PTR-MS MOBILE LABORATORY VAPOR MONITORING MONTHLY REPORT – MONTH 2

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Acronyms and Abbreviations

AOP	Abnormal Operating Procedure
ASTM	American Society of Testing and Materials
COPC	Chemical of Potential Concern
DR	Deficiency Report
MDL	Method Detection Limit
ML	Mobile Laboratory (Mobile Vapor Monitoring Laboratory)
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
QA	Quality Assurance
RL	Reporting Limit
SME	Subject Matter Expert
SOW	Statement of Work
TG	TerraGraphics
VOC	Volatile Organic Compound
WRPS	Washington River Protection Solutions, LLC

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.

During Month 2, field monitoring of the SX Paving Project was performed in order to collect data on the concentrations of chemical vapors in the area downwind from the SX Tank Farm during paving. The Mobile Laboratory monitored the AY-102 Rinse after SX Paving was completed. Area monitoring around A Farms was conducted in support of the Fugitive Emissions Team for the remainder of Month 2. Preventative maintenance, verifications, and calibrations were also performed on the Mobile Laboratory instrumentation.

1.0 DESCRIPTION OF TESTS CONDUCTED

During Month 2, spanning the dates of August 31, 2018, to September 30, 2018, the Mobile Laboratory (ML) was deployed to monitor chemicals of potential concern (COPCs) and characterize sources of potential odor causing compounds on the Hanford Site.

The ML was deployed to SX Farm on the Hanford Site to monitor the SX Paving Project from August 31, 2018, to September 24, 2018. Operation of the ML during the SX paving campaign was performed to collect concentrations of chemical vapors in the area downwind of the SX Tank Farm during paving and to characterize vapor sources during these activities. Once paving of SX Farm was completed on September 24, 2018, the ML began monitoring the septic tanks located east of the 242-A Evaporator on the Hanford Site for the remainder of Month 2.

Description of activities that were conducted are as follows:

- Week 5
 - Mobile Area Monitoring of SX Farms Paving
 - Mobile Area Monitoring of AY-102 Rinse Operations
- Week 6
 - Mobile Area Monitoring of SX Farms Paving
- Week 7
 - Mobile Area Monitoring of SX Farms Paving
- Week 8
 - Mobile Area Monitoring of SX Farms Paving
 - Source Characterization of Septic Tanks

Beyond monitoring, the tasks conducted during this period were performed to support proper function of the instruments in the ML. These tasks include calibrations, troubleshooting, verifications, and maintenance.

This report is structured based on reporting requirements, as defined in the original Statement of Work (SOW) #306312, "Mobile Laboratory Services and Lease."

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 2, 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 2. When deployed for monitoring, the ML used both the mast and the side port to perform air sampling. The side port was used for odor source characterization and the mast was used for area monitoring at the AY-102 and SX Farm.

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

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

2.1.1.1 Proton Transfer Reaction – Mass Spectrometer Sampling

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

The PTR-TOF 6000 X2 is used to quantify 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 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 Gesellschaft m.b.H., Innsbruck, Austria.

2.1.1.2 DAQFactory Sampling

DAQFactory^{®3} is a data acquisition and automation software system 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 (FY) 2018 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.

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.



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

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 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 of 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.

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 this study 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 850A. The Li-850A 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 parts per million by volume (ppmv) (0-2%), low power consumption (4W after powerup), and 1-second signal averaging to allow for real-time source apportionment (i.e., monitoring

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

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

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 the background study was operated using a factory calibration. Periodic checks of the unit were made with zero-air, ambient background air (ambient atmospheric CO₂ levels are approximately 400 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 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 CO₂ 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. 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. 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 ML. 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)

During Month 2, no confirmatory samples were taken.

3.0 CALIBRATION METHODS AND CALIBRATION GASES USED

Cylinder	ID#	Exp. Date
Carbon Dioxide	77-401243203-1	07/13/2026
Ammonia	48-401233442-1	06/21/2019
Zero-Air	330-2749, KI00052247, L0-000123	06/18/2019
VOC (Benzene)	TIBI-21-0.5-1	08/06/2022
VOC	160-401265983-1	02/28/2019

Table 3-1. Calibrated Gases in Use During Month 2.

4.0 MEASUREMENT UNCERTAINTY AND KNOWN SOURCES OF ERROR

4.1.1 **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, *Mobile Laboratory Operational Procedure*.

4.1.2 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 listed in the LI-COR factory specifications is \pm 3% of reading.

4.1.3 Ammonia Monitor

The Picarro Model 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.

4.1.4 Weather Station

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

4.2 Method Detection Limit

In order to gain insight into the limits of detection of the PTR-TOF 6000 X2, all zero-air checks run on the instrument from September 10, 2018, to September 27, 2018, were analyzed. A total of 33 zero-air checks were run during this time period. Each zero-air check consisted of roughly 100 data points, taken at 2 Hz. This period in particular was chosen because September 10, 2018, marked the first day in the field using the transmission curve generated by an improved and higher-accuracy VOC standard. This transmission curve takes into account what fraction of ions are successfully transmitted across the Time of Flight to the detector, as a function of mass, and corrects for this. Thus, it was very important for quantification purposes to base the Method Detection Limits (MDLs) off of the improved transmission curve.

The MDLs were calculated by taking the mean and standard deviation of the data collected during each zero-air check, for each compound detected. This takes into account the variance (or noise) present in the real-time data.

$$\mu = \frac{\sum_{i=1}^{n} x_i}{n}$$
$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \mu)^2}{n}}$$

Next, a grand mean of the mean values for each zero-air check for each compound was calculated by taking the mean of the 33 individual means calculated in the previous step.

$$\mu_T = \frac{\sum_{i=1}^n \mu_i}{n}$$

Using propagation of error, the standard deviations were combined. This was done by taking the square root of the average of the squares of each calculated standard deviation, i.e., the root of the average of the variances.

$$\sigma_T = \sqrt{\frac{\sum_{i=1}^n \sigma_i^2}{n}}$$

This ensured that the variances attributed to the discrete points of 2 Hz data were conserved. If a standard deviation of the mean of means was taken, the only variance taken into account would be the variance between calculated averages.

These combined standard deviations were then multiplied by the 2-tailed Student's t-value for 32 degrees of freedom at 95% CI, i.e., 2.037. This provided the MDLs for each compound detected by the PTR-TOF 6000 X2. As a conservative approach, an additional factor of 3 was then applied to the MDLs to obtain the Reporting Limits (RLs). Calculated MDLs and RLs for each COPC and odor compound are shown in the table below.

