and support of Washington River Protection Solutions LLC's Fugitive Emissions Team.

1.0 DESCRIPTION OF TESTS CONDUCTED

During Month 11, spanning the dates of August 1, 2019, to August 30, 2019, the Mobile Laboratory (ML) was deployed for the measurement of Volatile Organic Compounds (VOCs) after ML maintenance, modifications, operational testing, and continuous training were performed.

Description of activities that were conducted are as follows:

- Week 52
 - Area Monitoring
 - ML Testing
- Week 53
 - Area Monitoring
 - ML Testing
- Week 54
 - Area Monitoring
 - ML Testing
- Week 55
 - Area Monitoring
 - Fugitive Emissions
 - ML Testing and Maintenance
- Week 56
 - Area Monitoring
 - ML Testing and Modifications

2.0 MEASUREMENT SYSTEM DESIGN

This section describes the sampling methods, instrumentation, and confirmatory measurements used during this monitoring period.

2.1 Sampling Methods

2.1.1 Design of Sampling System

The ML is housed in a Chevrolet^{®1} 4500 14' Box Truck equipped with a 5.2L diesel engine. The box has been fully insulated to allow for the ML to maintain comfortable working temperatures for the Operators and the instrumentation. The ML has the option of utilizing either shore power or onboard diesel generator power for operation of the instruments. During Month 11, while the ML was located at the TerraGraphics warehouse in Pasco, WA, shore power was utilized. The ML was powered by the generator at all deployed locations during Month 11. When deployed for monitoring, the ML used both the mast and the side port to perform air sampling.

The layout of the ML and the sampling system is shown in the following drawings:

- 66409-18-ML-003, *Sampling Manifold Sketch*; and
- 66409-18-ML-004, *Mobile Lab Schematics*.

2.1.2 Proton Transfer Reaction – Mass Spectrometer Sampling

Proton Transfer Reaction – Time of Flight (PTR-TOF) 6000 X2 is the latest trace VOC analyzer from IONICON^{® 2}.

The PTR-TOF 6000 X2 is used to quantify chemicals of potential concern (COPCs) from the sampled air. The sampled air enters the PTR drift tube. In the drift tube, VOCs undergo chemical ionization via a fast proton transfer reaction using the reagent ion, hydronium. The hydronium is produced from water vapor via a series of reactions in the hollow cathode PTR ion source. This is a soft ionization method and VOC fragmentation is minimized. These ionized compounds and hydronium ions then travel through the drift tube to the transfer lens system, subsequently entering the Time of Flight – Mass Spectrometer (TOF-MS) where they are separated by mass and monitored. The signal from the TOF-MS is used to identify the VOCs based on their mass, as well as to calculate individual compound concentration based on the ratio of compound signal to hydronium signal.

¹ Chevrolet is a registered trademark of General Motors, LLC, Detroit, Michigan.

² IONICON is a registered trademark of Ionicon Analytik Gessellschaft m.b.H., Innsbruck, Austria.

2.1.3 DAQFactory Sampling

DAQFactory^{®3} is a data acquisition and automation software from AzeoTech that allows users to design custom applications with control and automatic output settings. In the ML, DAQFactory controls the sampling system through valves and flow controllers for the LI-COR^{®4} CO₂ monitor, Picarro Ammonia Analyzer, Airmar^{®5} Weather Station, and the PTR-TOF.

2.2 Instrumentation and Methods Used

2.2.1 Proton Transfer Reaction – Mass Spectrometer

Measurements performed by the ML during Fiscal Year 2019 utilized the IONICON PTR-TOF 6000 X2 system. The mass resolution of the PTR-TOF 6000 is sufficient to resolve some COPCs with high confidence (i.e., furan from isoprene) while other compounds have interferences which can potentially compromise their reliable detection and quantification. A full discussion of the reliability of COPC detection and quantification as performed by a PTR-TOF 4000, an instrument with less resolution, can be found in *Fiscal Year 2017 Mobile Laboratory Vapor Monitoring at the Hanford Site: Monitoring During Waste Disturbing Activities and Background Study*, September 2017. A brief summary of the instrument and its underlying chemistry that leads to the sensitive detection of vapor components will be provided herein. The general layout of the instrument is shown in Figure 2-1.



Figure 2-1. The General Configuration of an IONICON Proton Transfer Reaction – Time of Flight Instrument.

³ DAQFactory is a registered trademark of AzeoTech, Inc., Ashland, Oregon.

⁴ LI-COR is a registered trademark of LI-COR, Inc., Lincoln, Nebraska.

⁵ Airmar is a registered trademark of Airmar Technology Corporation, Milford, New Hampshire.

The VOCs are measured by chemical ionization, where the reagent ion H_3O^+ ionizes organics via a fast proton transfer reaction (R1).

$$R + H_3O^+ \rightarrow RH^+ + H_2O \tag{R1}$$

These reactions are normally non-dissociative, although there are some compounds that fragment to smaller ions upon protonation. The reaction takes place in a drift tube where the sample air stream reacts with H_3O^+ ions produced by a hollow cathode ion source. The number of ions counted per second for the reagent ion and protonated sample ion are monitored and used for the determination of estimated concentrations according to Equation 1.

$$[R] = \frac{1}{kt} \left(\frac{I_{RH+}}{I_{H3O+}} \right) \frac{\varepsilon_{RH+}}{\varepsilon_{H3O+}}$$
(1)

where k is the ion–molecule rate constant (molecules cm⁻³ s⁻¹), t is the reaction time (~ 100 microseconds), I_{RH+} and I_{H3O+} are the respective ion count rates, and \mathcal{E}_{RH+} and \mathcal{E}_{H3O+} are the ion transmission efficiencies through the TOF. It is important to note that estimated concentrations of compounds can be determined directly from Equation 1 (the "kinetic approach" to quantification). There is no need for the analysis of authentic standards and the generation of calibration curves. The system is essentially self-correcting as all measurements are made with respect to the ion count rate of the reagent ion.

The mixing ratio *X* of the organic R in the sample air is then determined by:

$$X_R (ppbV) = \frac{[R]}{[AIR]_{drift}} \times 1 \times 10^9$$
⁽²⁾

where [AIR] is the number density of air (molecules/cm³) in the drift tube given the drift tube pressure (typically ~ 2.4 mbar) and temperature (typically ~ 50°C).

The Proton Transfer Reaction – Mass Spectrometer (PTR-MS) technology has been used in numerous applications around the world with hundreds of peer-reviewed publications appearing in the literature over the past 20 years. Even though the technology is widely used in the research arena and has proven to be indispensable for many applications, there is no standard method among the United States regulatory agencies such as the U.S. Environmental Protection Agency, American Society for Testing and Materials (ASTM^{®6}), and National Institute for Occupational Safety and Health (NIOSH^{®7}). The end user of the technology is expected to provide the "best practice" in its use by adhering to established operational parameters governed by the scope of the project and the nature of the sample(s) to be measured.

⁶ ASTM is a registered trademark of American Society of Testing and Materials, West Conshohocken, Pennsylvania.

⁷ NIOSH is a registered trademark of U.S. Department of Health and Human Services, Bethesda, Maryland.

The kinetic approach provides quantitative estimates based on the use of relative ion signals of target compounds versus that of the reagent ion with an applied reaction rate constant found in the literature. This approach was chosen over the use of calibration standards due to the challenges associated with obtaining stable calibration mixtures for the Hanford COPC list. All quantification performed in Month 11 was accomplished by the kinetic approach.

2.2.2 Carbon Dioxide Monitor

Carbon dioxide is not a COPC; however, monitoring CO₂ is necessary for correlation of vapor signals to combustion processes or other sources. There are numerous combustion sources near the sampling sites of the background study including diesel and gas generators, all-terrain vehicles with no catalytic converters, and diesel and gasoline vehicles. These contribute VOCs to the vapor burden and are readily observed by the PTR-MS. It is necessary to distinguish these VOCs from tank farm related emissions resulting from normal work-related activities.

The CO₂ monitor used in the TerraGraphics ML was the LI-COR Model 840A. The Li840A is an absolute, non-dispersive infrared gas analyzer based upon a single path, dual wavelength infrared detection system. It is a low-maintenance, high performance monitoring solution that gives accurate, stable readings over a wide range of environmental conditions. It has a range of 0-20,000 ppm (0-2%), low power consumption (4W after power-up), and 1-second signal averaging to allow for real-time source apportionment (i.e., monitoring vehicle exhaust or other combustion sources on the fly). The instrument operates on a gas flow of less than 1 liter per minute.

It is interfaced to the ML's internal gas manifold at the same location as the PTR-MS sampling port to ensure that both instruments are simultaneously measuring the same source. The data from the CO₂ monitor are used to predict when VOC measurements from the PTR-MS come from combustion sources.

The CO₂ monitor used during Month 11 was operated using a factory calibration. Periodic checks of the unit were made with zero-air and ambient background air [ambient atmospheric CO₂ levels are approximately 400 parts per million by volume (ppmv)], and a certified reference standard to ensure continued system operation. The system has a continuous direct readout which can be displayed on the DAQFactory monitor in real time to aid in real-time decision making by the field analysts.

2.2.3 Ammonia Monitor

Ammonia is a compound on the COPC list of particular importance. It is believed to be associated with all high-level waste storage tanks on the Hanford Site. The global average background for ammonia is between 5-7 parts per billion by volume (ppbv). Previous studies of ammonia levels on the Hanford Site indicate the expected measurement range should be in the low ppbv range. Although relatively easy to measure at the parts per million by volume (ppmv) level, its measurement at the low ppbv level with high temporal resolution is not trivial. The purpose of measuring trace levels of NH₃ is the correlation of vapor data from the PTR-MS to

actual tank emissions. A measured vapor plume containing elevated COPCs with the same time correlation as an ammonia plume is reasonable evidence of a tank emission.

