PTR-MS MOBILE LABORATORY VAPOR MONITORING MONTHLY REPORT – MONTH 1

Report No. 53005-81-RPT-019
Revision 0
August 6, 2018 – August 28, 2018

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Record of Revision

Revision	Date	Pages/Sections Changed	Brief Description
0	10/2019	All	Original Issue.

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Acronyms and Abbreviations

ASTM	ASTM International, Inc.
COPC	Chemical of Potential Concern
DR	Deficiency Report
FY	Fiscal Year
MDL	Method Detection Limit
ML	Mobile Laboratory (Mobile Vapor Monitoring Laboratory)
NDMA	N-nitrosodiethylamine
NEMA	N-nitrosomethylethylamine
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
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). 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 1, field monitoring was performed in support of the Fugitive Emissions Team at sites located both on and off the Hanford Site. Preventative maintenance, verifications, and calibrations were performed on the Mobile Laboratory instrumentation.

1.0 DESCRIPTION OF TESTS CONDUCTED

During Month 1, spanning the dates of August 6, 2018, through August 28, 2018, the Mobile Laboratory (ML) was deployed to monitor chemicals of potential concern (COPCs) on the Hanford Site, and to characterize sources of potential odor-causing compounds both on and off the Hanford Site.

The ML was deployed to several locations around the A Farms on the Hanford Site for 9 days and off-site at Weston Mountain Onions for 4 days during Month 1.

Description of activities that were conducted are as follows:

- Week 1
    - Source Characterization of septic tanks
    - Source Characterization of onions at Weston Mountain Onions
    - Mobile Area Monitoring of A Farms
- Week 2
    - Source Characterization of onions at Weston Mountain Onions
    - Source Characterization of septic tanks
    - Mobile Area Monitoring of A Farms
- Week 3
    - Source Characterization of onions at Weston Mountain Onions
    - Source Characterization of septic tanks
    - Mobile Area Monitoring of A Farms
    - Mobile Area Monitoring in support of the AY-102 Rinse
- Week 4
    - Mobile Area Monitoring in support of the AY-102 Rinse
    - Source Characterization of onions at Weston Mountain Onions
    - Mobile Area Monitoring of A Farms
    - ML Demonstration for Washington River Protection Solutions, LLC (WRPS) personnel

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.

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 1, 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 1. 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*.

2.1.1.1 Proton Transfer Reaction – Mass Spectrometer Sampling

The 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 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.

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[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 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] CO_2 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)18 utilized the IONICON®[6] 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.

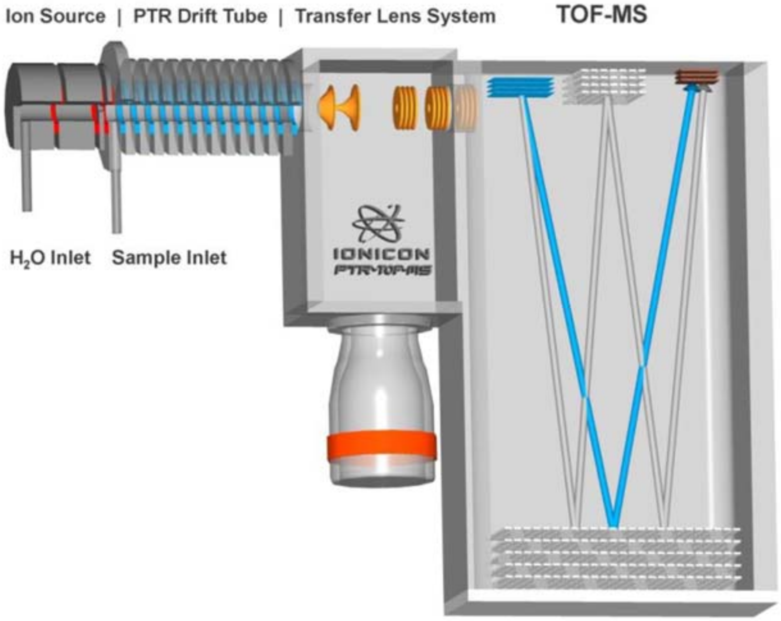

Figure 2-1. The General Configuration of an IONICON Proton Transfer Reaction – Time of Flight Instrument.

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[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.
[6] IONICON is a registered trademark of Ionicon Analytik Gesellschaft m.b.H., Innsbruck, Austria.

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.

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

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 ε_{RH+} and ε_{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:

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

where *[AIR]* is the number density of air (molecules/cm^3) 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 of Testing and Materials (ASTM)®[7], and National Institute for Occupational Safety and Health (NIOSH)®[8]. 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.

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

[8] 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 1 was accomplished by the kinetic approach.

2.2.2 Carbon Dioxide Monitor

Carbon dioxide is not a COPC; however, monitoring CO_2 is necessary for correlation of vapor signals to combustion processes or other sources. There are numerous combustion sources near the sampling sites during Month 1 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 CO_2 monitor used in the TerraGraphics ML was the LI-COR Model 840A. The Li-840A 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 CO_2 monitor are used to predict when VOC measurements from the PTR-MS come from combustion sources.

The CO_2 monitor used during Month 1 was operated using a factory calibration. Periodic checks of the unit were made with zero-air and ambient background air (ambient atmospheric CO_2 levels are approximately 400 ppm), 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 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 NH_3 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 NH_3 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 ± 0.005°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 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.

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

2.3 Confirmatory Measurements (if Applicable)

During Month 1, no confirmatory samples were taken. The sampling system within the ML was tested and verified using a Carbotrap®[9]-300 and Thermosorb® [10](n) cartridge that was analyzed by ALS Environmental.

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[9] Carbotrap is a registered trademark of Sigma-Aldrich Co., LLC, St. Louis, Missouri.
[10] Thermosorb is a registered trademark of Ellutia Limited Company, Cambridgeshire, United Kingdom.

3.0 CALIBRATION METHODS AND CALIBRATION GASES USED

Table 3-1. Calibrated Gases in use During Month 1.

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	TIBI-21-0.5-1	08/06/2022
VOC	THBI-21-0.5-2	07/18/2022

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 CO_2 Analyzer had no specific errors associated with 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 (±20%). The measurement accuracy of a properly calibrated instrument is listed in the LI-COR factory specifications as ±3% of reading.

4.1.3 Ammonia Monitor

The Picarro G2103 Ammonia Monitor had no specific errors associated with 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 (±20%). The measurement accuracy of a calibrated instrument listed in the Picarro factory specifications is ±5% of reading.

4.1.4 Weather Station

The Airmar 150WX Weather Station had no specific errors associated with 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*.

4.2 Method Detection Limit Study

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 TOF 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 three 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.

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

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)

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

Odor Name	MDL	RL
methyl mercaptan	0.047827	0.143481
dimethyl sulfide; ethanethiol	0.0362787	0.108836
allyl mercaptan	0.0448935	0.1346804
1-propanethiol; Isopropyl mercaptan	0.0292329	0.0876988
2-butene-1-thiol	0.029182	0.0875461
Diethyl Sulfide; 2-methylpropane-2-thiol	0.1569644	0.4708933
thiopropanal sulfuroxide	0.0239459	0.0718376
dimethyl disulfide	0.0237888	0.0713664
1-pentanethiol; 2,2-dimethylpropane-1-thiol	0.1251044	0.3753131
benzenethiol	0.0667393	0.2002179
diallyl sulfide	0.0757774	0.2273321
methyl propyl disulfide	0.0425556	0.1276668
methylbenzenethiol	0.0792234	0.2376702
dimethyl trisulfide	0.0488313	0.1464939
(1-oxoethyl) thiophene	0.1015274	0.3045822
(1-oxopropyl) thiophene	0.0761237	0.2283711
dipropyl disulfide	0.0625015	0.1875046
methyl propyl trisulfide	0.1212443	0.3637329
dimethyl tetrasulfide	0.0468888	0.1406663
dipropyl trisulfide	0.0708488	0.2125463
diphenyl sulfide	0.082742	0.248226

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 Septic Analysis

Seven days in August 2019 were focused on characterization and tracking of the septic tanks located east of the 242A Evaporator. Monitoring was performed at various locations downwind of the septic tanks. Vapors from the septic tank are hypothesized to travel downwind and result in workers smelling an unknown substance. These days included the initial studies to learn about the composition of the septic tanks, attempts to identify the odors, and investigation into how far downwind the septic plume can be detected.