COPC Name	OEL (ppbv)	MDL (ppbv)	RL (ppbv)
formaldehyde	300	0.246	0.738
methanol	200000	0.440	1.319
acetonitrile	20000	0.026	0.077
acetaldehyde	25000	0.289	0.868
ethylamine	5000	0.031	0.094
1,3-butadiene	1000	0.079	0.236
propanenitrile	6000	0.037	0.111
2-propenal	100	0.169	0.506
1-butanol + butenes	20000	0.098	0.293
methyl isocyanate	20	0.038	0.115
methyl nitrite	100	0.036	0.108
furan	1	0.024	0.071
butanenitrile	8000	0.023	0.069
but-3-en-2-one + 2,3-dihydrofuran + 2,5-dihydrofuran	100, 1, 1	0.020	0.059
butanal	25000	0.034	0.101
NDMA	0.3	0.033	0.098
benzene	500	0.083	0.250
2,4-pentadienenitrile + pyridine	300, 1000	0.028	0.083
2-methylene butanenitrile	30	0.017	0.052
2-methylfuran	1	0.022	0.065
pentanenitrile	6000	0.017	0.050
3-methyl-3-buten-2-one + 2-methyl-2-butenal	20, 30	0.026	0.077
NEMA	0.3	0.030	0.091
2,5-dimethylfuran	1	0.038	0.115
hexanenitrile	6000	0.032	0.097
2-hexanone (MBK)	5000	0.033	0.100
NDEA	0.1	0.114	0.342
butyl nitrite + 2-nitro-2-methylpropane	100, 30	0.115	0.344
2,4-dimethylpyridine	500	0.058	0.173
2-propylfuran + 2-ethyl-5-methylfuran	1	0.063	0.188
heptanenitrile	6000	0.056	0.169

Table 4-1. Method Detection Limits and Reporting Limits for Chemicals of Potential Concern. (2 Sheets)

TerraGraphics

COPC Name	OEL (ppbv)	MDL (ppbv)	RL (ppbv)
4-methyl-2-hexanone	500	0.055	0.164
NMOR	0.6	0.049	0.147
butyl nitrate	2500	0.054	0.163
2-ethyl-2-hexenal + 4-(1-methylpropyl)-2,3-dihydrofuran+ 3-(1,1-dimethylethyl)-2,3- dihydrofuran	100, 1, 1	0.053	0.160
6-methyl-2-heptanone	8000	0.051	0.152
2-pentylfuran	1	0.052	0.156
biphenyl	200	0.069	0.207
2-heptylfuran	1	0.106	0.319
1,4-butanediol dinitrate	50	0.071	0.214
2-octylfuran	1	0.033	0.100
1,2,3-propanetriol 1,3-dinitrate	50	0.055	0.164
PCB	1000	0.061	0.182
6-(2-furanyl)-6-methyl-2-heptanone	1	0.048	0.145
furfural acetophenone	1	0.095	0.284

Table 4-1. Method Detection Limits and Reporting Limits for Chemicals of Potential Concern. (2 Sheets)

Odor Name	MDL (ppbv)	RL (ppbv)
methyl mercaptan	0.0478	0.143
dimethyl sulfide; ethanethiol	0.0362	0.109
allyl mercaptan	0.0449	0.135
1-propanethiol; Isopropyl mercaptan	0.0292	0.0877
2-butene-1-thiol	0.0292	0.0876
Diethyl Sulfide; 2-methylpropane-2-thiol	0.157	0.471
thiopropanal sulfuroxide	0.0240	0.0718
dimethyl disulfide	0.0238	0.0714
1-pentanethiol; 2,2-dimethylpropane-1-thiol	0.125	0.375
benzenethiol	0.0667	0.200
diallyl sulfide	0.0758	0.227
methyl propyl disulfide	0.0426	0.128
methylbenzenethiol	0.0792	0.238
dimethyl trisulfide	0.0488	0.147
(1-oxoethyl) thiophene	0.102	0.305
(1-oxopropyl) thiophene	0.0761	0.228
dipropyl disulfide	0.0625	0.188
methyl propyl trisulfide	0.121	0.363
dimethyl tetrasulfide	0.0469	0.141
dipropyl trisulfide	0.0708	0.213
diphenyl sulfide	0.0827	0.248

Table 4-2. Method Detection Limits and Reporting Limits for Odor-Causing Compounds.

It is worth noting that while the RLs are calculated with the purpose of applying them to the data in an effort to reduce the likelihood of false positives at low concentrations, these calculated RLs will not be applied retroactively to the data discussed in this monthly report.

5.0 TEST RESULTS

This section details the test results found during this month's monitoring activities.

5.1 SX Farm

For 18 1/2 days, the focus was on monitoring asphalt-mix paving at SX Farm near the southern end of the 200W Tank Farms on the Hanford Site. The data collected in support of the SX Paving Project was visually inspected by the Subject Matter Expert (SME). The primary sources during this time are believed to be plumes from the asphalt, fumes from fuel used in the activities, and ML exhaust. The ML Operators were able to log observed influences from each of these three sources while in the field. The asphalt and fuel sources were identified by a dominant odor that coincided with a large plume identified by mobile laboratory instrumentation. The ML exhaust plumes were identified primarily by wind speed and direction related to the orientation of the inlet to the exhaust outlet. There were many asphalt and exhaust plumes observed over the observation period. Due to the large volume of plumes, representative plumes were chosen for analysis based on those identified in the logbook. There were only a few fuel plumes observed and as many as possible were included in this analysis.

Each plume was analyzed by taking the average of all resolved peaks for the duration. This average was then subtracted by an average background concentration before or after the plume occurred. The background was typically a 1- to 2-minute period. Subtracting this background ensures that only the plume response is accounted for within the analysis and removes the influence from ambient concentrations. Figure 5-1 exemplifies the way in which the plume average response was captured for one of the fuel plumes occurring on September 21, 2018, around 09:43. The green shaded area represents the plume attributed to fuel. This plume was identified by technicians in the logbook as coinciding with a strong smell of fuel. All resolved peaks were averaged within the green area. Since many species have an ambient background above zero, it is important to exclude this value if you want to look exclusively at the response within the plume. In Figure 5-1, the red area is where the background was identified for this plume. A background for each analyzed plume was established as shortly before or after the plume of interest occurred. This ensures that the background is accurately represented for each discrete plume.



Figure 5-1. Time Series Benzene Within a Fuel Plume (Green Shade) and the Period of Data Used to Quantify the Ambient Concentrations (Red Shade).