The ammonia monitor used was a Picarro model G2103 that is capable of measuring NH₃ with parts per trillion by volume (pptv) sensitivity. It is a sophisticated time-based measurement system that uses a laser to quantify spectral features of gas phase molecules in an optical cavity. It is based on cavity ring down spectroscopy. Gas phase spectroscopy measurements are subject to temperature and pressure fluctuations. The Picarro system features a $\pm 0.005^{\circ}$ C temperature stability and ± 0.0002 atm pressure stability to ensure low noise and high accuracy measurements. Sample flow rate to the instrument was provided by an external pump at 0.8 liters per minute at 760 Torr.

The analyzer is interfaced to the ML main sample stream to ensure the instrument measured the same gas sample as the PTR-MS and CO_2 monitor. The system outputs real-time data to a monitor, records data to its internal computer, and uses the ML Wi-Fi connection to automatically synchronize to a clock service. Daily data sets are retrieved and backed up similar to the other data collection instruments.

2.2.4 Weather Station

The weather station used in the ML is an Airmar 200WX-IPx7 with a control unit mounted in the server cabinet and the transducer mounted on the sampling mast located above the roof of the van. Real-time display of the output is visible on the DAQFactory monitor to aid field analysts in making sampling decisions in the field. The output data are fed to the server with a clock time-stamp that is synchronized to the other monitoring systems in the laboratory. The functions and outputs of the station include:

- Apparent wind speed and angle,
- True wind speed and angle,
- Air temperature,
- Barometric pressure,
- 2D Magnetic compass heading,
- Heading relative to true north, and
- Global positioning system (GPS).

The weather station transmitted data continuously at 2-second intervals to DAQFactory.

2.3 Confirmatory Measurements (if applicable)

Although PTR-MS has exceptional response time, sensitivity, and is an excellent instrument for quantification, it suffers from the inability to make qualitative determinations of complex

samples. Alternate analytical methods can provide important supporting evidence of the qualitative assignments made while interpreting the PTR-MS data as well as quantification validation of some COPCs. The Gas Chromatograph – Mass Spectrometer (GC/MS), High Performance Liquid Chromatograph (HPLC)/MS/MS, HPLC and GC methods used to support and confirm PTR-MS were performed using well-established methodology by accredited laboratories. Within the context of this month, one confirmatory method was utilized, EPA TO-17, "Volatile Organic Compounds," modified.

The ML has an onboard confirmatory sample collection system that allows up to four samples to be collected simultaneously through the same sampling inlet used by the PTR-MS and the other analytical equipment in the truck. This allows the ML Operators to collect co-located confirmatory samples simultaneously with the PTR-MS, carbon dioxide, and ammonia analyzer.

Commercially available traditional laboratory analytical techniques do not analyze for a large number of COPCs. Every attempt was made to find laboratory subcontract support for as large of a number of the COPCs as possible. However, in most cases, it was not feasible or possible for laboratories to analyze for the majority of the COPCs. In total, ten COPCs were analyzed quantitatively using valid confirmatory method full calibrations. Two more COPCs, furan and acetonitrile, were analyzed for tentatively identified compounds.

3.0 CALIBRATION METHODS AND CALIBRATION GASES USED

Table 3-1, shown below, highlights the type, identification number, and expiration date for each gas standard cylinder employed by the ML for calibration and testing purposes during Month 11.

Cylinder	ID#	Exp. Date
Carbon dioxide	77-401243203-1	07/13/2026
Ammonia	THBJ-14-50-3	07/10/2021
Zero-air	Lot #: 2191061	04/16/2020
Zero-air	Lot #: 2191762	06/25/2020
VOC	160-401380144-1	01/16/2020

 Table 3-1. Calibrated Gases in Use During Month 11.

During periods of deployment, Mobile Laboratory personnel operate under Report No. 66409-RPT-004, *Mobile Laboratory Operational Procedure*, which states that at least once during the scheduled shift, ML Operators shall perform a user-initiated zero-air and span check on the LI-COR, Picarro, and PTR-MS instruments. If a zero-air or span check fails, the ML Operators are instructed to inform the WRPS Project Manager, TerraGraphics Senior Scientist/Subject Matter Expert (SME), TerraGraphics Quality Assurance Representative, and TerraGraphics Project Manager. In the event that any recorded result in the procedure fails to conform to the acceptance criteria listed, the Quality Assurance Representative is notified, and the steps outlined in TG-DOE-QAP-002-1502, "Control of Nonconforming Processes," are followed.

Zero-air checks performed on each of the ML instruments allow a zero-point measurement to be recorded prior to initiation of the span check. Zero-air checks ensure no contamination or interferences have affected the instrument's readings.

Table 3-2 through Table 3-7 display the zero-air and span checks performed daily during Month 11. Table 3-4 and Table 3-5 show zero-air and span checks based on toluene (methyl benzene, 92.14 g/mol).

Date	Time	Instrument Check	Observed Result (ppmv)	Expected Result(ppmv)	% Difference	Acceptance Criteria (%)	Pass/Fail
08/01/2019	05:59	Zero	-5.9	<50	N/A	N/A	Pass
08/05/2019	05:32	Zero	-8.9	<50	N/A	N/A	Pass
08/06/2019	05:40	Zero	-7.9	<50	N/A	N/A	Pass
08/08/2019	05:52	Zero	-5.9	<50	N/A	N/A	Pass
08/09/2019	05:39	Zero	-7.9	<50	N/A	N/A	Pass
08/10/2019	07:00	Zero	-6.1	<50	N/A	N/A	Pass
08/12/2019	05:41	Zero	-5.9	<50	N/A	N/A	Pass
08/13/2019	06:44	Zero	-5.9	<50	N/A	N/A	Pass
08/14/2019	05:48	Zero	-6.0	<50	N/A	N/A	Pass
08/15/2019	05:49	Zero	-6.2	<50	N/A	N/A	Pass
08/22/2019	06:54	Zero	57.6	<50	N/A	N/A	Fail
08/22/2019	07:56	Zero	-6.5	<50	N/A	N/A	Pass

Table 3-2.	Zero-air	Checks for	the LI-COR	CO ₂ Monitor.
		CHECKS IOI		

Table 3-3. Span Checks for the LI-COR CO₂ Monitor.

Date	Time	Instrument Check	Observed Result (ppmv)	Expected Result (ppmv)	% Difference	Acceptance Criteria (%)	Pass/Fail
08/01/2019	06:01	Span	355	384	7.55	20	Pass
08/05/2019	05:34	Span	351	385.6	8.97	20	Pass
08/06/2019	05:42	Span	354	384.3	7.88	20	Pass
08/08/2019	05:55	Span	352	385	8.57	20	Pass
08/09/2019	05:41	Span	354	384	7.81	20	Pass
08/10/2019	07:02	Span	355	385	7.79	20	Pass
08/12/2019	05:43	Span	355	384.6	7.69	20	Pass
08/13/2019	06:46	Span	355	385	7.79	20	Pass
08/14/2019	05:50	Span	356	383	7.05	20	Pass
08/15/2019	05:51	Span	356	385	7.53	20	Pass
08/22/2019	06:56	Span	374	384.9	2.83	20	Pass
08/22/2019	07:58	Span	362	385.1	5.99	20	Pass

Date	Time	Instrument Check	Observed Result (ppbv)	Expected Result (ppbv)	% Difference	Acceptance Criteria (%)	Pass/Fail
08/01/2019	06:14	Zero	0.10	<0.5	N/A	N/A	Pass
08/01/2019	14:09	Zero	0.09	<0.5	N/A	N/A	Pass
08/05/2019	05:41	Zero	0.08	<0.5	N/A	N/A	Pass
08/05/2019	14:00	Zero	0.11	<0.5	N/A	N/A	Pass
08/06/2019	05:53	Zero	0.09	<0.5	N/A	N/A	Pass
08/06/2019	14:03	Zero	0.12	<0.5	N/A	N/A	Pass
08/08/2019	06:05	Zero	0.09	<0.5	N/A	N/A	Pass
08/08/2019	14:03	Zero	0.11	<0.5	N/A	N/A	Pass
08/09/2019	05:51	Zero	0.08	<0.5	N/A	N/A	Pass
08/10/2019	07:12	Zero	0.10	<0.5	N/A	N/A	Pass
08/10/2019	13:30	Zero	0.12	<0.5	N/A	N/A	Pass
08/11/2019	09:13	Zero	0.08	<0.5	N/A	N/A	Pass
08/12/2019	05:53	Zero	0.11	<0.5	N/A	N/A	Pass
08/12/2019	14:06	Zero	0.12	<0.5	N/A	N/A	Pass
08/13/2019	06:26	Zero	0.09	<0.5	N/A	N/A	Pass
08/13/2019	14:09	Zero	0.10	<0.5	N/A	N/A	Pass
08/14/2019	06:01	Zero	0.09	<0.5	N/A	N/A	Pass
08/14/2019	14:08	Zero	0.10	<0.5	N/A	N/A	Pass
08/15/2019	06:01	Zero	0.09	<0.5	N/A	N/A	Pass
08/15/2019	14:08	Zero	0.10	<0.5	N/A	N/A	Pass
08/22/2019	07:08	Zero	0.10	<0.5	N/A	N/A	Pass
08/22/2019	11:20	Zero	0.12	<0.5	N/A	N/A	Pass

Table 3-4. Zero-air Checks for the Proton Transfer Reaction – Mass Spectrometer.