To characterize the composition of the septic emissions, a 35' sample line heated to 60˚C was attached to the ML main sample line and replaced the standard 16' inlet. This allowed for the ML Operators to sample right at the emission point of the septic tanks. Figure 5-1 shows the response of methyl mercaptan and dimethyl sulfide + ethanethiol on August 7, 2018. The 35' line sampled next to one of the septic tanks from 8:33 to 9:25 am. The methyl mercaptan and dimethyl sulfide + ethanethiol were found to be among the most abundant species within the septic emissions.

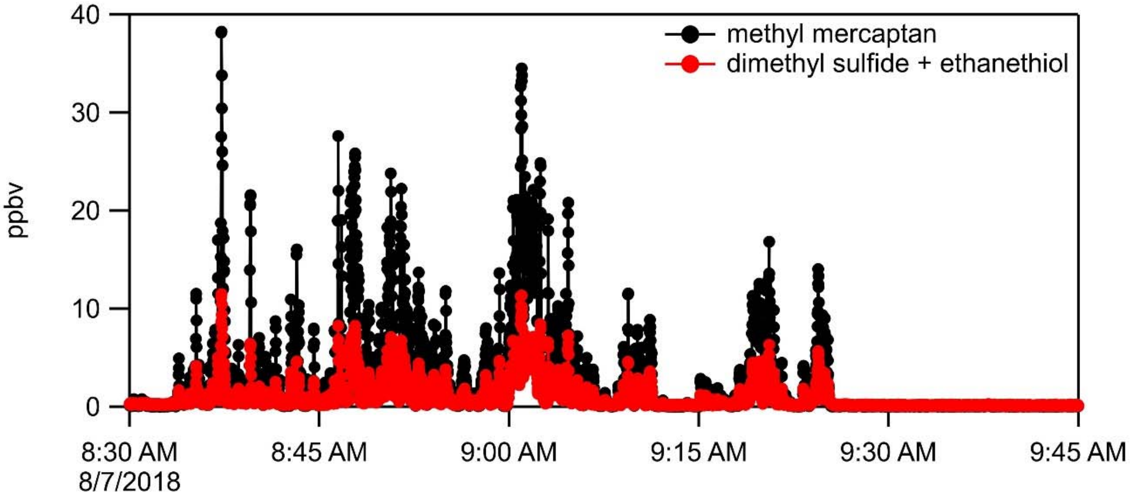

Figure 5-1. Time Series of the Response of Methyl Mercaptan and Dimethyl Sulfide + Ethanethiol During Mobile Laboratory Sampling near the Source of the Septic Plume.

A percent abundance was calculated for all resolved peaks within the data set. This is achieved by taking the average of the largest plume observed between 09:00 and 09:02 then subtracting the ambient mixing ratios approximated by the average between 09:30 and 09:45. The plume average was then summed to get a total response and each species divided by this total response to get a percentage contribution of the total abundance for each species. Figure 5-2 shows the abundance of the septic plume. Only species that contributed at least 0.5% of the total abundance are displayed. Ions used solely for diagnostic purposes (m/z 21, 30, 32, 37) were omitted from this analysis.

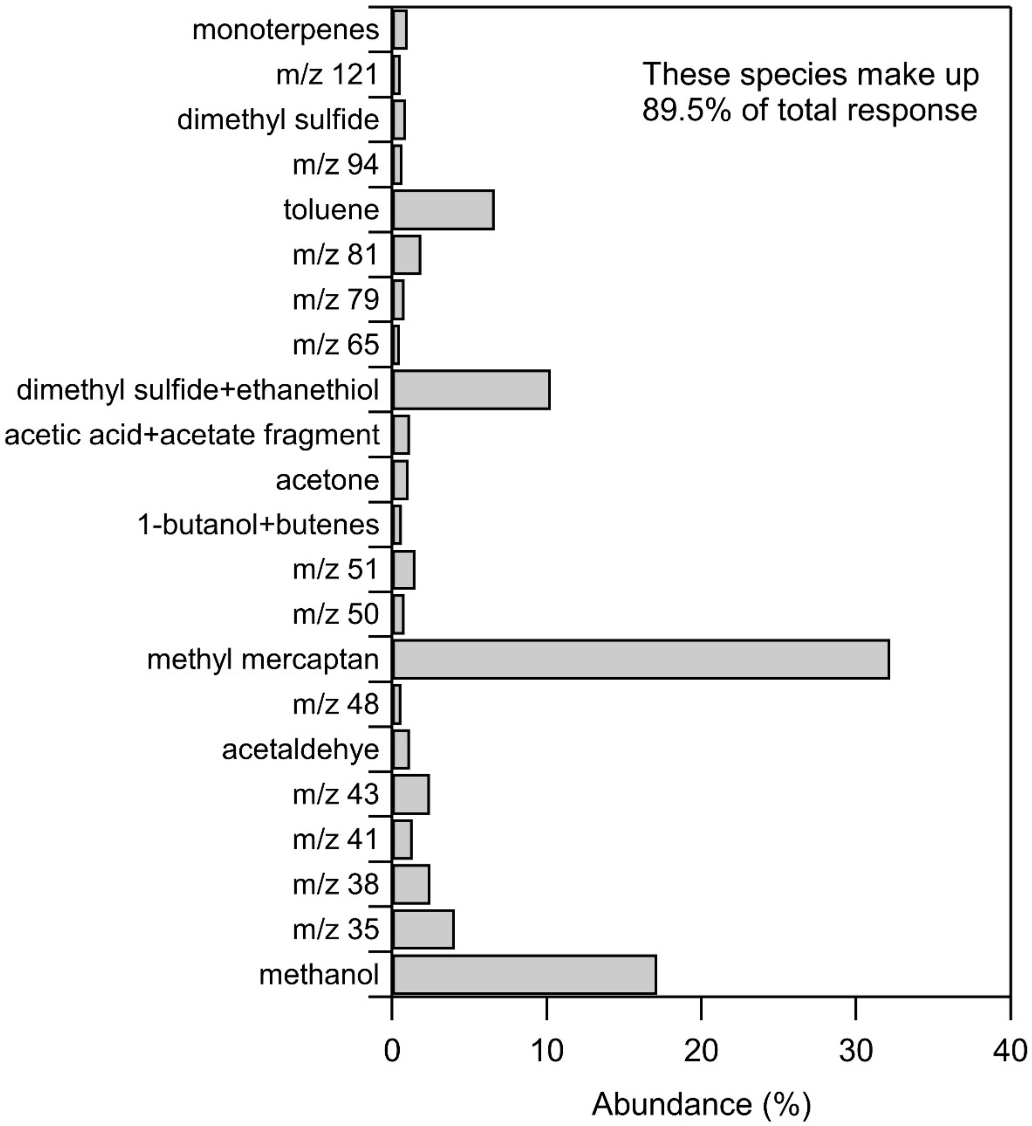

Figure 5-2. Relative Abundance of Species Within the Septic Plume.

With respect to Figure 5-2, most of the septic plume consists of methyl mercaptan (32.2%), methanol (17.1%), dimethyl sulfide + ethanethiol (10.2%), and toluene (6.6%) making up approximately 66% of the total abundance. Methyl mercaptan and dimethyl sulfide + ethanethiol are known odor-causing species which could be the primary cause of the strong smell when an observer is standing within the plume. These species are relatively unique and no other sources of the species in the area have been identified at this time. Hydrogen Sulfide is the next most abundant compounds and has a strong rotten egg smell with a very low odor threshold (0.5 ppb to 10 ppb).The presence of these species would act as a good indicator or fingerprint for assisting in source identification of an unidentified plume.