Once the plume response is calculated, the next step is to identify the important components of the plume. Any species that did not have a response of at least 0.05 ppbv was excluded from the analysis. The value of 0.05 ppbv was chosen as a threshold because it is approximately the same as the lowest RL value of the quantified compounds. The remaining species were summed up to get a total response of the plume. A relative abundance was then calculated for each species by taking its average value divided by the total plume response. This is what establishes a fingerprint for the source. Characterizing a source in this manner lends to understanding a source regardless of the magnitude of the concentrations. Many sources will emit the same species; therefore, their presence does not automatically translate to source identification. However, the relative abundance of the species within the plume can be different enough between sources to make them unique. Figure 5-2 shows the fingerprint for the fuel plume from Figure 5-1. For this analysis, species that did not have a relative abundance of at least 0.5% were excluded. An example and interpretation of the fuel fingerprint can be found below. This was performed for all the identified plumes for the different sources (exhaust, asphalt, fuel). The individual spectra for each source were then averaged together to get an average source fingerprint.



Figure 5-2. The Relative Abundance of Key Species Within the Fuel Plume from Figure 5-1.

5.1.1 Exhaust Fingerprint

During the monitoring around SX Farm, there were many instances where sporadic wind conditions resulted in sampling ML exhaust. These instances were inspected by the SME and a subset of seven were chosen to represent laboratory exhaust. The exhaust plumes used for the fingerprint analysis are listed in Table 5-1. The table also lists the relative abundance of the different groups within the fingerprint. Benzene was included in the aromatic group instead of the COPC group for this analysis. Figure 5-3 shows the plume on September 10, 2018, at 10:04. Only a few key species are displayed, but strong increases in multiple species was observed.

Date	09/07/2018	09/10/2018	09/11/2018	09/11/2018	09/18/2018	09/18/2018	09/21/2018	Average
Plume Start	14:42	10:04	09:54	11:32	11:29	12:04	11:18	-
Background Start	14:43	10:02	09:25	11:25	11:20	12:10	11:15	-
COPCs	86.3	62.4	63.8	69.3	38.8	37.3	54.5	58.9
Known	3.1	8.0	6.7	7.4	3.4	4.1	11.9	6.4
Aromatics	5.9	7.5	8.6	6.3	30.1	39.7	5.1	14.7
Odors	0.0	0.6	0.0	0.0	1.7	1.0	0.6	0.5
Unknown	4.7	21.5	20.9	17.0	26.0	18.0	27.9	19.4





Figure 5-3. Time Series of Key Species Within the Exhaust Plume for One of the Plumes Used in Analysis.

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Figure 5-4 shows the fingerprint for each of the seven plumes, the average of these plumes, and the exhaust fingerprint presented in the Month 1 Report (53005-81-RPT-019, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 1*). The most obvious feature is the large relative abundance of acetaldehyde, which is expected since it is a known component of vehicle exhaust. The next important feature is the presence of the aromatics benzene, toluene, C₂-benzenes, C₃-benzene, and C₄-benzenes. These are known components of fuel and exhaust; therefore, like acetaldehyde, their presence is expected. In similar fashion, formaldehyde and fragmentation ions at nominal m/z 41 and 43 are known components within exhaust. The COPCs comprise of 58.9% of the signal. Benzene was not included in this percentage and was grouped with the other aromatics which made up 14.7% of the fingerprint. Other known species contributed 6.4%, odors made up 0.5%, and unknowns accounted for the remaining 19.4%.

The analysis of an exhaust plume in the Month 1 Report (53005-81-RPT-019) during the AY-102 rinse activities reported fewer species, but the overall fingerprint compares well with the new results. The relative abundances are different, but the key species remained the same (acetaldehyde, formaldehyde, aromatics, acetone, methyl nitrate, nominal m/z 41 and 43). The fingerprint is not expected to always be the same since engine emissions can vary depending on temperature, running load, condition, and many other factors. However, even if the relative abundances can vary, the exhaust is expected to contain species common for fuel combustion. The presence of a high relative abundance of acetaldehyde accompanied by formaldehyde, aromatics, and methyl nitrite would be good indicators of potential engine exhaust influences.



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5.1.2 Asphalt Fingerprint

Under favorable wind conditions, the ML Operators were successful in monitoring multiple plumes from the asphalt paving activities. When the operators smelled a strong asphalt odor accompanied by an instrument response, it was entered into the logbook. A subset of these plumes were analyzed with the method described above and used to develop a representative fingerprint for asphalt. The asphalt plumes used for the fingerprint analysis are listed in Table 5-2. The table also lists the relative abundance of the different groups within the fingerprint. Benzene was included in the aromatic group instead of the COPC group for this analysis. Figure 5-5 shows the plume on September 14, 2018, at 11:15. Only a few key species are displayed, but strong increases in multiple species was observed.

Date	09/11/2018	09/14/2018	09/19/2018	09/19/2018	09/19/2018	09/22/2018	09/22/2018	Average
Plume Start	12:24	11:15	07:48	07:50	11:50	07:12	09:27	-
Background Start	12:21	11:18	07:45	07:45	12:05	06:56	09:24	-
COPCs	27.6	22.2	14.2	19.1	32.8	25.0	8.1	21.3
Known	4.5	4.4	3.7	5.1	4.7	5.5	13.4	5.9
Aromatics	12.7	11.9	42.7	20.5	17.4	8.7	11.8	18.0
Odors	2.6	2.9	2.7	2.1	2.0	2.6	2.4	2.5
Unknown	52.6	58.5	36.7	53.1	43.2	58.1	64.3	52.4

Table 5-2. Date and Time of Asphalt Plumes Used in the Analysis with Relative Abundances of Key Species Groups.

Figure 5-6 shows the fingerprint for each of the individual plumes and the average of these plumes. The largest signal occurred at nominal m/z 41, which is a common fragmentation ion. Alkenes, alkanes, cycloalkanes, and aromatics with large alkyl substitution groups have all been shown to produce fragmentation responses at nominal m/z 41 and 43 (Gueneron, 2015). Acetaldehyde, 1,3-butadiene, 1-butanol+butenes, and toluene showed similar and prominent abundances. Unknowns make up the largest portion of the asphalt fingerprint at 52.4%. The COPCs and aromatics have a similar abundance at 21.3% and 18.0%, respectively.

Figure 5-6. The Individual and Average Relative Abundances of Key Species in Asphalt.

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5.1.3 Fuel Fingerprint

During observations, there were rare occurrences where the ML Operators smelled a strong fuel odor accompanied by a large plume. These events were analyzed with the method described previously. The fuel plumes used for the fingerprint analysis are listed in Table 5-3. The table also lists the relative abundance of the different groups within the fingerprint. Benzene was included in the aromatic group instead of the COPC group for this analysis. The fuel plume observed on September 18, 2018, at 10:29, was also part of the detailed analysis performed in response to the Abnormal Operating Procedure (AOP)-015 event occurring at the SX Farm that day. Refer to 53005-81-RPT-015, *Special Communication – TerraGraphics Mobile Laboratory Monitoring for September 18, 2018*, for further details. Figure 5-7 shows the plume on September 18, 2018, at 10:29. Only a few key species are displayed, but strong increases in multiple species were observed.