Date	Time	Instrument Check	Observed Result (ppbv)	Expected Result (ppbv)	% Difference	Acceptance Criteria (%)	Pass/Fail
08/01/2019	06:22	Span	10.7	10.8	0.93	30	Pass
08/01/2019	14:19	Span	11.5	10.8	6.48	30	Pass
08/05/2019	05:50	Span	10.1	10.8	6.48	30	Pass
08/05/2019	14:09	Span	11.1	10.8	2.78	30	Pass
08/06/2019	05:58	Span	10.5	10.8	2.78	30	Pass
08/06/2019	14:13	Span	11.1	10.8	2.78	30	Pass
08/08/2019	06:14	Span	10.7	10.8	0.93	30	Pass
08/08/2019	14:13	Span	11.1	10.8	2.78	30	Pass
08/09/2019	06:00	Span	9.88	10.8	8.52	30	Pass
08/10/2019	07:23	Span	11.5	10.8	6.48	30	Pass
08/11/2019	09:23	Span	11.3	10.8	4.63	30	Pass
08/10/2019	13:39	Span	12.25	10.8	13.43	30	Pass
08/12/2019	06:03	Span	10.54	10.8	2.41	30	Pass
08/12/2019	14:14	Span	11.2	10.8	3.70	30	Pass
08/13/2019	07:07	Span	9.80	10.8	10.00	30	Pass
08/13/2019	14:18	Span	11.5	10.8	6.48	30	Pass
08/14/2019	06:10	Span	10.4	10.8	3.70	30	Pass
08/14/2019	14:18	Span	11.0	10.8	1.85	30	Pass
08/15/2019	06:11	Span	10.25	10.8	5.09	30	Pass
08/15/2019	14:18	Span	11.25	10.8	4.17	30	Pass
08/22/2019	07:17	Span	9.2	10.8	14.81	30	Pass
08/22/2019	11:11	Span	10.2	10.8	5.56	30	Pass

Table 3-5. Span Checks for the Proton Transfer Reaction – Mass Spectrometer.

Date	Time	Instrument Check	Observed Result (ppbv)	Expected Result (ppbv)	% Difference	Acceptance Criteria (%)	Pass/Fail
08/01/2019	05:40	Zero	3.2	< 20	N/A	N/A	Pass
08/05/2019	05:13	Zero	3.32	< 20	N/A	N/A	Pass
08/06/2019	05:25	Zero	3.08	< 20	N/A	N/A	Pass
08/08/2019	05:30	Zero	3.01	< 20	N/A	N/A	Pass
08/09/2019	05:19	Zero	3.07	< 20	N/A	N/A	Pass
08/10/2019	06:43	Zero	2.27	< 20	N/A	N/A	Pass
08/12/2019	05:24	Zero	3.02	< 20	N/A	N/A	Pass
08/13/2019	06:26	Zero	2.88	< 20	N/A	N/A	Pass
08/14/2019	05:31	Zero	3.00	< 20	N/A	N/A	Pass
08/15/2019	05:32	Zero	2.99	< 20	N/A	N/A	Pass
08/22/2019	06:30	Zero	2.79	< 20	N/A	N/A	Pass

Table 3-6.	Zero-air	Checks	for the	Picarro	Ammonia	Analyzer.

Table 3-7. Span Checks for the Picarro Ammonia Analyzer

Date	Time	Instrument Check	Observed Result (ppbv)	Expected Result (ppbv)	% Difference	Acceptance Criteria (%)	Pass/Fail
08/01/2019	05:55	Span	227	234	2.99	20	Pass
08/05/2019	05:27	Span	227	233	2.58	20	Pass
08/06/2019	05:37	Span	227	233	2.58	20	Pass
08/08/2019	05:45	Span	226	233	3.00	20	Pass
08/09/2019	05:52	Span	225	233	3.43	20	Pass
08/10/2019	06:56	Span	225	233	3.43	20	Pass
08/12/2019	05:34	Span	227	234	2.99	20	Pass
08/13/2019	06:40	Span	227	233	2.58	20	Pass
08/14/2019	05:44	Span	229	233	1.72	20	Pass
08/15/2019	05:45	Span	228	233	2.15	20	Pass
08/22/2019	06:45	Span	229	233	1.72	20	Pass

4.0 MEASUREMENT UNCERTAINTY AND KNOWN SOURCES OF ERROR

The sections below discuss the measurement uncertainty associated with each instrument employed in the ML, as well as studies conducted to quantify the Method Detection Limits (MDLs) of the PTR-MS.

4.1 **Proton Transfer Reaction – Mass Spectrometer**

All standards/zeroes performed by the field team to verify the accuracy of the instrument fell within acceptable administrative limits as described in 66409-RPT-004.

4.2 Carbon Dioxide Monitor

The LI-COR CO₂ Analyzer had no specific errors associated within the timeframe covered in this monthly report. All standards/zeroes performed by the field team and reported in this summary to verify the accuracy of the instrument fell within acceptable administrative limits ($\pm 20\%$). The measurement accuracy of a properly calibrated instrument is listed in the LI-COR factory specifications as $\pm 3\%$ of reading.

4.3 Ammonia Monitor

The Picarro G2103 Ammonia Monitor had no specific errors associated within the timeframe covered in this monthly report. Further detail regarding the errors associated with measuring ammonia using a Picarro instrument is discussed in *Fiscal Year 2017 Mobile Laboratory Vapor Monitoring at the Hanford Site: Monitoring During Waste Disturbing Activities and Background Study*, September 2017. All standards/zeroes associated with data reported in this summary performed by the field team to verify the accuracy of the instrument fell within acceptable administrative limits ($\pm 20\%$). The measurement accuracy of a calibrated instrument listed in the Picarro factory specifications is $\pm 5\%$ of reading.

4.4 Weather Station

The Airmar 200WX-IPx7 Weather Station had no specific errors associated within the timeframe covered in this monthly report. The Airmar 150 WX Weather Station is factory calibrated and is not user calibrated. The manual does not recommend periodic calibration. This is described in 66409-RPT-003, *Mobile Laboratory Operational Acceptance Testing Plan*.

5.0 **RESULTS**

This section details the test results found during Month 11 activities.

5.1 Discussion of Test Activities and Observations

During Month 11, there were thirteen days of area monitoring around the 200 West and 200 East Area of the Hanford Site. There were seven days spent on testing various laboratory components. Results from the area monitoring are presented in the following sections.

Week	Date	Description	Activities/Observations
52	08/01/2019	Area Monitoring	200 E and 200 W Area Monitoring
52	08/02/2019	ML Testing	Installation of FTIR and N ₂ O
	08/05/2019	Area Monitoring	200 E and 200 W Area Monitoring
	08/06/2019	Area Monitoring	200 E and 200 W Area Monitoring
52	08/07/2019	ML Testing	208-ft Heated Line
55	08/08/2019	Area Monitoring	200 E and 200 W Area Monitoring
	08/09/2019	Area Monitoring	AP106 to AP102 Waste Transfer
	08/10/2019	Area Monitoring	AP106 to AP102 Waste Transfer
	08/11/2019	Area Monitoring	AP106 to AP102 Waste Transfer/ML pickup
	08/12/2019	Area Monitoring	AP106 Rinse and Flush
54	08/13/2019	Area Monitoring	200 E Monitoring
54	08/14/2019	Area Monitoring	200 E and 200 W Area Monitoring
	08/15/2019	Area Monitoring	200 E and 200 W Area Monitoring
	08/16/2019	ML Testing	Multipoint calibrations
	08/19/2019	ML Testing	Multipoint calibration and long zero-air
55	08/20/2019	ML Testing and Maintenance	Generator exhaust characterization, generator maintenance, FTIR tech support
33	08/21/2019	ML Testing and Maintenance	Generator maintenance, ML truck exhaust characterization
	08/22/2019	Fugitive Emissions Monitoring	Side port sampled from soil fixant container
56	08/27/2019	ML Testing and Modifications	DAQFactory troubleshooting, multipoint calibrations

 Table 5-1. Mobile Laboratory Activities During Month 11.

5.2 Identification of Vapor Sources and Quantitative Analysis of Vapor Composition

5.2.1 Mobile Laboratory Diesel Generator and Diesel Truck Exhaust Testing – August 20, 2019, through August 21, 2019

On August 20, 2019, and August 21, 2019, the ML Operators conducted testing on the ML diesel generator and diesel truck exhaust. These experiments were conducted to characterize the exhaust profiles of the ML vehicle and generator so they could be more easily identified within the Area Monitoring data sets. The ML Operators performed these tests by connecting a 35-ft heated line to the ML inlet and first sampling charcoal-filtered air before testing the exhaust. During the testing, charcoal-filtered air was used for dilution in order to better characterize only the exhaust and to avoid instrument saturation issues caused by sampling pure sources.

The ML instrumentation combined require roughly 1800 sccm of flow in order to operate. When the supplied dilution flow exceeds the requirements of the instrumentation, the sampling system is only drawing dilution flow. When dilution flow drops below the total required flow of the ML, the difference between the instrument flow and the dilution flow indicate how much flow is being drawn through the ML inlet. In this case, the Operators began with a dilution flow of 2500 sccm to overflow the sample system by exceeding the required instrument flow and reduced the dilution air by 500 sccm increments down to a 1000 sccm dilution (4:9 dilution factor). Further discussion of the ML sample dilution system can be found in 53005-81-RPT-059, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 7*.

