

**PTR-MS MOBILE LABORATORY VAPOR MONITORING
MONTHLY REPORT – MONTH 9**

**Report No. 53005-81-RPT-073
Revision 0
May 1, 2019 – May 31, 2019**

Prepared for:

**Washington River Protection Solutions, LLC
P.O. Box 850
Richland, WA 99352**

Subcontract 53005, Release 81

Prepared by:

**TerraGraphics Environmental Engineering, Inc.
2926 E. Ainsworth
Pasco, WA 99301**



www.terragraphics.com

Approval Form

Prepared by:



Tyler Williams

Date: 10/03/2019

Reviewed by:



Matthew Erickson, Ph.D.

Date: 10/03/2019

Approved by:



Rich Westberg

Date: 10/03/2019

Record of Revision

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

Table of Contents

1.0	DESCRIPTION OF TESTS CONDUCTED	1
2.0	MEASUREMENT SYSTEM DESIGN.....	2
2.1	Sampling Methods	2
2.1.1	Design of Sampling System.....	2
2.2	Instrumentation and Methods Used	3
2.2.1	Proton Transfer Reaction – Mass Spectrometer	3
2.2.2	Carbon Dioxide Monitor.....	5
2.2.3	Ammonia Monitor	6
2.2.4	Weather Station.....	6
2.3	Confirmatory Measurements (if Applicable).....	7
3.0	CALIBRATION METHODS AND CALIBRATION GASES USED	8
4.0	MEASUREMENT UNCERTAINTY AND KNOWN SOURCES OF ERROR	15
4.1.1	Proton Transfer Reaction – Mass Spectrometer	15
4.1.2	Carbon Dioxide Monitor.....	15
4.1.3	Ammonia Monitor	15
4.1.4	Weather Station.....	15
4.1.5	Method Detection Limit Study	15
5.0	RESULTS	16
5.1	Discussion of Test Activities and Observations	16
5.2	Area Monitoring Data Scan	17
5.2.1	Exhaust Scan.....	17
5.2.2	Odor Scan.....	32
5.2.3	Methanol Plumes	32
5.2.4	Unique Plumes.....	39
5.2.5	Exhaust Plumes.....	43
5.2.6	Chemical of Potential Concern Statistics.....	45
5.3	Fugitive Emission	50
5.3.1	Location Investigation on May 21, 2019	50
5.3.2	Sewer Source Fingerprint on May 23, 2019	54
5.4	Laboratory Testing.....	60
5.4.1	208’ Sample Line Characterization	60
5.4.2	Charcoal Zero Source Characterization	64
6.0	QUALITY ASSESSMENT	66
6.1	Lessons Learned – DR19-010.....	66
7.0	CONCLUSION.....	67
8.0	REFERENCES	70

Appendices

Appendix A
Deficiency Report

Figures

Figure 2-1. The General Configuration of an IONICON Proton Transfer Reaction – Time of Flight Instrument.....	4
Figure 5-1. Fingerprints of the 28 Exhaust Plumes Identified with the Exhaust Scan of the May 2019 Data.....	19
Figure 5-2. Fingerprints of the Four Exhaust Plumes that Contained Increased Methanol Response Identified with the Exhaust Scan of the May 2019 Data.....	20
Figure 5-3. Fingerprints of the Eight Generator Exhaust Plumes Identified with the Exhaust Scan of the May 2019 Data.....	22
Figure 5-4. Comparison of the Generator Fingerprints to Month 7 and Month 8 Generator Fingerprints.....	23
Figure 5-5. Fingerprints of the Six Exhaust Plumes Identified with the Exhaust Scan Compared to the Month 2 Exhaust Fingerprint.....	25
Figure 5-6. Comparison of the Fingerprints from Three Different Combustion Exhaust Sources: Gasoline Vehicle, Diesel Vehicle, and Diesel Generator.....	26
Figure 5-7. Fingerprints of the Three Methanol Plumes Identified with the Exhaust Scan Compared to the Month 8 Methanol Plume Average Fingerprint.....	28
Figure 5-8. Fingerprints of the Four Toluene/C ₂ -benzene Plumes Identified with the Exhaust Scan.....	29
Figure 5-9. Location and Wind Direction During Observation of the Four Toluene and C ₂ -benzene Plumes.....	31
Figure 5-10. Location of the Mobile Laboratory when Observing the Methanol Plumes in the 200 East Area During May 2019.....	33
Figure 5-11. Fingerprints of Methanol Group A Plumes Observed on May 14, 2019, Along with the Average Methanol Plume Detailed in 53005-81-RPT-066.....	34
Figure 5-12. Wind Speed and Direction During Observations of Methanol Group A Plumes on May 14, 2019, from 09:52 to 09:57.....	35
Figure 5-13. Fingerprints of Methanol Group B Plumes Observed on May 15, 2019; May 29, 2019; and May 30, 2019, Along with the Exhaust + Methanol Fingerprint Described in Section 5.2.1.1, Figure 5-2.....	36
Figure 5-14. Fingerprints of Methanol Group C Plumes Observed on May 28, 2019, and May 30, 2019, Along with the Average Methanol Plume Detailed in the 53005-81-RPT-066.....	37
Figure 5-15. Comparison of Methanol Groups A, B, and C Fingerprints Along with the Methanol Fingerprint from 53005-81-RPT-066 and a Unique Methanol Plume Observed on May 21, 2019, at 09:45.....	39
Figure 5-16. Fingerprints of Unique Plumes Observed on May 2, 2019; May 6, 2019; and May 22, 2019, Along with the Average Fingerprint of the Unique Toluene Presented in 53005-81-RPT-066.....	40
Figure 5-17. Location of the Mobile Laboratory when Observing the Unique Plumes in the 200 East Area During May 2019.....	42

Figure 5-18. Wind Speed and Direction During Observations of the Unique Toluene Plumes on May 6, 2019, at 06:31 and 06:32.42

Figure 5-19. Wind Speed and Direction During Observations of Unique Plumes on May 2, 2019, at 11:38 and May 22, 2019, at 06:36.43

Figure 5-20. Fingerprints of Exhaust Plumes Observed on May 6, 2019 through May 9, 2019; May 16, 2019; May 20, 2019; and May 30, 2019, Along with Fingerprints Representing Gasoline Vehicle, Diesel Vehicle, and Diesel Generator Emissions.44

Figure 5-21. Time and Magnitude of the Maximum Value of Furan that Exceeded the Occupational Exposure Concentration on May 14, 2019.48

Figure 5-22. Time and Magnitude of the Maximum Value of NDMA that Exceeded the Occupational Exposure Concentration on May 6, 2019.49

Figure 5-23. Time and Magnitude of the Maximum Value of 2-methylfuran that Exceeded the Occupational Exposure Concentration on May 14, 2019.49

Figure 5-24. Time and Magnitude of the Maximum Value of NDEA that Exceeded the Occupational Exposure Limit on May 14, 2019.50

Figure 5-25. Location of the Mobile Laboratory During Location Investigation with the Fugitive Emission Group on May 21, 2019.51

Figure 5-26. Concentrations of Ammonia, CO₂, Acetonitrile, Acetaldehyde, 1-butanol + Butenes, Benzene, 2,4-dimethylpyridine, and 2-ethyl-2-hexanal + 4-(1-methylpropyl)-2,3-dihydrofuran and 3-(1,1-dimethyl)-2,3-dihydrofuran During the Fugitive Emission Location Investigation on May 21, 2019.52

Figure 5-27. Fingerprints of Plumes Occurring at 11:47, 12:10, and 12:24 on May 21, 2019, During the Fugitive Emission Location Investigation.53

Figure 5-28. Map of Location (Lat. = 46.5522555320531, Long. = -119.515415230273).54

Figure 5-29. Picture of Setup for May 23, 2019, Sewer Source Fingerprint.55

Figure 5-30. Concentrations of Key Species Within Septic Emissions Observed on May 23, 2019, While Sampling Directly from the Septic Tank.56

Figure 5-31. Fingerprint Taken from 09:06 to 09:22 in Unison with Sorbent Collection.57

Figure 5-32. Fingerprint Taken from 09:25 to 10:24 in Unison with Sorbent Collection.58

Figure 5-33. Comparison of Septic Fingerprints Generated in this Report to Previous Septic Fingerprints Developed in Month 2, Month 4, and Month 5.59

Figure 5-34. Proton Transfer Reaction – Mass Spectrometer Mass Spectra Over Time for Long Zero-air Measurement.60

Figure 5-35. Mass Spectra of the Average Response to 30 Minutes of Sampling Zero-air and 30 Minutes of Sampling Charcoal-filtered Zero-air.65

Tables

Table 3-1. Calibrated Gases in use During Month 9.8
Table 3-2. Zero-air Checks for the LI-COR CO₂ Monitor.9
Table 3-3. Span Checks for the LI-COR CO₂ Monitor.10
Table 3-4. Zero-air Checks for the Proton Transfer Reaction – Mass Spectrometer.11
Table 3-5. Span Checks for the Proton Transfer Reaction – Mass Spectrometer.12
Table 3-6. Zero-air Checks for the Picarro Ammonia Analyzer.13
Table 3-7. Span Checks for the Picarro Ammonia Analyzer.14
Table 5-1. Activity Details for Month 9.16
Table 5-2. Threshold Values of Species Used for the Exhaust Scanner.....17
Table 5-3. Date and Time of Potential Vehicle Exhaust Plumes Identified with the
Exhaust Scanner for May 2019.....18
Table 5-4. Chemicals of Potential Concern Statistical Information for the Monitoring
Period of May 2019. (2 Sheets)46
Table 5-5. 208’ Line Zero-air Sampling Test Results for Chemicals of Potential
Concern. (2 Sheets).....61
Table 5-6. 208’ Line Zero-air Sampling Test Results for Odors.....64

Acronyms and Abbreviations

ASTM	ASTM International
COPC	Chemical of Potential Concern
CSO	Central Shift Office
DR	Deficiency Report
FY	Fiscal Year
GC/MS	Gas Chromatograph – Mass Spectrometer
GPS	Global Positioning System
HPLC	High Performance Liquid Compounds
MDL	Method Detection Limit
MFC	Mass Flow Controller
ML	Mobile Laboratory (Mobile Vapor Monitoring Laboratory)
NDEA	N-Nitrosodiethylamine
NDMA	N-Nitrosodimethylamine
NIOSH	National Institute for Occupational Safety and Health
OEL	Occupational Exposure Limit
ppbv	parts per billion by volume
ppmv	parts per million by volume
pptv	parts per trillion by volume
PTR-MS	Proton Transfer Reaction – Mass Spectrometer
PTR-TOF	Proton Transfer Reaction – Time of Flight
R&D	Research and Development
SME	Subject Matter Expert
TIC	Tentatively Identified Compounds
TOF-MS	Time of Flight – Mass Spectrometer
VOC	Volatile Organic Compound

Executive Summary

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

This report of Month 9 operations spans the calendar month of May 2019.

During Month 9, Mobile Laboratory Operators performed maintenance, modifications, verifications, calibration, and received continuous training on Mobile Laboratory instrumentation.

The Mobile Laboratory performed area monitoring in the 200 East and 200 West Area of the Hanford Site in order to collect data on the concentrations of chemical vapors downwind of potential sources. This included monitoring an Abnormal Operating Procedure (AOP)-015 event near 241-A Farm on May 21, 2019.

Source characterization around the septic tanks near the 242-A Evaporator on the Hanford site was conducted in support of the Washington River Protection Solutions, LLC (WRPS) Fugitive Emissions Team.

1.0 DESCRIPTION OF TESTS CONDUCTED

During Month 9, spanning the dates of May 1, 2019, to May 31, 2019, the Mobile Laboratory (ML) was deployed for the measurement of volatile organic compounds (VOCs) after ML maintenance, modifications, operational testing, and continuous training were performed.

Description of activities that were conducted are as follows:

- Week 39
 - Area Monitoring and Testing
- Week 40
 - Area Monitoring and Testing
- Week 41
 - Area Monitoring and Testing
- Week 42
 - Area Monitoring and Testing
- Week 43
 - Area Monitoring and Testing

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 9, 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 9. 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

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

The PTR-TOF 6000 X2 is used to quantify Chemicals of Potential Concern (COPCs) from the sampled air. The sampled air enters the PTR drift tube. In the drift tube, VOCs undergo chemical ionization via a fast proton transfer reaction using the reagent ion, hydronium. The hydronium is produced from water vapor via a series of reactions in the hollow cathode PTR ion source. This is a soft ionization method and VOC fragmentation is minimized. These ionized compounds and hydronium 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.

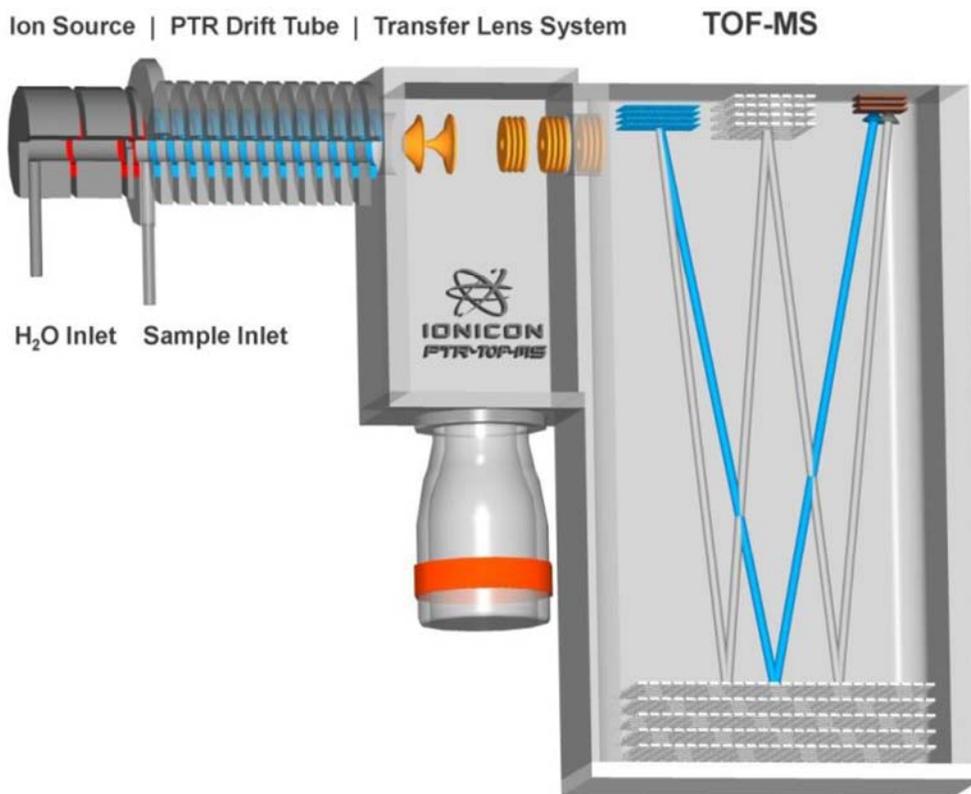


Figure 2-1. The General Configuration of an IONICON Proton Transfer Reaction – Time of Flight Instrument.

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



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.

$$[\text{R}] = \frac{1}{kt} \left(\frac{I_{\text{RH}^+}}{I_{\text{H}_3\text{O}^+}} \right) \frac{\epsilon_{\text{RH}^+}}{\epsilon_{\text{H}_3\text{O}^+}} \quad (1)$$

Where k is the ion–molecule rate constant ($\text{molecules cm}^{-3} \text{s}^{-1}$), t is the reaction time (~ 100 microseconds), I_{RH^+} and $I_{\text{H}_3\text{O}^+}$ are the respective ion count rates, and ϵ_{RH^+} and $\epsilon_{\text{H}_3\text{O}^+}$ 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:

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

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

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

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 Month 9 report 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 Month 9 including diesel and gas generators, all-terrain vehicles with no catalytic converters, and diesel and gasoline vehicles. These contribute VOCs to the vapor burden and are readily observed by the PTR-MS. It is necessary to distinguish these VOCs from tank farm related emissions resulting from normal work-related activities.

The CO₂ monitor used in the TerraGraphics ML was the LI-COR Model 840A. The Li840A is an absolute, non-dispersive infrared gas analyzer based upon a single path, dual wavelength infrared detection system. It is a low-maintenance, high performance monitoring solution that gives accurate, stable readings over a wide range of environmental conditions. It has a range of 0-20,000 parts per million by volume (ppmv) (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

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.

from the CO₂ monitor are used to predict when VOC measurements from the PTR-MS come from combustion sources.

The CO₂ monitor used during Month 9 was operated using a factory calibration. Periodic checks of the unit were made with zero air and ambient background air (ambient atmospheric CO₂ levels are approximately 400 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 $\pm 0.005^{\circ}\text{C}$ 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. 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)

Although PTR-MS has exceptional response time, sensitivity, and is an excellent instrument for quantification, it suffers from the inability to make qualitative determinations of complex samples. Alternate analytical methods can provide important supporting evidence of the qualitative assignments made while interpreting the PTR-MS data as well as quantification validation of some COPCs. The Gas Chromatograph – Mass Spectrometer (GC/MS), High Performance Liquid Chromatograph (HPLC)/MS/MS, HPLC, and GC methods used to support and confirm PTR-MS were performed using well-established methodology by accredited laboratories. Within the context of this month, one confirmatory method was utilized, EPA TO-17, “Volatile Organic Compounds,” modified.

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

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

3.0 CALIBRATION METHODS AND CALIBRATION GASES USED

Table 3-1, shown below, highlights the type, identification numbers, and expiration date for each gas standard cylinder employed by the ML for calibration and testing purposes during Month 9.

Table 3-1. Calibrated Gases in use During Month 9.

Cylinder	ID#	Exp. Date
Carbon Dioxide	77-401243203-1	07/13/2026
Ammonia	48-401233442-1	06/21/2019
Zero-air	Lot #: 2181802 (115421, C5438107, T-2768, 330-662, KI428)	06/29/2019
VOC	160-401380144-1	01/16/2020

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

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

Table 3-2 through Table 3-7 display the zero-air and span checks performed daily during Month 9.

Table 3-2. Zero-air Checks for the LI-COR CO₂ Monitor.

Date	Time	Instrument Check	Observed Result (ppm)	Expected Result (ppm)	Pass/Fail
05/01/2019	05:44	Zero	-1.52	<50	Pass
05/02/2019	05:34	Zero	-1.56	<50	Pass
05/06/2019	05:50	Zero	-1.74	<50	Pass
05/07/2019	06:28	Zero	-1.66	<50	Pass
05/08/2019	05:36	Zero	-1.71	<50	Pass
05/09/2019	05:52	Zero	-1.80	<50	Pass
05/13/2019	05:53	Zero	-2.06	<50	Pass
05/14/2019	05:43	Zero	-2.11	<50	Pass
05/15/2019	05:45	Zero	-2.24	<50	Pass
05/16/2019	05:43	Zero	-2.33	<50	Pass
05/20/2019	07:03	Zero	-2.02	<50	Pass
05/21/2019	06:37	Zero	-2.23	<50	Pass
05/22/2019	05:51	Zero	-2.17	<50	Pass
05/23/2019	05:39	Zero	-2.31	<50	Pass
05/28/2019	05:46	Zero	-2.47	<50	Pass
05/29/2019	05:51	Zero	-1.72	<50	Pass
05/30/2019	06:38	Zero	1.74	<50	Pass
05/31/2019	04:47	Zero	-1.75	<50	Pass

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

Date	Time	Instrument Check	Observed Result (ppbv)	Expected Result (ppbv)	% Difference	Acceptance Criteria (%)	Pass/Fail
05/01/2019	05:46	Span	362	384	7.4	20	Pass
05/02/2019	05:37	Span	362	383	5.8	20	Pass
05/06/2019	05:52	Span	355	384	8.1	20	Pass
05/07/2019	06:30	Span	369	385	4	20	Pass
05/08/2019	05:38	Span	364	386	5.9	20	Pass
05/09/2019	05:54	Span	363	385.3	5.7	20	Pass
05/13/2019	05:53	Span	352	384	-8.2	20	Pass
05/14/2019	05:45	Span	359	385.1	6.7	20	Pass
05/15/2019	05:47	Span	361	384	-6.1	20	Pass
05/16/2019	05:45	Span	361	384	-6.2	20	Pass
05/20/2019	07:05	Span	352	384	8.5	20	Pass
05/21/2019	06:37	Span	358	384	6.9	20	Pass
05/22/2019	05:53	Span	359	383	6.8	20	Pass
05/23/2019	05:41	Span	360	384.6	6.3	20	Pass
05/28/2019	05:48	Span	348	384	9.6	20	Pass
05/29/2019	05:53	Span	358	384	6.9	20	Pass
05/30/2019	06:38	Span	361	385.4	6.4	20	Pass
05/31/2019	04:49	Span	361	385	6.2	20	Pass

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

Date	Time	Instrument Check	Observed Result (ppbv)	Expected Result (ppbv)	Pass/Fail
05/01/2019	05:57	Zero	0.08	<0.5	Pass
05/02/2019	05:47	Zero	0.07	<0.5	Pass
05/06/2019	06:03	Zero	0.08	<0.5	Pass
05/07/2019	06:41	Zero	0.1	<0.5	Pass
05/08/2019	05:49	Zero	0.08	<0.5	Pass
05/09/2019	06:04	Zero	0.04	<0.5	Pass
05/13/2019	06:04	Zero	0.08	<0.5	Pass
05/14/2019	05:58	Zero	0.08	<0.5	Pass
05/15/2019	05:59	Zero	0.06	<0.5	Pass
05/16/2019	05:57	Zero	0.06	<0.5	Pass
05/20/2019	06:25	Zero	0.1	<0.5	Pass
05/21/2019	06:46	Zero	0.05	<0.5	Pass
05/22/2019	06:04	Zero	0.06	<0.5	Pass
05/23/2019	05:52	Zero	0.05	<0.5	Pass
05/28/2019	05:59	Zero	0.08	<0.5	Pass
05/29/2019	06:04	Zero	0.07	<0.5	Pass
05/30/2019	06:43	Zero	0.09	<0.5	Pass
05/31/2019	04:55	Zero	0.07	<0.5	Pass

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

Date	Time	Instrument Check	Observed Result (ppbv)	Expected Result (ppbv)	% Difference	Acceptance Criteria (%)	Pass/Fail
05/01/2019	06:06	Span	9.2	10.8	-14.8	30	Pass
05/02/2019	05:57	Span	9.1	10.8	-15.7	30	Pass
05/06/2019	06:13	Span	9.25	10.8	-14.4	30	Pass
05/07/2019	06:50	Span	9.6	10.8	-11.1	30	Pass
05/08/2019	05:59	Span	9.75	10.8	-9.7	30	Pass
05/09/2019	06:12	Span	9.7	10.8	-10.2	30	Pass
05/13/2019	06:14	Span	9.5	10.8	-12.0	30	Pass
05/14/2019	06:06	Span	9.3	10.8	-13.9	30	Pass
05/15/2019	06:09	Span	9.2	10.8	-14.8	30	Pass
05/16/2019	06:07	Span	9.1	10.8	-15.7	30	Pass
05/20/2019	06:27	Span	8.9	10.8	-17.6	30	Pass
05/21/2019	06:46	Span	9.9	10.8	-8.3	30	Pass
05/22/2019	06:14	Span	8.8	10.8	-18.5	30	Pass
05/23/2019	06:03	Span	9.1	10.8	-15.7	30	Pass
05/28/2019	06:09	Span	8.6	10.8	-20.4	30	Pass
05/29/2019	06:14	Span	8.75	10.8	-19.0	30	Pass
05/30/2019	06:43	Span	8.57	10.8	-20.6	30	Pass
05/31/2019	05:10	Span	8.7	10.8	-19.4	30	Pass

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

Date	Time	Instrument Check	Observed Result (ppb)	Expected Result (ppb)	Pass/Fail
05/01/2019	05:26	Zero	7	<20	Pass
05/02/2019	05:20	Zero	7	<20	Pass
05/06/2019	05:33	Zero	6.7	<20	Pass
05/07/2019	06:11	Zero	11.4	<20	Pass
05/08/2019	05:19	Zero	8.2	<20	Pass
05/09/2019	05:34	Zero	8	<20	Pass
05/13/2019	05:34	Zero	7.4	<20	Pass
05/14/2019	05:26	Zero	7.9	<20	Pass
05/15/2019	05:29	Zero	6.2	<20	Pass
05/16/2019	05:27	Zero	6.5	<20	Pass
05/20/2019	06:41	Zero	5.64	<20	Pass
05/21/2019	06:48	Zero	6	<20	Pass
05/22/2019	05:34	Zero	6.4	<20	Pass
05/23/2019	05:23	Zero	7.9	<20	Pass
05/28/2019	05:30	Zero	7.76	<20	Pass
05/29/2019	05:34	Zero	7.14	<20	Pass
05/30/2019	06:42	Zero	7	<20	Pass
05/31/2019	04:30	Zero	6.65	<20	Pass

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

Date	Time	Instrument Check	Observed Result (ppb)	Expected Result (ppb)	% Difference	Acceptance Criteria (%)	Pass/Fail
05/01/2019	05:38	Span	3585	3250	10.3	20	Pass
05/02/2019	05:30	Span	3660	3250	12.6	20	Pass
05/06/2019	05:46	Span	3625	3250	11.5	20	Pass
05/07/2019	06:24	Span	3585	3250	10.3	20	Pass
05/08/2019	05:31	Span	3600	3250	10.7	20	Pass
05/09/2019	05:44	Span	3540	3250	8.9	20	Pass
05/13/2019	05:47	Span	3610	3250	11.0	20	Pass
05/14/2019	05:40	Span	3576	3250	10.0	20	Pass
05/15/2019	05:41	Span	3625	3250	11.5	20	Pass
05/16/2019	05:39	Span	3625	3250	11.5	20	Pass
05/20/2019	06:58	Span	3370	3250	3.69	20	Pass
05/21/2019	06:48	Span	3457	3250	6.4	20	Pass
05/22/2019	05:47	Span	3500	3250	7.7	20	Pass
05/23/2019	05:33	Span	3508	3250	7.9	20	Pass
05/28/2019	05:45	Span	3632	3284	10.6	20	Pass
05/29/2019	05:47	Span	3547	3292	7.7	20	Pass
05/30/2019	06:42	Span	3445	3250	6	20	Pass
05/31/2019	04:41	Span	3626	3292	10.1	20	Pass

4.0 MEASUREMENT UNCERTAINTY AND KNOWN SOURCES OF ERROR

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

4.1.1 Proton Transfer Reaction – Mass Spectrometer

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

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

4.1.3 Ammonia Monitor

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

4.1.4 Weather Station

The Airmar 200WX-IPx7 Weather Station had no specific errors associated within the timeframe covered in this monthly report. The Airmar 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*.