Date	Date 09/18/2018		09/21/2018	Average
Plume Start	10:29	12:16	09:42	-
Background Start	10:25	12:05	09:40	-
COPCs	18.4	15.5	17.3	17.1
Known	4.7	4.1	4.6	4.4
Aromatics	12.4	17.1	17.0	15.5
Odors	2.8	3.1	2.2	2.7
Unknown	61.7	60.2	58.9	60.3

 Table 5-3. Date and Time of Fuel Plumes Used in the Analysis with Relative Abundances of Key Species Groups.

Figure 5-7. Time Series of Key Species Within the Fuel Plume for One of the Plumes Used in Analysis.

Figure 5-8 shows the fingerprint for each of the individual plumes and the average of these plumes. The largest responses were at nominal m/z 41, 1-butanol+butenes, and 1,3-butadiene. There is also a prominent presence of aromatics within the plume at 15.5%, but the unknowns make up most of the response contributing 60.3%. The COPCs are comparable to the aromatics at 17.1%.

5.1.4 Source Fingerprint Comparison

The exhaust, asphalt, and fuel sources were the primary observations while monitoring in support of the SX Paving Project. All three sources had very similar constituents, but there are differences in the relative abundances. Table 5-4 lists the average fingerprints for the three

sources for the relative abundance of the different groups. Benzene was included in the aromatic group instead of the COPC group for this analysis. The biggest difference is that most of the exhaust is attributed to COPCs while the asphalt and fuel are primarily unknowns. They all contain comparable amounts of aromatics and knowns. The asphalt and fuel sources seem to contain more odor compounds than that of the exhaust, but the odor compounds do not contribute a significant amount for all three. When grouped together in this manner, there does not appear to be much difference between the asphalt and fuel. Even though the asphalt and fuel smells are easily distinguished, the sources are co-located. The fuel is used to spray the equipment and miscellaneous equipment at the paving activity location. Given this, even though there was a strong fuel smell signifying its use, the proximity to the paving activities means there are likely asphalt influences within the fuel plumes. This could explain some of the similarities in this level of analysis, but there are differences once you look at relative abundances of specific species.

Date	Exhaust	Asphalt	Fuel
COPCs	58.9	21.3	17.1
Known	6.4	5.9	4.4
Aromatics	14.7	18.0	15.5
Odors	0.5	2.5	2.7
Unknown	19.4	52.4	60.3

Table 5-4. Relative Abundances of Key Groups Within Exhaust, Asphalt, and Fuel Plumes.

Figure 5-9 shows the average source fingerprints for the three sources. The different groups laid out in Table 5-4 are represented as different colors to illustrate the groups relative contribution to the fingerprint. All three sources have large contributions from the COPCs (red) and aromatics (blue). They all also contain most of the same COPCs with acetaldehyde, 1-butanol+butenes, 2-propenal, and 1,3-butadiene being present in all three sources. The noticeable difference is that the exhaust is dominated by acetaldehyde while the asphalt and fuel are dominated by 1-butanol+butenes and 1,3-butadiene. This difference could be attributed to the combustion process creating acetaldehyde within the exhaust while the asphalt and fuel sources do not. The trend in acetaldehyde between the three sources can also lend some insight into acetaldehyde within the plumes being a result of combustion. If the acetaldehyde is created during combustion, the fuel plume should have none present, but there is a response shown, if relatively small. This can be attributed to activities around the fuel since it was used at the same location of asphalt activities and machinery. Some of the emissions from paving activities are mixed with the fuel plume. The acetaldehyde becomes more prominent within the asphalt plume.

The general activities related to paving can result in the formation of acetaldehyde, in combination with the use of combustion engines from the paving vehicles. The mix of the equipment emissions with those of the asphalt itself create the unique fingerprint with acetaldehyde being a prominent species, but not dominant. The acetaldehyde becomes dominant when the exhaust from a combustion engine becomes the only emission source within the plume. Acetaldehyde contributes 1.2% to the fuel, 5.7% to the asphalt, and 32.8% to the exhaust

fingerprints. There is approximately a factor of 5 difference between fuel and asphalt with almost a factor of 6 difference between asphalt and exhaust. In a basic interpretation, the fuel plume is relatively free from exhaust, the asphalt is a mixture resulting in some dilution of exhaust with other emissions, and the exhaust is representative of a sole exhaust source fingerprint.

The 1-butanol+butenes and 1,3-butadiene appear to have the opposite relationship with their relative abundance being the highest in fuel, reduced in the asphalt, and much lower within the exhaust. The first inclination would be that it is transformed in the combustion process, but the lower abundance within the exhaust and asphalt could be dilution or the prominence of acetaldehyde. Toluene is a common species within all the fingerprints and its behavior within the PTR-MS is well understood. This qualifies it as a good species for comparing relative abundances within a fingerprint. If we divide the 1-butanol+butenes and the 1,3-butadiene relative abundances by that of toluene we can get a ratio to allow for comparison. Table 5-5 shows ratios of these COPCs to toluene. The ratios seen in the asphalt and fuel are relatively similar, with slightly lower ratios in the asphalt. There could be increased toluene emissions from the paving activities that drives this ratio lower for asphalt. For the exhaust, the 1-butanol+butenes and 1,3-butadiene relative abundances decrease drastically compared to the asphalt and fuel, but they increase in relation to toluene. The decrease in relative abundance compared to asphalt and fuel can be attributed to the high levels of acetaldehyde created within exhaust. The relative increase of the 1-butanol+butenes and 1,3-butadiene compared to the toluene could be more efficient combustion of toluene resulting in an increase in the ratio.

Ratio to Toluene	Exhaust	Asphalt	Fuel
formaldehyde	1.37	0.08	-
methanol	2.04	0.38	-
nominal m/z 41	1.42	1.61	3.66
nominal m/z 43	1.41	0.60	1.17
acetaldehyde	7.64	0.83	0.34
1,3-butadiene	0.35	0.75	1.82
1-butanol+butenes	0.68	0.89	2.50
acetone	0.90	0.30	-
methyl nitrate	0.71	-	-
furan	0.03	-	-
isoprene	0.17	0.38	0.96
COPCs at m/z 71	0.19	-	-
odors at m/z 91	0.07	0.23	0.49
odors at m/z 105	0.06	0.14	0.28
2,4-dimethylpyridine	0.06	0.03	-
monoterpenes	-	0.06	0.21

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Nominal masses m/z 41 and 43 are common fragmentation ions and are common among all three sources, with a decreased but still prominent presence in the exhaust. When looking at their ratio to toluene there is less of a difference between the three sources. Fuel has slightly higher nominal m/z 41 ratio and asphalt has a lower nominal m/z 43 ratio, but the ratios compare well. This could be a sign that all three sources contain a similar abundance of compounds susceptible to fragmentation that create a response at these ions. Alkenes, alkanes, cycloalkanes, and aromatics with large alkyl substitution groups are known to fragment to these ions and their presence would be expected in all three sources (Gueneron, 2015).