The ML diesel generator exhaust data generated on August 20, 2019, showed the presence of some compounds that are not present in the truck exhaust, such as formamide, formic acid, methyl acetate, as well as the ion signal response for acetic acid + acetate fragment. There was also a significant response at nominal mass m/z 43 (three times the response for ML truck exhaust), and methanol (twice the response for ML truck exhaust). Figure 5-1 shows the signal response for the ML diesel generator exhaust.

On August 21, 2019, the ML Operators performed testing on the ML diesel truck exhaust. The truck exhaust showed significantly larger responses of formaldehyde (5:1 to the generator exhaust), acetaldehyde (4:1 to the generator exhaust), and acetone (~4:1 to the generator exhaust). Figure 5-2 shows the signal response for the ML diesel truck exhaust, and Figure 5-3 combines the average signal observed by the ML diesel generator and truck exhaust for comparison.

Diesel sources found on site and the two diesel sources on the ML have their own exhaust profiles for many underlying reasons. Engine efficiency or tuning, drive state or load, the functioning of the catalytic converter (present in all vehicles manufactured since 1993), the fuel composition, and the combustion temperature of the engine itself all play a role in the observed organic signature of the exhaust. The use of Diesel Exhaust Fluid (DEF) in the ML Truck will also yield a higher presence of aldehydes (such as Formaldehyde and Acetaldehyde) and a lower yield of nitrous oxides than the ML Generator. While minor fluctuations are expected in the emission profile of a specific exhaust source from day to day, the organic signatures determined in these studies will be used to identify when the Area Monitoring activities were sampling ML based exhaust sources.



Figure 5-1. Diesel Generator Exhaust Fingerprint.



Figure 5-2. Diesel Truck Exhaust Fingerprint.



Figure 5-3. Diesel Generator and Diesel Truck Exhaust.

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5.2.2 Fugitive Emissions Testing – August 22, 2019

On August 22, 2019, the ML Operators performed testing for the Fugitive Emissions team sampling a soil-fixant container. The tote container (IBC poly tote) held a reddish-brown liquid used in the suppression of radiological contamination. The ML Operators positioned the 35-ft hose near the mouth of the container from 09:00-09:41 PST using approximately 1000 sccm dilution (1V zero-air). The resultant inlet flow was approximately 800 sccm (4:9 dilution factor).

There are many compounds detected by PTR-MS that differ by only a small mass. Their discrete ion signals are very close to one another and resolving them becomes problematic if the concentration of one compound becomes much greater than the neighboring ion signals. For example, N-Nitrosodimethylamine (NDMA), methyl acetate, and allyl mercaptan are all observed near 75 m/z. A high concentration of allyl mercaptan causes that peak to widen its footprint and elicit a response from minor ion signals nearby that have low concentrations and merely appear higher. Figure 5-4 shows the example of allyl mercaptan compromising the ability to resolve a small ion signal for NDMA and perhaps even the methyl acetate ion signal. Note the PTR-MS viewer file showing the multipeak of NDMA, methyl acetate and allyl mercaptan, where allyl mercaptan occurred at the height of the peak. The signal seen in each cycle can fluctuate, however, as the mass scale shifts due to saturation. The resulting signal ends up occasionally with a signal for NDMA or methyl acetate where the concentration may be low, but is actually the signal for Allyl Mercaptan at high concentration. The spectra for this phenomenon will have lines that connect from the baseline of the compound to the signal of allyl mercaptan (See Figure 5-5).

Since these spectra saturations are observed, it is difficult to characterize the source with any certainty; and the resulting fingerprints would be skewed by the supersaturation thus are not shown. There are significant responses registered by the PTR-MS; however, due to the oversaturation there are some shifts in the mass scale that create issue for quantifying these signals. Significant responses are noticed near the m/z for the following COPCs: ammonia, methanol, 1,3-butadiene, 2-propanal and 1-butanol (butenes), but-3-en-2-one (MVK + dihydrofurans), and butanal. The signals seen by the PTR-MS for 1,3-butadiene has interference from the reagent ion clusters. There is also a response at m/z 37 and m/z 39, where signal from the reagent ion water cluster is expected, which is influenced by water vapor concentrations in the sample.

As with the case of NDMA, allyl mercaptan, and methyl acetate, there are other multipeak signals that become difficult to quantify during saturation. These multi-peaks occur at m/z 57 (2-propenal, 1-butanol + butenes, and the reagent ion cluster), m/z 71 (but-3-en-2-one, known C₅H₁₀, and unknown m/z 71), and m/z 73 (butanal, known C₃H₄O₂, and unknown m/z 73). In this case, these two compounds have very similar masses, but the spikes in signal are due to a shift in the mass scale. Figure 5-6 displays the multipeak window from the PTR-MS viewer software showing m/z 57 where 2-propenal and 1-butanol + butenes are separated. Figure 5-7 shows the same multipeak window at a cycle when the mass scale has shifted and attributes the signal from 2-propenal to 1-butanol. Figure 5-8 shows the overall signal for these compounds overlaid to visualize the mass scale shifting (lines dropping to zero on the signal for 2-propenal signify the mass scale shift as the signal is attributed to 1-butanol).

As we expect with saturation, there are several COPC that are observed well over the OEL while sampling from a direct source. Given the issues with saturation, there are still some signals worth mentioning that could be potentially attributed to the following compounds: ammonia, methyl isocyanate, furan, but-3-en-2-one (MVK + dihydrofurans), NDMA (N-nitrosodimethylamine), 2-methylfuran, 2,5-dimethylfuran, 2-propylfuran + 2-ethyl-5-methylfuran, NMOR (N-nitrosomorpholine), 2-ethyl-2-hexenal + 4-(1-methylpropyl)-2,3-dihydrofuran + 3-(1,1-dimethylethyl)-2,3-dihydrofuran, 2-pentylfuran, and furfural acetophenone. In addition to the mass scale shifting, there are also known fragments that are seen in high concentration where the signal is significant; however, these signals are known to be propene and alkene fragmentations. Figure 5-9 shows the resulting spectra for some of these compounds over the OEL with signs of saturation (*when the charcoal filter is in use, the signal from the PTR-MS is higher).



Figure 5-4. Multipoint Peak Data at Mass 75 m/z.







Figure 5-6. Multipoint Peak Data at Mass 57 m/z.



Figure 5-7. Multipoint Peak Data at Mass 57 m/z with Mass Scale Shift.



Figure 5-8. Proton Transfer Reaction – Mass Spectrometer Signal at Mass 57 m/z.



Figure 5-9. Compounds over the Occupational Exposure Limit with Signs of Saturation.

5.2.3 Chemical of Potential Concern Fingerprint Analysis.

In order to generally assess trends in COPC data, statistical information was compiled for all Month 11 area monitoring activities. This information is presented below in Table 5-2.

COPC #	COPC Name	OEL (ppb)	MDL (ppb)	Ave. (ppb)	St. Dev. (ppb)	Rel St. Dev. (%)	Max. (ppb)	Median (ppb)
1	ammonia	25000	6.225	9.795†	3.045	31.084	25.970	10.178†
2	formaldehyde	300	0.141	0.262†	0.330	125.670	6.592	0.337†
3	methanol	200000	0.379	22.081	10.684	48.386	234.1	25.397
4	acetonitrile	20000	0.044	0.594	0.200	33.693	3.316	0.603
5	acetaldehyde	25000	0.220	3.530	2.143	60.698	28.758	3.804
6	ethylamine	5000	0.021	< 0.021	0.017	189.006	0.133	< 0.021
7	1,3-butadiene	1000	0.917	7.561	6.617	87.509	35.878	7.886
8	propanenitrile	6000	0.043	0.203	0.087	42.655	0.679	0.22
9	2-propenal	100	0.069	0.464	0.358	77.197	5.200	0.516
10	1-butanol + butenes	20000	0.050	0.098†	0.182	185.842	18.108	0.099†
11	methyl isocyanate	20	0.025	0.04†	0.033	82.723	0.308	0.046†
12	methyl nitrite	100	0.030	0.179	0.105	58.353	1.566	0.196
13	furan	1	0.021	0.042†	0.040	94.338	0.662	0.046†
14	butanenitrile	8000	0.013	0.014†	0.020	143.478	0.234	0.018†
15	but-3-en-2-one + 2,3- dihydrofuran + 2,5- dihydrofuran	1	0.017	0.164	0.142	86.359	N/A*	N/A*
16	butanal	25000	0.022	0.365	0.217	59.462	4.624	0.424
17	NDMA	0.3	0.015	0.050	0.053	106.148	0.512	0.055
18	benzene	500	0.066	0.364	0.537	147.401	74.997	0.374
19	2,4-pentadienenitrile + pyridine	300	0.018	0.075	0.065	87.210	4.518	0.078
20	2-methylene butanenitrile	300	0.008	0.022†	0.044	201.782	0.483	0.013†
21	2-methylfuran	1	0.016	0.072	0.056	78.170	0.746	0.075
22	pentanenitrile	6000	0.008	0.01†	0.013	124.935	0.155	0.011†
23	3-methyl-3-buten-2-one + 2- methyl-2-butenal	20	0.016	0.061	0.058	93.979	1.260	0.06
24	NEMA	0.3	0.010	0.014†	0.018	126.236	0.179	0.015†
25	2,5-dimethylfuran	1	0.013	0.084	0.133	156.998	1.366	0.055
26	hexanenitrile	6000	0.006	< 0.006	0.006	117.276	0.136	< 0.006
27	2-hexanone (MBK)	5000	0.010	0.027†	0.028	101.029	0.594	0.028†