4.1.5 Method Detection Limit Study

No MDLs were calculated during Month 9.

5.0 RESULTS

This section details the test results found during Month 9 monitoring activities.

5.1 Discussion of Test Activities and Observations

During Month 9, there were 18 days of area monitoring around the 200 West and 200 East Areas of the Hanford Site. There were 3 days spent on testing of various laboratory components. Results from the area monitoring are presented in the following sections.

Table 5-1. Activity Details for Month 9.

Week	Date	Activity
39	05/01/2019	Area Monitoring of the 200 E and 200 W Area
	05/02/2019	Area Monitoring of the 200 E and 200 W Area
	05/03/2019	ML Testing (multipoint calibration, acceptance testing, etc.)
40	05/06/2019	Area Monitoring of the 200 E and 200 W Area
	05/07/2019	Area Monitoring of the 200 E and 200 W Area
	05/08/2019	Area Monitoring of the 200 E and 200 W Area
	05/09/2019	Area Monitoring of the 200 E and 200 W Area
	05/10/2019	ML Testing (208' heated line)
41	05/13/2019	Area Monitoring of the 200 E and 200 W Area
	05/14/2019	Area Monitoring of the 200 E and 200 W Area
	05/15/2019	Area Monitoring of the 200 E and 200 W Area
	05/16/2019	Area Monitoring of the 200 E and 200 W Area
	05/17/2019	ML Testing (N2O instrument and PTR-MS multipoint)
42	05/20/2019	Area Monitoring of the 200 E and 200 W Area
	05/21/2019	Area Monitoring, AOP-015 Event, Fugitive Emissions
	05/22/2019	Area Monitoring of the 200 E and 200 W Area
	05/23/2019	Area Monitoring and Fugitive Emissions
43	05/28/2019	Area Monitoring of the 200 E and 200 W Area
	05/29/2019	Area Monitoring of the 200 E and 200 W Area
	05/30/2019	Area Monitoring of the 200 E and 200 W Area
	05/31/2019	AZ-102 to AN-106 Waste Transfer

5.2 Area Monitoring Data Scan

5.2.1 Exhaust Scan

The data scanner presented in 53005-81-RPT-066, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 8*, was used to scan the data for potential exhaust plumes. The exhaust scanner was modified from 53005-81-RPT-066 parameters to remove methyl nitrite from the list of scanned species. The remaining six (formaldehyde, nominal m/z 41, nominal m/z 43, acetaldehyde, benzene, toluene) were scanned for exceedances of the threshold. Table 5-2 lists the threshold values determined by the SME through visual inspection of the individual species response throughout the month. If at least five of these species exceeded their threshold at the same time it was identified as a potential plume. The width of the plume extends before and after this identified plume as long as four of the species still exceeded the threshold. The scan yielded 54 plumes throughout the month of May 2019. The SME reviewed the plumes and organized them into four general categories with 32 seeming to be vehicle exhaust plumes, 15 potentially from a generator source, three of them showing high methanol responses, and four having a large toluene and C₂-benzene influence.

Table 5-2. Threshold Values of Species Used for the Exhaust Scanner.

Species	Threshold (ppbv)
Formaldehyde	1.5
Nominal m/z 41	1.0
Nominal m/z 43	5.0
Acetaldehyde	3.0
Benzene	0.5
Toluene	0.5

5.2.1.1 Vehicle Exhaust A and B Plumes

The 32 vehicle exhaust plumes showed very similar response; however, there were some slight differences that allowed separation into two categories. All 32 plumes showed a high aromatic (benzene, toluene, C₂-benzenes, C₃-benzenes, C₄-benzenes) response along with strong signal at nominal m/z 41, nominal m/z 43, and acetaldehyde. Twenty-eight of the plumes showed a slight formaldehyde response but it is more suppressed than typically observed in exhaust plumes. It is important to note that ten of these 28 plumes were of short duration (<10 seconds) and are characterized as spikes. In 53005-81-RPT-066, spikes were omitted from analysis if the response did not seem stable or well defined. In this instance, these exhaust spikes seemed adequate for inclusion in the analysis. The 18 plumes occurred on May 9, 2019; May 15, 2019; and May 20, 2019, and the ten spikes occurred on May 15, 2019; May 16, 2019; and May 20, 2019. Table 5-3 lists the date and time the potential vehicle exhaust plumes occurred. The other four of the 32 exhaust plumes were on May 6, 2019, at 06:22; May 8, 2019, at 06:02; May 13, 2019, at 07:21; and May 15, 2019; at 12:27. They differed from the 28 exhaust plumes in the lack of formaldehyde and methyl nitrite along with higher methanol within the fingerprints.

Table 5-3. Date and Time of Potential Vehicle Exhaust Plumes Identified with the Exhaust Scanner for May 2019.

Date	Plume Times	Spike Times
May 9, 2019	10:52, 10:53, 13:45	
May 15, 2019	14 between 11:57 to 12:31	12:05, 12:15, Two at 12:32
May 16, 2019		10:45
May 20, 2019	12:25	Five between 07:51 to 07:53

The 28 potential vehicle exhaust plumes are shown in Figure 5-1 along with the average fingerprint, the exhaust fingerprint developed in 53005-81-RPT-027, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 2*, and the 53005-81-RPT-066 exhaust average fingerprint resulting from the exhaust scan. Compared to Month 2 exhaust, there are some distinct differences in the lower amounts of formaldehyde and acetaldehyde observed in the average fingerprint and the increased response in aromatics. The average fingerprint compares better with the Month 8 fingerprint showing the same response in formaldehyde, methanol, nominal m/z 41, nominal m/z 43, acetaldehyde, 2-propenal, and acetone. The big difference is the enhanced signal of aromatics which may be a function of the vehicle engine type. In general, gasoline fuel and gasoline engine exhaust contains more aromatics than diesel fuel and engine exhaust. The exact source is unknown and further investigation, observations, and analysis are needed to determine the likely cause but the composition suggests the plumes are exhaust in origin.

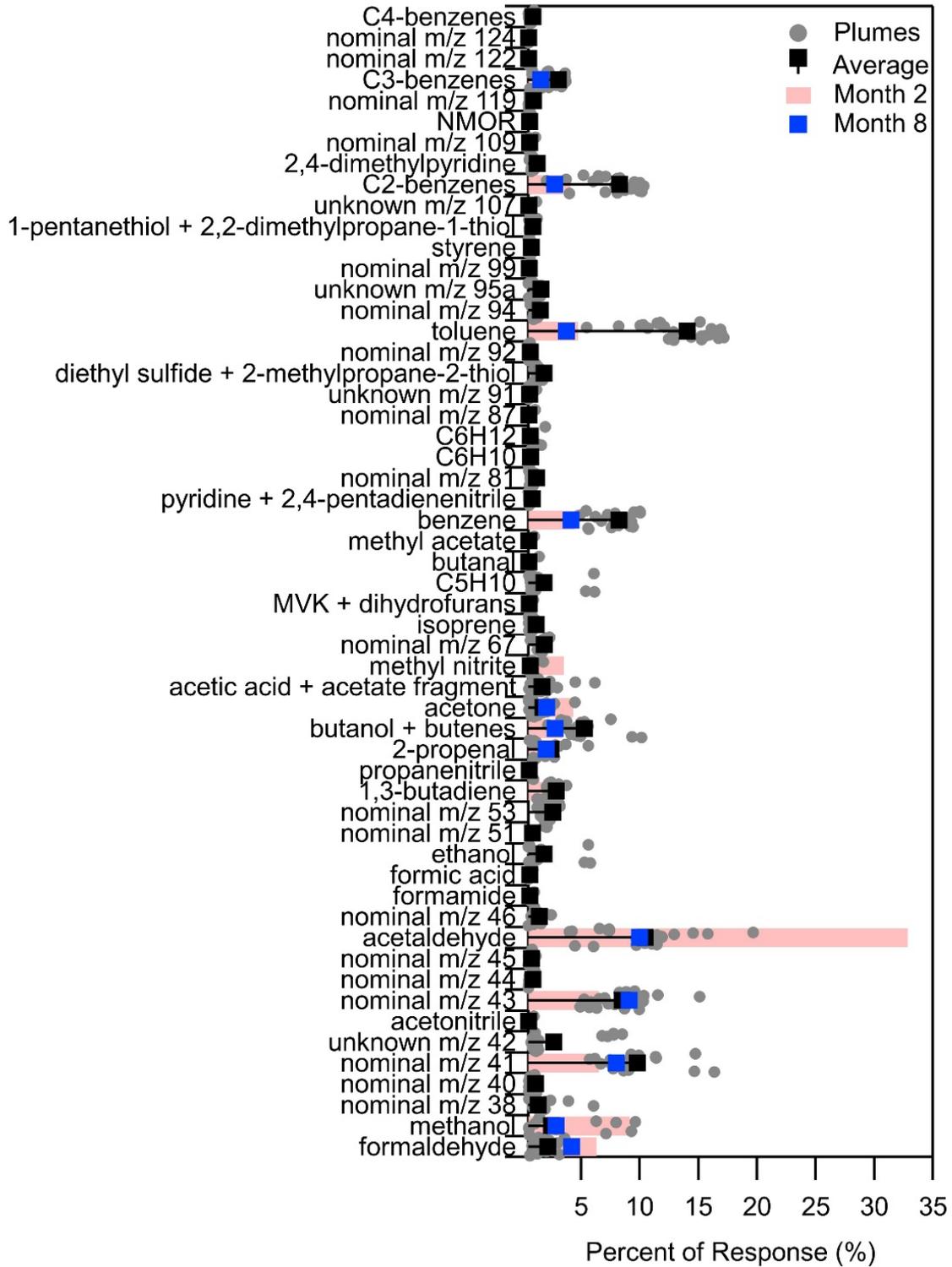


Figure 5-1. Fingerprints of the 28 Exhaust Plumes Identified with the Exhaust Scan of the May 2019 Data.

Figure 5-2 shows the other four of the 32 potential exhaust plumes. The average fingerprint is the same as the average fingerprint in Figure 5-1. The differences are the average fingerprint in Figure 5-2 has no response in formaldehyde and methyl nitrite plus a higher response in methanol. This is relatively minor and variability within the same or similar engine could account for the differences. As discussed in previous reports, window washer fluid typically contains high levels of methanol. The sole source of these plumes could be a gasoline vehicle with the exhaust being the major component with some influence from the window washer fluid.

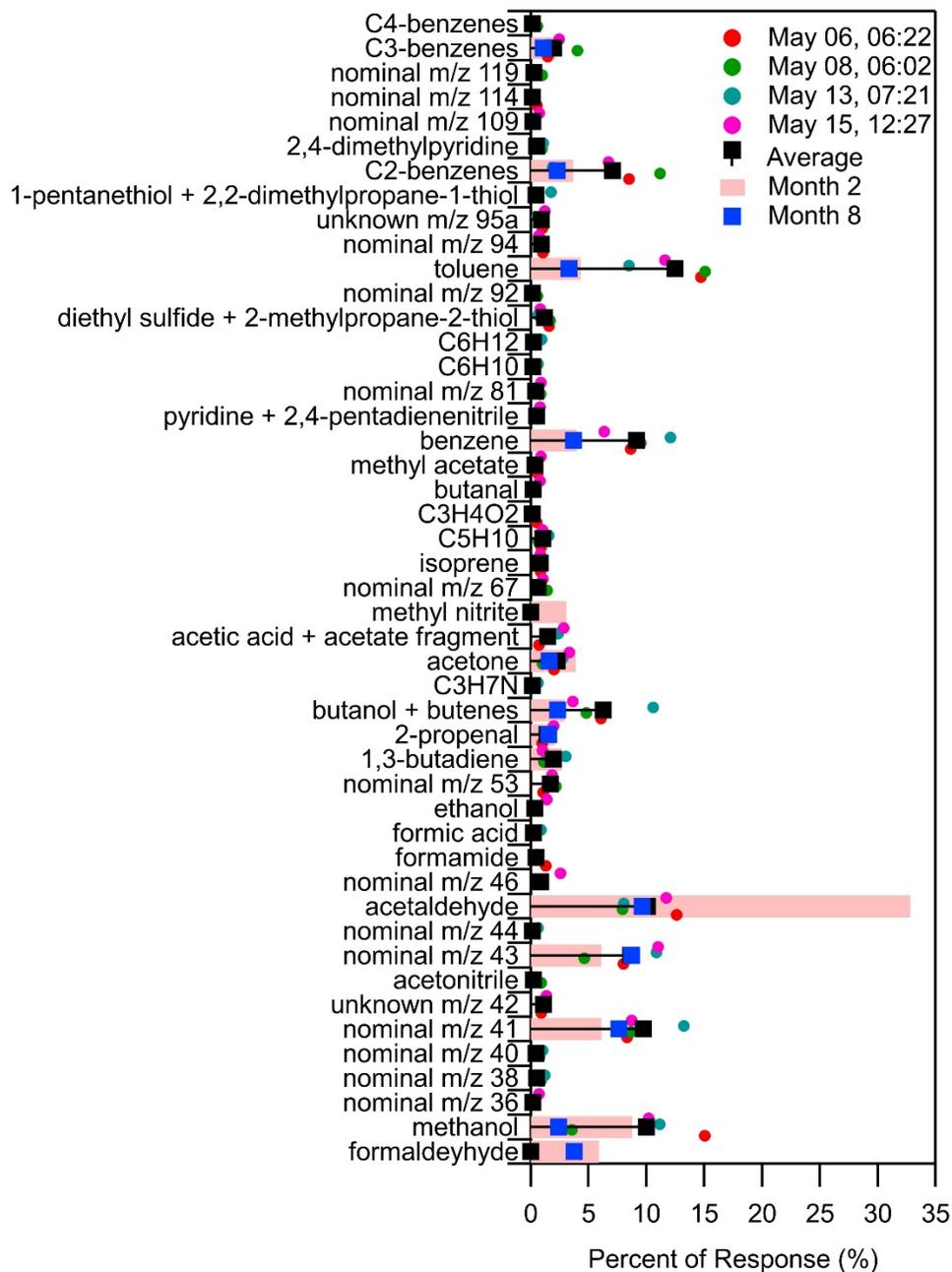


Figure 5-2. Fingerprints of the Four Exhaust Plumes that Contained Increased Methanol Response Identified with the Exhaust Scan of the May 2019 Data.

5.2.1.2 Generator Exhaust Plumes

There were 15 plumes that contained high enough nominal m/z 46 response to point towards generator exhaust as the potential source. In 53005-81-RPT-059, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 7*, and 53005-81-RPT-066, there was direct sampling of generator exhaust and it was determined that the nominal m/z 46 response was due to NO₂ within the exhaust. It seemed to be the most prominent species within the exhaust plume and is a good indicator to point towards generator sources. Eight of the 15 had strong NO₂ responses with five of them being plumes and three being spikes. Four of the plumes occurred on May 1, 2019, at 06:15, 13:10, 13:13, and 13:56 with the one occurring on May 2, 2019, at 10:54. Two of the spikes occurred on May 14, 2019 (both at 08:27), and one occurred on May 29, 2019, at 12:56. Figure 5-3 shows the eight plumes and the corresponding average. The highest responses are with formaldehyde, methanol, nominal m/z 41, nominal m/z 43, nominal m/z 45, acetaldehyde, and nominal m/z 46 which would be expected from a generator exhaust plume. There is some variability in the responses of these species, but the nominal m/z 46 and acetaldehyde maintain prominent response in every plume.

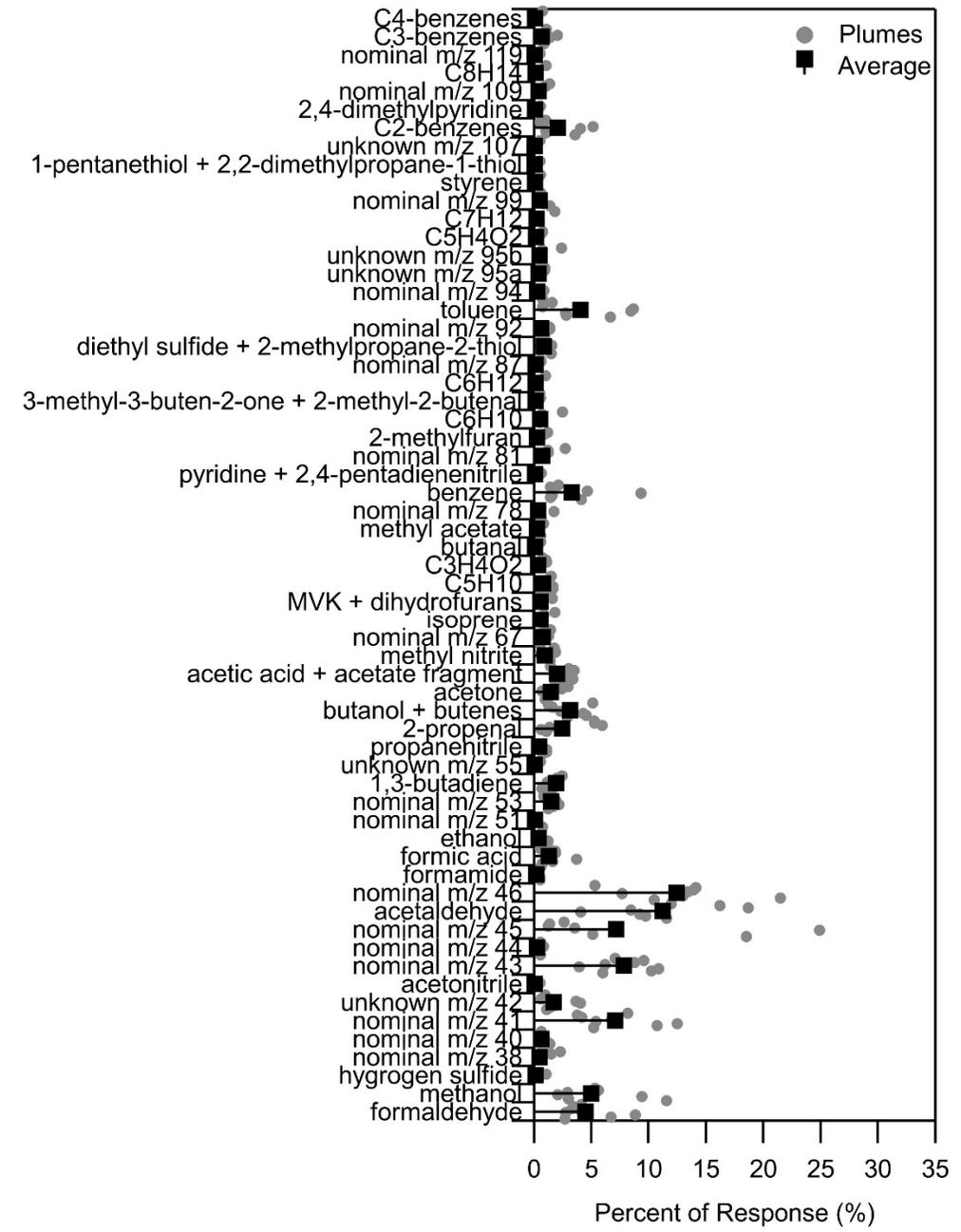


Figure 5-3. Fingerprints of the Eight Generator Exhaust Plumes Identified with the Exhaust Scan of the May 2019 Data.

Instead of relying on expected composition alone, the average fingerprint from Figure 5-3 can be compared to the generator exhaust characterization detailed in 53005-81-RPT-059 and 53005-81-RPT-066. Figure 5-4 shows the average generator exhaust fingerprint for the eight plumes along with the fingerprints from GEN2 in 53005-81-RPT-059 and the April 8, 2019, generator in 53005-81-RPT-066. GEN2 was described as less efficient than GEN1 in 53005-81-RPT-059 and contained a broader spectrum of species. The same conclusion was made for the April 8, 2019, generator compared to the April 15, 2019, generator in 53005-81-RPT-066 and a

reasonable comparison was shown between the GEN2 and April 8, 2019, fingerprints. The average fingerprint for the eight generator plumes identified in this report compares reasonably well with the GEN2 and April 8, 2019, fingerprints. The amount of acetaldehyde and nominal m/z 46 is only slightly offset from the April 8, 2019, fingerprint and the formaldehyde, methanol, nominal m/z 41, and nominal m/z 43 show a comparable response. This suggests the generator plumes are from the same or similar performing generator. Further analysis and investigation are required to attribute the plumes to a specific generator.

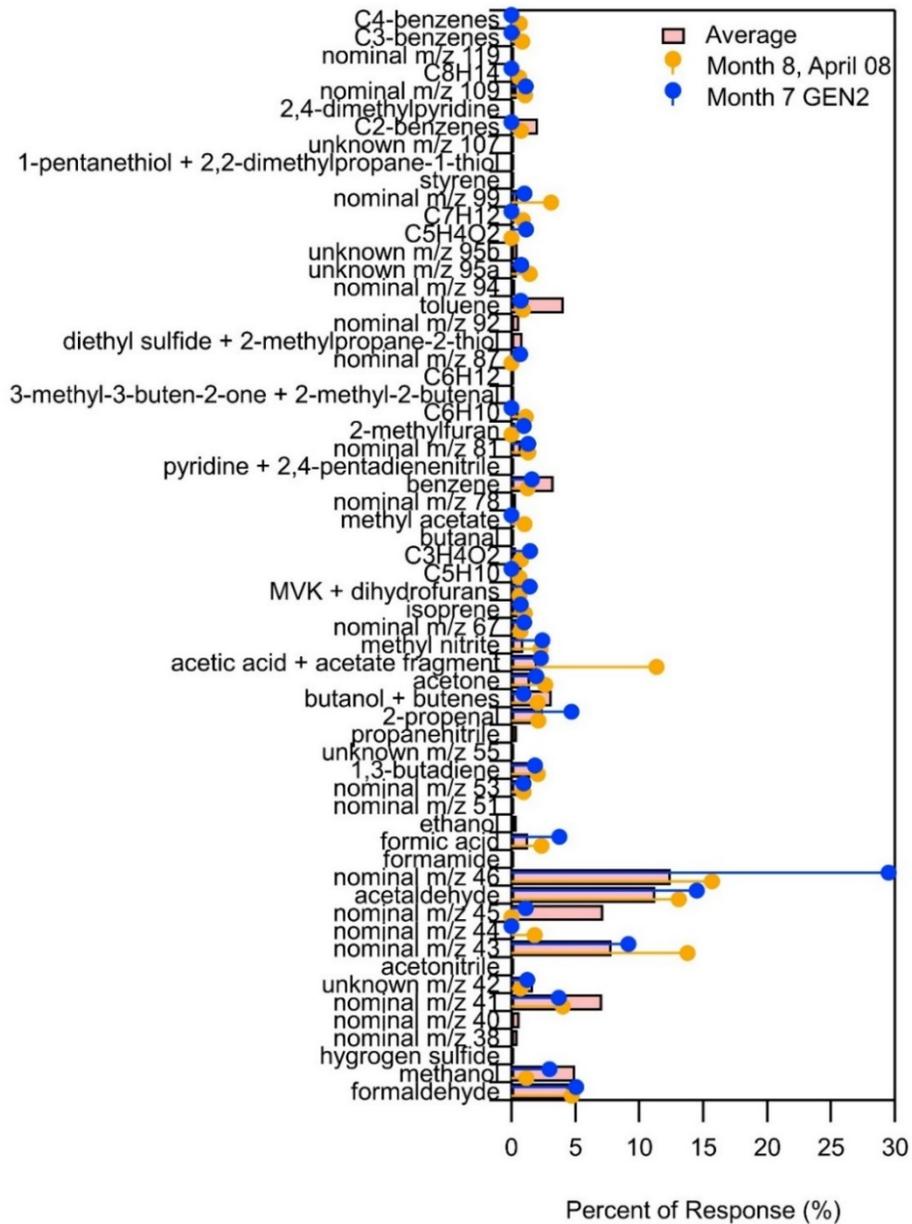


Figure 5-4. Comparison of the Generator Fingerprints to Month 7 and Month 8 Generator Fingerprints.

The Month 2 fingerprint has been the common fingerprint representing general exhaust sources in previous reports. The characterization of generator exhaust in 53005-81-RPT-059 and 53005-81-RPT-066 in combination with the exhaust scanner has evolved the understanding of exhaust fingerprints around site. The exhaust fingerprint from 53005-81-RPT-027 was identified as the representation of the exhaust from the ML itself. The exhaust scanner identified six plumes occurring on May 1, 2019, at 13:56 and 13:57; May 2, 2019, at 06:23; May 6, 2019, at 13:54; May 13, 2019, at 07:21; and May 30, 2019, at 09:35; with one spike occurring on May 6, 2019, at 06:23. The fingerprint from the six plumes and one spike are shown in Figure 5-5 along with the Month 2 ML exhaust fingerprint. The responses are slightly offset with the average compared to the Month 2 fingerprint, but they both follow the same pattern. Acetaldehyde is the largest constituent with prominent responses from nominal m/z 41, nominal m/z 43, and aromatics (benzene, toluene, C₂-benzene, C₃-benzenes, C₄-benzenes). The primary differences are the weaker response of formaldehyde, methanol, and methyl nitrite within the average plus the stronger aromatic response. The differences could be attributed to generator performance, runtime since last maintenance, or meteorological effects. To increase the understanding of the ML exhaust, laboratory tests could be performed to characterize the exhaust composition of the ML generator and the ML engine. Both the ML engine and generator use diesel; therefore, this fingerprint is representative of the output from the diesel combustion process and similar engines may produce a similar fingerprint.