Among the similar species among all three sources, isoprene and the odors at m/z 91 and m/z 105 stand out. Isoprene is a biogenic compound and it is not hypothesized that it is among the constituents generated by any of the three sources. This response could be attributed to an unidentified species present in the sources. Some cyclohexenes and cyclohexanes have been shown to fragment and generate a response at m/z 69, which would be expected to be a constituent of all three sources (Gueneron, 2015). The odors at m/z 91 and m/z 105 showed a comparable ratio to toluene for all three sources, with the exhaust being slightly lower than the other two.

While all three sources contain many similar species, there are some distinct differences. It is important to understand the common components among the sources, but the unique species offer valuable information for distinguishing the sources from one another. The exhaust has three key species that were not observed within the asphalt or fuel. Methyl nitrite, furan, and COPCs at m/z 71 appear to be unique to the exhaust and are all COPCs, with methyl nitrite being the most abundant and present in almost as much quantities as toluene. Formaldehyde, methanol, and 2,4-dimethylpyridine were present in both the exhaust and asphalt, but their ratio to toluene within the exhaust are an order of magnitude higher than the asphalt. 2,4-dimethylpyridine was also present within the exhaust and asphalt at minimal but comparable quantities. The only species that appear to be prominent and more unique to fuel are the monoterpenes. The ratio to toluene within fuel is three times higher than the ratio to toluene within asphalt. Like isoprene, monoterpenes are biogenic compounds, but none of these sources are suspected of emitting them. It is more probable that there is an unidentified species within asphalt and fuel that responds at the same ion signal as the monoterpenes.

This comparison helps develop valuable tools for future plume analysis. The ML Operators were present during sampling to observe and make observations of potential plume sources in real time, but that is not a feasible method for all types of deployment and operation. Taking this opportunity to understand the similarities and differences of these sources will help for plume identification when real-time observations are not feasible. A plume with high levels of acetaldehyde and the presence of methyl nitrate might be enough to distinguish the exhaust from asphalt or fuel. However, looking at the ratio to toluene for formaldehyde, methanol, nominal m/z 41, nominal m/z 43, and acetone would provide a reasonable benchmark for identification of exhaust. Essentially, comparing the fingerprint or ratios to toluene presented for any unknown plume will either help identify one of these sources or eliminate it as a candidate.

Figure 5-9. The Average Relative Abundances of Key Species in Exhaust, Asphalt, and Fuel.

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With CO₂ being a large constituent of combustion emissions, its presence can be a good indicator of engine emissions. The response of CO₂ within each of the exhaust, asphalt, and fuel plumes was determined and a ratio of CO₂ to toluene was calculated. Table 5-6 displays the resulting ratios. As expected, the CO₂ is prominent within exhaust with ratios to toluene spanning approximately 5 to 350 and averaging around 132 for the seven analyzed plumes. Comparing this to the average ratios of 2.22 in asphalt and 0.52 in fuel, the three sources are distinguishable. The variability within exhaust could be attributed to different operating conditions, engine performance, dilution dynamics, and unknown external influences. The variability within the asphalt could be attributed to changing activities related to paving operations, equipment performance, dilution dynamics, ambient conditions, and unknown external influences. However, engine-powered machinery was used in the paving process; thus some degree of CO₂ is expected to be within a plume identified as asphalt. This ratio is another tool that can help in the identification of plume sources. The presence of a high CO₂ to toluene ratio would suggest vehicle exhaust or at least the source has influence from a combustion process.

Exhaust		Asphalt		Fuel	
Time	CO ₂ :Toluene	Time	CO2:Toluene	Time	CO ₂ :Toluene
09/07/2018 14:42	14.3	09/11/2018 12:24	6.14	09/18/2018 10:29	0.94
09/10/2018 10:04	160	09/14/2018 11:15	1.10	09/19/2018 12:16	0.45
09/11/2018 09:54	207	09/19/2018 07:50	1.66	09/21/2018 09:42	0.17
09/11/2018 11:32	174	09/19/2018 11:50	0.94		
09/18/2018 11:29	8.56	09/22/2018 07:12	3.29		
09/18/2018 12:04	5.33	09/22/2018 09:27	0.19		
09/21/2018 11:18	352				
Average	132	Average	2.22	Average	0.52

 Table 5-6. Ratios of CO2 to Toluene within the Analyzed Plumes for

 Exhaust, Asphalt, and Fuel.

Due to its nature as a leading indicator for tank vapor, it is also important to consider the impact that ammonia had during this month. To date, there are no ammonia signals that have appeared to positively correlate to an increase in PTR signal. The table below shows statistical information for ammonia for each monitoring day during Month 2. Average values for ammonia throughout the month rarely exceeded 10 ppbv, and maximums only exceeded 20 ppbv twice. The case where the ammonia maximum was recorded to be 124 ppbv on September 10, 2018, was thoroughly investigated for any concurrent spikes in PTR signal. Figure 5-10 shows the key species identified within the exhaust, asphalt, and fuel during this unique event. There were increases in CO₂, acetaldehyde, and nominal m/z 43 just prior to seeing the ammonia plumes. The large response of CO₂ and acetaldehyde would lead to initial identification that this is an exhaust plume. Upon closer inspection, there is no response in other species associated with exhaust, asphalt, or fuel. The presence of CO₂ would indicate it is combustion related, but the source remains unidentified at this time.

Further analysis was performed for the plumes starting at 07:01 and 09:02. These plumes were associated with an increase in ammonia up to a max value of ~25 ppbv for the 07:01 plume and ~124 ppbv for the 09:02 plume. The response of ammonia was delayed compared to the other species due to instrument performance time and some sample line conditioning dynamics. The increase in ammonia during this period appear to coincide with the increases in CO_2 and acetaldehyde, but correlation of ammonia: CO_2 , or ammonia:acetaldehyde do not appear to be consistent between the plumes. Using maximum plume response values within the plumes would lead to ammonia: CO_2 ratios of approximately 1.1 and 25.5 for the 07:01 and 09:02 plumes respectively, which are more than an order of magnitude different. The ammonia: acetaldehyde ratios are slightly closer being 0.24 and 1.3 for the 07:01 and 09:02 plumes respectively, but there is still over a factor of 5 difference. A fingerprint for this source was calculated using the same criteria as the previous analysis for the plumes starting at 07:01 and 09:02.