5.2 Onion Analysis

Multiple days were spent identifying a fingerprint of onion emissions. At Weston Mountain Onion, the procedure for getting rid of onions that did not pass their quality assurance (QA) inspection is to load them into a large semi-trailer. During this time, the onions begin to rot. In addition, Weston Mountain Onion filled a more accessible crate with onions for the ML to monitor. During the 4 days on site, the onions in the crate were at varying stages of rot. To characterize the emissions, a 35’ sample line heated to 60˚C was attached to the ML main sample line and replaced the standard 16’ inlet. This allowed the ML Operators to sample at appropriate locations to capture the onion emissions. The following analysis focuses on the data collected on August 14, 2018, when both fresh and aged onions were sampled individually near the inlet. This produced a significant signal which allowed for easier characterization of the onion emission composition.

The best responses were a result of sampling a fresh onion and an aged onion directly at the inlet. This was done by holding the onion in hand and squeezing until juices formed. Figure 5-3 shows the resulting signal of methyl acetate and ethyl acetate for both instances. The fresh onion was introduced at 10:18 and the aged onion at 10:20. Due to the high concentrations observed, both onions were only sampled for a brief period to reduce the chance of oversaturation or contamination within the PTR-TOF. Methyl acetate and ethyl acetate are shown because they were discovered to be among the most abundant signals within both the fresh and aged onions. The difference in magnitude shown in Figure 5-3 is not attributed to the relative abundances between the two emissions and is a result of variable sampling conditions. The distance at which the onion was held from the inlet is the primary factor in the observed magnitude.

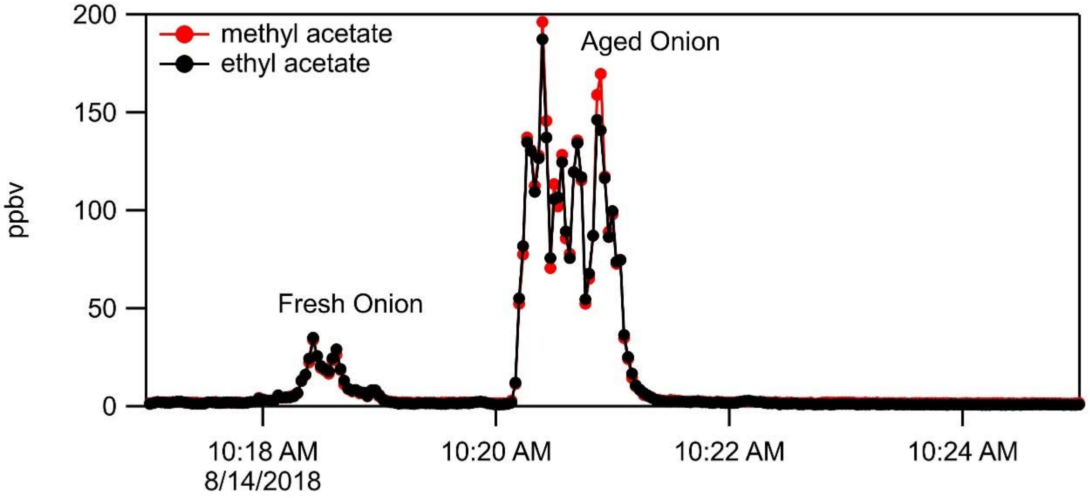

Figure 5-3. Time Series of Methyl Acetate and Ethyl Acetate while Sampling a Fresh Onion and an Aged Onion near the Inlet.

While it is important to characterize the abundant species within the onion emissions, it is also important to understand the emission composition as completely as possible to help identify unique signatures or important interferences. To accomplish this, an abundance was calculated for all resolved peaks within the data set. This was accomplished by averaging the signals of the plume and subtracting the average ambient background signal (10:23 to 10:25) to result in an emission plume average. The signal was then summed to get a total response and each species divided by this total response to get a percentage contribution of the total abundance for each species. Figure 5-4 shows the abundance of a fresh onion and an aged onion. Only species that contributed at least 0.5% of the total abundance are displayed. Ions used solely for diagnostic purposes (m/z 21, 30, 32, 37) were omitted from this analysis.

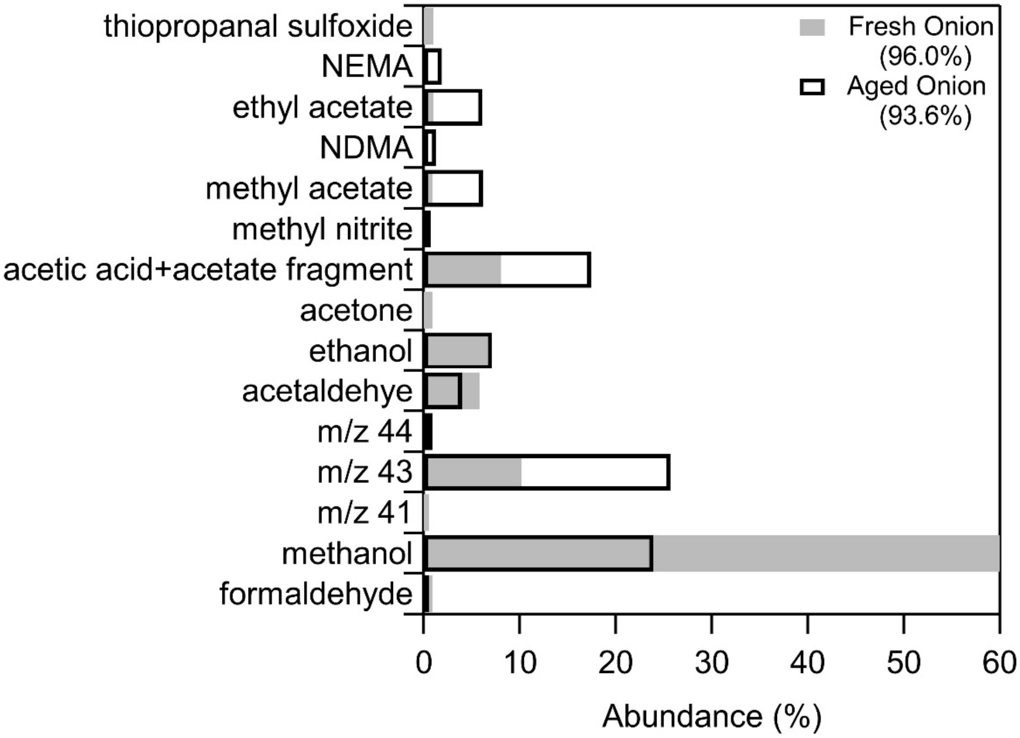

Figure 5-4. Percentage Contribution of each Species to the Total Abundance for Fresh and Aged Onions.

Only species that contributed at least 0.5% are displayed in Figure 5-4. The percentage with the '( )' in the legend is how much of the total abundance is attributed to the species shown.

For the species shown in Figure 5-4, they account for 96% and 93.6% for the total abundance for fresh and aged onions, respectively. When considering all species, it is clear the methanol, m/z 43, and acetic acid + acetate fragment are the most abundant species in the onion emissions regardless of age. Ethanol and acetaldehyde are also present in both onions and account for over 10% of the total abundance. The five species account for approximately 91% and 78% of the abundance for fresh and aged onions, respectively. They are all relatively common in ambient air and have a variety of sources, which does not make them useful for determining unique fingerprints of sources. They hide the response of less abundant but important and unique ions. Given this, a second analysis was performed omitting the diagnostic ions (e.g., m/z 21, 30, 32, 37), common fragmentation ion (m/z 43), methanol, acetaldehyde, ethanol, acetone, and acetic acid + acetate fragment. Figure 5-5 shows the resulting abundance for the fresh and aged onion. Only species that contributed at least 0.5% of the total abundance are displayed.