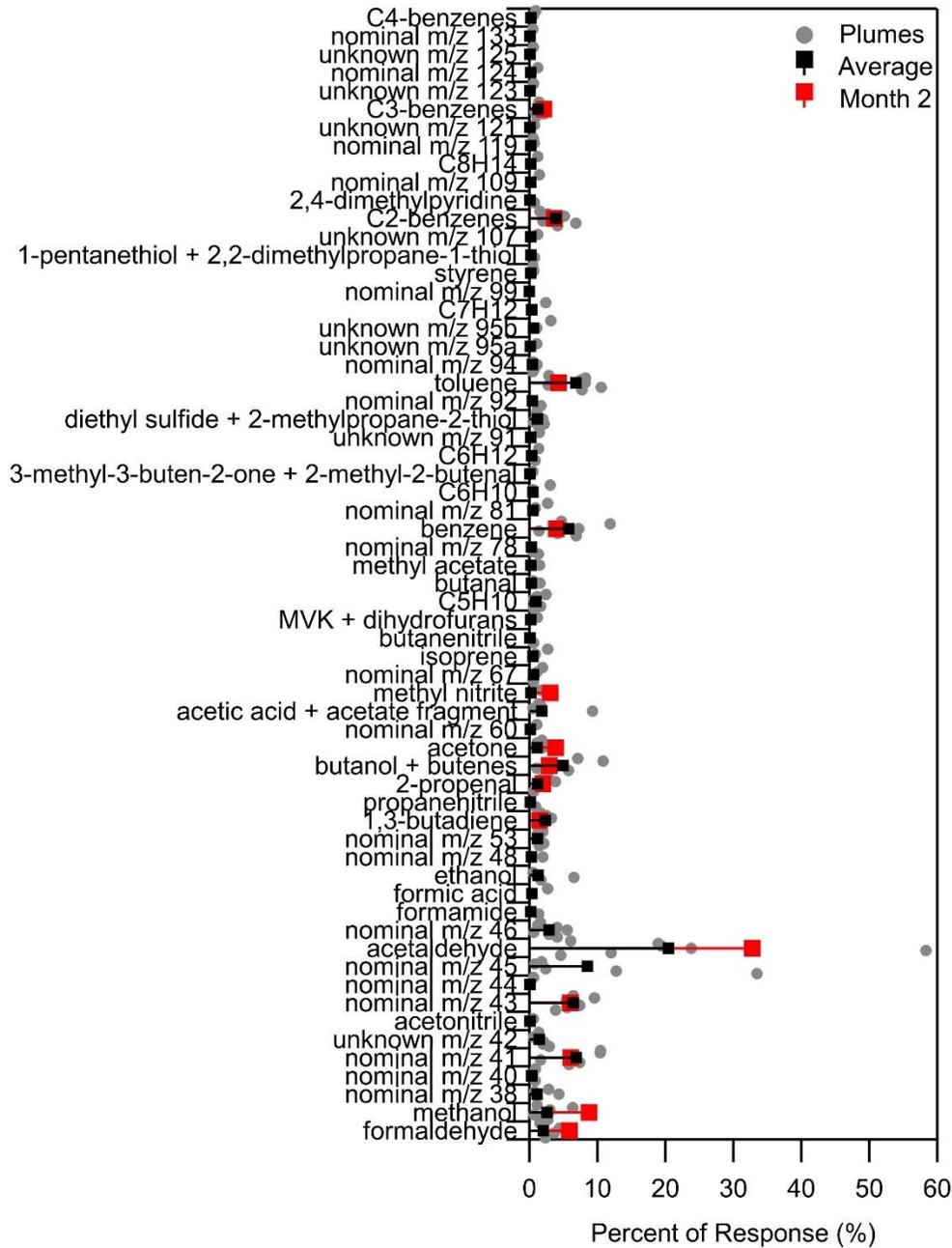


Figure 5-5. Fingerprints of the Six Exhaust Plumes Identified with the Exhaust Scan Compared to the Month 2 Exhaust Fingerprint.

5.2.1.3 Exhaust Fingerprint Comparisons

This analysis of exhaust fingerprints identified by the exhaust scanner has enhanced the understanding of exhaust sources on site. Enough information has been collected and analyzed to propose fingerprints for three different exhaust sources: gasoline vehicles, diesel vehicles, and generators. Figure 5-6 shows the representative fingerprints from these three types of exhaust sources. The gasoline vehicle is best represented by the strong aromatic response compared and

was shown previously in Figure 5-1. The nominal m/z 41, nominal m/z 43, and acetaldehyde still have a strong presence within gasoline exhaust, but the aromatics contribute a higher fraction to the overall signal compared to the diesel vehicle and generator. The diesel vehicle is best identified by the strong acetaldehyde response and the diesel generator by the strong NO₂ response (nominal m/z 46). These are minor differences, but these distinctions were identifiable during these observations. This is also just the initial proposal of fingerprints that represent these three exhaust sources. Further testing, investigation, and analysis is required to determine their accuracy and reliability, but this provides a metric for future plume source identification.

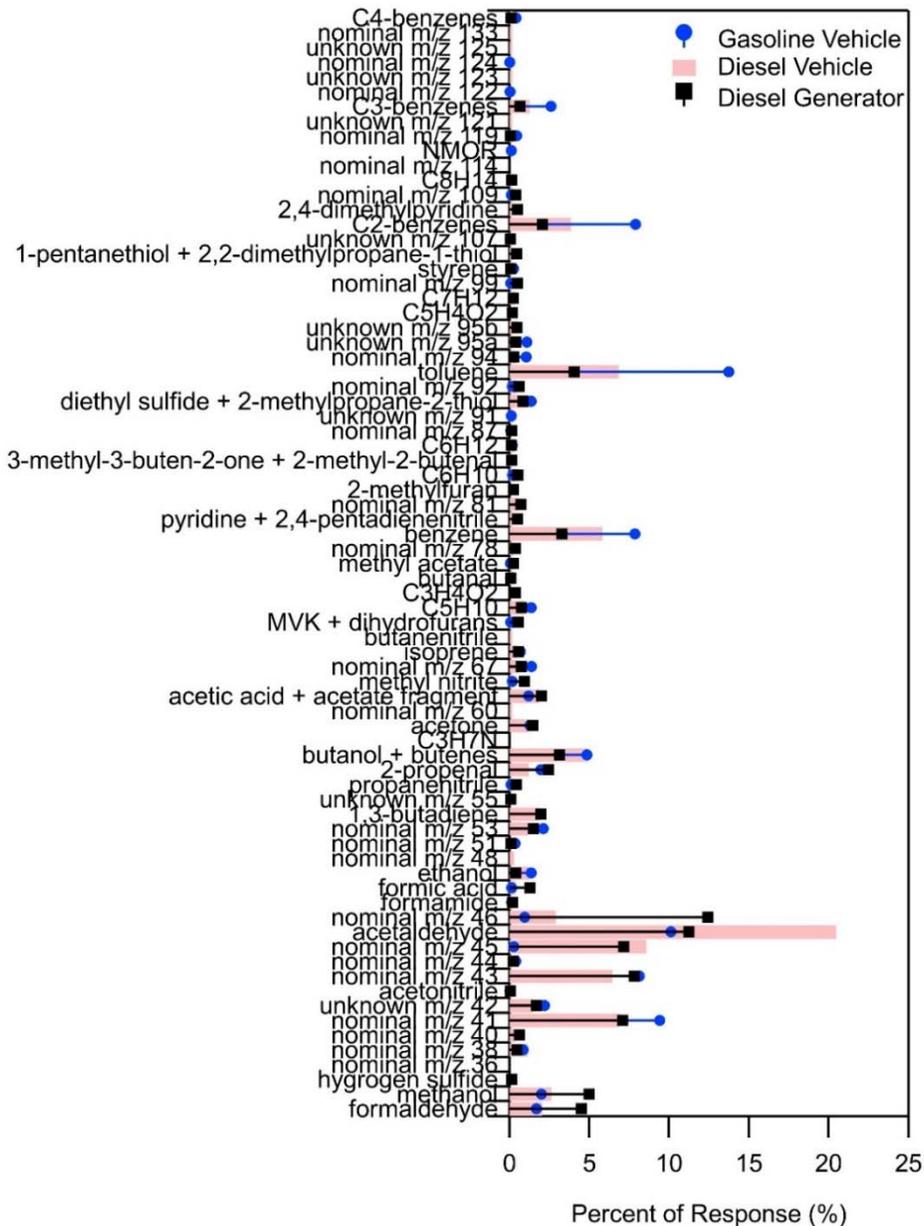


Figure 5-6. Comparison of the Fingerprints from Three Different Combustion Exhaust Sources: Gasoline Vehicle, Diesel Vehicle, and Diesel Generator.

5.2.1.4 Methanol Plumes

There were instances of high methanol response identified by the exhaust scan. A plume occurred on May 13, 2019, at 07:35 and two spikes occurred on May 6, 2019, at 06:21 and 06:36. Figure 5-7 shows the resulting fingerprints included with the average methanol plume fingerprint reported in 53005-81-RPT-066. 53005-81-RPT-066 suggests that the source of the methanol plumes may be vehicle related due to the presence of exhaust species and windshield washer fluid contains high amounts of methanol. The May 6, 2019, and May 13, 2019, fingerprints compare well to the Month 8 fingerprint with a majority of the response from methanol and secondary responses at unknown m/z 42 and nominal m/ 43. Even with the strong response in methanol, the concentrations are relatively low compared to the Occupational Exposure Limit (OEL). The May 6, 2019, spikes at 06:21 and 06:36 reached maximum concentrations of 28 ppbv and 16 ppbv, respectively, and the May 13, 2019, plume reached 21 ppbv. The OEL for methanol is 200,000 ppbv which is four orders of magnitude higher than the max concentrations in the plume and spikes. The exhaust scan does not look for methanol plumes and larger ones occur than those identified here. During the month of May 2019, the maximum observed concentration of methanol was 165 ppbv which is equivalent to 0.08% of the OEL. A separate scan can be developed to identify large methanol plumes; however, method development in this manner is better focused towards plumes and sources that have a higher potential for worker safety impact.

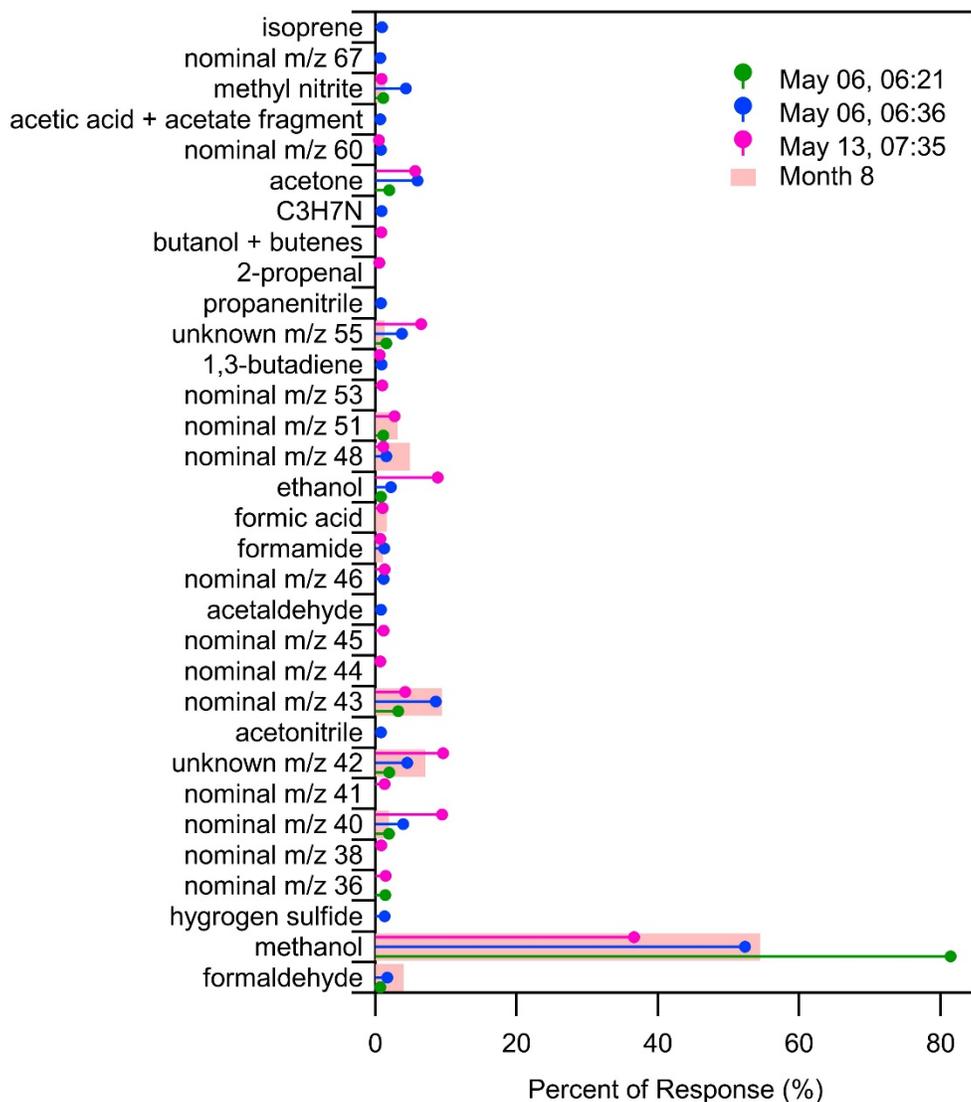


Figure 5-7. Fingerprints of the Three Methanol Plumes Identified with the Exhaust Scan Compared to the Month 8 Methanol Plume Average Fingerprint.

5.2.1.5 Toluene and C₂-Benzene Plumes

The last four plumes of the 54 identified with the exhaust scanner showed strong toluene and C₂-benzene responses. Figure 5-8 shows the fingerprints of the four plumes occurring on May 9, 2019, at 10:53; May 15, 2019, at 06:18 and 11:01; and May 30, 2019, at 11:41 along with the average. Toluene had the highest contribution and there was surprising consistency within all four plumes. The percent of response of toluene ranged from 20.6% to 21% for the four plumes for an average of 20.8%. The C₂-benzenes did not show as much consistency as the toluene and averaged 14.5%. Other main contributors were nominal m/z 41 at 8.6%, benzene at 8%, acetaldehyde at 6.6%, butanol + butenes at 6%, nominal m/z 43 at 5.4%, and C₃-benzenes at 4.4%. These eight species accounted for ~74% of the total response. In 53005-81-RPT-066, there were unique plumes containing either large amounts of toluene or C₂-benzenes but not a

strong response of both within the same plume. The Month 8 toluene plumes contained ~58% toluene and the C₂-benzene plumes were ~62% C₂-benzenes. One possibility is the four plumes shown in Figure 5-8 are a mixture of the Month 8 plumes. If the Month 8 plumes mixed evenly, they would be expected to each contribute ~30% of the response to the combined plume and account for ~60%. The combined response with the May 2019 plumes is 35.3% which is a little over half the expected response. This suggests that it is not likely to be a combination of the Month 8 plumes. The strong aromatic response may be the result of fuel emissions rather than combustion emissions. The presence of acetaldehyde means there is likely some combustion influence so these plumes could be a mixture of combusted and pure fuel emissions.

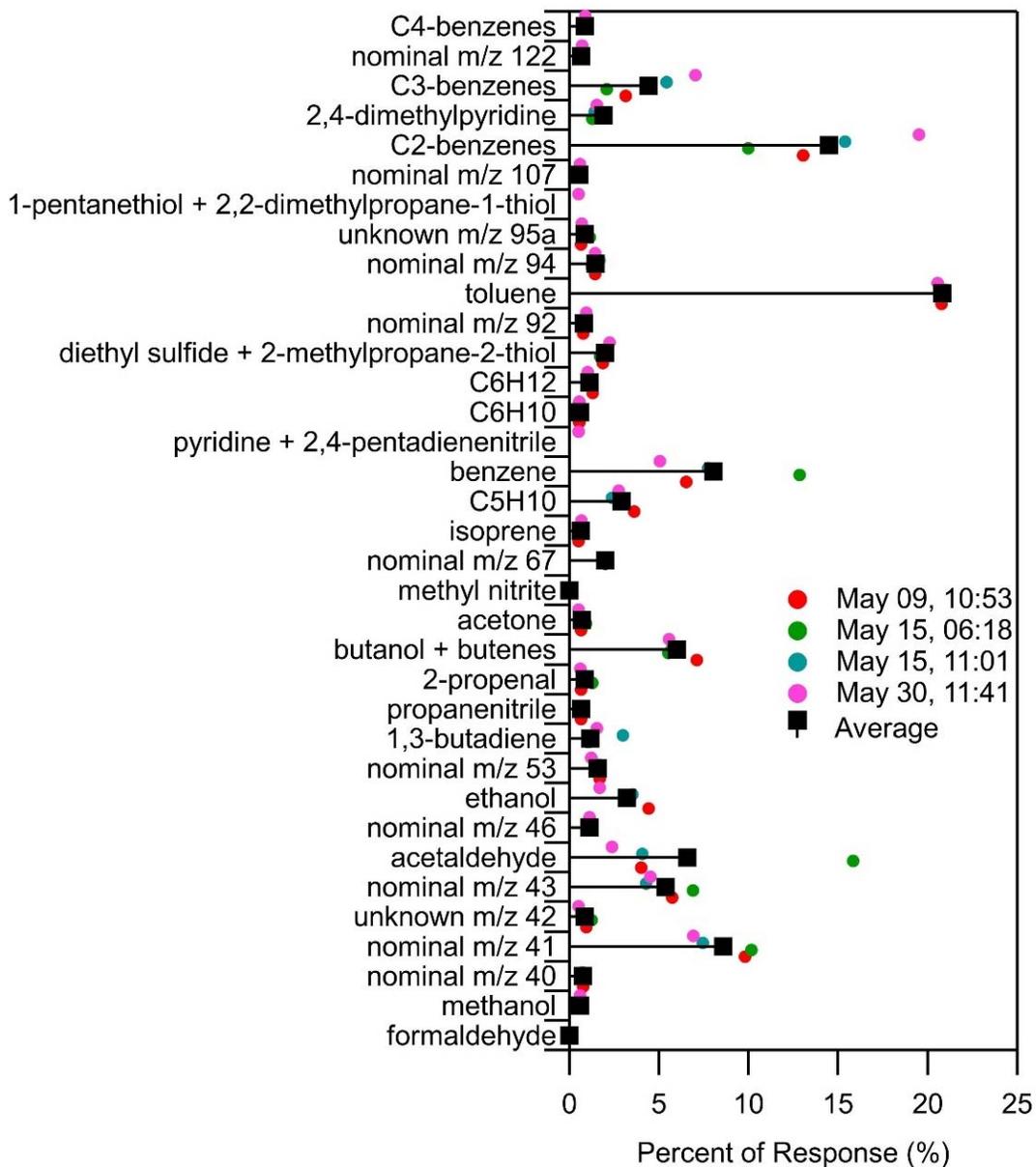
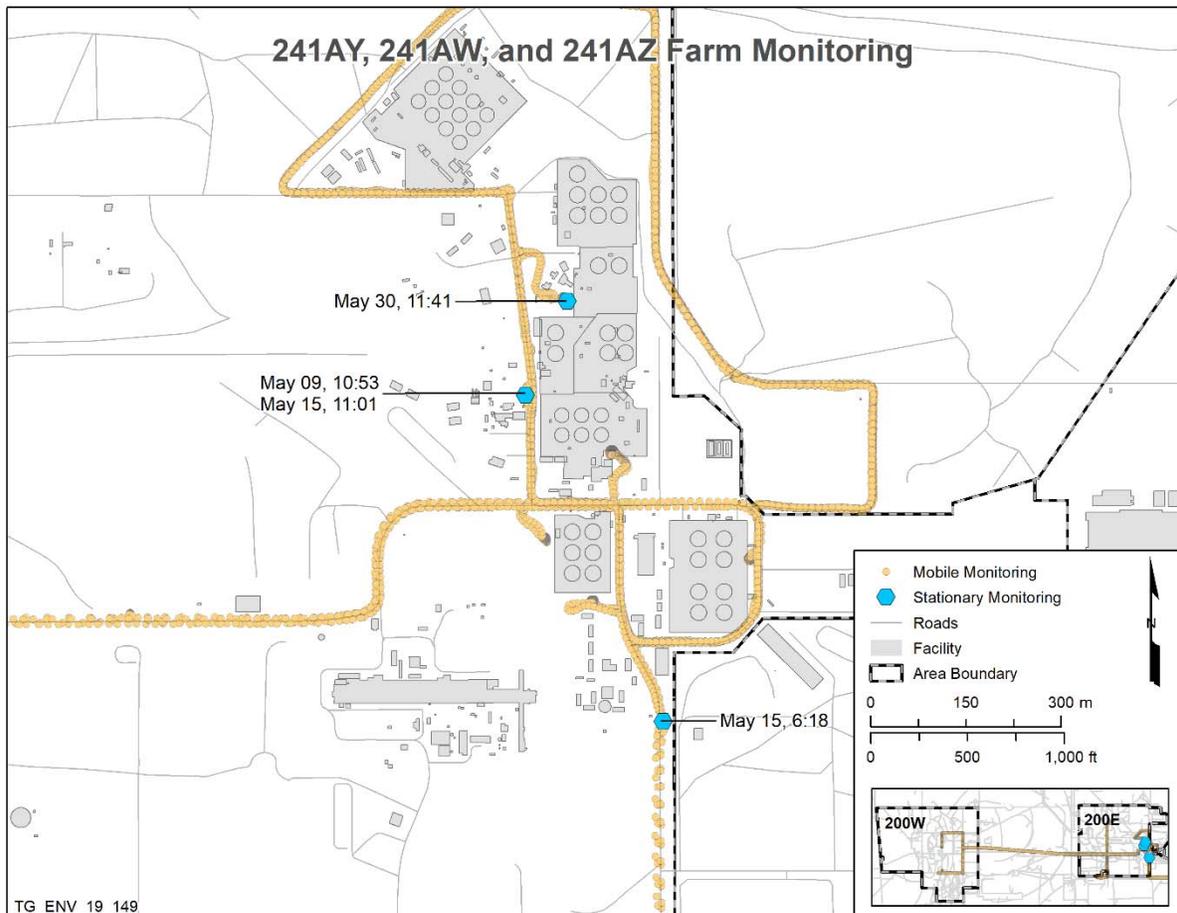


Figure 5-8. Fingerprints of the Four Toluene/C₂-benzene Plumes Identified with the Exhaust Scan.

The location of three of the plumes was around 241-AY Farm. Figure 5-9 shows the location of each plume along with the wind direction observed around the time of observation. The May 9, 2019, plume occurred near the southwest corner of 241-AY and had steady northeast wind greater than 4 m/s pointing towards 241-AY as the source. The May 15, 2019, 06:18 plume occurred on the southeast of 241-AW with consistent 2 to 5 m/s northwest wind from that direction. The May 15, 2019, 11:01 plume occurred at the same location as the May 9, 2019, plume near the southwest corner of 241-AY, but the wind was primarily from the north at 1 to 3 m/s with some periodic 1 to 2 m/s northeast wind which suggests the plume could originate from 241-AY. The May 30, 2019, 11:41 plume was observed west of 241-AZ and north of 241-AY with some variability in the wind ranging from 1 to 4 m/s from the southwest to northwest. Wind from the southwest could still suggest 241-AY as the potential source of the plume. Further investigation is needed to identify the actual source, but this fingerprint can be used in future analysis to identify plumes from the same or similar source.



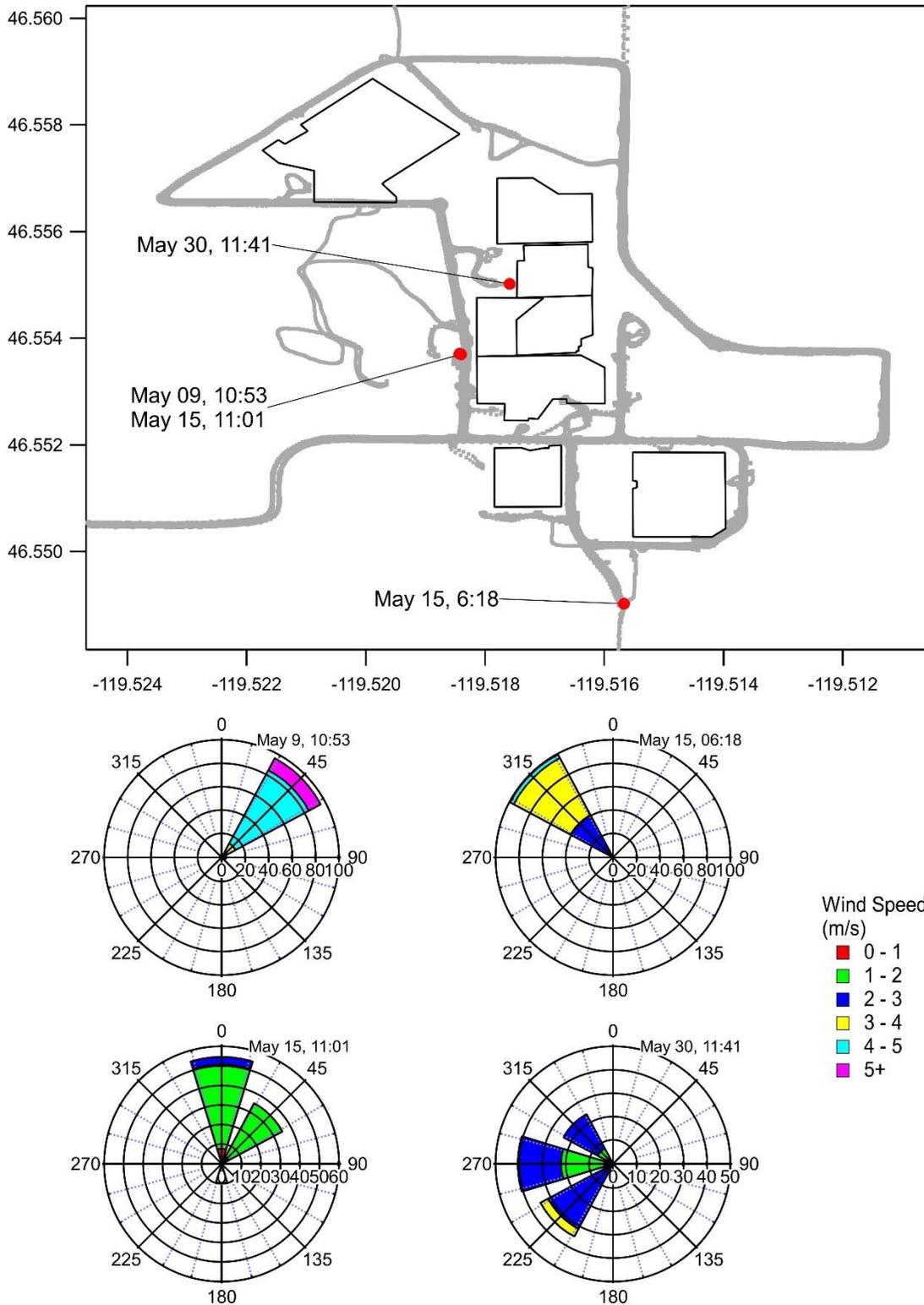


Figure 5-9. Location and Wind Direction During Observation of the Four Toluene and C₂-benzene Plumes.