Date	Ave. (ppbv)	St. Dev. (ppbv)	Rel St. Dev. (%)	Max (ppbv)	Median (ppbv)
08/31/2018	8.881	4.891	55.072	31.021	7.171
09/04/2018	5.916	1.906	32.214	14.216	5.060
09/05/2018	4.922	0.434	8.815	6.375	4.810
09/06/2018	7.855	2.294	29.206	13.434	6.954
09/07/2018	8.210	2.273	27.688	13.751	7.462
09/08/2018	5.279	1.450	27.473	9.738	4.692
09/10/2018	8.268	11.037	133.496	123.761	5.239
09/11/2018	3.854	0.786	20.403	8.498	3.660
09/12/2018	4.896	1.323	27.021	12.840	4.797
09/13/2018	4.166	0.697	16.723	6.965	3.983
09/14/2018	4.196	0.492	11.716	7.290	4.132
09/15/2018	4.205	0.774	18.408	7.492	3.949
09/17/2018	4.083	0.786	19.250	7.166	4.005
09/18/2018	4.633	0.814	17.572	8.453	4.378
09/19/2018	4.603	1.151	24.999	9.824	4.142
09/20/2018	4.146	1.313	31.677	10.424	3.631
09/21/2018	6.003	0.840	13.988	8.618	5.666
09/22/2018	5.978	1.046	17.491	9.964	5.950
09/24/2018	3.553	0.618	17.404	6.286	3.390
09/25/2018	10.767	1.648	15.304	13.488	11.148
09/26/2018	11.405	1.920	16.835	16.667	11.110
09/27/2018	9.640	0.880	9.131	11.958	9.518

Table 5-7. Statistical Information for NH₃ for Each Monitoring Day of Month 2.

Figure 5-10. Time Series During the Unique Source Observations of Key Species Identified Within the Exhaust, Asphalt, and Fuel Plumes.

Figure 5-11 shows the resulting fingerprint for the September 10, 2018, plumes starting at 07:01 and 09:02. The acetaldehyde is the most prominent VOC within the plume. The acetic acid + acetate fragment, nominal m/z 43, and nominal m/z 44 make up a majority of the remaining signal. Some influences from formaldehyde, methanol, and acetone are worth noting, but they are not significant. The presence of methyl nitrite is of interest since it was only found to be

significant within the previous exhaust analysis and does not show up within the asphalt or fuel fingerprints. Minor amounts of nominal m/z 99 were observed in the exhaust, asphalt, and fuel, but it appears to be more prominent within these unique plumes. One of the key components of the fingerprint is the lack of aromatics, which contributed significantly to the exhaust, asphalt, and fuel sources. As stated previously, the presence of CO₂ points towards a combustion-related source, but the lack of aromatics suggests that this combustion source is not from a gasoline or diesel engine. The ratio of CO₂ to toluene within the 07:01 plume was ~535, which is higher than observed in the exhaust, but this ratio is driven by the low abundance or lack of toluene within the plume. Only 0.06 ppbv of toluene was detected within the 07:01 plume, which passes the 0.05 ppbv threshold set by the analysis, but that signal contributed to less than 0.5% of the signal and is classified as negligible within the fingerprint. In the case of the 09:02 plume, there was no response in the toluene; thus no ratio can be calculated. Future analysis of unique plumes may benefit from exploring different ratios of abundant species beyond comparison to toluene to create a more comprehensive suite of metrics in identifying plume sources.

Figure 5-11. Relative Abundance of Key Species Within the 07:01 and 09:02 Unique Plumes on September 10, 2018.

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5.2 AY-102 Rinse

On September 7, 2018, the ML monitored downwind of AY-102 during tank rinsing activities. This was similar to the monitoring on August 24, 2018, and August 26, 2018, reported in the Month 1 Report (53005-81-RPT-019) where the ML monitors for COPCs downwind of AY-102 before, during, and after the activities. The SME inspected all the resolved peaks to identify potential plumes of interest and a response and fingerprint for each plume was calculated. Species within the plume that had a response of at least 0.05 ppbv and contributed at least 0.5% to the overall plume signal were included in further analysis. The ten plumes that were analyzed began at 06:38, 10:12, 11:08, 11:43, 13:41, 13:46, 14:08, 14:12, 14:45, and 14:50. After inspection of the fingerprints of these plumes, some of them were determined to be from the same source. The six plumes occurring at 06:38, 11:08, 13:41, 13:46, 14:45, and 14:50 were identified as exhaust plumes. The two plumes occurring at 10:12 and 11:43 were identified as potential exhaust from a vehicle cold start. The remaining two plumes occurring at 14:08 and 14:12 showed similar fingerprints, but from an unknown source. These groups of plumes were averaged and the results are displayed in Figure 5-12.

Figure 5-12 also includes the average exhaust fingerprint observed during the SX paving monitoring. The average exhaust fingerprint observed during the AY-102 rinse when compared to the SX Paving displays a recognizable pattern. Both are dominated by acetaldehyde, with prominent responses from aromatics, formaldehyde, nominal masses m/z 41 and 43, and methyl nitrite. It was these key species within the plumes that led the SME to identify them as exhaust plumes. The AY exhaust does appear to have a lower relative abundance of all the species, but this is a result of more species being identified within the AY fingerprint versus the SX fingerprint. This difference could be attributed to other sources in the area contributing a small amount to the exhaust plume, differing engine performance, or the conditions and plume magnitude were more conducive for minor species to be identified.

The ML Operators placed an entry in the logbook at 10:12 stating that there was a vehicle cold start in front of the ML and that a benzene spike was observed. This plume was inspected and the plume occurring at 11:43 had a similar fingerprint and was classified as a vehicle cold start. As expected, when comparing the average of these two fingerprints in Figure 5-12 to the exhaust signatures, it is found that they both contain the same key species. The distinguishing feature is that acetaldehyde no longer dominates the vehicle cold start fingerprint. Acetaldehyde is still the most prominent species, but the aromatics contribute a larger portion to the abundance. When an engine is first started after being off for an extended period, the engine is operating below running efficiency. The combustion of the fuel will not be as complete during this time. This is displayed clearly in the fingerprint with components of the fuel (aromatics) contributing to a large portion of the abundance and combustion products (acetaldehyde) showing a reduced contribution.