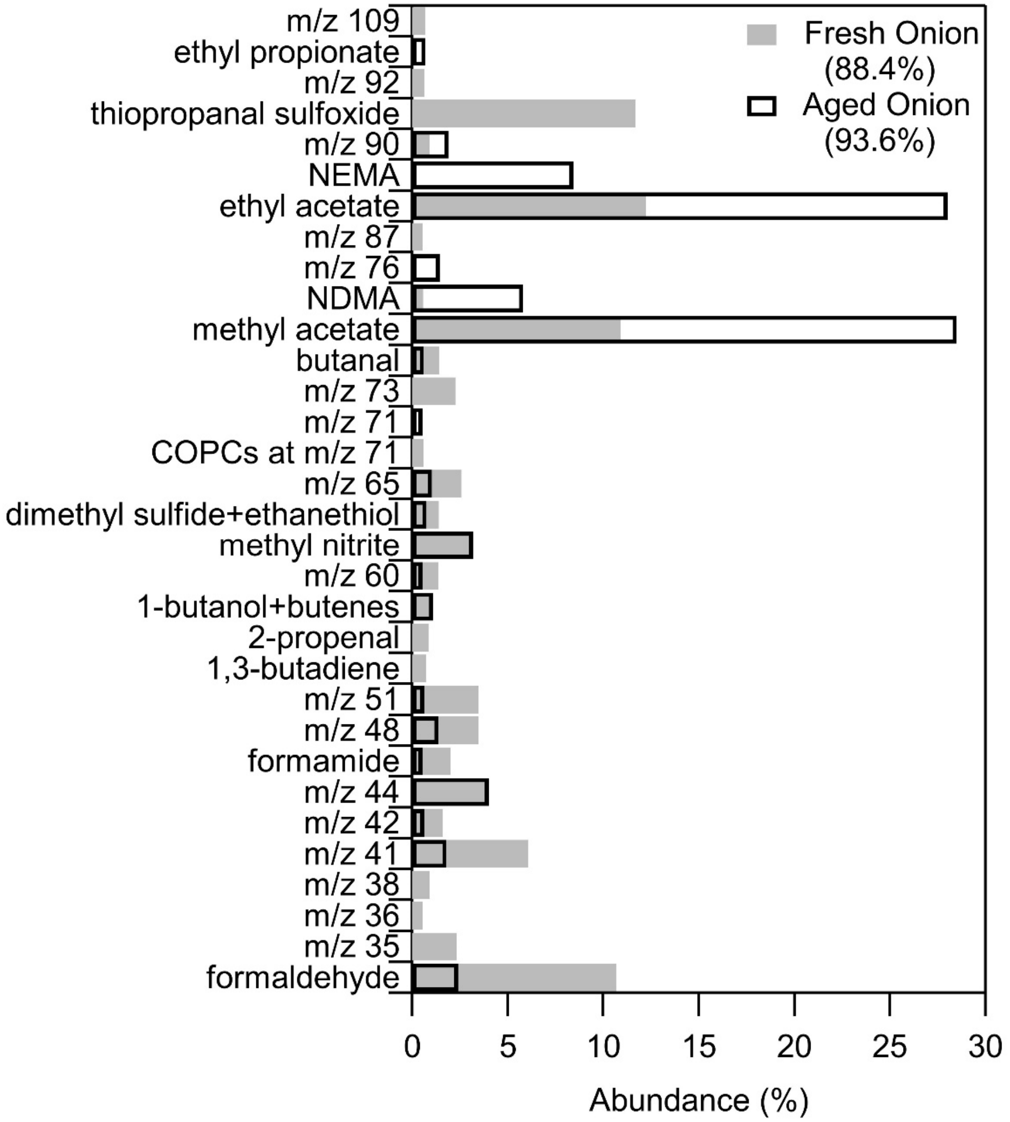

Figure 5-5. Percentage Contribution of each Species to the Total Abundance for Fresh and Aged Onions.

Only species that contributed at least 0.5% are displayed in Figure 5-5. The percentage in the legend signifies the total abundance that is accounted for by the species shown. Diagnostic ions (e.g., m/z 21, 30, 32, 37), common fragmentation ion (m/z 43), methanol, acetaldehyde, ethanol, acetone, and acetic acid + acetate fragment were omitted from the analysis. The COPCs at m/z 71 refers to but-3-en-2-one + 2,3-dihydrofuran + 2,5-dihydrofuran.

It is with the new analysis that the differences in the onion signatures become apparent. The largest difference is the relative abundance of methyl acetate and ethyl acetate. In the aged onion, they compose of roughly 56% of the abundances while only 23% in the fresh onion. The COPCs make up 21.5% in the aged onion and 19% in the fresh onion, which is largely due to N-nitrosodiethylamine (NDMA) and N-nitrosomethylethylamine (NEMA) in the aged onion. The NDMA and N-nitrosomethylethylamine (NEMA) signals also show more prominence within the aged onion, but this signal increase is not attributed to increased levels of NDMA and NEMA. When integrating the peaks during the data workup process, the software has difficulty separating peaks when a species within a similar mass range is present at high levels. During sampling of the aged onion, the methyl acetate and ethyl acetate ranged from 50 to 200 ppbv. Figure 5-6 shows the resulting peak within the data workup software. The left graph shows methyl acetate in green, NDMA in light blue, and the dark blue is the summed response of all species at that mass. When one species is present in a high abundance, the peak will extend into the mass range of other species. In this case, the methyl acetate signal was so high that it overlapped the NDMA signal. Since there is a signal where the software expects to find NDMA, it will then attribute a portion of the signal to NDMA. This creates a false response at NDMA because of the high abundance of methyl acetate. The right graph in Figure 5-6 shows the false response of NEMA (light blue) due to the high abundance of ethyl acetate (green). Additionally, Figure 5-6 shows the center of mass for the odor compounds allyl mercaptan (left graph) and 2-butene-1-thiol (right graph). No signal was attributed to either of these compounds and they do not appear to be present in the onion emissions.

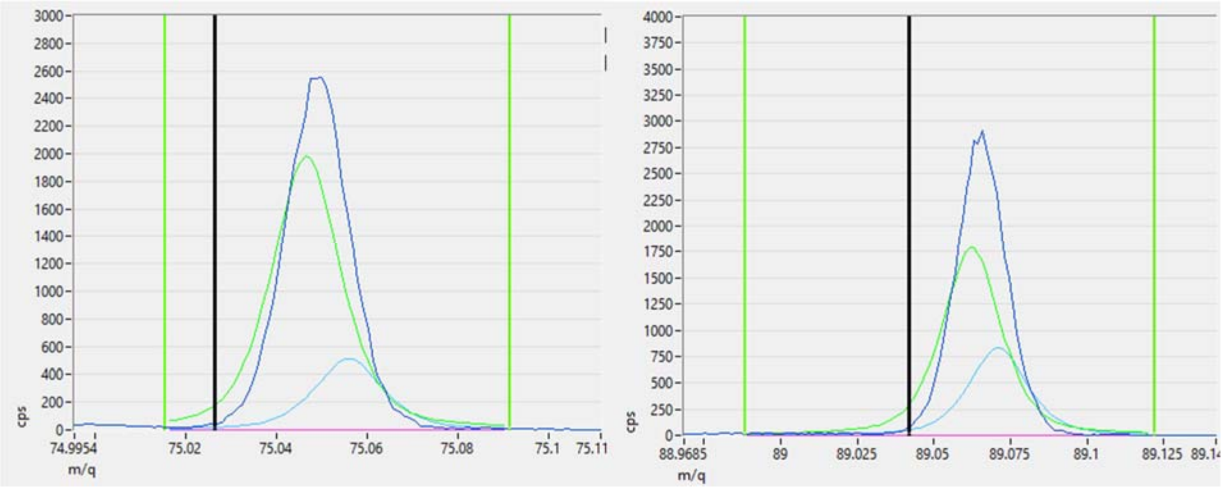

Figure 5-6. Peak Responses at m/z 75 (Left) and m/z 89 (Right).

The dark blue lines in Figure 5-6 are the summed response of all species. The green lines are methyl acetate (left) and ethyl acetate (right). The light blue lines are NDMA (left) and NEMA (right). The black vertical lines signify the center of mass for the odor compounds allyl mercaptan (left) and 2-butene-1-thiol (right).