5.2.2 Odor Scan

The odor scanner was performed using refined thresholds. The SME reviewed the time-series for each odor and adjusted the threshold values to optimize plume identification. There were instances where the Reporting Limit (RL) of the odor species was not adequate to capture smaller plumes and those thresholds were lowered. This resulted in the identification of 77 plumes. Ten of the plumes were determined to have too low of concentrations or were too short lived for analysis. Upon comparison with the exhaust scan rests, 30 of the plumes were previously identified during that scan and will not be analyzed again. This leaves 37 plumes for analysis and were grouped into 14 potential exhaust plumes, 19 methanol related plumes, and four unique plumes. Even though this scan is intended to identify potential odor plumes, none of the plumes were dominated by odor species. This means that there were no significant odor plumes containing the odor species from the scan list during this month.

5.2.3 Methanol Plumes

The 19 potential methanol plumes were further organized into three groups based on similar composition. The different groups will be given an alphabetic designation based on order of occurrence. Methanol Group A (MA) consists of two plumes and six short-lived spikes all occurring on May 14, 2019, between 09:52 and 09:57. Methanol Group B (MB) occurred on May 15, 2019, with a plume at 11:56; May 29, 2019, with a spike at 11:17; and May 30, 2019, with two spikes at 06:44 and 11:17. Methanol Group C (MC) had two plumes and a spike within a short time span around 06:22 on May 28, 2019, and three spikes on May 30, 2019, with two at 06:33 and one at 07:03. There was a final plume that occurred on May 21, 2019, at 09:45 that did not fit within the three methanol groups. The locations of the observations of these methanol groups around 200 E is shown in Figure 5-10. Note that the MB spike on May 30, 2019, at 06:44 occurred at the same location as the MC spikes on May 20, 2019, at 06:33.

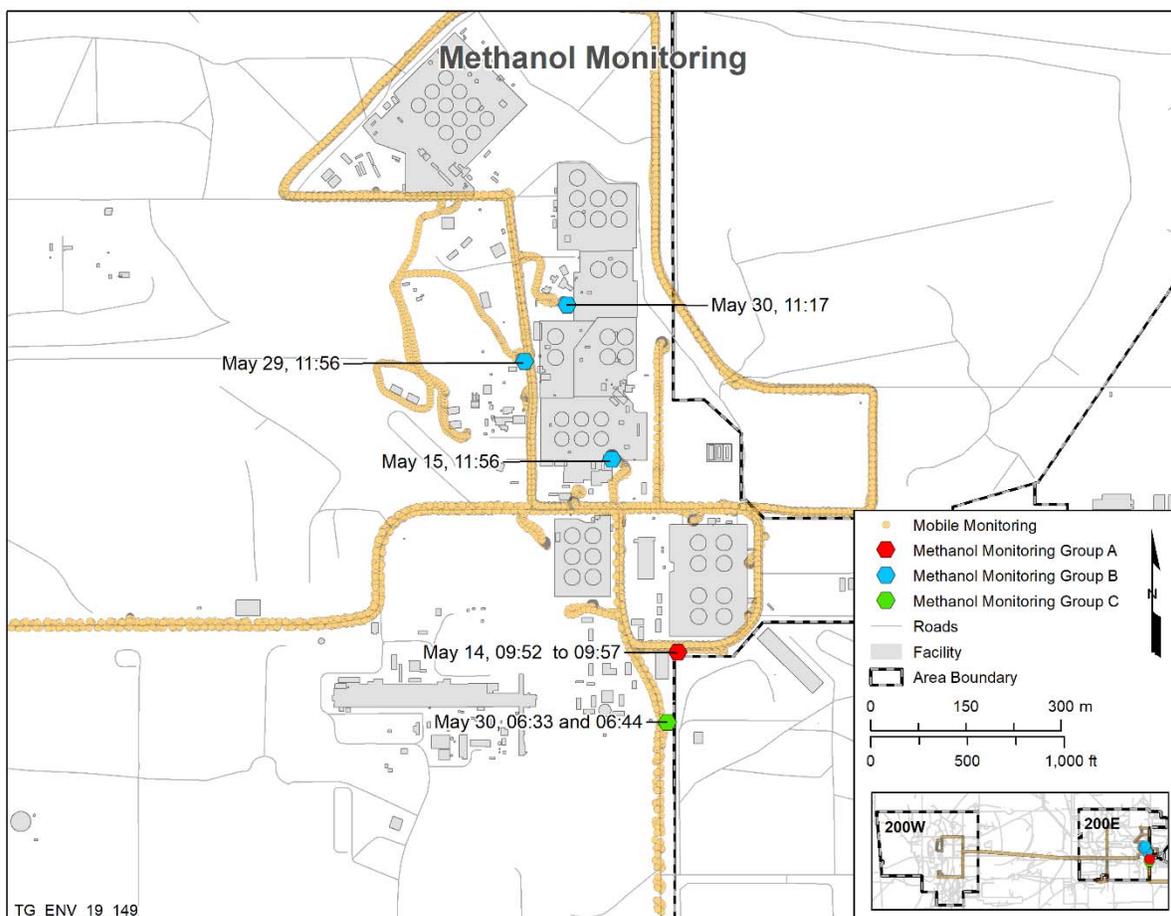


Figure 5-10. Location of the Mobile Laboratory when Observing the Methanol Plumes in the 200 East Area During May 2019.

5.2.3.1 Methanol Group A

The ML was located near the southwest corner of 241AP Farm when the multiple plumes and spike between 09:52 and 09:57 on May 14, 2019 were observed. Figure 5-11 shows the resulting fingerprints and overall average along with the methanol plume signature presented in 53005-81-RPT-066. The Month 8 fingerprint was derived from four plumes observed on April 3, 2019; April 23, 2019; and April 25, 2019. The MA fingerprints followed a different pattern and have a more suppressed methanol response with an average of 16% versus the Month 8 methanol response of 54%. The dominant responses were from nominal m/z 43 at 28%, acetic acid + acetate fragment at 19%, and acetaldehyde at 7%. Combined with methanol, these four species account for 70% of the total response. While these species are commonly found within exhaust, the fingerprint pattern is distinctly different and seems to be from a unique source.

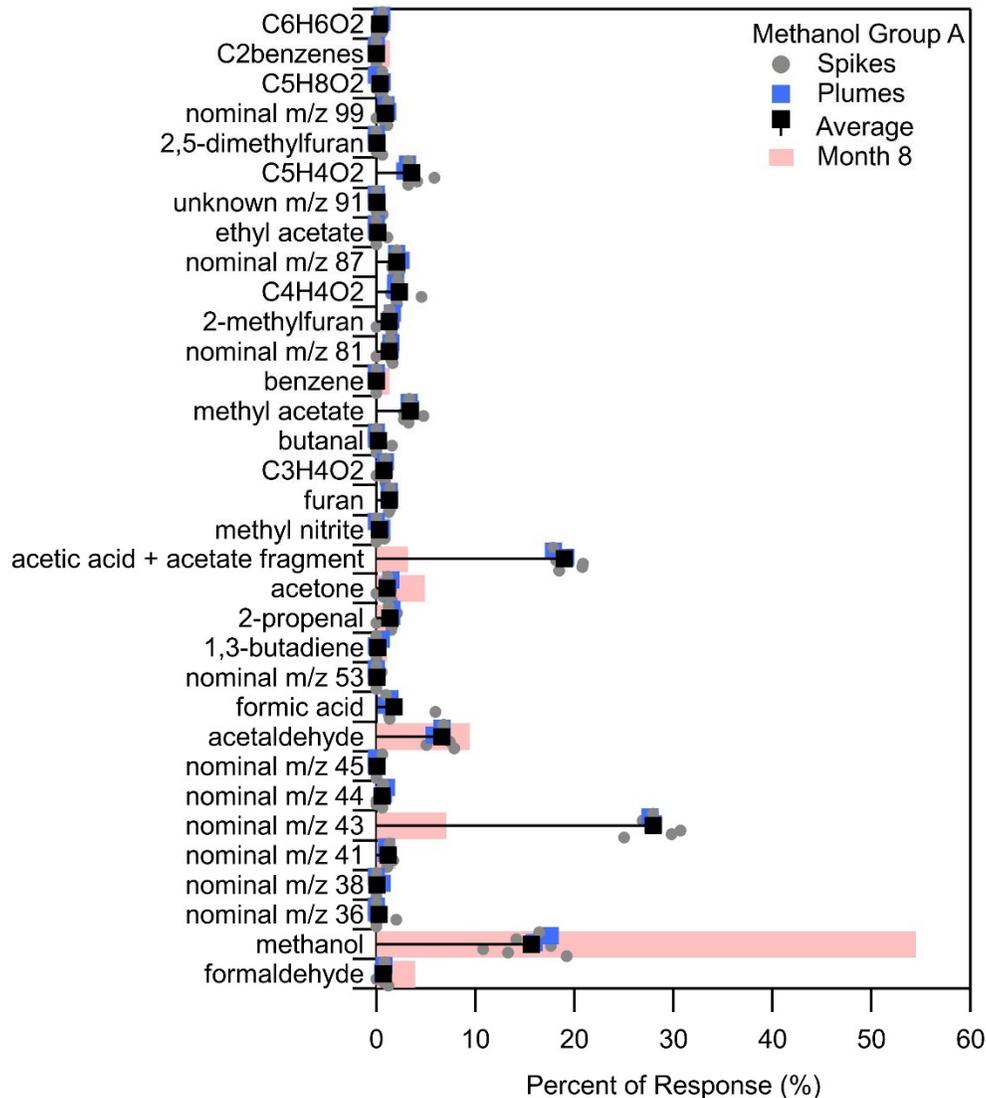


Figure 5-11. Fingerprints of Methanol Group A Plumes Observed on May 14, 2019, Along with the Average Methanol Plume Detailed in 53005-81-RPT-066.

The wind direction between 09:52 and 09:57 on May 14, 2019, was predominately from the west. Figure 5-12 shows the wind direction around the beginning and the end of the MA plume observations. The wind speed varied from 1 to 5 m/s with gusts exceeding 5 m/s. The ML was located near the southwest corner of 241-AP Farm and in the west direction is primarily mobile offices and Canton Avenue. Further investigation is required to determine if the mobile offices or traffic along the road could be the source of these plumes.

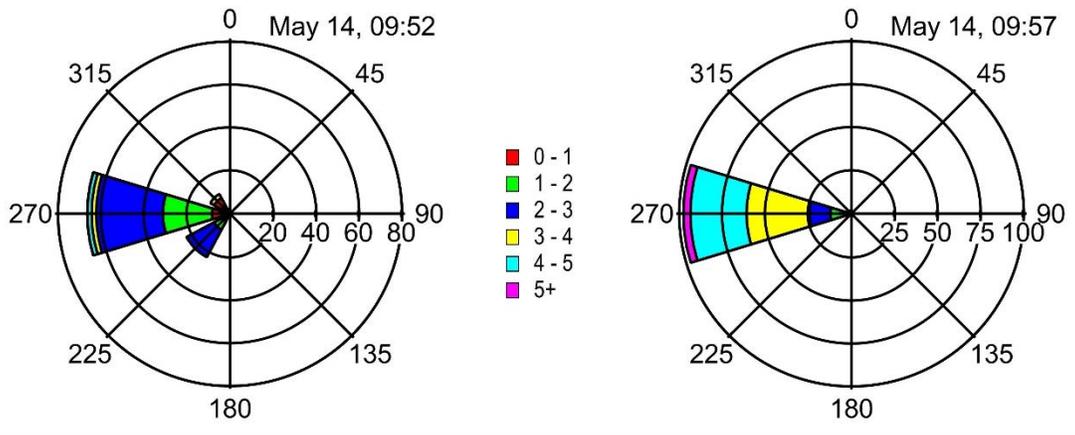


Figure 5-12. Wind Speed and Direction During Observations of Methanol Group A Plumes on May 14, 2019, from 09:52 to 09:57.

5.2.3.2 Methanol Group B

The location of the ML varied with observations of the plume on May 15, 2019, at 11:56; spikes on May 29, 2019, at 11:17; and spikes on May 30, 2019, at 06:44 and 11:17. Figure 5-10 shows these observations occurred around 241-A, AX, AY, and AZ except for the May 30, 2019, 06:44 plume south of 241-AP and the Central Shift Office (CSO). Figure 5-13 shows the fingerprints of each plume and the average along with the combination exhaust and methanol plume signature presented in Section 5.2.1.1, Figure 5-2. The plume fingerprints follow the same pattern and the likely source is vehicle exhaust. The exhaust scanner potentially missed identifying these plumes due to higher threshold values compared to the ones used for this odor scan. For example, nominal m/z 43 and formaldehyde did not respond above the threshold of the exhaust scan for the plume on May 15, 2019, at 11:56. Future iterations of the exhaust scanner could include reducing the thresholds to identify potential exhaust plumes at lower levels.

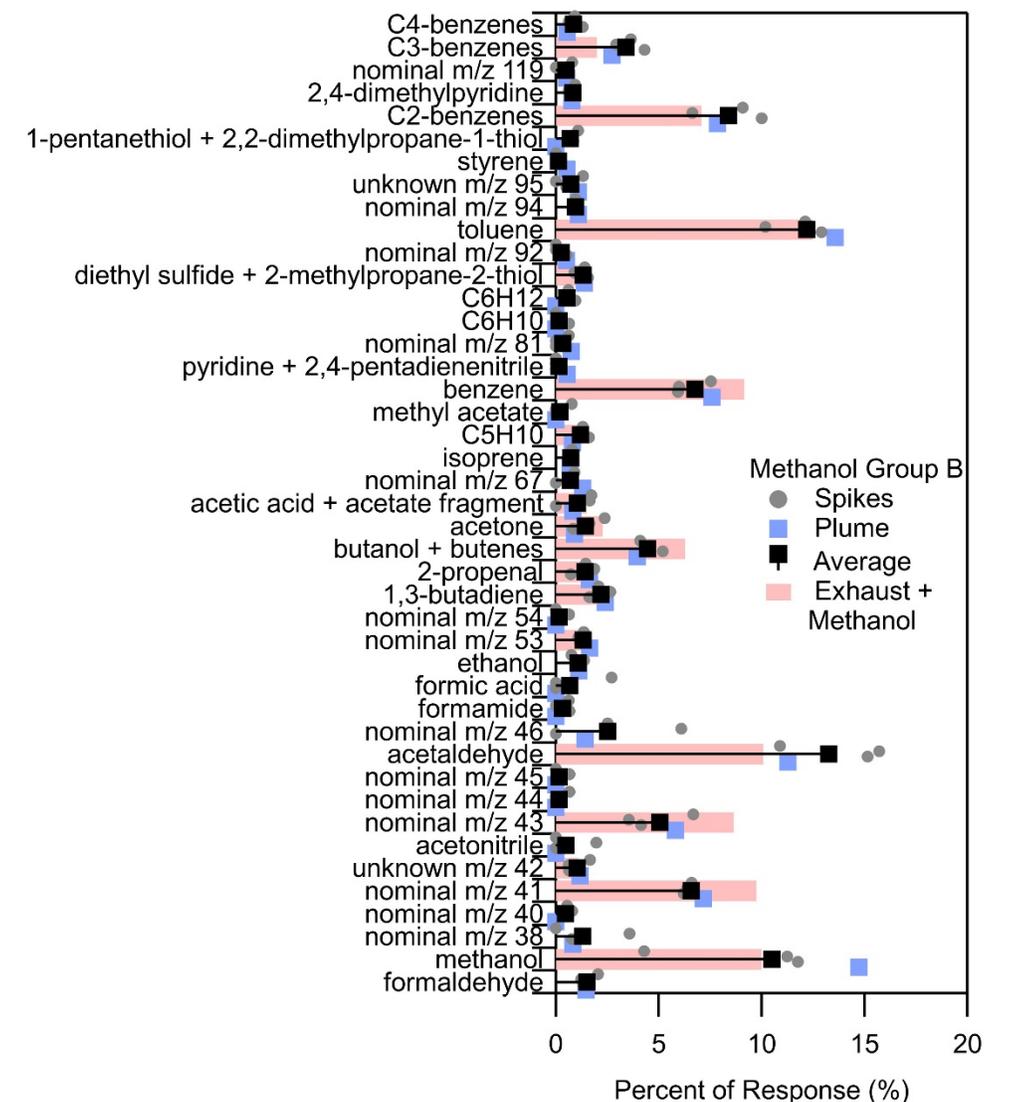


Figure 5-13. Fingerprints of Methanol Group B Plumes Observed on May 15, 2019; May 29, 2019; and May 30, 2019, Along with the Exhaust + Methanol Fingerprint Described in Section 5.2.1.1, Figure 5-2.

5.2.3.3 Methanol Group C

The third methanol groups had the highest methanol contribution within the fingerprint. Figure 5-14 shows the fingerprints for the two plumes and spike on May 28, 2019, occurring at 06:22, the two spikes at 06:33, and spike at 07:03 on May 30, 2019. These plumes were observed at different locations. The May 28, 2019, plumes occurred while the ML was in transit from the Wye Barricade to 200E. The May 30, 2019, plumes at 06:33 occurred while the ML was parked south of the CSO. The May 30, 2019, plume at 07:03 occurred near TX/TY Farms. The average methanol response was 41% and ranged from 30% to 53%. This is similar to what was observed in Month 8 which saw a slightly higher methanol response averaging 54%. In addition, both MC and Month 8 showed response at nominal m/z 43, acetaldehyde, acetone, and acetic acid + acetate fragment. Looking back at 53005-81-RPT-019, *PTR-MS Mobile*

Laboratory Vapor Monitoring Monthly Report – Month 1, there was a plume observed that was attributed to the windshield wiper fluid of the ML. This was characterized by a strong methanol response contributing 78% and is shown in Figure 5-14 as the windshield fingerprint. While the MC and Month 8 fingerprints have a lower methanol response, the consistency of seeing multiple plumes at variable locations supports that the source is either very common around the site or is relocated frequently. The fact that some of these were observed while the ML was in transit is the strongest evidence to support source identification as ML windshield wiper fluid. The ML was not near typical site sources and the fast speeds would make it difficult to observe a transient plume since the ML would pass through it quickly.

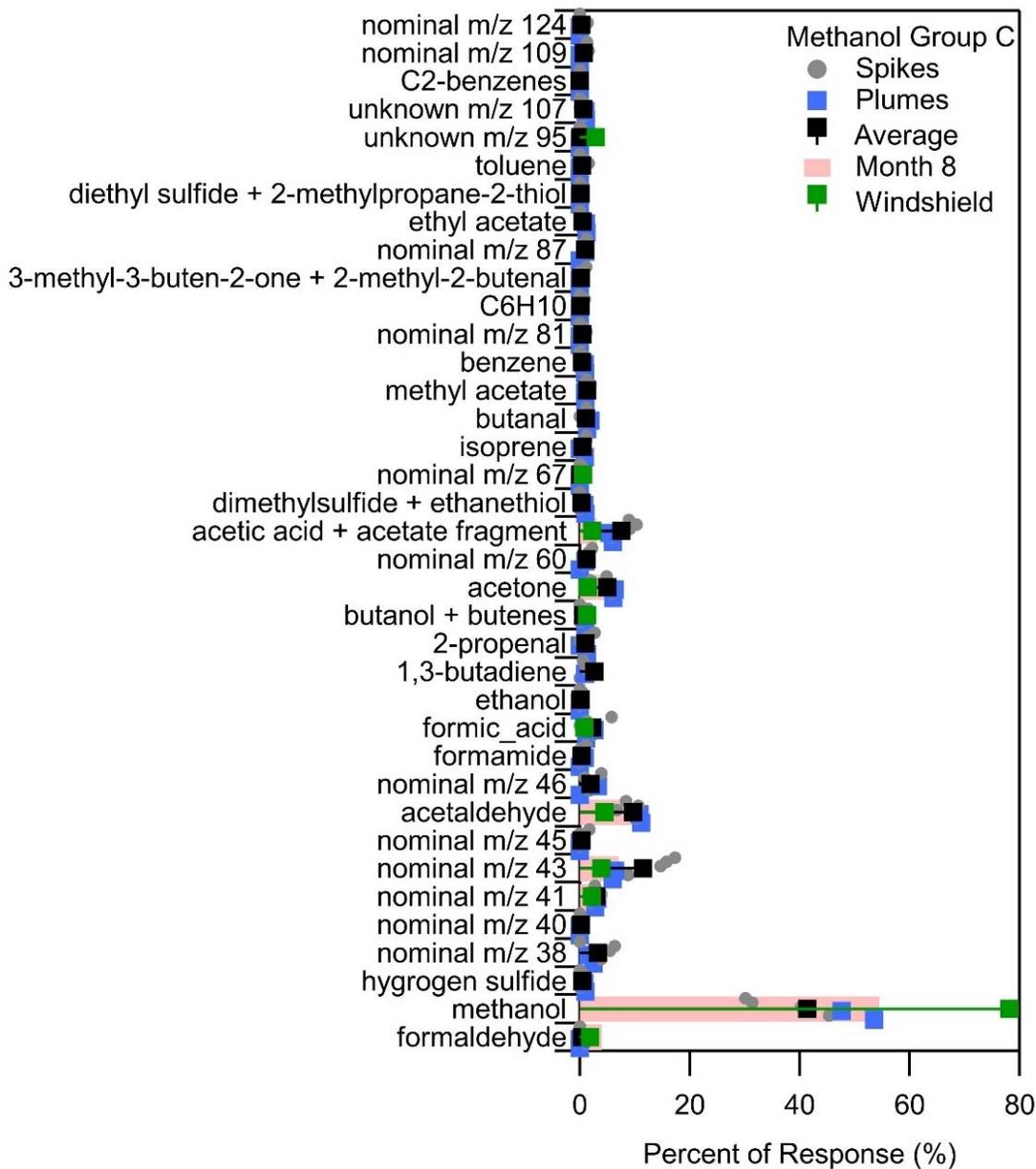


Figure 5-14. Fingerprints of Methanol Group C Plumes Observed on May 28, 2019, and May 30, 2019, Along with the Average Methanol Plume Detailed in the 53005-81-RPT-066.

5.2.3.4 Methanol Comparison

Figure 5-15 shows the average fingerprints of MA, MB, and MC along with the fingerprints from Month 8 and a plume on May 21, 2019, at 09:45. The May 21, 2019, plume is similar to the MB in that it appears to be an exhaust + methanol plume with exhaust having a larger contribution than methanol. There was a lack of response in the aromatics which is the main reason it was not included in the MB fingerprint. It is unknown if this is from a similar or same source as the MB. It was already detailed that MC and Month 8 were likely ML windshield wiper influenced and MB appears to be a mixture of exhaust with a methanol source or influence. The MA was unique and the source is unknown but the fingerprint has enough defining characteristics that may lend to future scanning and identification of plumes from the same or similar source.

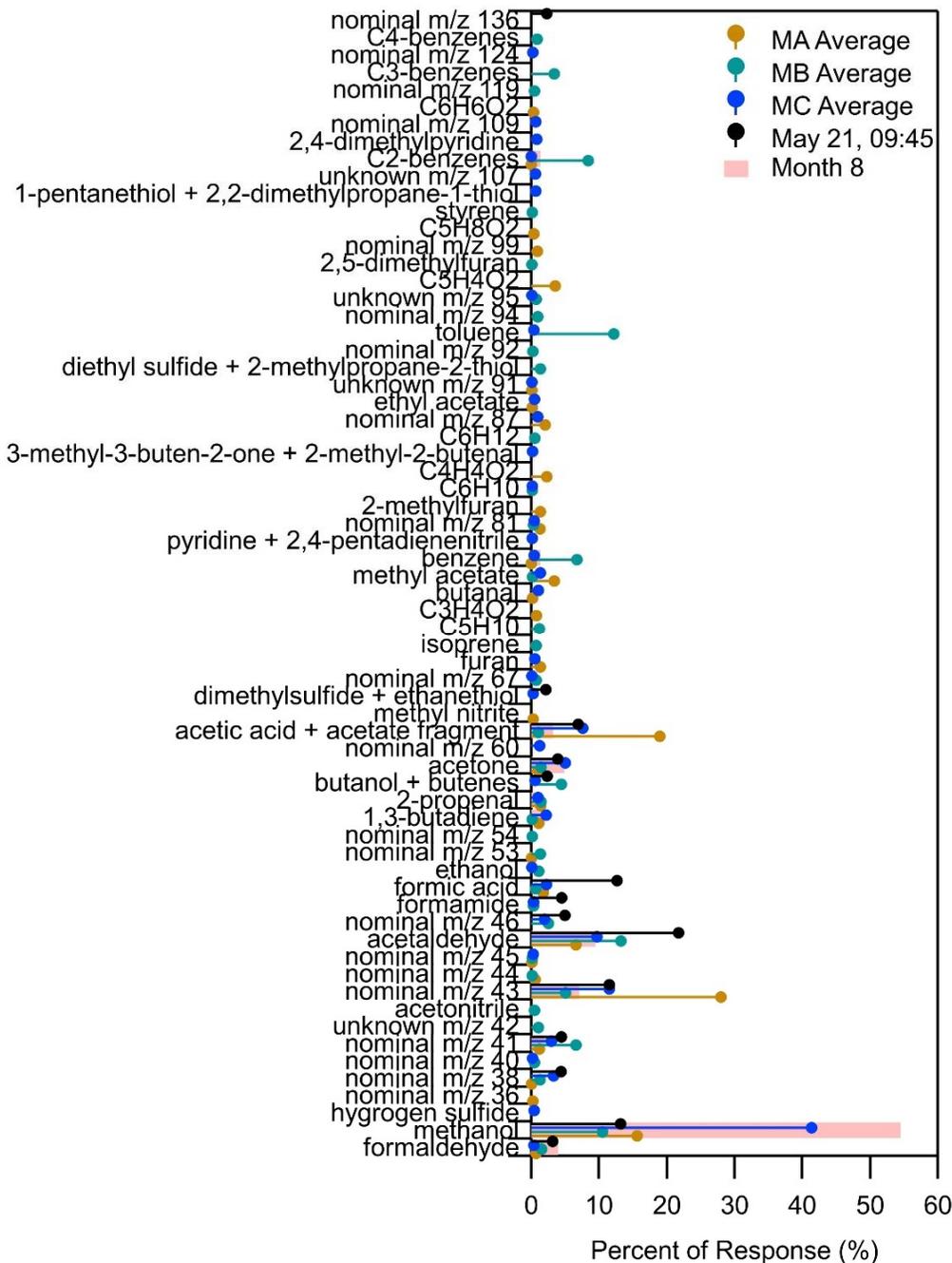


Figure 5-15. Comparison of Methanol Groups A, B, and C Fingerprints Along with the Methanol Fingerprint from 53005-81-RPT-066 and a Unique Methanol Plume Observed on May 21, 2019, at 09:45.