Table 5-2. Chemical of Potential Concern Statistical Information for the Area Monitoring Period of August 1, 2019, through August 15, 2019. (2 Sheets)

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Table 5-2. Chemical of Potential Concern Statistical Information for the AreaMonitoring Period of August 1, 2019, through August 15, 2019. (2 Sheets)

COPC #	COPC Name	OEL (ppb)	MDL (ppb)	Ave. (ppb)	St. Dev. (ppb)	Rel St. Dev. (%)	Max. (ppb)	Median (ppb)
28	NDEA	0.1	0.011	< 0.011	0.009	210.601	0.117	< 0.011
29	butyl nitrite + 2-nitro-2- methylpropane	30	0.006	0.024	0.016	66.518	0.120	0.025
30	2,4-dimethylpyridine	500	0.008	0.01†	0.026	276.575	4.043	0.008†
31	2-propylfuran + 2-ethyl-5- methylfuran	1	0.010	0.028†	0.042	149.166	0.449	0.021†
32	heptanenitrile	6000	0.004	< 0.004	0.004	312.164	0.061	< 0.004
33	4-methyl-2-hexanone	500	0.008	< 0.008	0.014	186.815	0.334	< 0.008
34	NMOR	0.6	0.009	0.011†	0.015	137.200	0.347	0.012†
35	butyl nitrate	2500	0.004	< 0.004	0.004	293.240	0.109	< 0.004
36	2-ethyl-2-hexenal + 4-(1- methylpropyl)-2,3- dihydrofuran + 3-(1,1- dimethylethyl)-2,3- dihydrofuran	1	0.007	0.011†	0.012	113.181	0.217	0.011†
37	6-methyl-2-heptanone	8000	0.006	0.011†	0.013	124.512	0.280	0.011†
38	2-pentylfuran	1	0.006	0.035	0.033	92.126	0.309	0.034
39	biphenyl	200	0.008	< 0.008	0.008	147.281	0.063	< 0.008
40	2-heptylfuran§	1	0.023	< 0.007	0.022	365.228	0.238	< 0.007
41	1,4-butanediol dinitrate	50	0.005	< 0.005	0.002	213.878	0.012	< 0.005
42	2-octylfuran	1	0.004	< 0.004	0.005	340.656	0.048	< 0.004
43	1,2,3-propanetriol 1,3- dinitrate	50	0.002	< 0.002	0.001	798.450	0.014	< 0.002
44	РСВ	1000	0.006	< 0.006	0.002	79.480	0.014	< 0.006
45	6-(2-furanyl)-6-methyl-2- heptanone	1	0.003	< 0.003	0.003	142.918	0.028	< 0.003
46	furfural acetophenone	1	0.006	< 0.006	0.005	119.428	0.048	< 0.006
N/A*	The maximum peak value for but-3- 0.155 ppb. The PTR-MS results for concentrations because: 1) the result concentrations that occasionally exc that differ by a factor of 200, which	en-2-one + 2 but-3-en-2-et is suspect d eed the dihy provide wid	2,3 dihydrofu one + 2,3 dih ue to a know drofuran OE ely variant ba	rran + 2,5 dih ydrofuran + 1 m biogenic ir L, and 2) this ases for these	ydrofuran was 2,5 dihydrofur aterferant (met combination numbers.	s 1.224 ppb and an are not comp hacrolein) that of COPCs have	the median pared to OEI is expected to OEL concer	value was o be in ntrations
**	Nitrosamine results are suspect due background [53005-81-RPT-007, P and Fiscal Year 2017 Mobile Labor Activities and Background Study, R.	to isobaric in TR-MS Mobi atory Vapor I Lee Group,	terferants can le Laborator Monitoring a Inc.].	using positiv y Vapor Mor at the Hanfor	e bias that hav nitoring Backg rd Site: Monito	e been encounte round Study, (3 pring During Wa	ered during p 2/18/2018 – 4 aste Disturbi	revious //20/2018), ng
§	Denotes compounds calculated	using Kinet	tic methods	•				
<	COPC Averages below the MDL.							
Ť	COPC Averages between the RL an	d the MDL.						
	COPC Averages >100% of the OEL							
	COPC Averages 50-100% of the OF	EL.						
	COPC Averages 10-50% of the OEI	L.						

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The average concentration over the course of 11 monitoring days for NDMA exceeded 10% of occupational exposure limit (OEL) concentrations. Further investigation was conducted by comparing the instantaneous maxima for the COPCs against their time-weighted average OELs. While an instantaneous concentration does not represent an exceedance from an occupational health perspective, it does provide insight into compounds of interest. This metric naturally resulted in focusing on compounds with very low OEL concentrations with NDMA at 0.3 ppbv, 2,3-dihydrofuran + 2,5-dimethylfuran at 1 ppbv, and N-nitrosodiethylamine (NDEA) at 0.1 ppbv. It is important to note that but-3-en-2-one responds at the same ion as 2,3-dihydrofuran + 2,5-dihydrofuran and has an OEL concentration of 200 ppbv. For the purpose of this analysis, the species are assumed to be either 2,3-dihydrofuran and 2,5-dihydrofuran to be as conservative as possible with OEL concentration exceedances. It is possible that the response was from but-3-en-2-one instead of the dihydrofurans meaning there would be no exceedance above the OEL concentration.

Using this lens, a time-series plot showing those traces along with CO_2 , a general combustion marker, was generated. This plot is shown below in Figure 5-10.



Figure 5-10. Time Series Plot of Chemicals of Potential Concern of Interest in Month 11.

This plot immediately drew focus to three consecutive monitoring days, specifically August 9, 2019, through August 11, 2019. During this time, the ML was supporting the AP-106 to AP-102 Tank Waste Transfer. The transfer was announced to have started at 08:45 on August 9, 2019, and was announced to have concluded at 07:08 on August 11, 2019. The ML, when staffed, was generally positioned such that the sampling mast was downwind of AP-Farm. At the end of shift, the ML was deployed in a stationary position overnight.

Visible in the plot above are four events that will be discussed in-depth in the following section. They are detailed in Table 5-3 below.

Plume	Date	Time Range
1	08/09/2019	22:05 - 23:12 PST
2	08/10/2019	03:20 - 04:57 PST
3	08/10/2019	21:34 - 23:30 PST
4	08/11/2019	03:50 - 08:30 PST

 Table 5-3.
 Selected Month 11 Events.

These events have several factors in common. Primarily, they all generally occurred while the ML was unstaffed, either late at night or very early in the morning. In addition, each of these events exhibit a CO₂ response which closely followed the pattern of the VOC plume. Furthermore, after going more in-depth to characterize these plumes, their VOC fingerprints share many commonalities. The fingerprints showing percentages of the major constituents of each plume are shown below in Figure 5-11.



Figure 5-11. Fingerprints for Month 11 Plumes.

Each fingerprint above represents over 85% of the response of any given plume. Many ion signal ratios between the different plumes showed stark similarities. For example, each plume had a very prominent methanol signal. Other common signals between all four plumes included nominal m/z 41, nominal m/z 43, acetaldehyde, nominal m/z 51, nominal m/z 53, 1,3-butadiene, 2-propenal, acetone, nominal m/z 67, butanal, benzene, nominal m/z 81, and nominal m/z 153. Many of these ion signals are very common in typical exhaust patterns. However, there are some differences that drive comparison between the sets of plumes. It seems that even for shared species, the ratios vary enough to break the plumes into two distinct groups.

The first group, represented by Plumes 1 and 3, showed higher ratios of the shared species like methanol and acetaldehyde as opposed to Plumes 2 and 4. Additionally, this group did not exhibit as much of a response in the higher masses above m/z 81. This includes not showing a response for toluene, 2,5-dimethylfuran, and the substituted benzenes. It is possible that these plumes were more mixed or diluted than Plumes 2 and 4, and this is further enforced by examining the time series plot, in which Plumes 1 and 3 clearly exhibited a lower response above baseline. Another possible explanation for the apparent difference is that the two sets of plumes came from differing sources. These possibilities are explored in more detail below, including local meteorological conditions and ML spatial positioning.



Figure 5-12. Plume 1 and Plume 2 Location (Shown in Green).

Plumes 1 and 2 were detected to the south of the AP Farm fence line. Since the ML was unattended for the duration of overnight monitoring, the ML's location and orientation did not change between events. As such, the ML was oriented with the nose to the northeast, placing the generator exhaust pipe to the south or southwest of the mast inlet. Wind roses showing the prevailing wind patterns for Plumes 1 and 2 are shown below in Figures 5-13 and 5-14.



Figure 5-13. Plume 1 Wind Rose.

From 22:05 to 23:12 PST on August 9, 2019, the wind was predominantly from the west, generally mild to moderate. Some gusts above 8 mph were observed, mostly from the southwest. This strongly indicates that the plume did not come from the direction of the tank farms. Furthermore, there is a possibility that the ML sampled its own diesel generator during this time due to the vehicle heading placing the exhaust pipe slightly upwind of the mast. This is further supported by the fingerprint for Plume 1 being generally more in line with other diesel exhaust fingerprints (i.e., no larger aromatics like toluene or substituted benzenes, no diethyl sulfide + 2-methylpropane-2-thiol, and lower acetaldehyde and m/z 43 ratios).