The odor compounds make up 13% of the fresh onion abundance with a large contribution to thiopropanal sulfoxide and a smaller amount of dimethyl sulfide + ethanethiol. This is one of the more pronounced differences between the aged and fresh onions with the odor compounds in the aged onion being present in less than 1%. The aged onion odor is primarily the dimethyl sulfide + ethanethiol and thiopropanal sulfoxide is present in negligible amounts.

The presence of methyl acetate and ethyl acetate could act as a signature for onion emissions regardless of age. If thiopropanal sulfoxide is also present, it would point toward the emissions suggesting the onions are relatively fresh. The formaldehyde and m/z 41 species are present at reasonable amounts but are not unique to onions and would not act as a good indicator of onion emissions. All other species are not present in a high enough abundance to add value to the fresh or aged onion signature.

5.3 AY-102 Rinse

The ML was deployed to support the AY-102 rinsing on August 24, 2018, and August 26, 2018. The objective was to position the ML downwind from the AY-102 activities and monitor for COPCs. For these days, every resolved peak was visually inspected by the Subject Matter Expert (SME) for trends and peaks/plumes of interest. When a response is identified, the wind speed/direction and location of the ML was taken into consideration when determining the potential source.

5.3.1 Mobile Laboratory Exhaust Fingerprint

Figure 5-7 shows a variety of species that showed varying degrees of response on August 24, 2018. Plumes were largely observed during the second half of the monitoring period. Most of these were suspected to be exhaust from the ML when wind has shifted from the primary direction to the direction of the exhaust or become stagnant, which makes it more likely to monitor sources within close proximity.

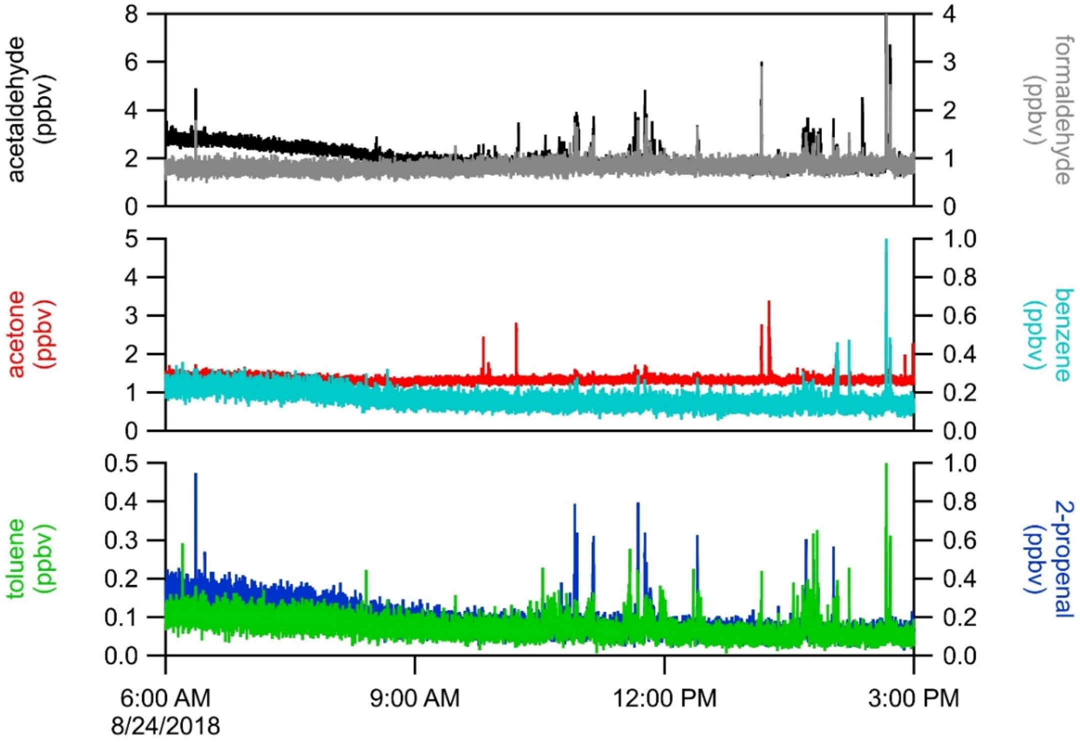

Figure 5-7. Time Series of Acetaldehyde, Formaldehyde, Acetone, Benzene, Toluene, and 2-propenal During Monitoring on August 24, 2018.

Figure 5-8 takes a closer look at two plumes that are suspected to be ML exhaust. The wind during these plumes was coming from the direction of the exhaust outlet. Acetaldehyde, formaldehyde, and aromatics (benzene, toluene, xylenes, etc.) are expected to be within the exhaust emissions. Their presence is a good indicator that the plume is exhaust resulting from a gasoline or diesel engine. Figure 5-9 shows the composition in greater detail for the plume that began at 13:09 and provides a first analysis of the ML exhaust fingerprint. Acetaldehyde (40.7%) and formaldehyde (14.4%) are the most abundant and make up 55.2%. Another 26.4% consists of acetone (9.4%), methyl nitrite (4.7%), and unknown responses at nominal masses m/z 41 (6.5%) and m/z 43 (5.8%). The aromatics (benzene, toluene, C_2-benzenes, and C_3-benzenes) make up 7.5%. Establishing a source fingerprint for the ML exhaust provides an important tool to assist in identifying further cases of sampling this exhaust occurred. Further analysis of ML exhaust will be performed to strengthen understanding of its composition.

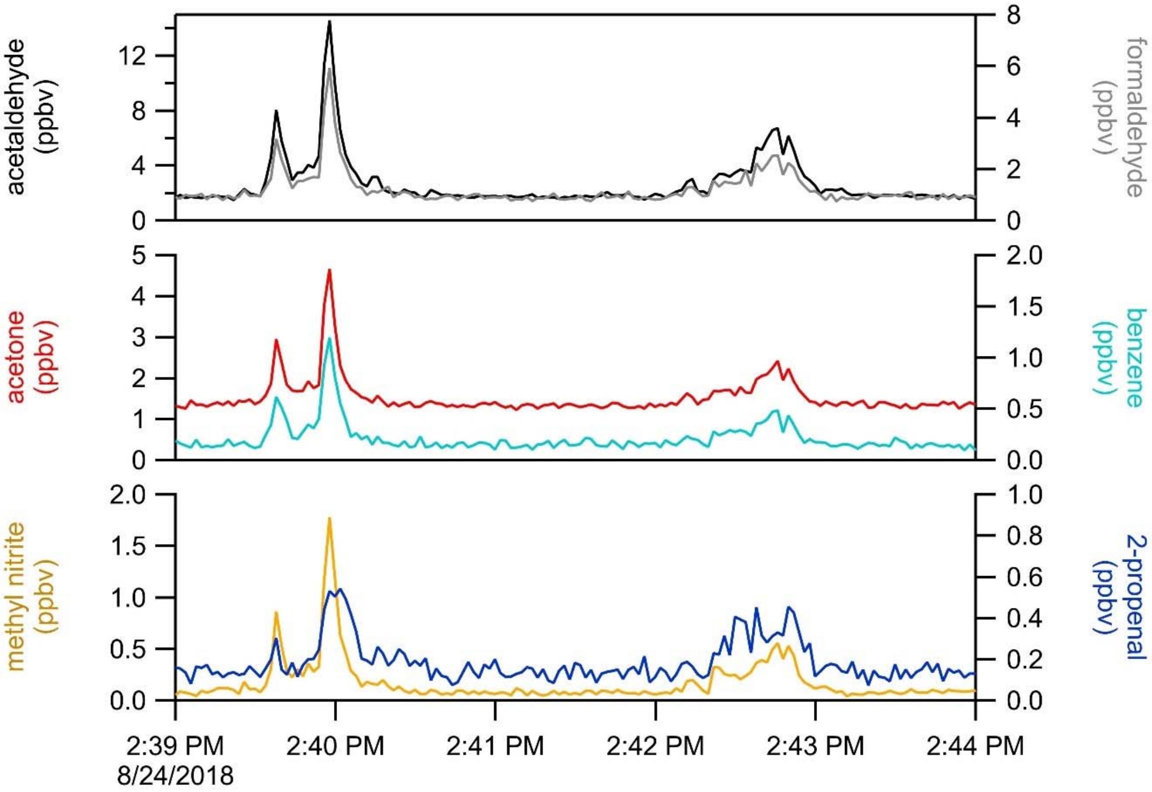

Figure 5-8. Time Series of Acetaldehyde, Formaldehyde, Acetone, Benzene, Methyl Nitrite, and 2-propenal During Two Plumes Observed on August 24, 2018, that are Suspected to be Mobile Laboratory Generator Exhaust.