5.2.4 Unique Plumes

There were four plumes that did not follow the patterns of the methanol or exhaust plumes. On May 2, 2019, at 11:38, there was a short spike dominated by nominal m/z 45. There was a spike and plume of toluene at 06:31 and 06:32, respectively, on May 6, 2019. A spike with a strong

nominal m/z 43 signal occurred on May 22, 2019, at 06:36. The fingerprints of these four plumes are shown in Figure 5-16 along with the toluene plume fingerprint presented in 53005-81-RPT-066. There were five toluene plumes observed in Month 8 identifying the location of the sources as TY/TX Farms and 241-A. The May 6, 2019, spike and plume fingerprints are dominated by toluene and follow similar patterns to Month 8. The May 2, 2019, and May 22, 2019, plumes contained negligible amounts toluene and their fingerprints are shifted more towards the smaller mass range.

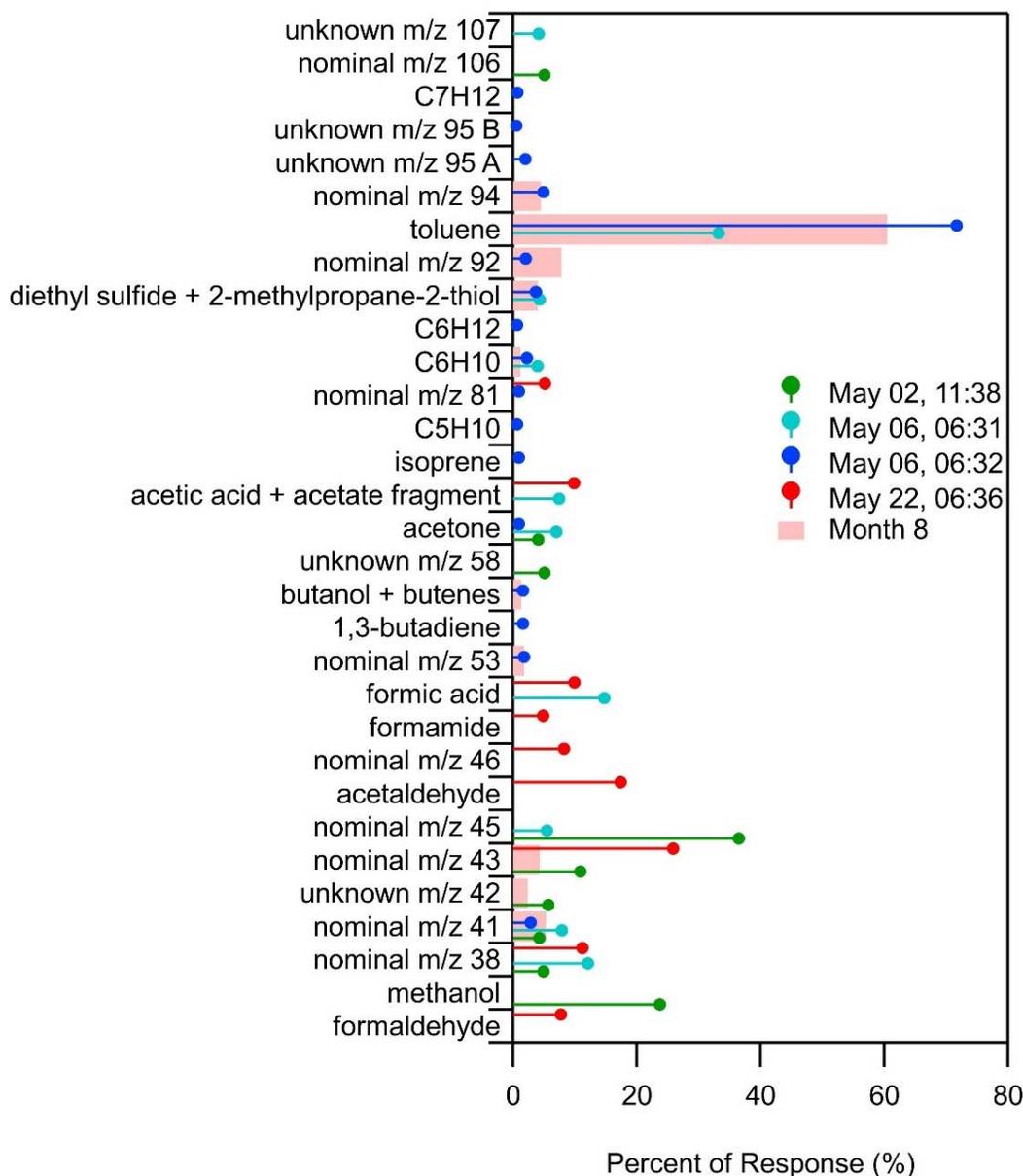


Figure 5-16. Fingerprints of Unique Plumes Observed on May 2, 2019; May 6, 2019; and May 22, 2019, Along with the Average Fingerprint of the Unique Toluene Presented in 53005-81-RPT-066.

Figure 5-17 shows the location of the ML while observing the four plumes. There was a short time difference between the two May 6, 2019, observations at 06:31 and 06:32 which means the ML was mobile during these observations. Figure 5-18 shows the wind speed and direction around the time of observation of both the May 6, 2019, toluene plumes and Figure 5-19 shows the wind speed and direction for the May 2, 2019, and May 22, 2019, plumes. On May 6, 2019, the wind direction was primarily from the northwest with speeds ranging from 1 to 5 m/s. May 2, 2019, showed similar wind direction predominantly from the northwest with slightly lower wind speeds ranging from 1 to 4 m/s. May 22, 2019, had mostly wind from the southeast with some variation to the south at speeds from 1 to 3 m/s. The strong toluene plume on May 6, 2019, was first observed near the southwest corner of 241-AP but the wind direction suggests the source is from the direction of 241-AW. The ML then observed a similar plume with an even stronger toluene response about a minute later near the northeast corner of 241-AW. The wind direction did not change so this observation further upwind suggests the source is in the direction of 241-A. Both the 06:31 and 06:32 plumes seem to be from a similar source and the weaker toluene response observed further downwind would support this explanation. Since these strong toluene plumes have been observed during consecutive months of observations. Future plume identification will continue to look for and analyze their composition and identify potential source locations.

The May 2, 2019, plume is primarily nominal m/z 45 and methanol. Acetaldehyde responds around m/z 45, but nominal m/z 45 is separate from the acetaldehyde response. It is unclear what the source of this plume is, but the wind direction and location suggest it is from the direction of 241-AX and 241-AZ. On May 22, 2019, it appears as if ML exhaust is the likely source of the plume. While checking in with the CSO upon arrival to 200E to begin a shift, the ML is parked facing north. A wind direction from the southeast would be the direction of the truck and generator exhaust. Presence of nominal m/z 46, which is attributed to NO₂, along with formaldehyde, nominal m/z 43, and acetaldehyde is typical of diesel combustion vehicle exhaust. There is a lack of aromatic presence which is typically a significant component. To better understand the ML exhaust, laboratory tests could be performed to establish fingerprints for the ML truck and generator exhaust.

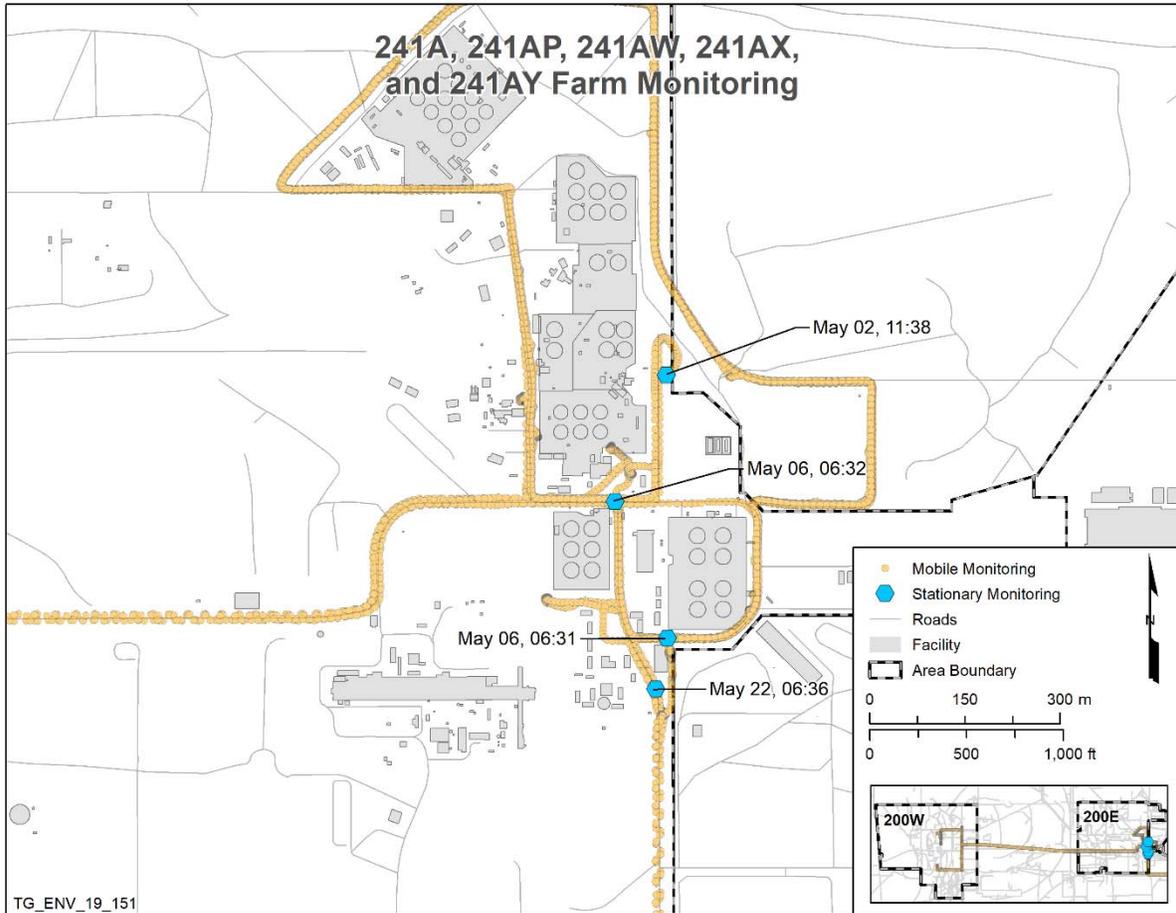


Figure 5-17. Location of the Mobile Laboratory when Observing the Unique Plumes in the 200 East Area During May 2019.

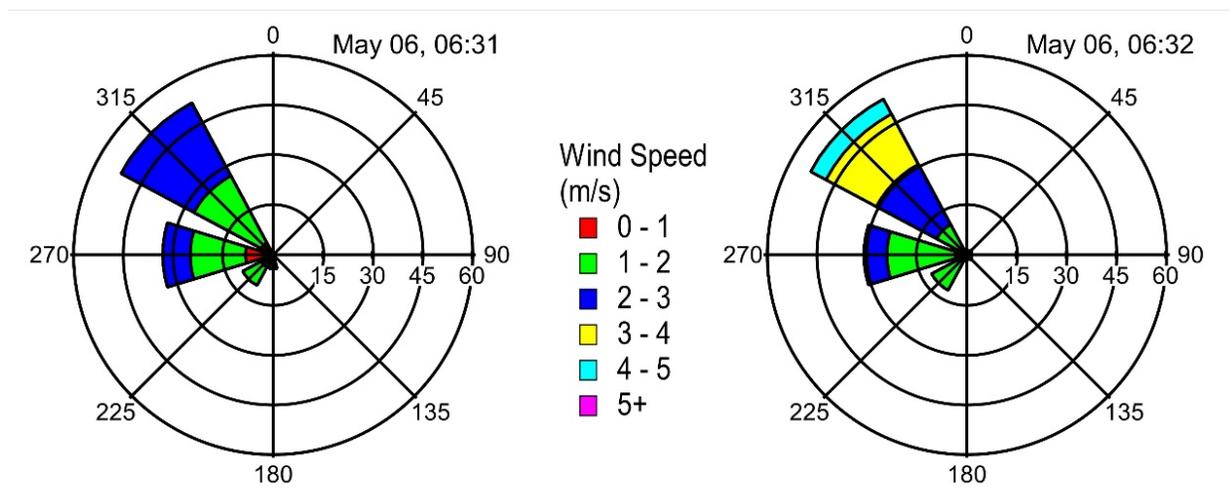


Figure 5-18. Wind Speed and Direction During Observations of the Unique Toluene Plumes on May 6, 2019, at 06:31 and 06:32.

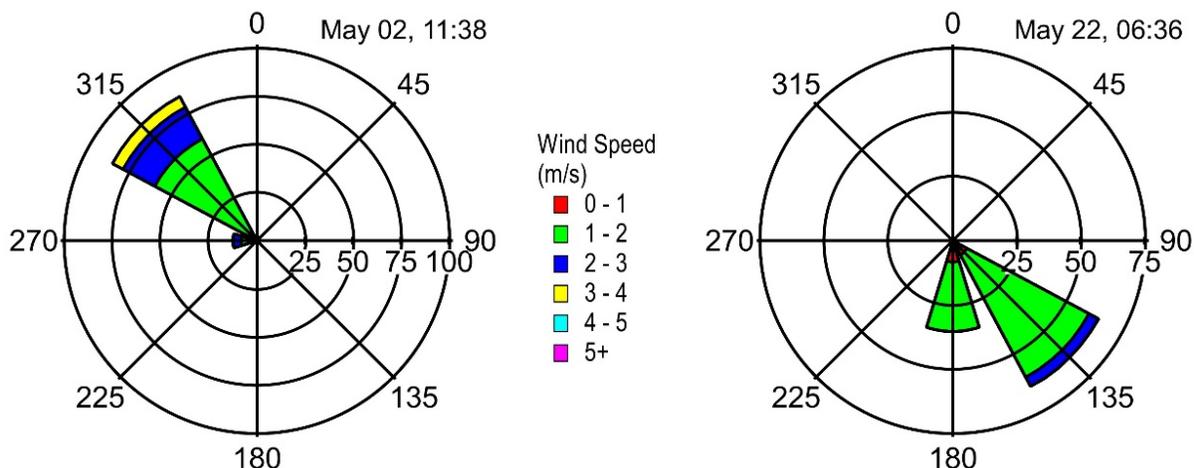


Figure 5-19. Wind Speed and Direction During Observations of Unique Plumes on May 2, 2019, at 11:38 and May 22, 2019, at 06:36.

5.2.5 Exhaust Plumes

Figure 5-20 shows the fingerprints of the 14 exhaust signatures consisting of eight plumes and six spikes along with the gasoline vehicle, diesel vehicle, and diesel generator fingerprints previously in Section 5.2.1.3, Figure 5-6. The plumes occurred on May 6, 2019, at 13:47; May 7, 2019, at 10:55; May 8, 2019, at 06:02; May 9, 2019, at 12:19 and 13:32; May 16, 2019, at 7:58; and May 30, 2019, at 11:17 and 11:18. The spikes occurred on May 16, 2019, at 09:54; May 20, 2019, at 07:50, 08:07, and 09:42; and two on May 30, 2019, at 11:43. These plumes were not identified during the exhaust scan. As was the case with MB, the threshold values were higher for the exhaust scan which can cause some exhaust plumes to lack the strength to surpass the threshold of all six required species. Future implementation of the exhaust scan could be refined to lower these threshold values. All the fingerprints shown follow a similar pattern with the differences explained by the differences between gasoline vehicles, diesel vehicles, and diesel generators. Most of them appear to have a strong toluene signal which is more in line with gasoline vehicle emissions. There is the presence of higher nominal m/z 46 (attributed to NO_2) and signifies that a few diesel generators were sampled. There seems to be less influence from diesel vehicles with only one plume having an acetaldehyde abundance high enough. Exhaust is the most commonly observed source onsite due to the quantity and variable locations of vehicles and generators. The odor scan often finds exhaust plumes that the exhaust scan missed due to the stricter criteria of the exhaust scan. Future implementations of this analysis could be aided by lowering the exhaust scan threshold values to identify additional potential exhaust plumes.

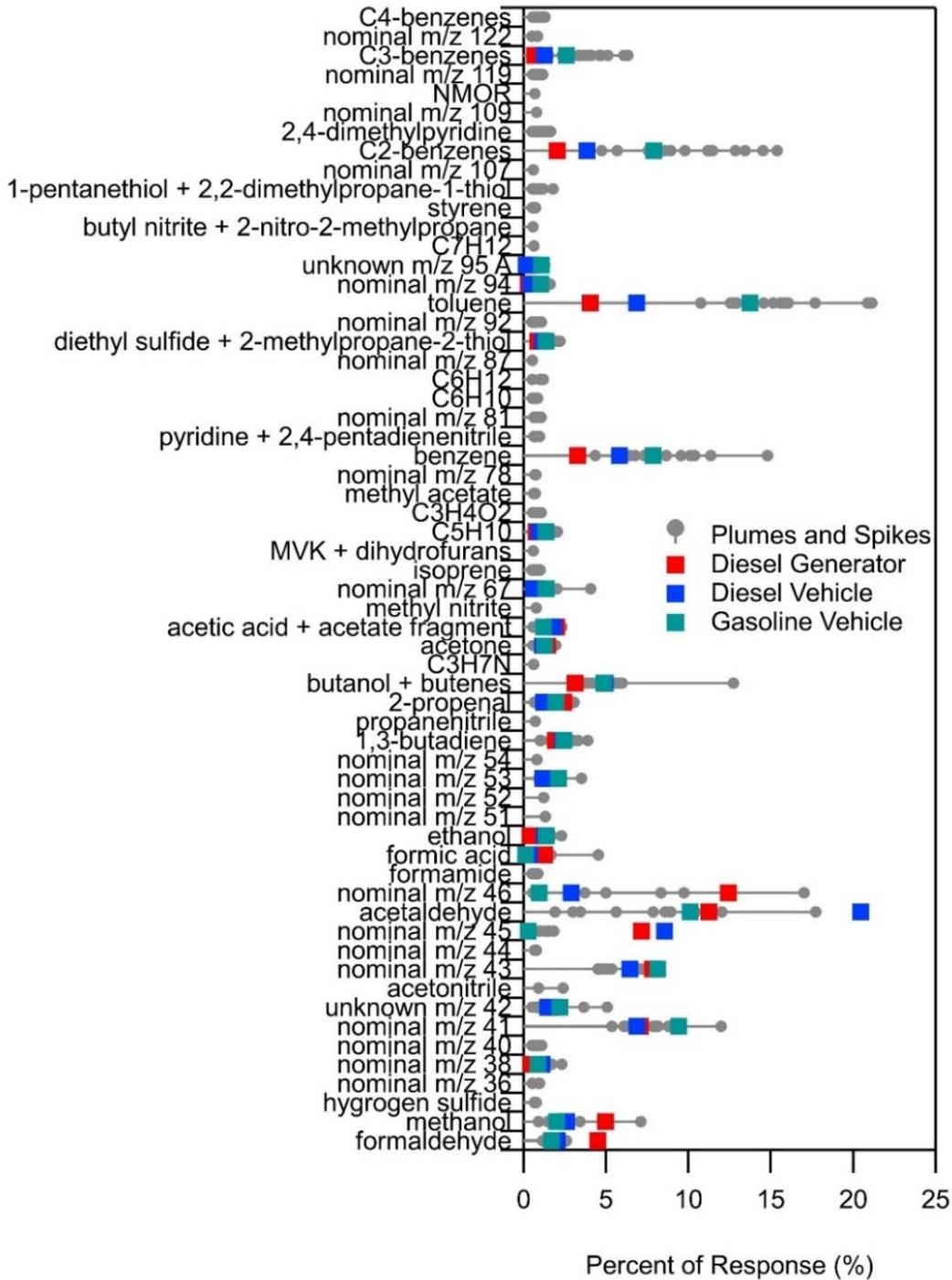


Figure 5-20. Fingerprints of Exhaust Plumes Observed on May 6, 2019 through May 9, 2019; May 16, 2019; May 20, 2019; and May 30, 2019, Along with Fingerprints Representing Gasoline Vehicle, Diesel Vehicle, and Diesel Generator Emissions.

5.2.6 Chemical of Potential Concern Statistics

The same statistics as the weekly reports were performed for the entire May 2019 area monitoring dataset to quantify the average, standard deviation, relative standard deviation, maximum, and median for each COPC. No averages or medians exceeded OELs. Table 5-2 shows the resulting statistics along with flags in the average column to signify if the average was below the MDL or within a certain value range. The average and median of all but seven COPCs was below the detection limit. Ammonia, methanol, acetonitrile, acetaldehyde, methyl nitrite, but-3-en-2-one + 2,3-dihydrofuran + 2,5-dihydrofuran, and butanal had averages and medians between their respective MDL and RL. Ammonia, methanol, and acetaldehyde are commonly observed in the atmosphere; therefore, so it is not surprising that their averages and medians are above the detection limit. The detection limit of methyl nitrite is 0.098 ppbv and the average was just barely above at 0.099 ppbv. Methyl nitrite has commonly been in exhaust so it is possible that observations of high concentration exhaust plumes have skewed the monthly average slightly higher. A similar effect could be increasing the but-3-en-2-one + 2,3-dihydrofuran + 2,5-dihydrofuran signal to 0.056 ppbv which is above the 0.041 ppbv MDL. Acetonitrile and butanal have averages more than double the MDL and are potentially true detects. The OELs for acetonitrile and butanal are 20,000 ppbv and 25,000 ppbv, respectively; therefore, this slight detect is multiple orders of magnitude lower than any level of concern.

Table 5-4. Chemicals of Potential Concern Statistical Information for the Monitoring Period of May 2019. (2 Sheets)

COPC #	COPC Name	OEL (ppb)	MDL (ppb)	Ave. (ppb)	St. Dev. (ppb)	Rel St. Dev. (%)	Max. (ppb)	Median (ppb)
1	ammonia	25000	6.225	10.106†	4.486	44.4	42.7	11.127†
2	formaldehyde	300	1.721	<1.721	0.252	40.9	12.2	<1.721
3	methanol	200000	5.758	7.693†	2.742	35.6	165	8.137†
4	acetonitrile	20000	0.085	0.172†	0.049	28.7	0.832	0.192†
5	acetaldehyde	25000	1.027	1.705†	0.976	57.2	180	1.801†
6	ethylamine	5000	0.069	<0.069	0.020	78.2	0.233	<0.069
7	1,3-butadiene	1000	0.183	<0.183	0.091	63.2	3.98	<0.183
8	propanenitrile	6000	0.107	<0.107	0.023	51.6	1.53	<0.107
9	2-propenal	100	0.340	<0.34	0.094	67.2	2.28	<0.34
10	1-butanol + butenes	20000	0.214	<0.214	0.111	107.3	15.3	<0.214
11	methyl isocyanate	20	0.069	<0.069	0.025	55.8	0.272	<0.069
12	methyl nitrite	100	0.098	0.099†	0.044	44.6	1.20	0.11†
13	furan	1	0.062	<0.062	0.026	83.9	1.63	<0.062
14	butanenitrile	8000	0.039	<0.039	0.014	76.0	0.496	<0.039
15	but-3-en-2-one + 2,3-dihydrofuran + 2,5-dihydrofuran	200, 1, 1	0.041	0.056†	0.040	70.3	0.628	0.061†
16	butanal	25000	0.061	0.145†	0.070	48.1	0.741	0.159†
17	NDMA**	0.3	0.082	<0.082	0.023	186.0	0.422	<0.082
18	benzene	500	0.236	<0.236	0.118	102.4	8.37	<0.236
19	2,4-pentadienenitrile + pyridine	300, 1000	0.085	<0.085	0.018	54.1	0.794	<0.085
20	2-methylene butanenitrile	300	0.036	<0.036	0.010	79.4	0.353	<0.036
21	2-methylfuran	1	0.043	<0.043	0.032	82.6	1.81	<0.043
22	pentanenitrile	6000	0.036	<0.036	0.011	84.3	0.192	<0.036
23	3-methyl-3-buten-2-one + 2-methyl-2-butenal	20, 30	0.043	<0.043	0.028	74.9	0.427	<0.043
24	NEMA**	0.3	0.058	<0.058	0.018	161.4	0.209	<0.058
25	2,5-dimethylfuran	1	0.032	<0.032	0.018	83.1	0.374	<0.032
26	hexanenitrile	6000	0.031	<0.031	0.008	100.3	0.112	<0.031
27	2-hexanone (MBK)	5000	0.036	<0.036	0.013	93.2	0.143	<0.036
28	NDEA**	0.1	0.034	<0.034	0.010	153.7	0.106	<0.034
29	butyl nitrite + 2-nitro-2-methylpropane	100, 300	0.058	<0.058	0.013	52.1	0.161	<0.058

Table 5-4. Chemicals of Potential Concern Statistical Information for the Monitoring Period of May 2019. (2 Sheets)

COPC #	COPC Name	OEL (ppb)	MDL (ppb)	Ave. (ppb)	St. Dev. (ppb)	Rel St. Dev. (%)	Max. (ppb)	Median (ppb)
30	2,4-dimethylpyridine	500	0.036	<0.036	0.015	152.3	1.51	<0.036
31	2-propylfuran + 2-ethyl-5-methylfuran	1	0.027	<0.027	0.011	99.5	0.190	<0.027
32	heptanenitrile	6000	0.027	<0.027	0.007	102.4	0.096	<0.027
33	4-methyl-2-hexanone	500	0.033	<0.033	0.010	98.4	0.098	<0.033
34	NMOR**	0.6	0.021	<0.021	0.008	188.1	0.319	<0.021
35	butyl nitrate	2500	0.022	<0.022	0.006	127.4	0.061	<0.022
36	2-ethyl-2-hexenal + 4-(1-methylpropyl)-2,3-dihydrofuran + 3-(1,1-dimethylethyl)-2,3-dihydrofuran	100, 1, 1	0.028	<0.028	0.009	97.0	0.080	<0.028
37	6-methyl-2-heptanone	8000	0.028	<0.028	0.009	93.9	0.081	<0.028
38	2-pentylfuran	1	0.026	<0.026	0.010	85.8	0.081	<0.026
39	biphenyl	200	0.022	<0.022	0.007	131.5	0.068	<0.022
40	2-heptylfuran	1	0.067	<0.067	0.013	47.2	0.122	<0.067
41	1,4-butanediol dinitrate	50	0.036	<0.036	0.008	94.8	0.088	<0.036
42	2-octylfuran	1	0.020	<0.02	0.007	211.7	0.083	<0.02
43	1,2,3-propanetriol 1,3-dinitrate	50	0.011	<0.011	0.004	388.6	0.066	<0.011
44	PCB	1000	0.034	<0.034	0.008	78.5	0.073	<0.034
45	6-(2-furanyl)-6-methyl-2-heptanone	1	0.025	<0.025	0.007	108.7	0.066	<0.025
46	furfural acetophenone	1	0.064	<0.064	0.012	48.1	0.110	<0.064
N/A*	The maximum peak value for but-3-en-2-one + 2,3 dihydrofuran + 2,5 dihydrofuran was 0.354 ppb and the median value was 0.062 ppb. The PTR-MS results for but-3-en-2-one + 2,3 dihydrofuran + 2,5 dihydrofuran are not compared to OEL concentrations because: 1) the result is suspect due to a known biogenic interferant (methacrolein) that is expected to be in concentrations that occasionally exceed the dihydrofuran OEL, and 2) this combination of COPCs have OEL concentrations that differ by a factor of 200, which provide widely variant bases for these numbers.							
**	Nitrosamine results are suspect due to isobaric interferants causing positive bias that have been encountered during the previous Spring 2018 background study [53005-81-RPT-007, PTR-MS Mobile Laboratory Vapor Monitoring Background Study, (3/18/2018 – 4/20/2018)], and Fiscal Year 2017 Mobile Laboratory Vapor Monitoring at the Hanford Site: Monitoring During Waste Disturbing Activities and Background Study, RJ Lee Group, Inc., 2017].							
<	COPC Averages below the MDL.							
†	COPC Averages between the RL and the MDL.							
	COPC Averages >100% of the OEL.							
	COPC Averages 50-100% of the OEL.							
	COPC Averages 10-50% of the OEL.							