Figure 5-14. Plume 2 Wind Rose.

From 03:20 to 04:47 PST on August 10, 2019, winds were mild (below 5 mph) and generally out of the southeast. The ML was still unmanned overnight. Once again it is unlikely that the source of Plume 2 was from AP Farm, which was directly to the north of the ML. Plume 2 exhibited responses from many constituents of vehicle exhaust, specifically responses typically observed to be associated with gasoline exhaust, such as higher acetone ratios, presence of acetic acid + the acetate fragment, and presence of higher mass aromatic compounds. While it cannot definitively be said that the source of this plume was not the ML's own diesel exhaust, all evidence seems to point to another nearby source, likely burning gasoline. It is also likely that this source was either somewhat close to the ML or present in much higher concentrations directly next to the source, as the time series plot shows much more elevated signals with respect to the baseline at this time. Combined with the extremely mild winds, this plume likely was not diluted as strongly between the source and the ML inlet as others.



Figure 5-15. Plume 3 and Plume 4 Location.

Plumes 3 and 4 were detected while the ML was in a stationary position near the northeast corner of AP-Farm. The ML was parked in this location with the nose oriented towards the west after the end of shift on August 10, 2019, and remained in this position until the end of the waste transfer the morning of August 11, 2019. This placed the exhaust of the ML's diesel generator generally to the east of the mast inlet for the entire time period in question. Wind roses showing the prevailing wind patterns for Plumes 3 and 4 are shown below in Figures 5-16 and 5-17.



Figure 5-16. Plume 3 Wind Rose.

From 21:34 to 23:30 on August 10, 2019, winds were mild to moderate and predominantly out of the south, with occasional shifts to the southwest and the east. Once again, it would be unlikely that the source of this plume came from within the AP-Farm fence line. The occasional shifts to the east suggest that it is possible that the source of this plume was the ML's generator exhaust, and this is further supported by the similarity between Plumes 1 and 3. It is unclear what sources could be positioned directly to the ML's south from this location that would produce this signal response, especially because it is unlikely it could be caused by any passing vehicle due to the longer duration of the event. Like Plume 1, there is a chance this source was further away from the ML and was being carried by the stronger winds from the south, mixing and diluting the plume somewhat before being sampled. This is corroborated by the lower signal response from COPCs shown in the time series plot, as well as the absence of some species that may have been diluted below the threshold for significance in the fingerprint tool.



Figure 5-17. Plume 4 Wind Rose.

From 03:50 to 08:30 PST on August 11, 2019, winds were moderate and fairly variable. This is likely due to the rather large period of time encompassed by this event. However, as evidenced in the time series plot above, elevated signals of several COPCs persisted for several hours during the early morning of this day. This time window additionally lined up with the start of morning work activities for the Hanford Site. Because the ML's generator exhaust is positioned to the east of the inlet, it is unlikely that the PTR-MS sampled the exhaust at this time. The plume in question exhibited ratios closer to Plume 2, which is more in line with gasoline exhaust for the reasons outlined above. In addition, the overall magnitude of the concentration for the constituents of this plume were much higher than the others, implying much lower mixing or much greater proximity to the source of the signal. This could be explained through the ML's overall proximity to work activities associated with the tank waste transfer, especially considering that the transfer was stated to have officially concluded at around 07:00 PST.

5.2.4 Odor Fingerprint Analysis

In order to generally assess trends in odor data, statistical information was compiled for all Month 11 area monitoring activities. This information is presented below in Table 5-4.

Odor Compound #	Odor Name	MDL (ppb)	Ave. (ppb)	St. Dev. (ppb)	Rel St. Dev. (%)	Max. (ppb)	Median (ppb)
1	hydrogen sulfide	0.139	< 0.139	0.082	102.422	0.556	< 0.139
2	methyl mercaptan	0.026	0.044†	0.035	80.724	0.277	0.051†
3	dimethylsulfide; ethanethiol	0.034	0.782	0.098	12.587	1.608	0.804
4	allyl mercaptan	0.058	< 0.023	0.018	205.213	0.077	< 0.023
5	1-propanethiol; isopropyl mercaptan	0.087	< 0.03	0.053	373.048	0.935	< 0.03
6	2-butene-1-thiol	0.019	0.072	0.064	88.845	0.549	0.083
7	diethyl sulfide; 2-methylpropane- 2-thiol	0.087	0.174†	0.314	180.169	50.735	0.16†
8	thiopropanal sulfuroxide	0.010	< 0.01	0.002	444.302	0.039	< 0.01
9	dimethyl disulfide	0.013	< 0.013	0.015	455.457	0.129	< 0.013
10	1-pentanethiol; 2,2- dimethylpropane-1-thiol	0.022	< 0.022	0.011	239.231	1.237	< 0.022
11	benzenethiol	0.012	< 0.012	0.017	187.704	0.186	< 0.012
12	diallyl sulfide	0.015	0.024†	0.027	108.770	0.297	0.028†
13	methyl propyl disulfide	0.011	< 0.011	0.010	839.045	0.075	< 0.011
14	methylbenzenethiol	0.008	< 0.008	0.006	186.710	0.075	< 0.008
15	dimethyl trisulfide	0.026	0.193	0.049	25.582	0.559	0.206
16	(1-oxoethyl) thiophene	0.010	< 0.01	0.005	175.338	0.051	< 0.01
17	(1-oxopropyl) thiophene	0.008	< 0.008	0.006	77160.086	0.059	< 0.008
18	dipropyl disulfide	0.005	< 0.005	0.004	388.079	0.036	< 0.005
19	methyl propyl trisulfide	0.003	< 0.003	0.002	376.557	0.019	< 0.003
20	dimethyl tetrasulfide	0.003	< 0.002	0.004	285.888	0.026	< 0.002
21	dipropyl trisulfide	0.004	< 0.004	0.002	109.082	0.016	< 0.004
22	diphenyl sulfide	0.005	< 0.005	0.003	163.102	0.022	< 0.005
ş	Denotes compounds calculated usin	g kinetic m	ethods.				
<	COPC average/median below the M	IDL.					
Ť	Average/median between the RL an	d the MDL					

Table 5-4. Odor Statistical Information for the Area Monitoring
Period of August 1, 2019, Through August 15, 2019.

Very few odor compounds exhibited an average response over 11 monitoring days above the detection limit. The odors that did exceed the detection limit on average include dimethylsulfide + ethanethiol, 2-butene-1-thiol, diethyl sulfide + 2-methylpropane-2-thiol, diallyl sulfide, and

dimethyl trisulfide. Of those compounds, the one that merited further investigation was the ion signal for diethyl sulfide + 2-methylpropane-2-thiol at m/z 63. It was far and away the most predominant odor-causing compound throughout the entire dataset. Shown below in Figure 5-18 is a time-series plot showing an odor plume of interest from August 8, 2019.



Figure 5-18. Time Series Plot of Diethyl Sulfide + 2-methylpropane-2-thiol.

This odor signal peaked around 09:44 PST. No other odors were observed to trend with this plume. However, the plume was deemed to be interesting on the merit that it did not seem to exhibit a strong mirroring CO_2 response. In order to further characterize the other constituents of this plume, a fingerprint was taken. This is shown below in Figure 5-19.



Figure 5-19. Month 11 Odor Plume Fingerprint.

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This is an interesting fingerprint in that it is relatively unique compared to others. Compared to the other fingerprints in this section, there was a notable absence of many constituents, including nominal m/z 43, acetaldehyde, acetone, acetic acid + acetate fragment, or any furans. This plume was not significantly dominated by any one species, unlike the previous plumes which exhibited methanol percentages anywhere from 20 - 40% of the total plume. However, the odor compound at m/z 63, diethyl sulfide + 2-methylpropane-2-thiol exhibited the highest percentage overall, at nearly 15%. Also notable was the presence of ethanol and nominal m/z 46, which were not present in other plumes from this month. Finally, this plume lasted only a few minutes, instead of hours. While this plume did not present any obvious clues as to the identity of its source, the lack of very common combustion products like CO₂ and aldehydes, combined with elevated ratios of benzene and higher mass substituted benzenes point to the conclusion that this source could be fuel, as opposed to combustion exhaust. The location of the ML during this event is shown below in Figure 5-20.



Figure 5-20. Odor Plume Location During Mobile Monitoring.

One notable fact about this plume is that it was detected while the ML was moving to the west along the south side of C Farm in 200E. Figure 5-21 below is a wind rose showing the predominant wind patterns over the course of this measurement.



Figure 5-21. Odor Plume Wind Rose.

Wind speed measurements use the ML's GPS position to factor out erroneous speed readings caused by the movement of the ML. This is evidenced by the fact that there is a lack of wind coming predominantly from the direction of travel. As such, wind was relatively stagnant over these few minutes, hardly exceeding 4 mph. What wind that was present came mainly from the northeast, leading to the conclusion that the source of the plume may either be just to the side of the road from the ML or on the other side of the C Farm fence line.

5.2.5 Exhaust Scan

As with previous months, the exhaust scanner was tuned by the SME to specify thresholds that best fit the data. The exhaust scan resulted in the identification of 43 potential exhaust plumes. The plumes were split into four categories with nine having a high acetaldehyde response, nine

had many aromatics (benzene, toluene, C₂-benzenes, C₃-benzenes, C₄-benzenes), 21 had a large methanol signal, and four plumes did not fit well within any of those three categories. These plumes were further analyzed to determine the general composition through generation of fingerprints and comparing them to fingerprints developed in previous reports to determine the potential source.