The unknown source fingerprint is dominated by the acetic acid + butenes, methanol, and nominal m/z 43 signals, along with lower contributions of acetaldehyde and formaldehyde. These species are common in the atmosphere except for nominal m/z 43 which is a common fragmentation ion. Even though the exhaust contains some of these species, the fingerprints are distinguishable and do not appear to be related to exhaust emissions. Identification of the source is difficult at this time, but this fingerprint provides a valuable comparison if this unknown source is monitored in future operations.

Figure 5-12. Average Relative Abundances of Key Species in Exhaust, Cold Start Exhaust, and a Unique Plume During AY Support Operations Along with the Average Exhaust Fingerprint Observed During the SX Paving Support Operations.

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5.3 Septic Analysis

From September 24, 2018, through September 27, 2018, the ML was monitoring around A Farm. One of the goals was to track the fugitive emissions from the septic tanks located east of the 242-A Evaporator. The operators were successful in monitoring the septic emissions downwind from the source. Using knowledge of the constituents of the septic plume analysis in the Month 1 Report (53005-81-RPT-019) and ML logbook notes, eight septic plumes were analyzed to generate a fingerprint using the same method described previously. The location of the ML during the eight septic plumes analyzed are displayed in Figure 5-13. On September 24, 2018, the ML Operators observed possible septic plumes at 10:57 and inspection of the data led to analysis of plumes occurring at 11:04 (Plume 1) and 11:30 (Plume 2). On September 25, 2018, septic plumes were monitored repeatedly from 08:15 until past 09:00 as recorded in the logbook and the plumes occurring at 08:36 (Plume 3) and 09:02 (Plume 4) were selected for analysis. On September 26, 2018, the ML Operators recorded a strong septic smell at 08:15, which led to using the plumes at 08:15 (Plume 5) and 08:37 (Plume 6) for analysis. On September 27, 2018, a strong septic smell observed by the ML Operators at 07:15 led to analysis of plumes occurring at 07:14 (Plume 7) and 07:21 (Plume 8). The resulting fingerprints for these eight plumes are displayed in Figure 5-14.

Figure 5-13. The Location of the Mobile Laboratory During the Eight Septic Tank Plumes.

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The grey sticks in Figure 5-14 are the fingerprints of each of the eight plumes. The sticks are only present if the species was detected within the fingerprint. This indicates that plumes that did not contain that species will not have a stick. Based on this, the common constituents within a septic plume are clear. All eight plumes observed strong responses from hydrogen sulfide, methyl mercaptan, and toluene. Nominal m/z 48 and nominal m/z 51 also showed a response within four of the plumes. The other species listed were only present within one or two of the plumes. The red bars in Figure 5-14 show the average of all eight septic plumes. As reference, the septic emission fingerprint presented in the Month 1 Report (53005-81-RPT-019) is represented by the blue sticks in Figure 5-14. When comparing the Month 1 fingerprint to the average of the eight plumes, there are similarities as expected, but also some stark differences. The toluene and methyl mercaptan are major constituents of both in comparable relative abundances with the Month 1 fingerprint being slightly larger. The most drastic difference is in the relative abundance of hydrogen sulfide. The eight plume average shows hydrogen sulfide as the largest response while it is only a minor constituent in the Month 1 fingerprint. There was also a large presence of methanol and dimethyl sulfide + ethanethiol within the Month 1 fingerprint while the eight plumes only saw small contributions within only two and three of the plumes, respectively. More monitoring and analysis is required to resolve the reason for these differences, but it would be influences from other nearby sources, changes in weather, use of the septic system, or a mechanism not well understood at this time. Even with these differences, the important components of septic emissions are further defined. Methyl mercaptan and toluene remain the best indicators of septic emissions with the presence of hydrogen sulfide as a good secondary indicator. Further exploration and monitoring will help define the importance of the other species detected within some of the plumes.

Figure 5-14. The Individual and Average Relative Abundances of Key Species Within the Septic Plumes Along with the Septic Fingerprint Presented in 53005-81-RPT-019 (Month 1 Report) for Reference.

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6.0 QUALITY ASSESSMENT

During the August 31, 2018, to September 30, 2018, monitoring campaign, quality control procedures were followed by the TerraGraphics Vapor Team: Data Collection and Data Processing. Data were collected and quality documents completed according to Procedure 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. All potential quality-affecting deviations have been captured in Deficiency Reports (DRs) and are summarized below with some interpretation.

During the August 31, 2018, to September 30, 2018, monitoring campaign, there was one (1) DR. Deficiency Report DR18-007 documents an error that occurred on September 5, 2018, on the PTR-MS 6000 X2 that resulted in two hours of data and required a software restart to resolve the issue. See Appendix A for a copy of this DR.

6.1 Lessons Learned – DR18-007

On September 5, 2018, the PTR-MS experienced a software-related glitch that resulted in loss of approximately two hours of PTR data. The WRPS Project Manager, TerraGraphics Quality Assurance (QA) Representative, and SME were notified of the issue. Through remote access, the SME resolved the issue by restarting the software and restoring funnel settings. A span check was performed to confirm the PTR-MS was operating correctly and the PTR-MS was collecting data shortly after the span passed.

IONICON, the PTR-MS instrument manufacturer, was notified of the software error and the TerraGraphics QA Representative continues to monitor this glitch for DR trend purposes.

7.0 CONCLUSION AND RECOMMENDATIONS

This report deeply explores source characterization for a variety of sources and establishes a number of important fingerprints. Supporting the SX paving activities provided a large dataset for analyzing exhaust, asphalt, and fuel sources. The Month 1 Report (53005-81-RPT-019) contains the first analysis of exhaust which was greatly expanded by the further analysis in this report. Key species, both common and unique, were identified for each of the sources and will assist in future identification of plumes from unknown sources.

The exhaust fingerprint showed the prominence of acetaldehyde, aromatics, formaldehyde, methanol, nominal m/z 41, nominal m/z 43, and methyl nitrite. The characteristic species is acetaldehyde, but its presence alone is not enough to definitively distinguish it from other sources. The fingerprint was dominated by approximately 59% COPCs, 19% unknown, and 15% aromatics with the remaining consisting of known species and odors. The asphalt fingerprint was similar to the exhaust with acetaldehyde, aromatics, methanol, nominal m/z 41, and nominal m/z 43 being large constituents, but also had significant abundances of 1-3-butadiene and 1-butanol+butenes. There was a larger contribution of unknown species within the asphalt compared to the fuel. The fingerprint was dominated by unknowns making up 52%, with COPCs at 21%, aromatics at 18%, and the remaining contributed to known species and odors. Like the exhaust and asphalt, the fuel fingerprint had large influences from nominal m/z 41, nominal m/z 43, and aromatics. It also followed along the asphalt containing large abundance of 1,3-butadiene and 1-butanol+butenes plus seeing large responses of unknown species. The unknowns accounted for 60% of the signal, the COPCs for 17%, aromatics for 16%, and the remaining from known species and odors.