There were four species that had a maximum value that briefly exceeded their OEL concentrations during the month of May 2019. These four excursions above OEL concentrations ranged from lasting approximately two to twenty seconds. OELs are defined by an 8-hour time weighted average, therefore these five species that had values that exceeded OEL concentrations temporarily did not exceed OSHA guidelines for acute exposures. Figures 5-21 through 5-24 show the timeseries for furan, N-Nitrosodimethylamine (NDMA), 2-methylfuran, and N-Nitrosodiethylamine (NDEA) when the maximum value exceeded the OEL concentration.

The furan exceedance shown in Figure 5-21 occurred on May 14, 2019, between 09:52 and 09:54. There were four small plumes that exceeded the OEL concentration within this time period. The maximum concentration was 1.63 ppbv and each exceedance was less than 0.64 ppbv above the OEL concentration and the longest consecutive period of exceedance was less than 20 seconds. These were the only exceedances of furan above the OEL concentration. In addition, these plumes were already detected by the odor scan in Section 5.2.2 and were designated as Methanol Group A. Figure 5-11 has the associated fingerprints.

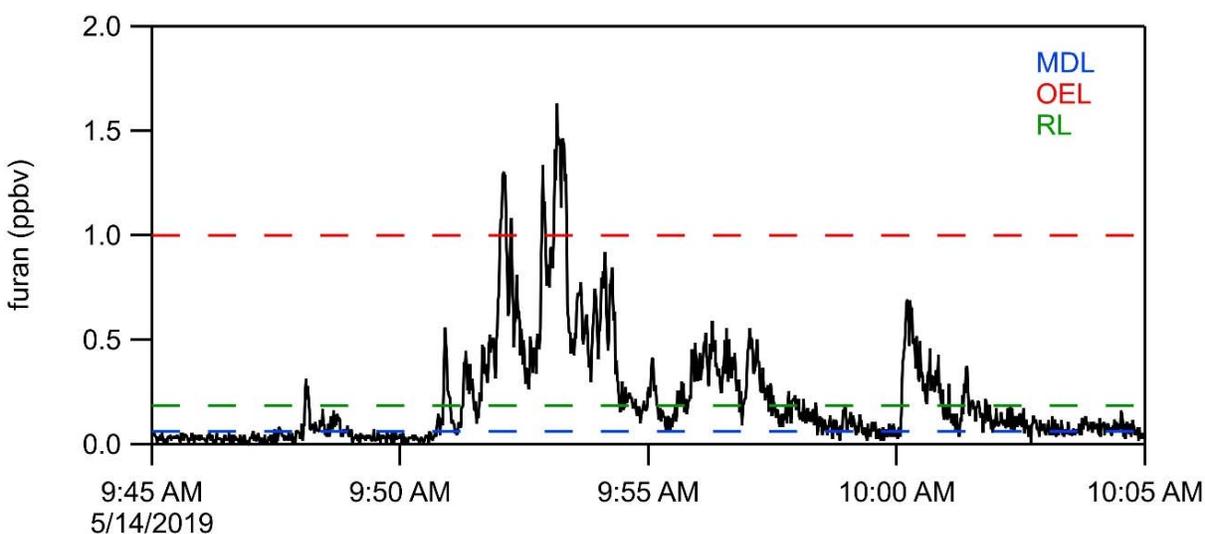


Figure 5-21. Time and Magnitude of the Maximum Value of Furan that Exceeded the Occupational Exposure Concentration on May 14, 2019.

The NDMA exceedance shown in Figure 5-22 occurred on May 6, 2019, between 06:54 and 07:10. There were multiple small plumes that exceeded the OEL concentration within this time period. The maximum concentration was 0.422 ppbv and each exceedance was less than 0.43 ppbv above the OEL concentration and the longest consecutive period of exceedance was less than 6 seconds. These were the only exceedances of NDMA above the OEL concentration. In addition, the odor scan in Section 5.2.2 identified some plumes around this time but the total concentration of the plume was too low to warrant further analysis.

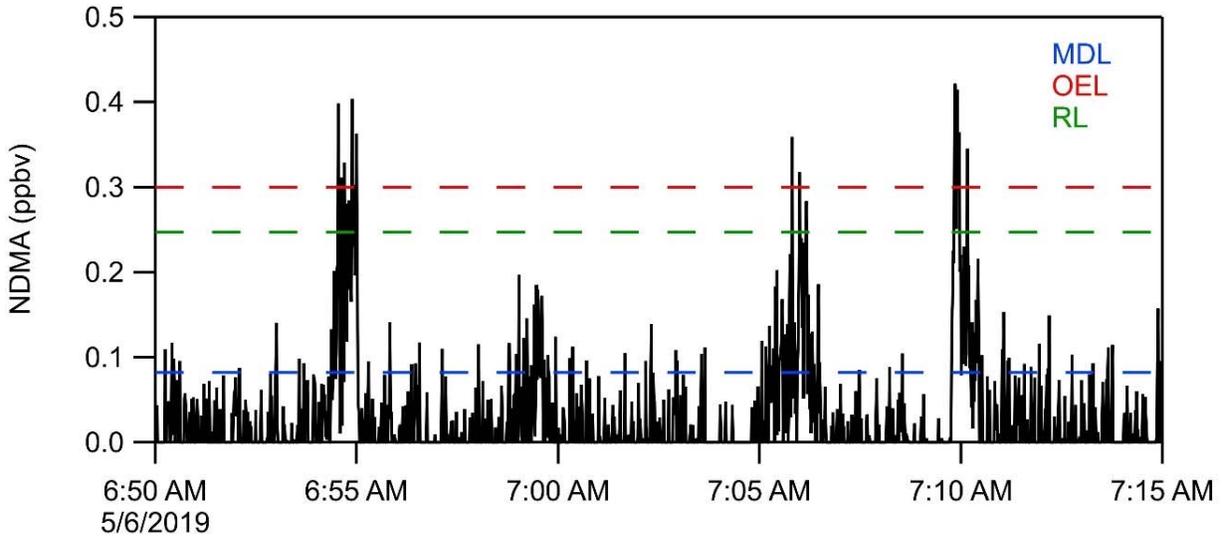


Figure 5-22. Time and Magnitude of the Maximum Value of NDMA that Exceeded the Occupational Exposure Concentration on May 6, 2019.

The 2-methylfuran exceedance shown in Figure 5-23 occurred on May 14, 2019, between 09:52 and 09:54. There were four small plumes that exceeded the OEL concentration within this time period. The maximum concentration was 1.81 ppbv and each exceedance was less than 0.82 ppbv above the OEL concentration and the longest consecutive period of exceedance was less than 20 seconds. These were the only exceedances of 2-methylfuran above the OEL concentration. This is also the same time window as the furan excursion and the plumes follow the same pattern which suggests both the 2-methylfuran and furan are from the same source. In addition, these plumes were already detected by the odor scan in Section 5.2.2 and were designated as Methanol Group A. Figure 5-11 has the associated fingerprints.

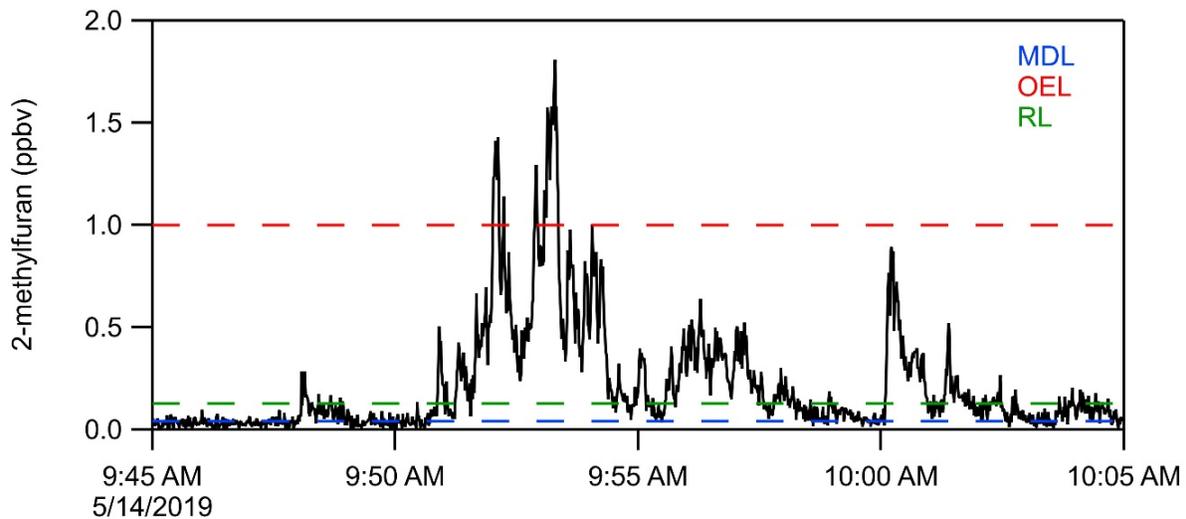


Figure 5-23. Time and Magnitude of the Maximum Value of 2-methylfuran that Exceeded the Occupational Exposure Concentration on May 14, 2019.

The NDEA exceedance shown in Figure 5-24 occurred on May 14, 2019, at 09:53 reaching 0.106 ppbv and exceeded the OEL concentration by 0.006 ppbv for no more than 2 seconds. This was the only exceedance of NDEA above the OEL concentration. This was in the same time window as the furan and 2-methylfuran exceedances which suggests it could be from the same source. In addition, plumes occurring around this time were already detected by the odor scan in Section 5.2.2 and were designated as Methanol Group A. Figure 5-11 has the associated fingerprints.

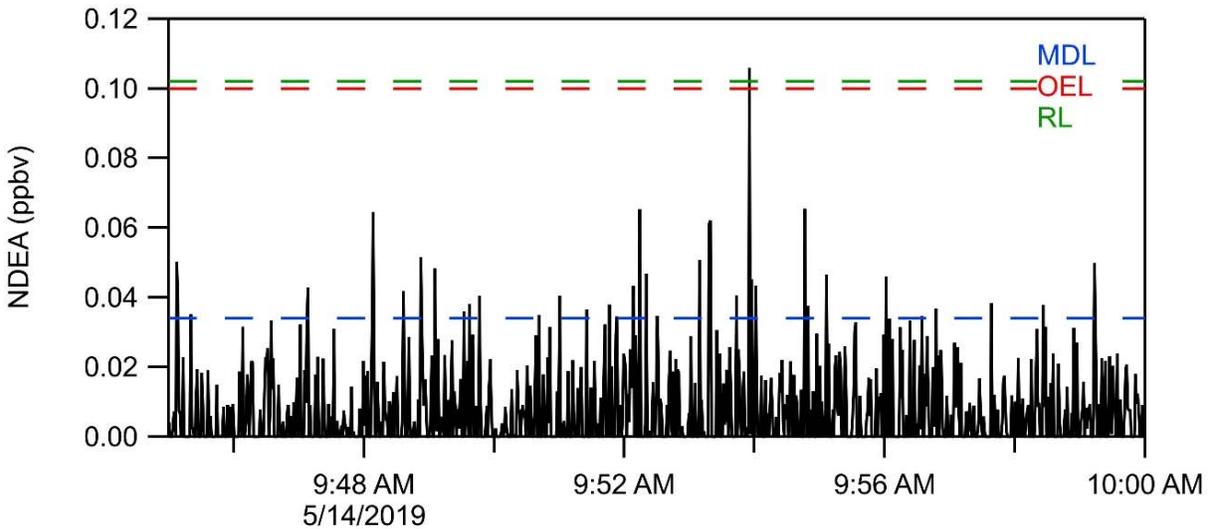


Figure 5-24. Time and Magnitude of the Maximum Value of NDEA that Exceeded the Occupational Exposure Limit on May 14, 2019.

5.3 Fugitive Emission

5.3.1 Location Investigation on May 21, 2019

From 11:13 until 12:38, on May 21, 2019, the ML supported the Fugitive Emissions group in the investigation of a location of interest shown in Figure 5-25. This was done by using the 35' inlet to sample from a designated spot and assist the Fugitive Emissions group with sampling sorbents. Two sorbents were collected in duplicate for 60 minutes from 11:33 until 12:33 using the ML sorbent sampling system with PTR-MS, LI-COR, and Picarro sampling from the same inlet during this time. For the course of these observations, no odors or increases in ammonia were detected.

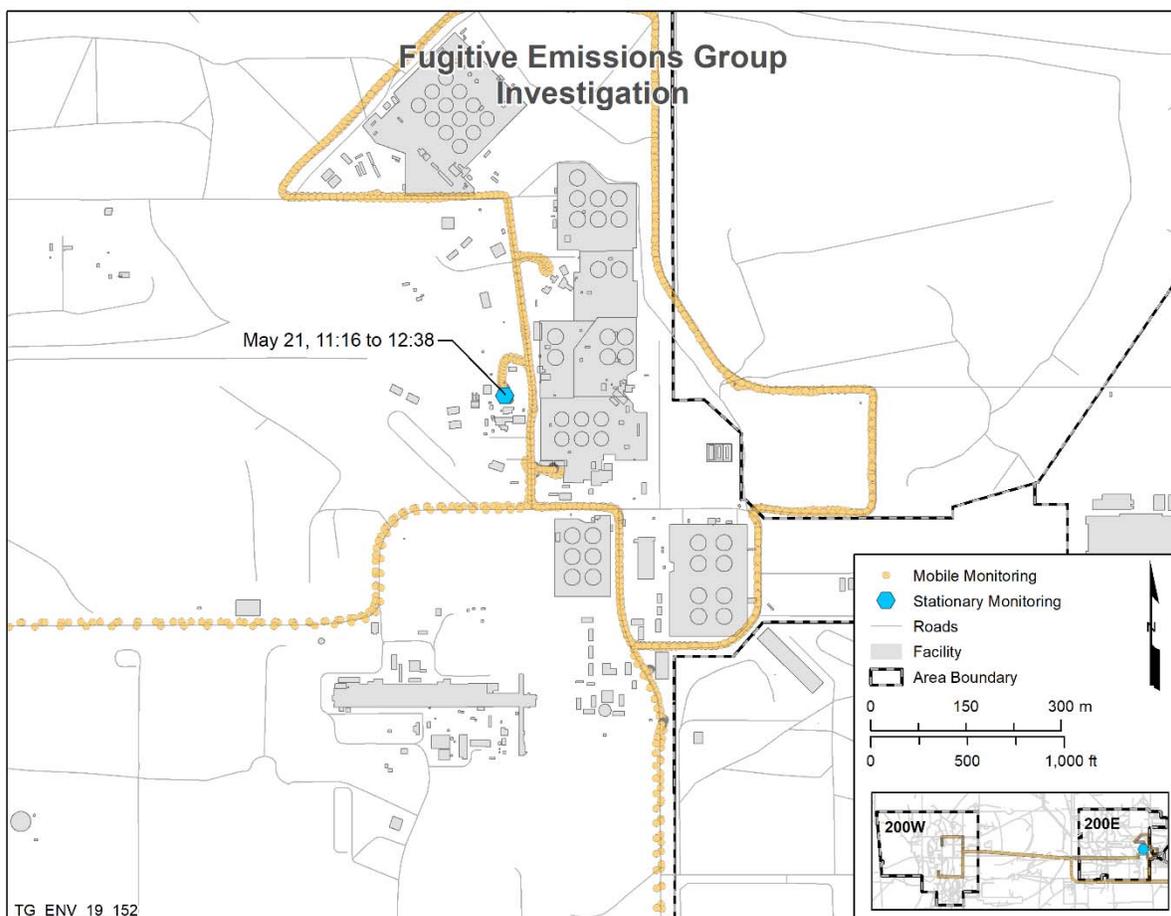


Figure 5-25. Location of the Mobile Laboratory During Location Investigation with the Fugitive Emission Group on May 21, 2019.

Figure 5-26 shows the concentrations of key species that showed a response during these observations. The ammonia stayed constant at around 13 ppbv other than the increase in the beginning which is a conditioning effect of switching to the 35' hose. There were numerous spikes in CO₂ suggesting heavy influence from a nearby combustion source or multiple sources. These are likely due to engine exhaust with the largest plume occurring at 12:10. There were two unique plumes with an increase in 2-ethyl-2-hexanal + substituted dihydrofurans [4-(1-methylpropyl)-2,3-dihydrofuran and 3-(1,1-dimethyl)-2,3-dihydrofuran] observed at 11:47 and a broader plume of acetonitrile occurring at 12:24. Fingerprint analysis was performed for the 2-ethyl-2-hexanal plume at 11:47, the benzene plume at 12:10, and the acetonitrile plume at 12:24.

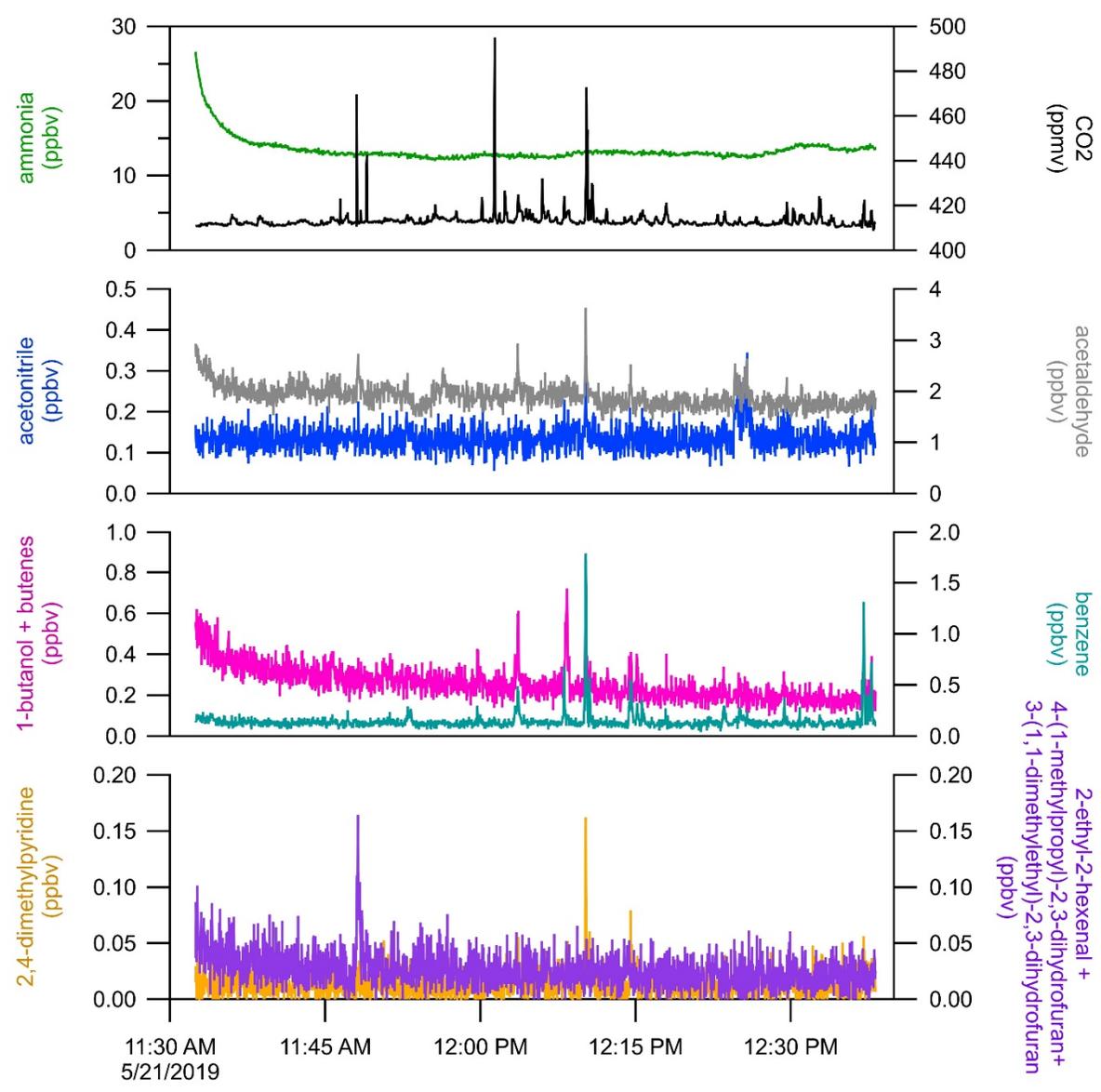


Figure 5-26. Concentrations of Ammonia, CO₂, Acetonitrile, Acetaldehyde, 1-butanol + Butenes, Benzene, 2,4-dimethylpyridine, and 2-ethyl-2-hexenal + 4-(1-methylpropyl)-2,3-dihydrofuran and 3-(1,1-dimethyl)-2,3-dihydrofuran During the Fugitive Emission Location Investigation on May 21, 2019.

Figure 5-27 shows the fingerprints of the plumes occurring at 11:47, 12:10, and 12:24. The 11:47 plume lasted for approximately 26 seconds with concentrations of 2-ethyl-2-hexenal + substituted dihydrofurans reaching 0.16 ppbv, which accounts for 5% of the fingerprint response. The fingerprint consists mostly of acetone, nominal m/z 43, and acetaldehyde which make up 75% of the response. The remaining 25% is acetic acid + acetate fragment, nominal m/z 109, and 2-ethyl-2-hexenal + substituted dihydrofurans. The responses of these six species adds up to 100%, which means these were the only species to have an average response above 0.05 ppbv. The 12:10 plume lasted about 20 seconds and the highest constituent was toluene which reached 2.5 ppbv. The fingerprint looks similar to that typically observed with exhaust from a

combustion engine with large response in aromatics (benzene, toluene, C₂-benzenes, C₃-benzenes) and acetaldehyde. This was the largest exhaust plume, but multiple of the same were observed during this time notably at 12:03, 12:08, and 12:14. The 2,4-dimethylpyridine spike seen in Figure 5-26 occurred at the same time as this plume, but the average concentration was below 0.05 ppbv and considered to have a negligible effect on the fingerprint.

The duration of the 12:22 plume was approximately 100 seconds with elevated levels of methanol, nominal m/z 41, acetonitrile, nominal m/z 43, acetaldehyde, and acetone. Acetaldehyde had the largest contribution at 36.5% with nominal m/z 41 and nominal m/z 43 each making up around 16.5%. The most interesting feature is the presence of acetonitrile, which accounted for 9.2% of the fingerprint. It is often a product of combustion of wood or other products but is not typically found within combustion engine exhaust. In instances of large wildfires, background levels of acetonitrile would increase, but would not create a plume as was observed. This suggests that there was a source in proximity to the ML. At 12:24, ML Operators noted that someone was smoking a cigar upwind of sampling. The observed fingerprint fits well with expected composition of this type of source and is attributed to tobacco combustion.