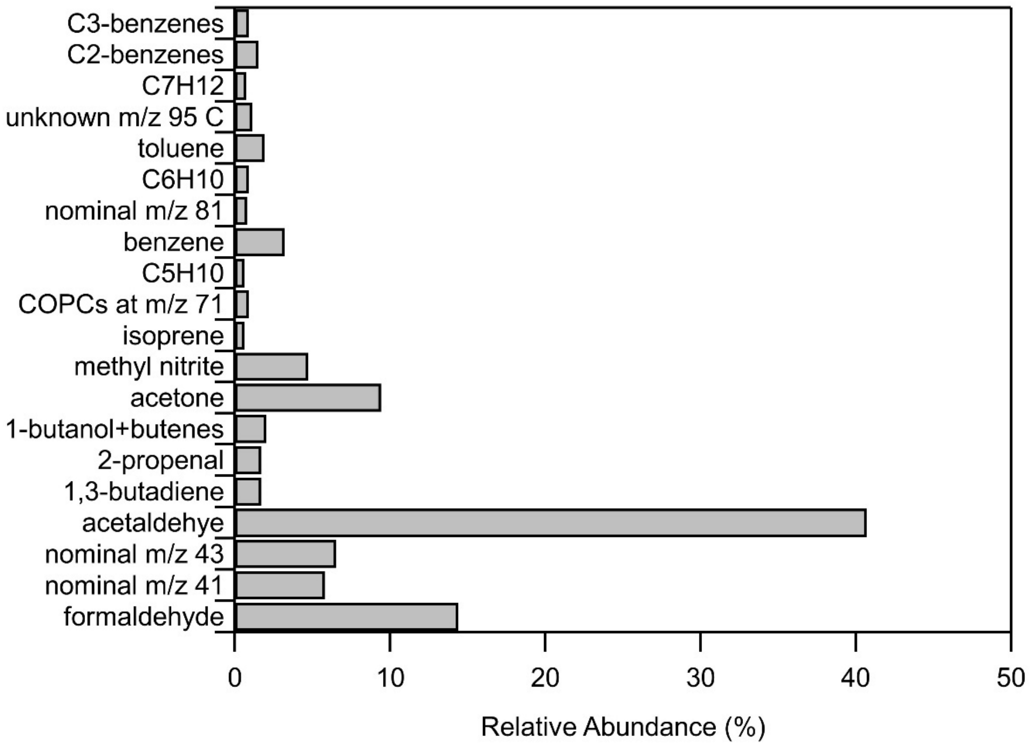

Figure 5-9. Relative Abundance of Key Species Within the Mobile Laboratory Generator Exhaust.
Species that showed a response of at least 0.5 ppbv and contributed at least 0.5% to the total response are included in Figure 5-9.

5.3.2 Windshield Wiper Fluid Fingerprint

The peak at 13:09 is an exception. The average wind direction prior to the plume was approximately 340˚. The ML was parked to the east-southeast in relation to AY Farm and the location is marked in Figure 5-10. At this time, the ML Operators had decided to do a survey loop, which they began at approximately 13:15. Figure 5-11 shows methanol, acetaldehyde, 1-butanol + butenes, and a response from an unknown species at m/z 95 during the 13:09 plume, which lasted a little over 30 seconds. The methanol sees a large increase and reaches almost 100 ppbv. Windshield wiper fluid contains methanol. Given the operators were getting ready to relocate the ML at this time, it is possible that this included using the windshield wiper fluid to clean up the windows. All this suggests that the increase was resultant of these activities rather than emissions from the AY-102 activities. Figure 5-12 shows the relative abundance of the key species within the windshield wiper fluid fingerprint. It is dominated by methanol (78.1%), with acetaldehyde being the second most abundant (4.5%).

Figure 5-10. Mobile Laboratory Location on August 24, 2018, at 13:09.
The red arrow represents the approximate wind direction.

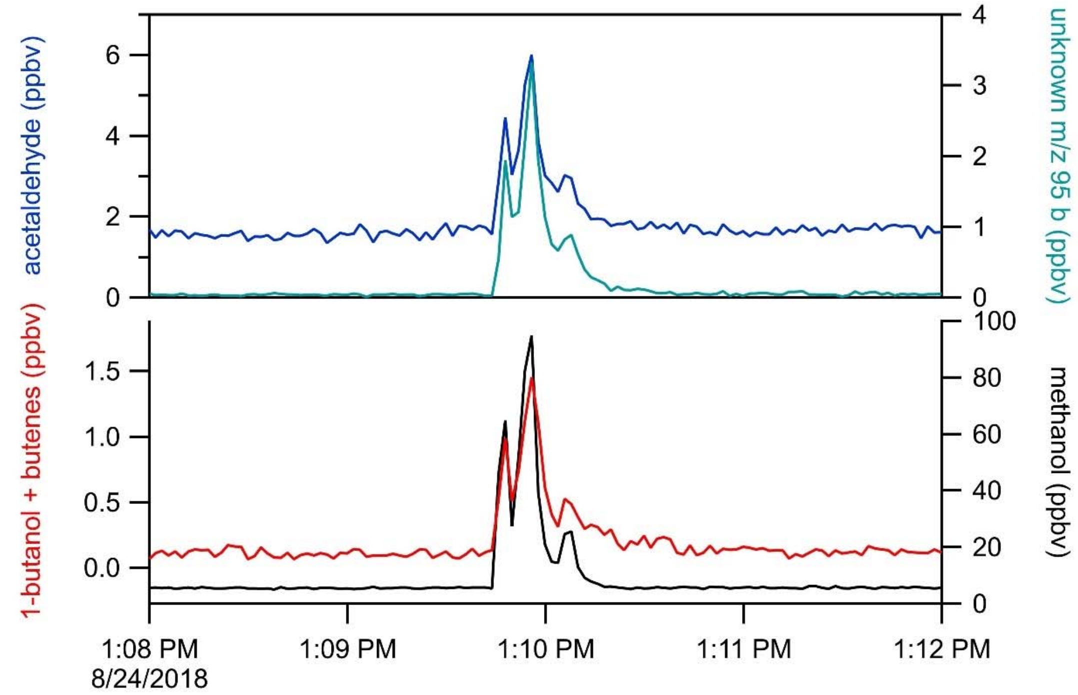

Figure 5-11. Time Series of Methanol, Acetaldehyde, 1-butanol + Butenes, and Unknown Species at m/z 95 During a Plume from an Unidentified Source.