5.2.5.1 Diesel Vehicle Exhaust – Engine Exhaust Group A

The nine plumes with high acetaldehyde response occurred on August 6, 2019 (12:43, 12:45, 13:36), August 8, 2019 (two at 06:43, 12:10, 12:11, 12:14), and August 14, 2019 (13:14). Figure 5-22 shows the resulting fingerprints along with the corresponding average and the fingerprint of Engine Exhaust Group A (EEGA) from 53005-81-RPT-076, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 10*. The average fingerprint is primarily composed of acetaldehyde (29.0%), acetone (7.6%), methanol (6.2%), nominal m/z 43 (5.9%), formaldehyde (4.8%), nominal m/z 41 (3.8%), 1,3-butadiene (3.1%), benzene (2.6%), nominal m/z 46 (2.1%), and methyl nitrite (2.0%) which makes up 67.1% of the overall fingerprint. This followed a comparable pattern to that observed with the Month 10 EEGA, which was attributed to diesel vehicle exhaust, with the biggest difference being a more pronounced acetaldehyde and acetone response. The likely source of these plumes was diesel vehicle exhaust due to the general composition, similarity to Month 10 EEGA, and presence of nominal m/z 46 (NO₂) which is a good indicator of diesel combustion emissions.



Percent of Response (%)



5.2.5.2 Gasoline Vehicle Exhaust – Engine Exhaust Group B (EEGB)

The nine plumes with a prominent aromatic response occurred on August 8, 2019 (two at 09:10), August 9, 2019 (06:24, 06:39, 06:56, 09:16), August 12, 2019 (06:50), and August 13, 2019 (12:32, 13:04). Figure 5-23 shows the resulting fingerprints and corresponding average along with the fingerprints for Engine Exhaust Group B (EEGB) from 53005-81-RPT-076 and a typical gasoline vehicle exhaust fingerprint. The key species within the average fingerprint are diethyl sulfide + 2-methylpropane-2-thiol (8.5%), toluene (8.1%), benzene (7.5%), C₂-benzenes (7.2%), nominal m/z 43 (6.5%), acetaldehyde (6.2%), nominal m/z 41 (5.7%), butanol + butenes (4.4%), unknown m/z 95c (4.1%), nominal m/z 53 (3.2%), and C₃-benzenes (3.2%). These 11 species make up 64.6% of the total fingerprint. The fingerprint compared well with the Month 10 EEGB except for the signal is shifted towards higher aromatics and lower methanol and acetaldehyde. The general pattern had some similarity to the gasoline exhaust but the magnitude of the aromatic, nominal m/z 41, and nominal m/z 43 is diminished. The presence of diethyl sulfide + 2-methylpropane-2-thiol is the most interesting feature and this was expressed in 53005-81-RPT-076 as well. Five plumes were observed in 53005-81-RPT-076 for EEGB occurring on 3 different days. This report adds nine more plumes throughout 4 days to total 14 plumes over 7 days. The reoccurrence suggests that there was either a common source frequently observed by the ML or it originated from the ML itself.



Figure 5-23. Fingerprints of Engine Exhaust Group B and the Corresponding Average for Plumes Occurring on August 8, 2019; August 9, 2019; August 12, 2019; and August 13, 2019; Along with the Gasoline Vehicle Exhaust and Month 10 EEGB Fingerprints.

5.2.5.3 Methanol Group A (MA)

The 21 plumes with a large methanol response occurred on August 8, 2019 (17 between 06:25 and 06:40) and August 9, 2019 (four between 22:13 and 22:30). Figure 5-24 shows the resulting fingerprints and corresponding average along with the fingerprints for Methanol Group A (MA) from both 53005-81-RPT-073, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 9*, and 53005-81-RPT-076. The largest responses in the average fingerprint were methanol (27.4%), nominal m/z 43 (24.1%), acetic acid + acetate fragment (12.2%), acetaldehyde (7.6%), acetone (6.2%), 1,3-butadiene (3.6%), and formic acid (2.7%) which totals 83.8% of the fingerprint. The average closely resembled the Months 9 and 10 MA fingerprints except there was a lower methanol response and higher response in nominal m/z 43 and acetic acid + acetate fragment. In 53005-81-RPT-073, it was proposed the potential source could be traffic among the road, but it was suggested that the lack of response from key species within exhaust (aromatics, butanol + butenes) meant it might be more unique than vehicle exhaust. There was the presence of nominal m/z 46 (NO₂) within all three fingerprints which would point towards diesel combustion as the potential source or having some level of influence on the plume.



Figure 5-24. Fingerprints of Methanol Group A and the Corresponding Average for Plumes Occurring on August 8, 2019; and August 9, 2019; Along with the Methanol Group A Fingerprints from 53005-81-RPT-073 and 53005-81-RPT-076.

Figure 5-25 shows the location of the ML while observing these plumes. On August 9, 2019, the ML was stationary just south of 241AP. On August 8, 2019, the ML was initially parked south of the Central Shift Office for the morning check-in before it proceeded west to monitor around TX/TY and U Farms as part of the typical area monitoring routine. The plumes occurred along the stretch of road marked red in the map below. The consistency in the fingerprint supports that they are from the same source. Since the ML covered a large distance while observing these plumes, it is likely that there was an elevation of many species within a plume covering a large area. The exhaust scan was consistently picking up parts of it along the way. A broad plume like this would be from a source further upwind and is unlikely to originate within the A-Farm area due to the ML route extending a fair distance away.



Figure 5-25. Location of the Mobile Laboratory on August 8, 2019, from 06:25 to 06:40; and August 9, 2019, from 22:13 to 22:30.

Figure 5-26 shows the wind speed and direction during the observations. On August 8, 2019, between 06:25 and 06:40, the wind was exceeded 5 m/s for most of the time and was stable from the southeast direction. The key species within the fingerprint are common in ambient air; therefore, given the broad shape and high winds, it is suggested that the elevated signals were due to an ambient airmass change increasing signals above typical background levels. On August 9, 2019, stable wind was observed from the west between 22:13 and 22:30 with wind speeds ranging from 2 to 5 m/s with some gusts exceeding 5 m/s. Upwind of the ML are primarily mobile offices and Canton Avenue, which are potentially the source(s) of the plume. Since the plume is similar to August 8, 2019, it is also possible there was just a brief airmass change resulting in background concentrations raising above typical levels.



Figure 5-26. Location of the Mobile Laboratory on August 8, 2019, from 06:25 to 06:40 and August 9, 2019, from 22:13 to 22:30.

5.2.5.4 Other Plumes

There were four plumes identified by the exhaust scan that did not follow the same pattern as the EEGA, EEGB, and MA fingerprints. They occurred on August 8, 2019, at 09:11; August 9, 2019, at 22:06 and 23:00; and August 12, 2019 at 07:32. Figure 5-27 shows the fingerprints of these four plumes. The August 8, 2019, plume is composed of methanol (36.0%), nominal m/z 43 (8.9%), nominal m/z 41 (6.5%), 1,3-butadiene (4.6%), butanol + butenes (3.9%), ethanol (3.7%), acetaldehyde (3.6%), and benzene (3.2%) for a total of 72.4% of the total response. The presence of these species and the response of aromatics suggests this is exhaust related. The lack of nominal m/z 46 (NO₂), which is typical of diesel exhaust, within the fingerprint leads towards the source of this plume being gasoline vehicle emissions. The August 9, 2019, 22:06 plume composition was acetone (25.1%), nominal m/z 43 (14.6%), 1,3-butadiene (14.3%), acetaldehyde (11.4%), acetic acid + acetate fragment (4.1%), nominal m/z 41 (4.0%), and butanal (3.1%) which accounts for 76.6% of the fingerprint. This is comparable to gasoline exhaust except there was not much aromatic presence and the large response in acetone was not

typical. Increased activity in CO₂ during this plume suggests it was still combustion related. The main constituents of the August 9, 2019, 23:00 plume were methanol (36.5%), nominal m/z 43 (14.5%), acetone (8.9%), acetic acid + acetate fragment (5.6%), nominal m/z 81 (4.5%), and acetaldehyde (3.1%) which contributed 73.1% of the total fingerprint. These species are common in typical ambient air; therefore, this could be a function of an airmass change except the presence of nominal m/z 81 suggests there could be biogenic influence. In 53005-81-RPT-066, *PTR-MS Mobile Laboratory Vapor Monitoring – Month 8*, a plume with a large response in nominal m/z 81 was observed and attributed to species known to be emitted by plants (monoterpenes, 2-hexanal, d-limonene, sesquiterpenes). The August 12, 2019, plume was primarily methanol (66%) and benzene (6.5%) with smaller influence from aromatics, nominal m/z 41, nominal m/z 41, acetaldehyde and other species typically found within exhaust. Plumes such as this have been observed in previous reports and are suspected to be mixtures of windshield wiper fluid to produce the methanol response and vehicle exhaust.



Figure 5-27. Fingerprints of the Plumes Observed on August 8, 2019, at 09:11; August 9, 2019, at 22:06 and 23:00; and August 12, 2019, at 07:32.

6.0 QUALITY ASSESSMENT

From August 1, 2019, through August 31, 2019, quality control procedures were followed by the TerraGraphics Vapor Team: Data Collection and Data Processing. Data were collected and quality documents completed according to 66409-RPT-004. All data were accepted, processed, and reported according to the Procedure 17124-DOE-HS-102, "Mobile Laboratory Data Processing – Analysis." All exceptions have been noted and any potential quality-affecting issues were resolved prior to report or are noted in this report. Any potential quality-affecting deviations have been captured in Deficiency Reports (DRs) and are summarized below with some interpretation.