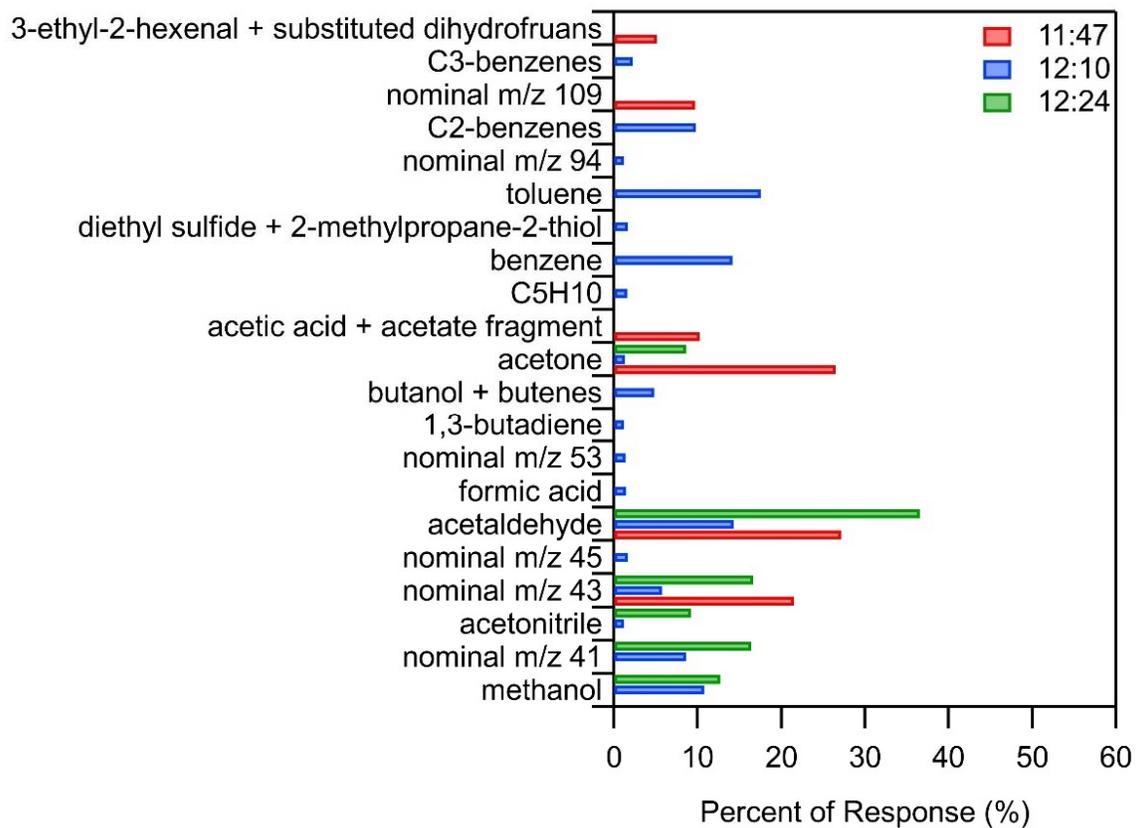


Figure 5-27. Fingerprints of Plumes Occurring at 11:47, 12:10, and 12:24 on May 21, 2019, During the Fugitive Emission Location Investigation.

5.3.2 Sewer Source Fingerprint on May 23, 2019

On May 23, 2019, the ML was deployed to support the Fugitive Emissions group with characterizing septic system emissions located as shown in Figure 5-28. The ML sampled through the 35' inlet through the side port which was connected to an additional sampling system located inside the septic system. Figure 5-29 shows pictures of the setup. This activity is part of an ongoing effort to characterize potential sources of odors and other fugitive emissions around site. Sampling was conducted from 08:28 and continued until 10:24. The PTR-MS sampled continuously from the sewer during this time along with two sets of sorbent tube collections. The sorbent tubes were sampled in duplicate from 09:06 until 09:21 for the first set and from 09:25 until 10:24 for the second set. Sorbent results have not been received at the time of writing this report; therefore, no comparison can be made at this time.

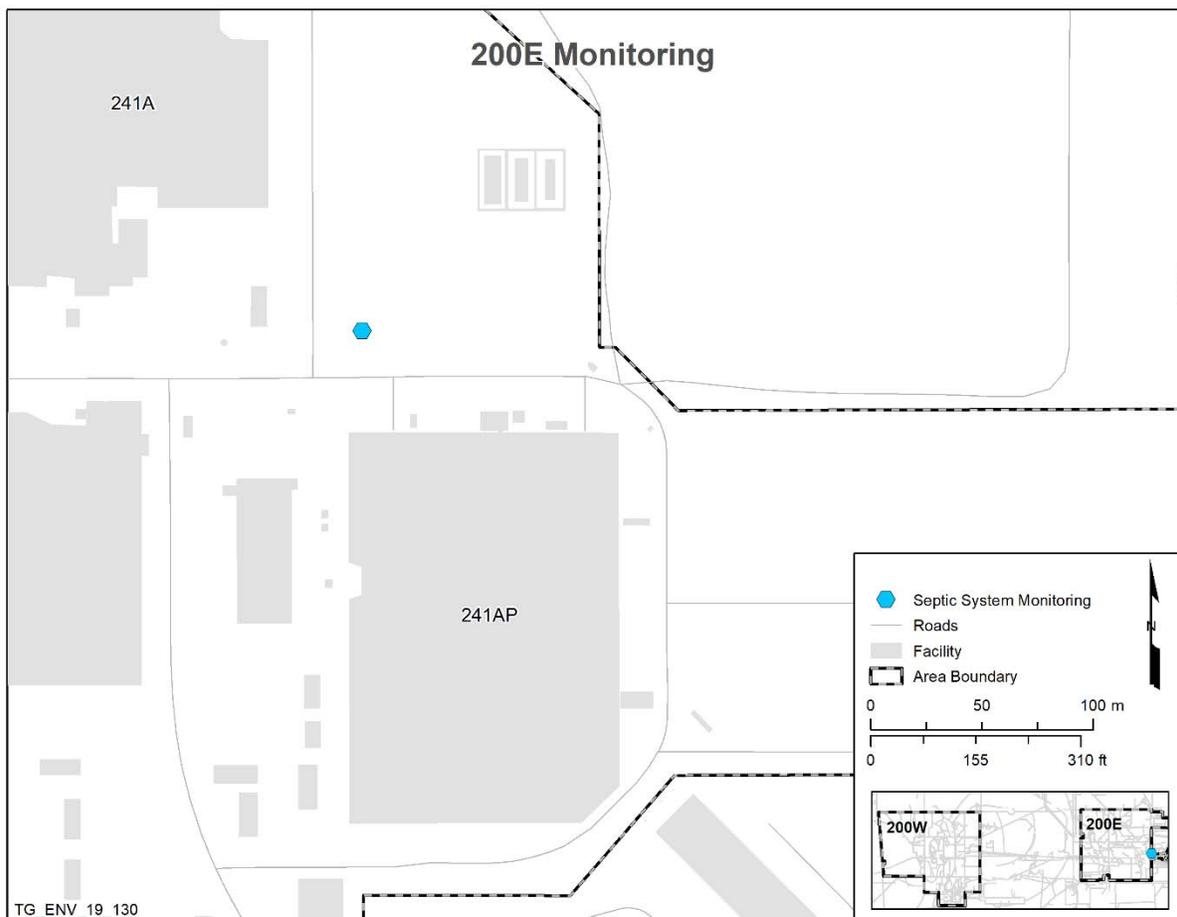


Figure 5-28. Map of Location (Lat. = 46.5522555320531, Long. = -119.515415230273).



Figure 5-29. Picture of Setup for May 23, 2019, Sewer Source Fingerprint.

Figure 5-30 shows the concentrations of key species monitored by the PTR-MS, Picarro, and LI-COR instruments. Carbon dioxide reached levels above 700 ppmv in the beginning. Ammonia seemed to slowly build up over the course of sampling and was steadily above 3500 ppbv in the latter half of sampling. The highest concentrations of sulfur compounds were observed with methyl mercaptan reaching up to 350 ppbv and dimethylsulfide + ethanethiol reaching up to 30 ppbv. There was also a strong presence of methanol which reached a maximum of 29 ppbv and remained above 7 ppbv for the duration of sampling.

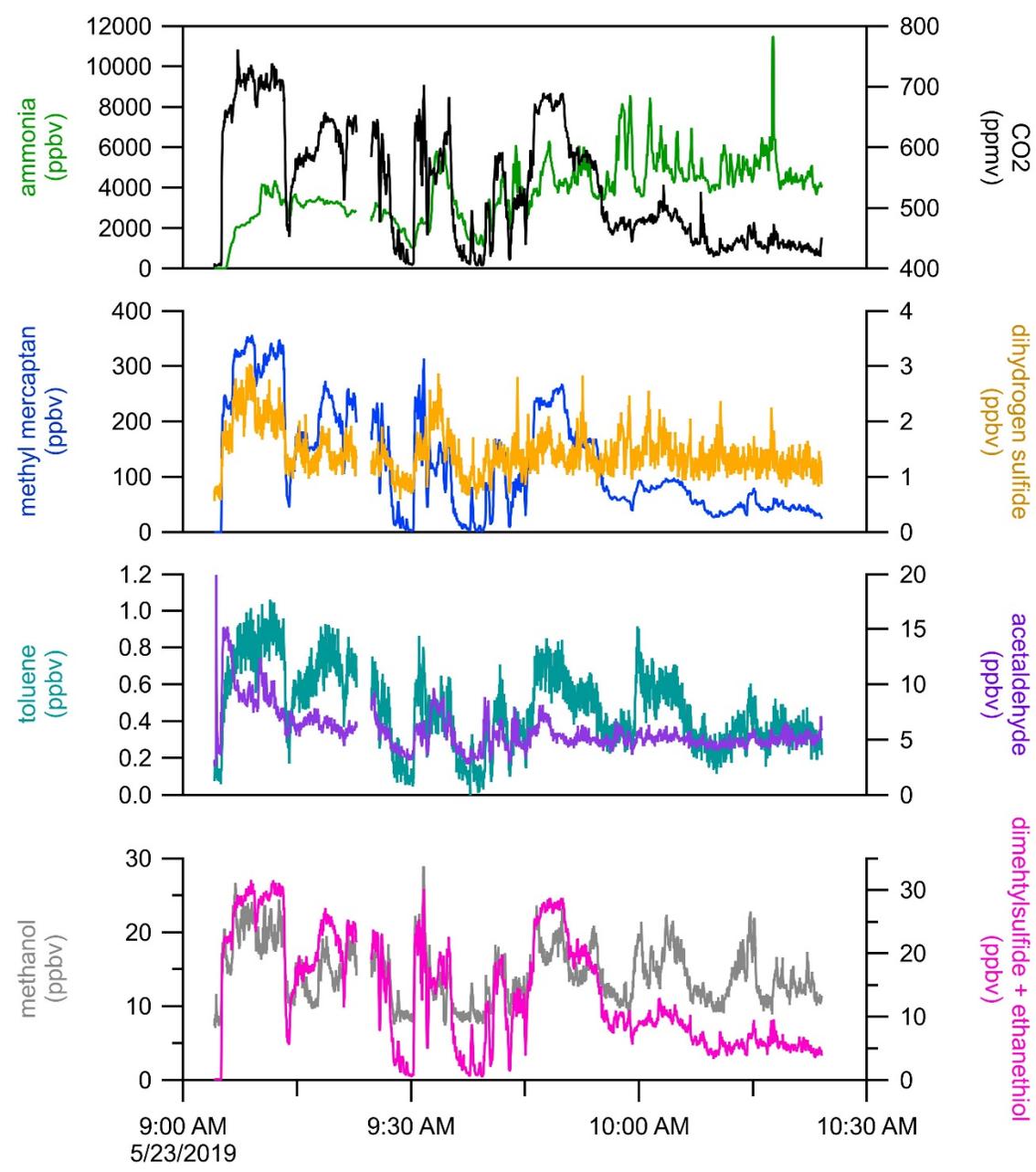


Figure 5-30. Concentrations of Key Species Within Septic Emissions Observed on May 23, 2019, While Sampling Directly from the Septic Tank.

Fingerprints were generated encompassing both periods where sorbent sampling occurred. Figure 5-31 shows the fingerprint for the data collected from 09:06 until 09:21. Methyl mercaptan makes up 64% of the fingerprint and dimethylsulfide + ethanethiol accounts for an additional 6% for a total of 70% of the fingerprint comprised of sulfur compounds. Nominal m/z 43 is the third highest at 3.8% with methanol, nominal m/z 51, acetone, and acetic acid + acetate fragment each contributing between 2% and 3%. Overall, these seven species account for 84% of the total response.

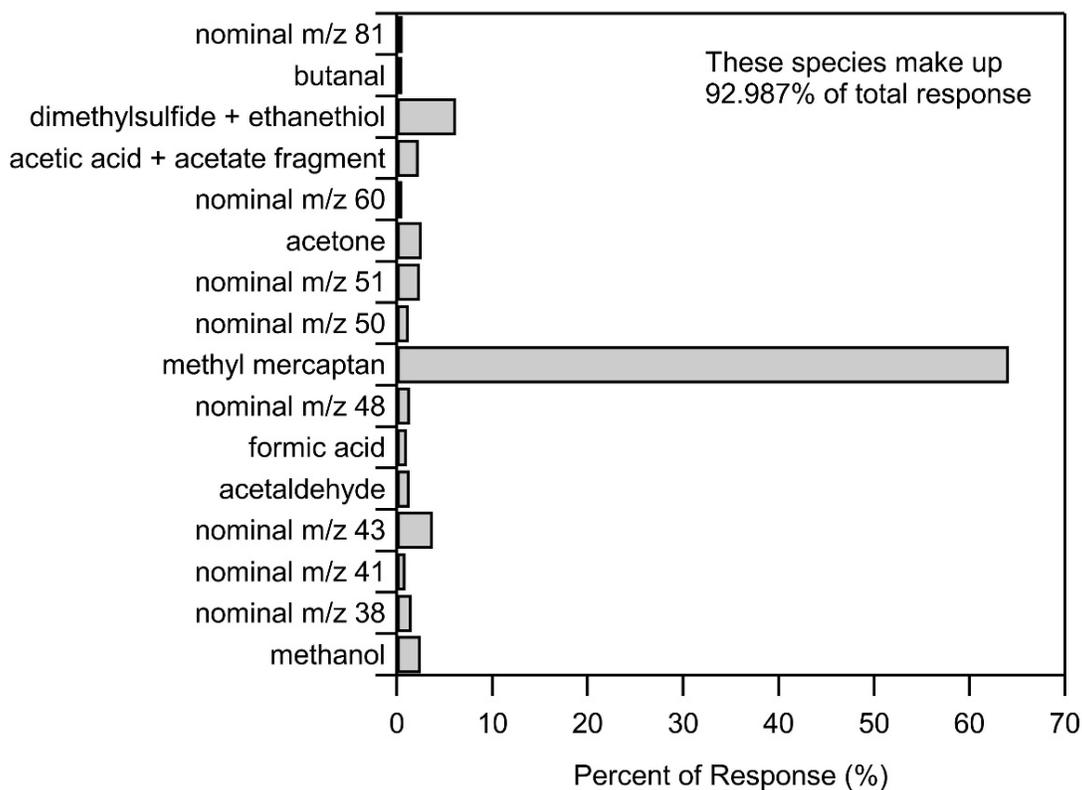


Figure 5-31. Fingerprint Taken from 09:06 to 09:22 in Unison with Sorbent Collection.

Figure 5-32 shows the fingerprint derived from observations between 09:25 and 10:24. The overall shape is similar to that of Figure 5-31 which is expected since the source did not change. The relative contributions of the species did shift with methyl mercaptan contribution lowering to 52.6% but dimethylsulfide + ethanethiol remained consistent at 6%. Acetone became the third highest within the fingerprint at 4.2% and there was an increase in methanol and nominal m/z 38. The contribution of the seven most prominent species in Figure 5-32 decreased from 84% to 74%. The methyl mercaptan decreasing from 64% to 52.5% was the main driving force of this reduction; however, increases in other species offset and minimized the total reduction to 10%.

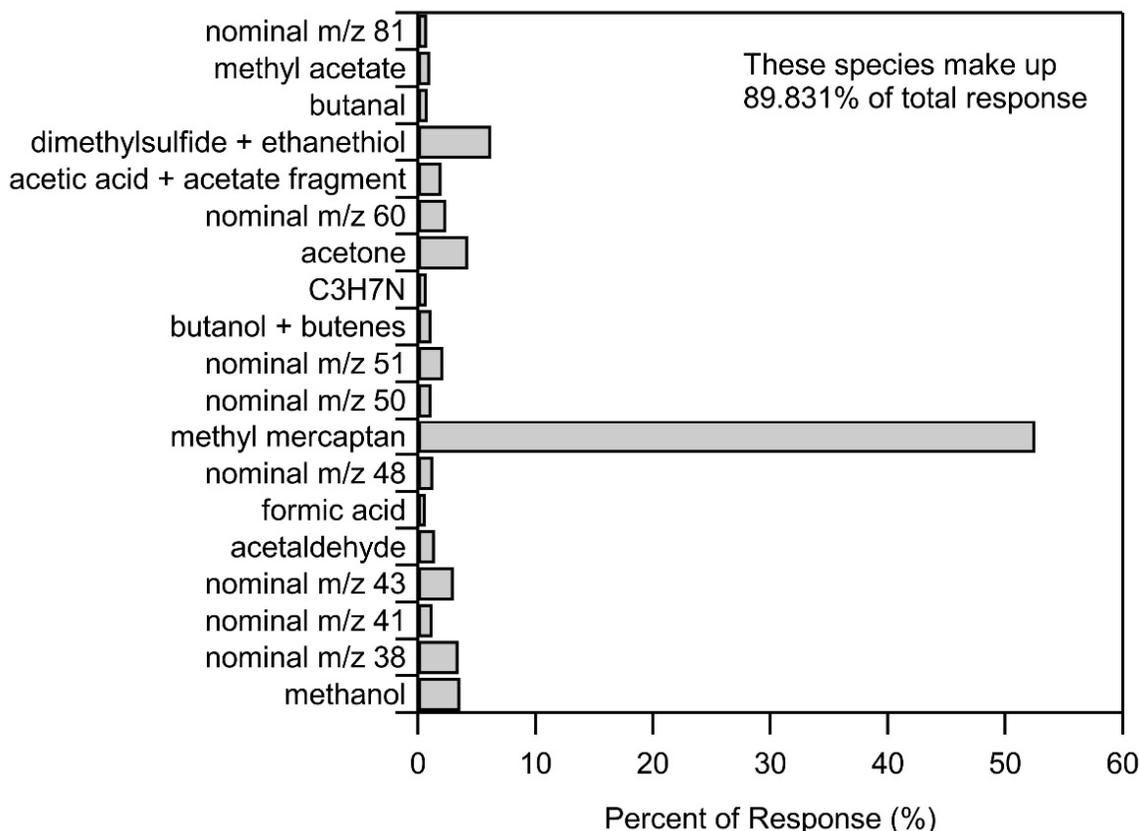


Figure 5-32. Fingerprint Taken from 09:25 to 10:24 in Unison with Sorbent Collection.

As mentioned previously, characterization of sources around site has been an ongoing effort and includes multiple observations of septic emissions over the course of the last year. Sewer fingerprints were previously reported in 53005-81-RPT-027; 53005-81-RPT-039, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 4*; and 53005-81-RPT-048, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 5*. Figure 5-33 shows the sewer fingerprints from these past reports along with the two fingerprints generated for this report. All the fingerprints show a strong response in methyl mercaptan. The biggest difference is strong response of dihydrogen sulfide and the OSC fragment at m/z 93 in previous reports and the lack of response in this report’s fingerprints. Looking back at Figure 5-26, both dihydrogen sulfide and OSC fragment at m/z 93 (toluene) are shown and there is a response. The dihydrogen sulfide peaked at approximately 3 ppbv and the OSC fragment at m/z 93 peaked at 1 ppbv. Even though there is a noticeable response for both these species it was considered to have a negligible contribution to the overall fingerprint. Both have concentrations 2 orders of magnitude lower than methyl mercaptan which was over 300 ppbv. This highlights the variability that can be observed from a source that may be assumed to be consistent. Until this report, the general constituents remained consistent even though the relative contributions were variable; however, the latest report shows that is not always the case. There was some consistency with the methanol, nominal m/z 43, and nominal m/z 51 all showing approximately the same response in all the fingerprints. Dimethyl sulfide + ethanethiol was more prominent in this month’s fingerprints, but a similar response was observed in the Month 5 fingerprint.

Acetone was either not present or limited in response in previous months but was much more prominent in the new fingerprints. Even though there are some differences, the identification of septic emissions remains the same. A strong methyl mercaptan signal is the initial indicator of septic emissions and the presence of methanol, dihydrogen sulfide, acetone, dimethyl sulfide + ethanethiol, and the OSC fragment at m/z 93 will increase confidence in this source identification.

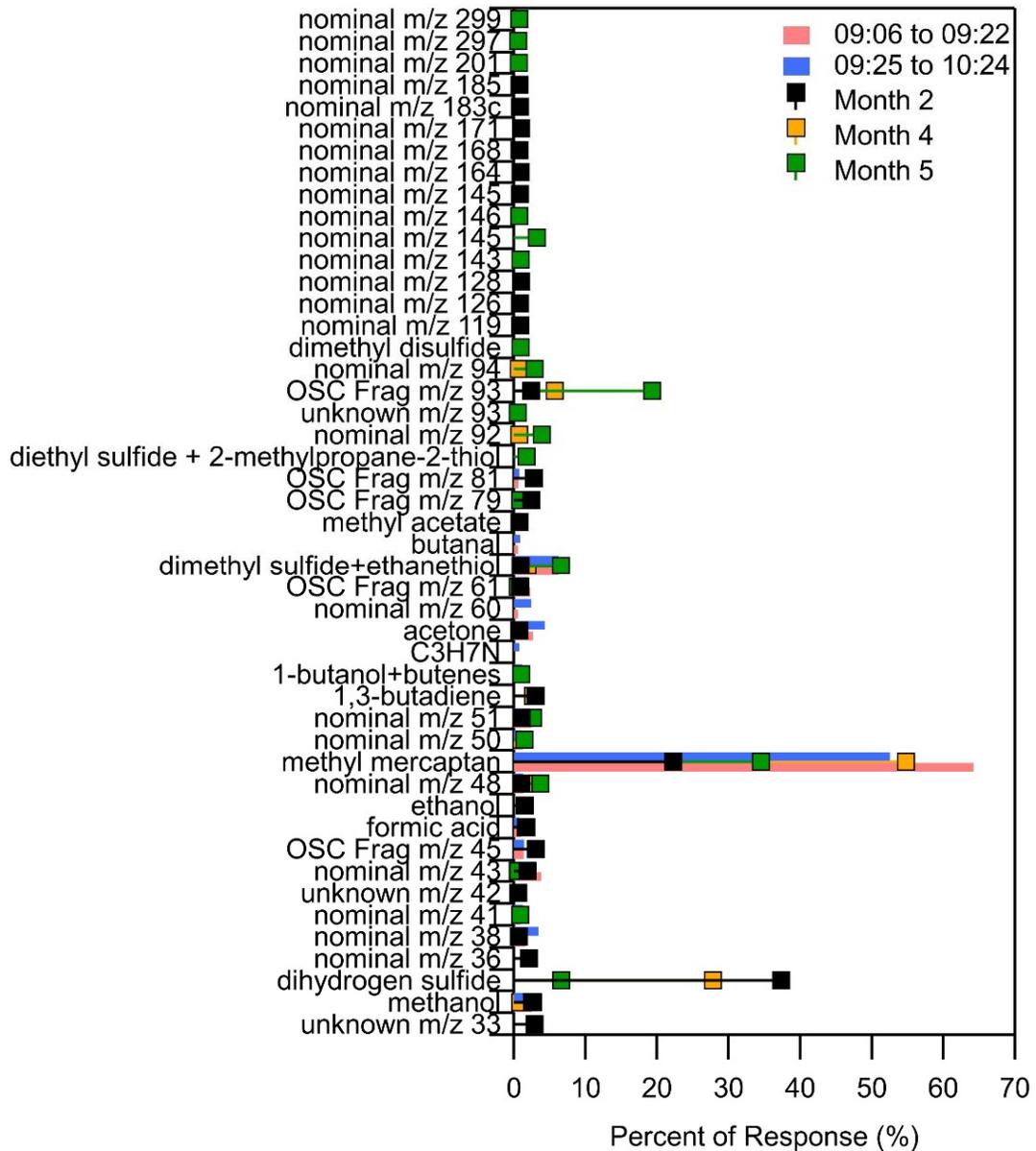


Figure 5-33. Comparison of Septic Fingerprints Generated in this Report to Previous Septic Fingerprints Developed in Month 2, Month 4, and Month 5.

5.4 Laboratory Testing

5.4.1 208' Sample Line Characterization

During Month 9, efforts were made to characterize the 208' heated line's response to prolonged sampling of a zero-air cylinder. The purpose of this test was to understand the PTR-MS and Picarro instrument response to only the heated line, without interference from ambient air. This was prompted by the observation that many ion signals as detected by PTR-MS did indeed appear to be elevated when sampling ambient air through the heated line. In addition, it had been observed that heating the line while measuring caused a characteristic “hump” in the time series data due to the increased temperature driving off VOCs from the inside of the heated line, before settling back down to a steady-state measurement.

Thus, it became crucial to understand which compounds could be attributed to the use of the heated line. Running a continuous zero-air measurement for several hours would also allow us to observe which species are present regardless of ambient background, and which species could naturally be driven off over the course of the measurement, as well as how long it took to achieve that reduction in signal. As was expected, many ion signals showed a marked decrease over three hours of sampling zero-air, while many showed no response at all over the course of sampling zero-air. This is illustrated below for PTR-MS in Figure 5-34.

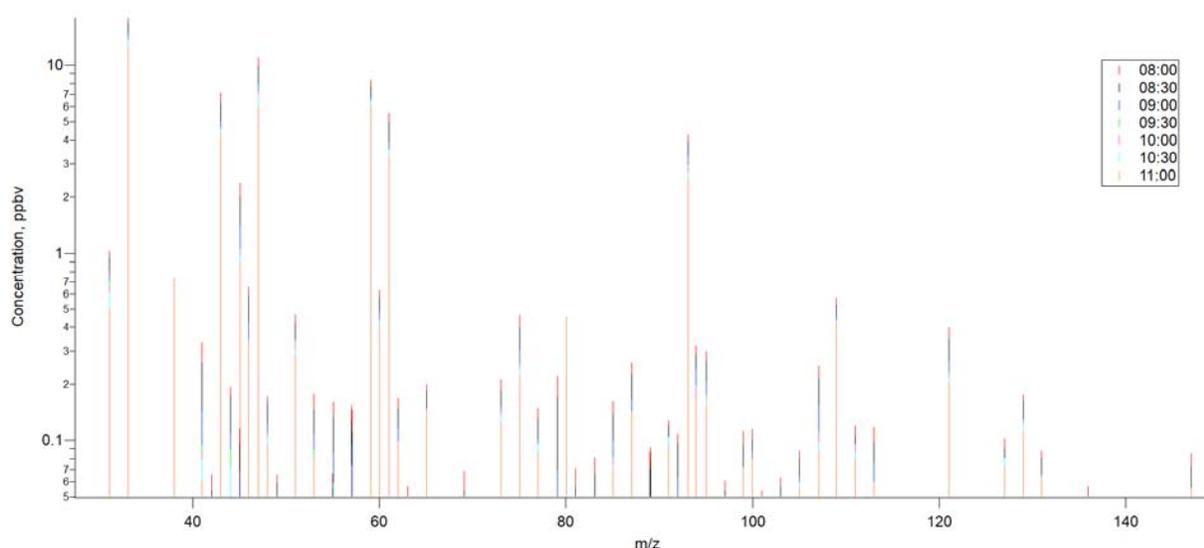


Figure 5-34. Proton Transfer Reaction – Mass Spectrometer Mass Spectra Over Time for Long Zero-air Measurement.