Looking at the relative contribution of the different groups, the exhaust is different from the asphalt and fuel with the COPCs contributing most of the signal versus the unknowns. They all have a similar abundance of aromatics and the other known species and odors contributed the least within all three sources, with the odors being more prominent within the asphalt and fuel. One distinguishable feature is the abundance of acetaldehyde. All three sources contain it, but the relative abundance within exhaust is approximately five times larger than asphalt and 30 times larger than fuel.

The ratios of the key species to toluene offered the most insight into the abundance dynamics. This stresses the similarities and difference between the three sources. Nominal m/z 41, nominal m/z 43, odors at m/z 91, odors at m/z 105, and the signal at isoprene showed similar ratios to toluene. The methyl nitrite, furan, and COPCs at m/z 71 seemed to only be present within the exhaust and the ratios to toluene compared to formaldehyde, methanol, and 2,4-dimethylpyridine was an order of magnitude higher than in the asphalt. The fuel had fewer unique species, but it appears that the signal at monoterpenes is slightly more prominent than within the asphalt. The ratios of CO₂ to toluene also show it as a good indicator of exhaust. This is expected since CO₂ will be prominent in combustion source plumes. The average ratio within exhaust was approximately 60 and 250 times greater than within the asphalt and fuel, respectively. These ratios will lead to future identification of unknown plumes and help develop the methods for identifying other key ratios from sources of interest.

There was not much activity in ammonia during the SX paving monitoring with daily average concentrations rarely exceeding 10 ppbv. The unique plumes on September 10, 2018, were the only exception with influence from an unidentified source resulting in ammonia up to 124 ppbv. The increased ammonia looks to be associated with CO₂ and acetaldehyde, but further investigation of two plumes at 07:01 and 09:02 showed that there seems to be an inconsistent correlation. Fingerprint analysis of the source showed acetaldehyde, nominal m/z 41, nominal m/z 43, and acetic acid + acetate fragment accounting for a majority of the response. The presence of methyl nitrite along with CO₂ and acetaldehyde, suggests a combustion source since these things were all prominent within the exhaust. The lack of aromatics within the source is unexpected and could be the more distinguishable feature of this unidentified source when compared to exhaust, asphalt, and fuel.

The September 7, 2018, deployment to monitor downwind of AY-102 during rinse activities yielded additional exhaust plumes, vehicle cold start plumes, and another unique source. The exhaust plumes closely resembled those observed during SX paving monitoring, as expected. The relative abundances for the AY exhaust were lower because additional species were identified. The vehicle cold start plumes showed that the relative abundance is much higher which is expected due to the engine not at running performance and not burning fuel as efficiently. The unknown source consisted primarily of methanol, nominal m/z 43, and acetic acid + acetate fragment, with a lesser influence from formaldehyde, acetaldehyde, and methyl acetate. These species are common, so identification of this source is difficult without further information.

The eight septic plumes analyzed during the 4 days of monitoring A Farm showed similar results to the Month 1 septic analysis. Methyl mercaptan and toluene remain importance septic tracers. There were significant differences with these eight plumes showing dominance of hydrogen sulfide, and the Month 1 plume showing a lesser contribution. There was also a prominent presence of methanol and dimethyl sulfide + ethanethiol in the Month 1 fingerprint. There are potential mechanisms that are not well understood that have led to this difference, but the eight septic plumes analyzed in this report show good continuity regarding composition.

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APPENDIX A

DEFICIENCY REPORT DR18-007

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TerraGraphics	
DEFICIENCY REPORT	
Deficiency Report No.:	Page:
DR18-007	1 of 1
Originator (Print Name):	Signature: Date:
Matt Erickson	What h 09/07/2018
Project No./Title:	
18-66409-01 Mobile Laboratory Servic	e and Lease
PAAA Reportable:	10 CFR 21 Reportable:
🛛 No 🗌 Yes	🛛 No 🗌 Yes
Description of Requirement that was Violate	d and of Deficiency:
On 09/05/2018, the PTR-MS in the Mo that resulted in loss of approximately tw	bile Laboratory experienced a software related glitch vo hours of PTR-MS data.
Concurrently during this same time peri returned to the CSO to retrieve a new ra	iod, the CSO radio ran low on batteries and the ML adio. This took approximately one hour
COD	
COR	RECTIVE ACTION
Corrective Action: Per 66409-RPT-004, Rev.03, Mobile La followed: "If any itam in this proceedure	RECTIVE ACTION
Corrective Action: Per 66409-RPT-004, Rev.03, Mobile La followed: "If any item in this procedure for the scope of work, the ML operator problem persists, inform the WRPS PM, Section 5.0 Deficiencies."	ERECTIVE ACTION aboratory Operational Procedure para. 2.0 General was fails to conform to the appropriate acceptance criteria may perform the step again to verify the result. If the Senior Scientist/SME, QAR, and PM and refer to
Corrective Action: Per 66409-RPT-004, Rev.03, Mobile La followed: "If any item in this procedure for the scope of work, the ML operator is problem persists, inform the WRPS PM, Section 5.0 Deficiencies." On 09-05-18, the corrective action was to PM (11:00), TG QA Representative of to contacted at 9:41, and the issue was reso Completion Date: 09/05/2018 Deficiency Cause and Extent of Condition:	aboratory Operational Procedure para. 2.0 General was fails to conform to the appropriate acceptance criteria may perform the step again to verify the result. If the Senior Scientist/SME, QAR, and PM and refer to to inform the WRPS PM (09:54), TerraGraphics' project he PTR-MS data loss. The Subject Matter Expert was olved through remote access.
Corrective Action: Per 66409-RPT-004, Rev.03, Mobile La followed: "If any item in this procedure for the scope of work, the ML operator is problem persists, inform the WRPS PM, Section 5.0 Deficiencies." On 09-05-18, the corrective action was PM (11:00), TG QA Representative of t contacted at 9:41, and the issue was reso Completion Date: 09/05/2018 Deficiency Cause and Extent of Condition: The PTR-MS 6000 X2 is state of the sec	aboratory Operational Procedure para. 2.0 General was fails to conform to the appropriate acceptance criteria may perform the step again to verify the result. If the Senior Scientist/SME, QAR, and PM and refer to to inform the WRPS PM (09:54), TerraGraphics' project he PTR-MS data loss. The Subject Matter Expert was olved through remote access.