During Month 11, there was one documented DR. DR19-016 documents a deviation from 66409-RPT-004 on August 9, 2019.

6.1 Lessons Learned – DR19-016

On August 9, 2019, the ML Operators deviated from the 66409-RPT-004 by not performing the end-of-day PTR-MS zero-air and span check. The ML Operators assumed that because the ML was performing continuous monitoring that the vapor team would not want an end-of-day PTR-MS span performed since that would require the data to be cut, and therefore noncontinuous. To avoid this confusion in the future, the next revision of 66409-RPT-004 will include a statement to define when the end-of-day PTR-MS span check is to be performed, dependent on deployment type.

7.0 CONCLUSION

As part of the ongoing effort to identify and characterize fugitive emissions on-site, studies to understand the ML emissions and a soil-fixant container were performed. Due to proximity to the inlet, the ML vehicle and generator exhaust are important sources to understand. There were some defining differences between the ML vehicle and generator exhaust. The ML generator had a higher nominal m/z 43 and methanol response. The ML vehicle exhaust was shown to have a much larger response in formaldehyde, acetaldehyde, and acetone. There was also a much larger presence of formamide, formic acid, methyl acetate and acetic acid + acetate fragment within the generator exhaust compared to the vehicle exhaust. This information can be used in future data analysis to attribute suspected exhaust plumes to the ML exhausts and potentially provide the basis to distinguish between the two. The observations of the soil-fixant container on August 22, 2019, showed one of the difficulties of sampling directly from a source. The saturation of the signal meant the fingerprint analysis would be skewed; therefore, it was not performed for this data set. The lesson learned with the test is that sampling directly from a source requires careful planning to ensure the signals are within quantifiable range. Prior planning and development of the sample dilution system and setup will help reduce the chance of this occurring when sampling future high concentrations sources.

During the air monitoring activities, none of the COPCs had averages above OEL concentrations. Only NDMA had an average that exceeded 10% of the OEL concentration but it remained below the 50% OEL concentration. There were only four plumes of interest all occurring between August 9, 2019, through August 11, 2019, which was during the AP-106 to AP-102 transfer. Additional analysis showed that the composition of these plumes of interest was synonymous with vehicle exhaust and had a corresponding response in CO₂ to support to notion that the origin of the plumes is combustion related. The wind conditions for two of the plumes (Plume 1: August 9, 2019, 22:05 to 23:12; Plume 3: August 10, 2019, 21:34 to 23:30) suggested that the source was ML generator exhaust. The composition and similarity of the fingerprints for these plumes supports the attribution of the signal to the generator exhaust. The other two plumes (Plume 2: August 10, 2019, 03:20 to 04:47; Plume 4: August 11, 2019, 03:50 to 08:30) were also similar and the composition followed the pattern of gasoline exhaust rather than diesel exhaust. The wind conditions also pointed that the ML exhaust is unlikely to be the source and the wind had shifted to position the ML upwind of 241AP, so the potential source is not from within the farm. The time and wind direction suggest that the source could be related to early morning worker activity.

There was little response in odor species during the month's observations except for diethyl sulfide + 2-methylpropane-2-thiol. On August 8, 2019, around 09:44, there was a plume consisting of a strong diethyl sulfide + 2-methylpropane-2-thiol response with some aromatics, ethanol, and nominal m/z 46. This is typical of exhaust but there is a lack of response in other key species (acetaldehyde, nominal m/z 43, CO₂) during this time and the fingerprint pattern was more consistent with fuel. The ML was moving west along the southern side C Farm with wind coming from the northeast which suggests that the source could be within C Farm.

The exhaust scan identified 43 potential exhaust plumes and categorized into fingerprint groups developed in previous reports. There were nine plumes following the diesel vehicle exhaust (EEGA) pattern, nine following the gasoline vehicle exhaust (EEGB) pattern, and 21 following

the Methanol Group A (MA) pattern. The remaining four plumes were attributed to exhaust (August 8, 2019, 09:11), combustion related (August 9, 2019, 22:06), airmass change and biogenic influenced (August 9, 2019, 23:00), and a combination of windshield wiper fluid and vehicle exhaust (August 12, 2019, 07:32).

8.0 **REFERENCES**

- 17124-DOE-HS-102, 2018, "Mobile Laboratory Data Processing Analysis," Revision 2, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 53005-81-RPT-007, 2018, *PTR-MS Mobile Laboratory Vapor Monitoring Background Study* (3/18/2018 – 4/20/2018), Revision 0, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 53005-81-RPT-066, *PTR-MS Mobile Laboratory Vapor Monitoring Month 8*, Revision A, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 53005-81-RPT-073, 2019, PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report Month 9, Revision A, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 53005-81-RPT-076, 2019, PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report Month 10, Revision A, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 66409-18-ML-003, 2018, *Sampling Manifold Sketch*, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 66409-18-ML-004, 2018, *Mobile Lab Schematics*, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 66409-RPT-003, 2018, *Mobile Laboratory Operational Acceptance Testing Plan*, Revision 0, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 66409-RPT-004, 2018, *Mobile Laboratory Operational Procedure*, Revision 15, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- EPA 821-R-16-006, 2016, "Definition and Procedure for the Determination of the Method Detection Limit, Revision 2," U.S. Environmental Protection Agency, Washington, D.C.
- EPA TO-17, "Volatile Organic Compounds," U.S. Environmental Protection Agency, Washington, D.C.
- Fiscal Year 2017 Mobile Laboratory Vapor Monitoring at the Hanford Site: Monitoring During Waste Disturbing Activities and Background Study, September 2017, RJ Lee Group, Inc., Pasco, Washington.
- Statement of Work 306312, 2018, "Mobile Laboratory Services and Lease," Revision 2, Washington River Protection Solutions, LLC, Richland, Washington.
- TG-DOE-QAP-002, 2018, *TerraGraphics Quality Assurance Procedure Manual*, Revision 5, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.

APPENDIX A

DEFICIENCY REPORT DR19-016

TerraGraphics

TerraGraphics DEFICIENCY REPORT	AUTHENTIC QUALITY RECORDS	
Deficiency Report No.:		Page:
DR19-016	0	1 of 1
Originator (Print Name): Adrielle Olson	adrielle KOlson	Date: 08/09/19
Project No./Title: 66409 Mobile Laboratory Service & Lease		
PAAA Reportable: No Yes	10 CFR 21 Reportable:	Yes
Description of Requirement that was Violated and On 08/09/19 the Mobile Laboratory (ML) op Operational Procedure, by not performing the	of Deficiency: perators deviated from 66409-RF he end of the day PTR-MS span	PT-004, <i>ML</i> check.
CORREC Corrective Action:	CTIVE ACTION	
CORREC Corrective Action: Improved Section 4.7.1 of 66409-RPT-004, 1 perform the end of the day PTR-MS span che Completion Date: 08/09/19 Deficiency Cause and Extent of Condition: This deficiency and extent of condition was a documents the isolated incident and indicates delivery process. Action to Preclude Recurrence: Proceduralized when it is appropriate for ope continue the Quality Assurance/Quality Cont Completion Date: 08/20/19	CTIVE ACTION ML Operational Procedure, by deck. an isolated incident. This deficie is areas of improvement for the e erators to perform a secondary P trol checks currently in place.	le fining when to ncy report stablished data TR-MS span and
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CORREC Corrective Action: Improved Section 4.7.1 of 66409-RPT-004, <i>I</i> perform the end of the day PTR-MS span che Completion Date: 08/09/19 Deficiency Cause and Extent of Condition: This deficiency and extent of condition was a documents the isolated incident and indicates delivery process. Action to Preclude Recurrence: Proceduralized when it is appropriate for ope continue the Quality Assurance/Quality Cont Completion Date: 08/20/19 Resp. Manager/TL (Print & Sign): Mult Erster Mult 08/20/19 CI Comments and Notes (if applicable): Refer to section 4.7.1 of Revision 16a of 664	CTIVE ACTION ML Operational Procedure, by deck. an isolated incident. This deficie is areas of improvement for the e erators to perform a secondary P trol checks currently in place. QA Rep. (Print & Sign): Heath Low Mult OSURE 09-RPT-004: "If the Mobile Lab	le fining when to ncy report stablished data TR-MS span and Date: Date: 28/28/19 poratory is required
CORREC Corrective Action: Improved Section 4.7.1 of 66409-RPT-004, <i>I</i> perform the end of the day PTR-MS span che Completion Date: 08/09/19 Deficiency Cause and Extent of Condition: This deficiency and extent of condition was a documents the isolated incident and indicates delivery process. Action to Preclude Recurrence: Proceduralized when it is appropriate for ope continue the Quality Assurance/Quality Cont Completion Date: 08/20/19 Resp. Manager/TL (Print & Sign): Matt Erster Matter 08/20/19 CI Comments and Notes (if applicable): Refer to section 4.7.1 of Revision 16a of 664 to collect data overnight, depending on the so and Span Check will be required at the discret	CTIVE ACTION ML Operational Procedure, by o eck. an isolated incident. This deficie s areas of improvement for the e rators to perform a secondary P rol checks currently in place. QA Rep. (Print & Sign): Heath Low LOSURE 09-RP T-004: "If the Mobile Lab cope of work/shift orders, End oj etion of the SME or delegate."	le fining when to ncy report stablished data TR-MS span and Date: D
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