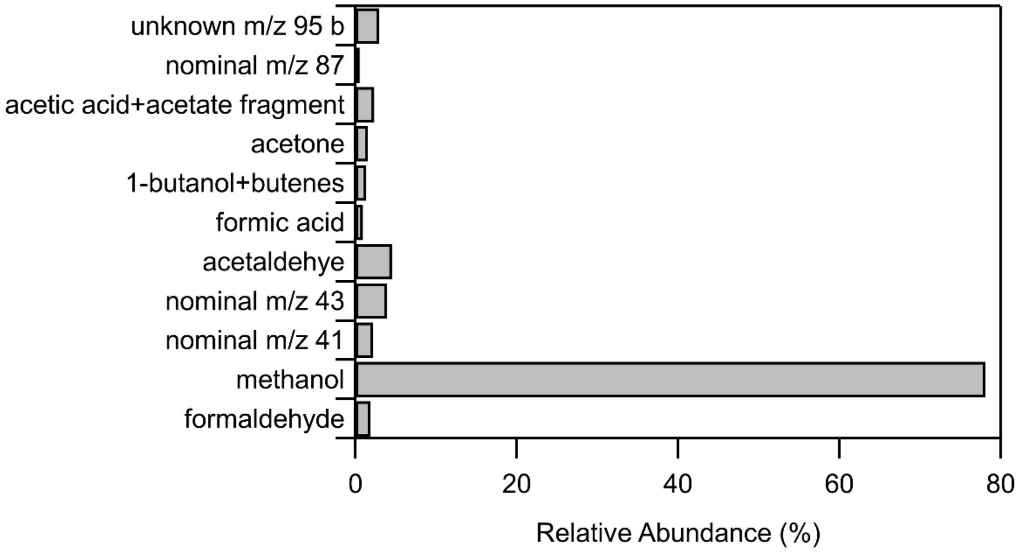

Figure 5-12. Composition of the Plume Occuring at 13:09 on August 24, 2018.
Species that showed a response of at least 0.5 ppbv and contributed at least 0.5% to the total response are included.

5.3.3 Unidentified Source Fingerprint

The August 26, 2018, observations were similar to August 24, 2018, in that most of the spikes and plumes observed were generally caused by the ML exhaust as a result of shifting and stagnant winds. However, there were a pair of more sustained, unique plumes that occurred around 09:00. Figure 5-13 shows these plumes starting at 08:59 and 09:18 on August 26, 2018. The plumes lasted approximately 8 and 16 minutes for the 08:59 and 09:18 plumes, respectively. The shape, duration, and stability of the plumes are more representative of the behavior of a well-mixed, continuous source located a moderate distance from the ML. Nearby sources tend to show short-lived, high signal spikes and have a sporadic behavior (e.g., Figures 5-8 and 5-11). These plumes were then analyzed to determine the relative abundances of the key species and develop a source fingerprint.

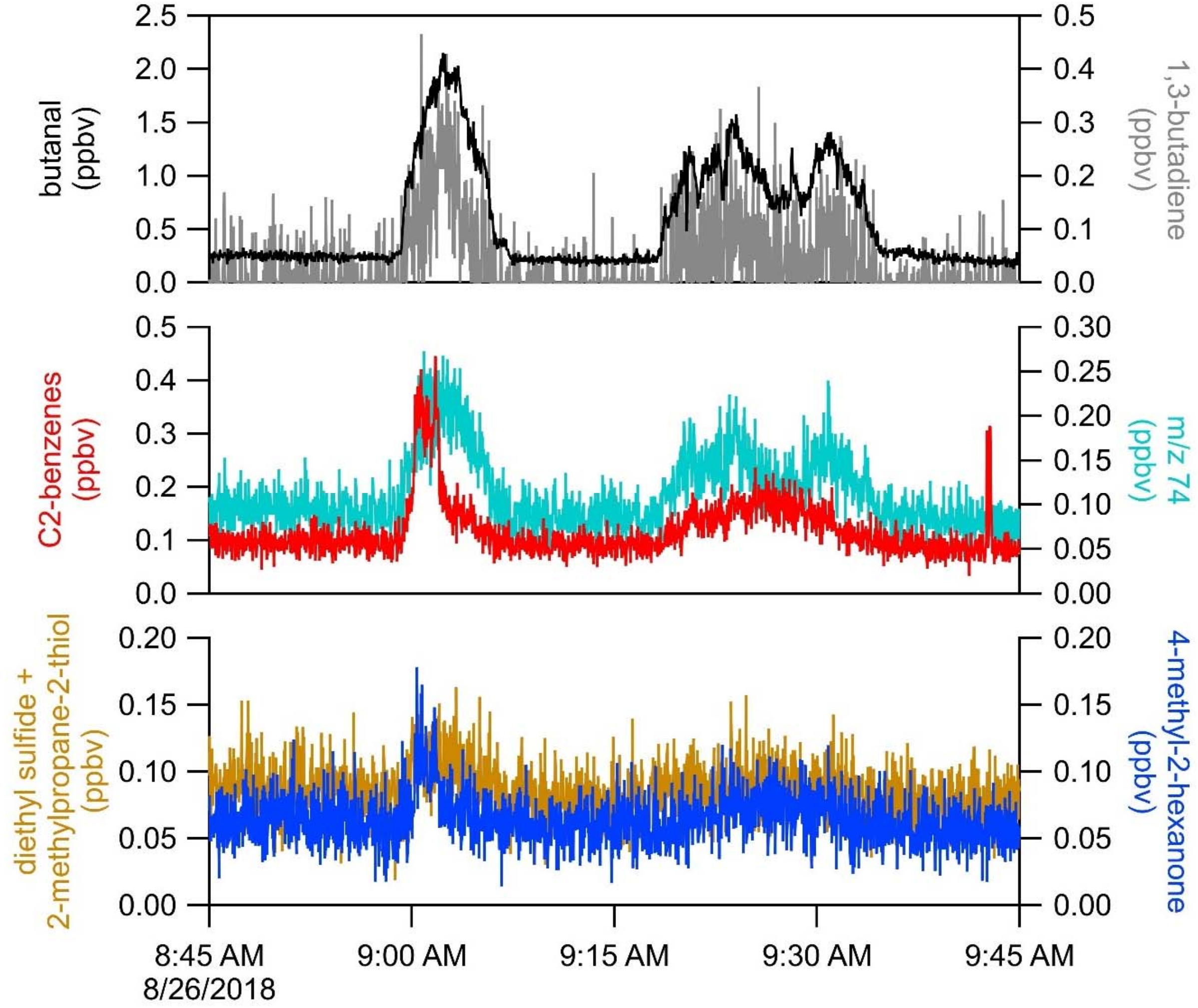

Figure 5-13. Time Series of Key Species Observed Within the 08:59 and 09:18 Plumes on August 26, 2018.

Figure 5-14 shows the relative abundance of the key species within both of the observed plumes. A plume response was calculated for every resolved peak and visually inspected by the SME to qualify the response and determine its validity as part of the source fingerprint. The basic criteria were that the average response within the plume had to be at least 0.05 ppbv, contribute at least 0.5% of the total response, and follow the same general trend along the plume as other key species. With respect to Figure 5-14, the most prominent species within the plumes is butanal with smaller responses from 1,3-butadiene, diethyl sulfide + 2-methylpropane-2-thiol, C_2-benzene, 4-methyl-2-hexanone, and a response from an unknown species at nominal m/z 74. As expected, the composition of the plumes is the same with only minor differences in relative abundance. This plume contains three COPCs (1,3-butadiene, butanal, and 4-methyl-2-hexanone), an odor response (diethyl sulfide + 2-methylpropane-2-thiol), commonly emitted C_2-benzenes (xylenes, ethylbenzene), and an unidentified species (m/z 74) making this signature very distinguishable. All concentrations were well below 50% Occupational Exposure Limit (OEL) thresholds during the duration of the plume. A source that would produce this mixture is undetermined at this time, but the location of the ML and wind direction assist in narrowing down the suspects.