Every half hour of the long zero-air measurement, starting at 08:00 PST, a fingerprint of all masses detected by PTR-MS, as well as ammonia measured by the Picarro, was taken, with a cutoff threshold of 0.05 ppbv, below which it was decided to no longer be of sufficient concern. A response at or below 50 pptv would not be unreasonable to expect when measuring zero-air, even without the heated line. This provided average concentrations at each half-hour interval, allowing for visualization of the degree of reduction in signal at each mass. This is shown in the plot above, which depicts layered colored lines representing each half-hour period. For some

masses, their signals reduced to negligible levels over the course of the measurement; for others, they presented a consistent response in the PTR-MS even after hours of sampling zero-air. The latter case is represented by the orange-colored lines in the plot above, which represents the average mass spectrum in concentration as detected by PTR-MS at 11:00 PST and is overlaid on top. The mass axis is cut off at 150 m/z because no mass signals above that range responded above the 50 pptv threshold. Prominent non-odor, non-COPC mass signals that did not decay over the course of three hours include m/z 43, m/z 47a (formic acid), m/z 59 (acetone), m/z 61 (acetic acid/acetate fragment), and m/z 93 (toluene), all of which had maintained a concentration of 1 ppbv or greater by the end of sampling. Both m/z 47a and m/z 61 maintained an average concentration of over 6 ppbv by the end of sampling, suggesting that these sustained mass signals in particular would never be expected to reasonably decay under normal sampling conditions. The tables below summarize the results of this test for ammonia as detected by the Picarro and all COPCs and odors detected by the PTR-MS.

Table 5-5. 208' Line Zero-air Sampling Test Results for Chemicals of Potential Concern. (2 Sheets)

COPC Name	Initial Conc. (ppbv)	Final Conc. (ppbv)	Reduction to <0.05 Achieved After: (hrs)	Total % Reduction
ammonia	6.164	5.337	Never	13%
formaldehyde	1.031	0.503	Never	51%
methanol	17.85	12.45	Never	30%
acetonitrile	<0.05	<0.05	Not Present	Not Present
acetaldehyde	2.377	0.905	Never	62%
ethylamine	<0.05	<0.05	Not Present	Not Present
1,3-butadiene	0.161	<0.05	3	N/A
propanenitrile	<0.05	<0.05	Not Present	Not Present
2-propenal	0.153	0.070	Never	55%
1-butanol + butenes	0.145	<0.05	1.5	N/A
methyl isocyanate	<0.05	<0.05	Not Present	Not Present
methyl nitrite	0.168	0.099	Never	41%
furan	<0.05	<0.05	Not Present	Not Present
butanenitrile	<0.05	<0.05	Not Present	Not Present
but-3-en-2-one + 2,3-dihydrofuran + 2,5-dihydrofuran	<0.05	<0.05	Not Present	Not Present
butanal	0.213	0.126	Never	41%
NDMA	<0.05	<0.05	Not Present	Not Present
benzene	0.221	<0.05	1.5	N/A
2,4-pentadienenitrile + pyridine	<0.05	0.456	N/A	N/A

**Table 5-5. 208' Line Zero-air Sampling Test Results for
 Chemicals of Potential Concern. (2 Sheets)**

COPC Name	Initial Conc. (ppbv)	Final Conc. (ppbv)	Reduction to <0.05 Achieved After: (hrs)	Total % Reduction
2-methylene butanenitrile	<0.05	<0.05	Not Present	Not Present
2-methylfuran	<0.05	<0.05	Not Present	Not Present
pentanenitrile	<0.05	<0.05	Not Present	Not Present
3-methyl-3-buten-2-one + 2-methyl-2-butenal	<0.05	<0.05	Not Present	Not Present
NEMA	<0.05	<0.05	Not Present	Not Present
2,5-dimethylfuran	<0.05	<0.05	Not Present	Not Present
hexanenitrile	<0.05	<0.05	Not Present	Not Present
2-hexanone (MBK)	<0.05	<0.05	Not Present	Not Present
NDEA	<0.05	<0.05	Not Present	Not Present
butyl nitrite + 2-nitro-2-methylpropane	<0.05	<0.05	Not Present	Not Present
2,4-dimethylpyridine	<0.05	<0.05	Not Present	Not Present
2-propylfuran + 2-ethyl-5-methylfuran	<0.05	<0.05	Not Present	Not Present
heptanenitrile	<0.05	<0.05	Not Present	Not Present
4-methyl-2-hexanone	<0.05	<0.05	Not Present	Not Present
NMOR	<0.05	<0.05	Not Present	Not Present
butyl nitrate	<0.05	<0.05	Not Present	Not Present
2-ethyl-2-hexenal + 4-(1-methylpropyl)-2,3-dihydrofuran+ 3-(1,1-dimethylethyl)-2,3-dihydrofuran	<0.05	<0.05	Not Present	Not Present
6-methyl-2-heptanone	<0.05	<0.05	Not Present	Not Present
2-pentylfuran	<0.05	<0.05	Not Present	Not Present
biphenyl	<0.05	<0.05	Not Present	Not Present
2-heptylfuran	<0.05	<0.05	Not Present	Not Present
1,4-butanediol dinitrate	<0.05	<0.05	Not Present	Not Present
2-octylfuran	<0.05	<0.05	Not Present	Not Present
1,2,3-propanetriol 1,3-dinitrate	<0.05	<0.05	Not Present	Not Present
PCB	<0.05	<0.05	Not Present	Not Present
6-(2-furanyl)-6-methyl-2-heptanone	<0.05	<0.05	Not Present	Not Present
furfural acetophenone	<0.05	<0.05	Not Present	Not Present

The standout COPC results for this test are ammonia, formaldehyde, methanol, and acetaldehyde, which never dropped to below 0.5 ppbv in the line over the course of the zero-air measurement. However, while formaldehyde and acetaldehyde achieved more than a 50% reduction over the course of three hours and were below 1 ppbv, methanol only achieved a 30% reduction, from 17.85 ppbv to 12.45 ppbv. This is by far the highest signal observed while sampling zero-air through the heated line. However, methanol has a relatively permissive OEL of 200,000 ppbv and despite the relatively high background signal produced by the heated line, it is still safe to assume that any significant rises in ambient methanol concentration would be observed above a consistent baseline. Regarding the performance of ammonia as detected by the Picarro instrument, only a 13% reduction in concentration was achieved, dropping from 6.164 ppbv to 5.337 ppbv. Once again, the OEL for ammonia is several orders of magnitude higher than this background response. However, without characterizing the additional residence time and spread introduced to sampling ammonia by using the heated line, it is not clear how well significant increases in ammonia concentration would be captured by the considerably longer sampling system. It is recommended to conduct future tests to characterize this. The ion signal for 2,4-pentadienenitrile and pyridine exhibited unique behavior in that it was the only compound to show an increase in concentration throughout the test. This is likely the result of slow-moving contamination in either the zero air tank, regulator, calibration system, or the 208' line itself. It likely wasn't observed until the end of the test due to low concentrations and strong interactions with the walls of the line, such that equilibrium concentration had to be reached before sample could reach the instrument. No COPC above m/z 80 was observed to respond above the 50 pptv threshold during this test.

Table 5-6. 208' Line Zero-air Sampling Test Results for Odors.

Odor Name	Initial Conc. (ppbv)	Final Conc. (ppbv)	Reduction to <0.05 Achieved After: (hrs)	Total % Reduction
hydrogen sulfide	<0.05	<0.05	Not Present	Not Present
methyl mercaptan	0.065	<0.05	1	N/A
dimethyl sulfide; ethanethiol	0.057	<0.05	0.5	N/A
allyl mercaptan	<0.05	<0.05	Not Present	Not Present
1-propanethiol; Isopropyl mercaptan	<0.05	<0.05	Not Present	Not Present
2-butene-1-thiol	<0.05	<0.05	Not Present	Not Present
diethyl Sulfide; 2-methylpropane-2-thiol	<0.05	<0.05	Not Present	Not Present
thiopropanal sulfuroxide	0.128	0.095	Never	26%
dimethyl disulfide	<0.05	<0.05	Not Present	Not Present
1-pentanethiol; 2,2-dimethylpropane-1-thiol	<0.05	<0.05	Not Present	Not Present
benzenethiol	0.120	0.080	Never	33%
diallyl sulfide	<0.05	<0.05	Not Present	Not Present
methyl propyl disulfide	<0.05	<0.05	Not Present	Not Present
methylbenzenethiol	<0.05	<0.05	Not Present	Not Present
dimethyl trisulfide	<0.05	<0.05	Not Present	Not Present
(1-oxoethyl) thiophene	<0.05	<0.05	Not Present	Not Present
(1-oxopropyl) thiophene	<0.05	<0.05	Not Present	Not Present
dipropyl disulfide	<0.05	<0.05	Not Present	Not Present
methyl propyl trisulfide	<0.05	<0.05	Not Present	Not Present
dimethyl tetrasulfide	<0.05	<0.05	Not Present	Not Present
dipropyl trisulfide	<0.05	<0.05	Not Present	Not Present
diphenyl sulfide	<0.05	<0.05	Not Present	Not Present

The only two odor compounds which never dropped below 50 pptv were thiopropanal sulfuroxide and benzenethiol. They also did not reduce more than 33% over the course of the zero-air measurement. However, they did reduce to below 100 pptv. In addition, methyl mercaptan and dimethyl sulfide + ethanethiol were observed to drop below significant levels after less than an hour.

5.4.2 Charcoal Zero Source Characterization

Another testing effort conducted during Month 9 involved employing a charcoal filter connected in line with the zero-air tank. The purpose of the test was to observe the signal response in the PTR-MS for both the zero-air only, and the zero-air in line with a charcoal filter. It was theorized that the charcoal filter would provide some reduction in the observed PTR-MS signal, as it is generally assumed that, while conventional zero-air cylinders are generally very clean, some small trace amounts of VOCs can be left in the cylinder, and an adequately sensitive instrument such as the PTR-MS might be able to detect these trace amounts. Since zero-air measurements are crucial for characterizing the instrument background, if the charcoal filter

offered an improvement the ML's ability to conduct zero-air measurements, it would be worth investigating. Figure 5-35 below exhibits the average PTR-MS response for half an hour of sampling zero-air, overlaid with the average PTR-MS response for half an hour of sampling zero-air passed through a charcoal filter, across the mass spectrum.

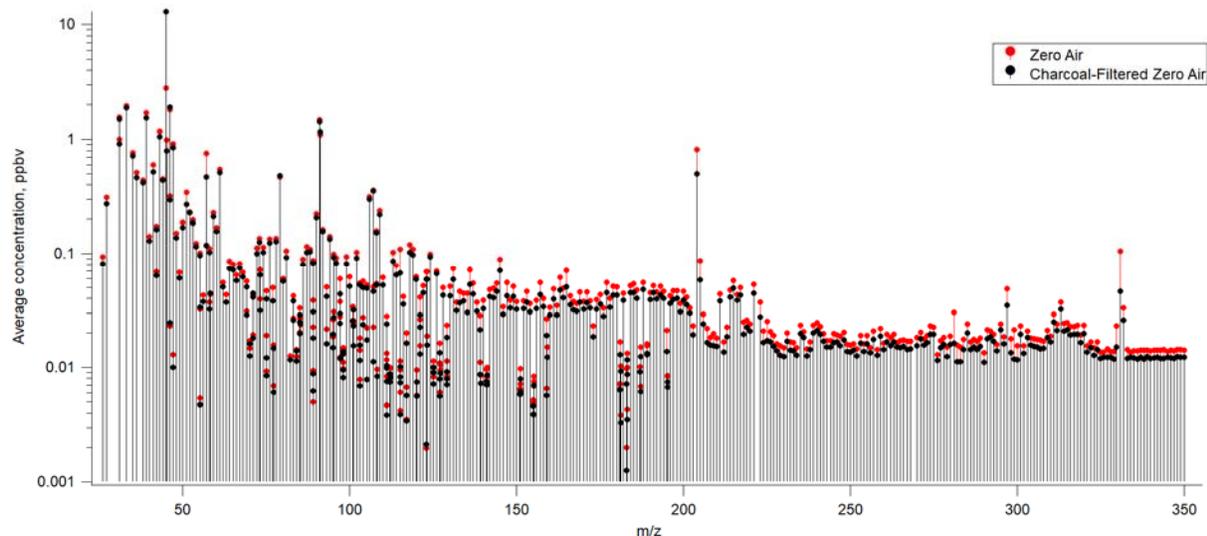


Figure 5-35. Mass Spectra of the Average Response to 30 Minutes of Sampling Zero-air and 30 Minutes of Sampling Charcoal-filtered Zero-air.

As shown above, the charcoal-filtered, zero-air measurement produced generally lower results across the mass spectrum. The results showed an average percent difference of $-13 \pm 20\%$ between the zero-air measurement and the charcoal-filtered measurement across all masses measured by PTR-MS. This means that generally speaking, the charcoal filter reduced the amount of observed VOCs in the zero-air by up to 33% but select species showed no reduction or a slight increase up to 7%.

It is worth discussing prominent mass signals which fell outside one standard deviation of the average. Compounds that generally showed a much higher than average decrease in signal in the charcoal-filtered, zero-air include m/z 107 (C₂-benzenes), m/z 121 (C₃-benzenes), m/z 135 (C₄-benzenes), m/z 57a (2-propenal), m/z 183 (1,2,3-propanetriol-1,3-dinitrate), m/z 101 (2-hexanone), and m/z 75 (1-propanethiol + isopropyl mercaptan).

Compounds that showed an increase in signal in the charcoal-filtered, zero-air include m/z 79 (benzene), m/z 91a (diethyl sulfide + 2-methylpropane-2-thiol), and m/z 45 (nominal 45). While the signals for benzene and the sulfur compounds at m/z 91 only demonstrated a marginal increase in the charcoal filter (3% and 6%, respectively), nominal 45 is notable in that it exhibited a 364% increase in the charcoal filter test, and averaged 12.98 ppbv over the course of the measurement.

6.0 QUALITY ASSESSMENT

During the May 1, 2019, to May 31, 2019, period, 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 the writing of this report or are noted in this report. Any potential quality-affecting deviations have been captured in Deficiency Reports (DRs) and are summarized below with some interpretation.

During Month 9, there was one DR recorded. DR19-010 documents a corrupt data file from the morning of May 23, 2019, that was deemed unsalvageable.

6.1 Lessons Learned – DR19-010

A file from the morning of May 23, 2019, was found to be corrupt during analysis of the data. During the day’s set-up for monitoring, a pressure drop on the PTR-MS occurred, which the instrument attempted to correct internally. Upon contacting the SME, Dr. Matthew Erickson, and restarting the instrument’s software, the Operators considered the problem to be resolved. On May 29, 2019, when data analysts began processing the day’s data, they discovered that the pressure drop had caused the first set of data from that day to be unusable and would not be reported. This event was deemed an anomaly and required no specific actions to be taken.

7.0 CONCLUSION

The exhaust scan found 54 potential plumes with 32 identified as vehicle exhaust, 15 as generator exhaust, three with high methanol, and four of them having toluene and C2-benzene responses. Of the 32 vehicle exhaust plumes, 28 were found to be similar to the Month 8 fingerprint except there were enhanced signals in aromatics suggesting the source is potentially a gasoline vehicle. The other four vehicle exhaust plumes are also suspected to be gasoline exhaust in origin with some influence from a methanol source. Of the 15 generator exhaust plumes, eight were found to compare with the Month 8, April 8, 2019, generator with only slight differences in key species and seven were found to compare with the Month 2 ML exhaust fingerprint, suggesting the ML was the source. This information was used to classify the results and typical fingerprints for gasoline vehicles, diesel vehicles, and diesel generators to use as a comparison in future reports. The three high methanol plumes compared well to the Month 8 methanol plume fingerprint which shows these plumes are common but should not remain a focus due to the magnitude of the plumes being well below the OEL and posing no risk to worker safety. The four toluene and C2-benzene plumes are suspected to be a combination of combustion and fuel emissions with the potential sources within 241-AY and 241-AW.

The odor scan found 77 potential plumes with 10 being too low in concentration for analysis and 30 previously identified as exhaust with the exhaust scanner. None of the remaining 37 plumes were found to be dominated by odor species. Fourteen were identified as exhaust, 19 methanol related, and four as unique plumes. The 19 methanol plumes were organized into three groups. The eight MA plumes showed a unique fingerprint with a potential source in the direction of the mobile offices and Canton Avenue. The four MB plumes have a composition of methanol + exhaust and were similar to four of the plumes identified with the exhaust scan. The six MC plumes had the highest abundance of methanol with windshield wiper fluid as the potential source. There was a final methanol plume that did not fit within the three groups but appeared to be a variation of the MB fingerprint with a higher contribution of exhaust compared to methanol. The four unique odor plumes had two with high toluene, similar to the Month 8 toluene fingerprint suggesting potential sources within 214-A and 241-AW. One unique odor plume had high nominal m/z 45 and methanol response with a potential source within 241-AX and 241-AZ. The last unique odor plume is suspected to be generator exhaust due to the presence of nominal m/z 46 (NO₂) and acetaldehyde. The 14 exhaust plumes identified with the odor scan generally had a strong toluene response suggesting gasoline vehicle exhaust as the source with a few of the plumes from generator exhaust due to the high nominal m/z 46 (NO₂) response.

The statistical analysis of COPCs concentrations for the entire month showed that no averages or medians exceeded OEL concentrations. Averages were below detection limits except for seven species (ammonia, methanol, acetonitrile, acetaldehyde, methyl nitrite, but-3-en-2-one + 2,3-dihydrofuran + 2,5-dihydrofuran, butanal) whose averages were between their respective MDLs and RLs. There were four species with a maximum value that briefly exceeded OEL concentrations. Furan exceeded the OEL concentration four times in a short window with the highest exceedance being 0.64 ppbv above the OEL concentration and the longest plume was less than 20 seconds. N-Nitrosodimethylamine had multiple short duration plumes that exceeded the OEL concentration by less than 0.43 ppbv and never for more than six seconds. 2-methylfuran exceeded the OEL concentration four times in a short period; however, never went beyond 0.82 ppbv above the OEL concentration and lasted less than 20 seconds. N-Nitrosodiethylamine had a small spike that exceeded the OEL concentration by 0.006 ppbv lasting no more than 2 seconds.

The ML supported the Fugitive Emission group with a location investigation on May 21, 2019. Sampling occurred for approximately 85 minutes through the 35' heated sampling line. Three plumes were analyzed at 11:47, 12:10, and 12:24. The 11:47 plume was primarily acetone, nominal m/z 43, and acetaldehyde; however, there was a response in 2-ethyl-2-hexanal + substituted dihydrofurans reaching 0.16 ppbv but no potential source was identified. The 12:10 plume closely resembled combustion engine exhaust and is representative of multiple smaller exhaust hits during the monitoring period. The 12:22 plume contained a large amount of acetonitrile and was identified as cigar smoke by the ML Operators and was consistent with the expected fingerprint composition.

Characterization of septic emissions on May 23, 2019, showed that methyl mercaptan was the dominant species within the fingerprint accounting for over 50% of the composition. Dimethylsulfide + ethanethiol was the second most abundant. This was compared to previous characterizations of septic emissions in 53005-81-RPT-027, 53005-81-RPT-039, and 53005-81-RPT-048. The previous reports showed a large methyl mercaptan response but had a much stronger response in OSC fragment at m/z 93 and dihydrogen sulfide compared to Month 9. This demonstrates that there is some variability in septic emissions; however, methyl mercaptan still remains the best initial indicator of septic emissions. The presence of other key septic species (dihydrogen sulfide, OSC fragment at m/z 93, dimethylsulfide + ethanethiol) would further support source attribution to septic emissions.

Continued characterization of the 208' sample hose was performed to quantify important interferences and conditioning. Running a continuous zero for several hours showed that there is no interference for most of the COPCs and odors. The species that have an increased signal within the heated 208' sample hose either showed a marked decrease in signal in the range of 26 – 62% or the concentration reduced to less than 0.05 ppbv. The only species that remained above 0.05 ppbv for the entire test were seven COPCs (formaldehyde, methanol, acetaldehyde, 2-propenal, methyl nitrite, butanal) and two odors (thiopropenal sulfuroxide, benzenethiol). Despite this interference within the line, the lowest OEL for the COPCs listed is 100 ppbv for 2-propenal and methyl nitrite which is much higher than the observed interferences (<0.2 ppbv). This means there is no risk of these interferences affecting the ability of the PTR-MS to accurately measure COPCs well below the OEL.

Further tests were performed to determine if cleaner zero-air is achievable using a charcoal filter to scrub the zero-air from the cylinder. The zero-air tanks are certified to a low level for VOC content, but the sensitivity of the PTR-MS can detect trace amounts of VOCs below certified levels. Adding the charcoal filter as an additional VOC scrubber reduced the VOC responses by approximately 13% across the entire mass range. A decrease beyond 13% was observed in C₂-benzenes, C₃-benzenes, C₄-benzenes, 2-propenal, 1,2,3-propanetriol-1,3-dinitrate, 2-hexanone, and 1-propanethiol + isopropyl mercaptan indicating these species benefit even further from the addition of a charcoal filter. However, there was an increase in signal for benzene and diethyl sulfide + 2-methylpropane-2-thiol as well as a large increase in nominal m/z 45. Implementation of a charcoal filter in line with the zero-air would provide an overall benefit as long as the increased signal in benzene, diethyl sulfide + 2-methylpropane-2-thiol, and nominal m/z 45 does not affect the objectives or data quality.

8.0 REFERENCES

- 17124-DOE-HS-102, 2018, “Mobile Laboratory Data Processing – Analysis,” Revision 2, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 53005-81-RPT-007, 2018, *PTR-MS Mobile Laboratory Vapor Monitoring Background Study (3/18/2018 – 4/20/2018)*, Revision 0, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 53005-81-RPT-019, 2018, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 1*, Revision A, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 53005-81-RPT-027, 2018, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 2*, Revision A, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 53005-81-RPT-039, 2018, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 4*, Revision A, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 53005-81-RPT-048, 2019, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 5*, Revision A, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 53005-81-RPT-059, 2019, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 7*, Revision A, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 53005-81-RPT-066, 2019, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 8*, Revision A, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 66409-18-ML-003, 2018, *Sampling Manifold Sketch*, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 66409-18-ML-004, 2018, *Mobile Lab Schematics*, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 66409-RPT-003, 2018, *Mobile Laboratory Operational Acceptance Testing Plan*, Revision 0, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- 66409-RPT-004, 2018, *Mobile Laboratory Operational Procedure*, Revision 15, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.
- EPA TO-17, “Volatile Organic Compounds,” U.S. Environmental Protection Agency, Washington, D.C.
-

Fiscal Year 2017 Mobile Laboratory Vapor Monitoring at the Hanford Site: Monitoring During Waste Disturbing Activities and Background Study, September 2017, RJ Lee Group, Inc., Pasco, Washington.

Statement of Work 306312, 2018, “Mobile Laboratory Services and Lease,” Revision 2, Washington River Protection Solutions, LLC, Richland, Washington.

TG-DOE-QAP-002, 2018, *TerraGraphics Quality Assurance Procedure Manual*, Revision 4, TerraGraphics Environmental Engineering, Inc., Pasco, Washington.

APPENDIX A
DEFICIENCY REPORT

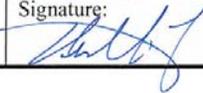


DEFICIENCY REPORT

Deficiency Report No.: DR19-010_Rev.01		Page: 1 of 1	
Originator (Print Name): Kimberly Boone		Signature: <i>Kimberly Boone</i>	Date: 08/06/19
Project No./Title: 66409 Mobile Laboratory Service & Lease			
PAAA Reportable: <input checked="" type="checkbox"/> No <input type="checkbox"/> Yes		10 CFR 21 Reportable: <input checked="" type="checkbox"/> No <input type="checkbox"/> Yes	
Description of Requirement that was Violated and of Deficiency: A PTR-MS data file from 05/23/19 monitoring, "SourceCharacterization_190523_A", was found to be corrupt during analysis of the data on 05/29/19.			
CORRECTIVE ACTION			
Corrective Action: Since the data analyst was unable to separate peaks in the data using PTR-MS Viewer software, approximately one hour of area monitoring data will not be included in the respective weekly report.			
AUTHENTIC QUALITY RECORDS Initials <i>AW</i> Date <i>08/05/19</i> TERRAGRAPHS			
Completion Date: 05/29/19			
Deficiency Cause and Extent of Condition: The corruption occurred on the PTR-MS when pressure dropped, and the PTR-MS attempted to correct the drop internally. When the ML operators contacted the SME and restarted the instrument software, the issue appeared to be resolved.			
Upon processing the data, the analyst found this data set, the first set of the day, to be corrupt. This hour of data was deemed unusable and will not be reported.			
Action to Preclude Recurrence: There are no specific actions identified to preclude recurrence at this time. Due to the unique monitoring conditions this instance is currently being treated as an anomaly. Should the condition persist, further analysis will be performed to determine the extent of condition and identify appropriate actions to preclude recurrence.			
Completion Date: 05/29/19			
Resp. Manager/TL (Print & Sign): Rich Westberg <i>[Signature]</i>		Date: 08/06/19	QA Rep. (Print & Sign): Heath Low <i>[Signature]</i>
		Date: 08/06/19	
CLOSURE			
Comments and Notes (if applicable): As of 08/06/19, the PTR-MS 6000x2 has been exchanged for another PTR-MS 6000x2 and there have been no corrupt files unique to the type of monitoring conditions.			



DEFICIENCY REPORT

QA Manager (Print Name): Heath Low	Signature: 	Date: 08/06/19
---------------------------------------	---	-------------------

Deficiency Report (01-2018)