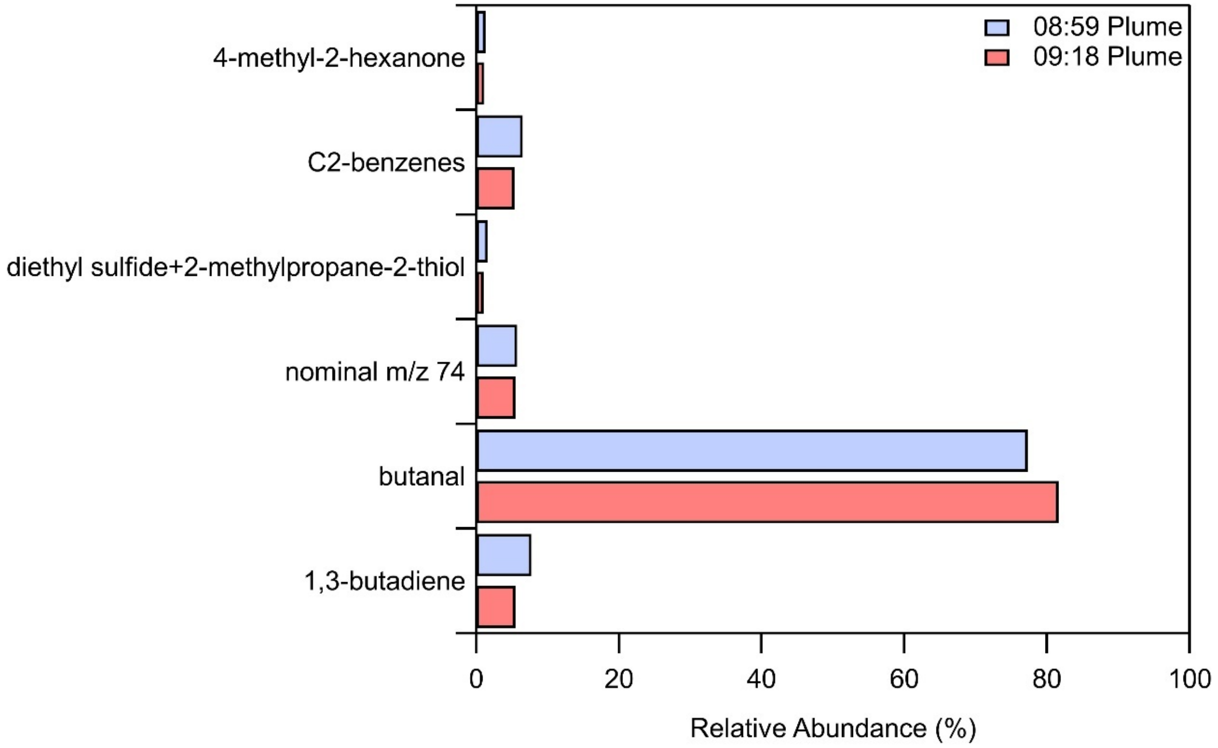

Figure 5-14. Relative Abundance of Key Species for the 08:59 and 09:18 Plumes Observed on August 26, 2018.

Species that showed a response of at least 0.5 ppbv and contributed at least 0.5% to the total response are included.

Figure 5-15 shows the location and wind direction of the ML when the two plumes were observed. At 09:07, the first plume had ended, but the ML stayed at that location until 09:17 at which time ML relocation began. The plume was observed again while the ML was in transit and at 09:26, the ML was in the location labeled as 09:18 in Figure 5-15. The plume persisted until 09:34. The wind direction while the ML was stationary was from the direction of the A Farms and suggests that the source of the plumes could be a result of activities within that area.

Figure 5-15. Location of the Mobile Laboratory on August 26, 2018, near A Farm at 08:59 (Blue Pin) and 09:18 (Orange Pin).

The red and yellow arrows represent the wind direction around 08:59 (72.8⁰ wind direction) and 09:18 (66.2⁰ wind direction), respectively.

6.0 QUALITY ASSESSMENT

During the August 6, 2018 through August 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 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 potentially quality-affecting issues were resolved prior to report or are noted in this report. All potentially quality-affecting deviations have been captured by Deficiency Reports (DRs) and are summarized below with some interpretation.

During the August 6, 2018 through August 30, 2018, monitoring campaign, there was one (1) DR. DR18-006 documents a communication loss with the ML's Weather Station (Airmar) and carbon dioxide analyzer (LI-COR).

6.1 Lessons Learned – DR18-006

On August 6, 2018, a communication error with the AirMar Weather Station and LI-COR CO_2 Analyzer occurred. TerraGraphics' investigation led to a rare occasion communication loss between the RS232 serial and the USB. This resulted in a restart of DAQFactory to reestablish communication. After the DAQFactory software was restarted, the weather data began collecting data within a couple minutes. The LI-COR monitor, however, did not collect data after the first-restart. DAQFactory was restarted again, and data began collecting again for both the AirMar and LI-COR.

Per SME recommendation, a more reliable communication serial type was purchased and installed by August 23, 2018.

7.0 CONCLUSION AND RECOMMENDATIONS

The ML was assigned to the following tank farm related tasks:

- Source Characterization of septic tanks,
- Mobile Area Monitoring of A Farms, and
- Mobile Area Monitoring in support of the AY-102 Rinse.

The ML was also involved in the following off-site activities in support of the overall project:

- Source characterization of onions at Weston Mountain Onions, and
- Demonstration of the ML for WRPS personnel.

7.1 Conclusion

The ML was able to identify and characterize several sources during the first month of operation. This resulted in unique fingerprints that will be tools for assisting in plume identification for all future data analysis. Multiple days were focused on characterization of septic and onion emissions by sampling directly at the source. The AY-102 rinse operation provided some secondary source characterization when the ML sampled its own exhaust or windshield wiper fluid when the conditions were favorable. Understanding these emissions is an integral aspect of continuing improvements of ML operations. Further monitoring and analysis of these sources will increase the ability to identify or exclude their presence in future studies.

The septic emissions provided the most unique signature with the largest constituents being methyl mercaptan, methanol, dimethyl sulfide + ethanethiol, and toluene. The most important within this fingerprint is the methyl mercaptan since it has not been identified or observed in any of the other sources and is an odor-producing species. Future observations containing methyl mercaptan will prompt initial comparison to the septic fingerprint.

The onion emissions provided another unique signature, but the changing composition during the aging process does make comparisons to future observations conditional. The presence of methyl acetate and ethyl acetate would suggest that a future observation could be a general onion emission. To distinguish whether it is a fresh or aged onion, the presence of thiopropanal sulfoxide will be the biggest indicator that emission points toward an aged onion.

Whenever the ML is deployed, the closest source will always be the exhaust generated by the ML itself. Therefore, it is imperative to analyze and understand the associated emissions. The AY-102 rinse operations provided the first look at the exhaust fingerprint. It is important to note that exhaust emission composition can vary depending on many factors (ambient temperature, time since last service, fuel composition, engine load); therefore, continual analysis of exhaust plumes under different conditions is important. However, the general constituents within the emissions would not be expected to change drastically. Beyond the commonly abundant species (formaldehyde, acetaldehyde, acetone), the most useful species are the presence of methyl nitrate and aromatics (benzene, toluene, C_2-benzenes, and C_3-benzenes). The presence of these things in addition to the commonly abundant species within an observed plume should prompt a comparison to the exhaust fingerprint.

Another important source pertaining to ML emissions is the windshield wiper fluid. While its presence is situational, identifying and characterizing it in the early stages of ML deployment is useful. Additionally, with the presence of other vehicles being common to some deployment locations, there is potential for the ML to observe the windshield wiper fluid emissions from a neighboring vehicle. The primary fingerprint for this source is the drastic increase of methanol with minimal or negligible increases of any other species.

Understanding these sources helps to analyze any plumes, spikes, or trends observed by the ML. It was useful in understanding the unique plume observed on August 26, 2018, during the AY-102 rinse operation. While the plume did contain C_2-benzenes which are common to vehicle exhaust, the rest of the composition was unique with the leading indicator being butanal. Even though the source of the plumes is unidentified at this time, the presence of butanal, 1,3-butadiene, C_2-benzenes, nominal m/z 74, diethyl sulfide + 2-methylpropane-2-thiol, and 4-methyl-2-hexanone in any future observations may suggest the same or similar source. For this reason, characterization of unknown sources is equally as important as known sources.

7.2 Recommendations

The following recommendations have been compiled for improvement in further ML deployments:

- Investigate saturation of the PTR-MS with odor-releasing compounds,
- Develop a system of switching to NO^+ from H_3O for SRI research, and
- Develop an automated sampling system for confirmatory samples to be used in the fall background study.

8.0 REFERENCES

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