PTR-MS MOBILE LABORATORY VAPOR MONITORING MONTHLY REPORT – MONTH 7

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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

TerraGraphics

www.terragraphics.com

Approval Form

Prepared by:

Tyler Williams Date: 09/26/2019

Tyler Williams

Reviewed by:

Date: 09/26/2019

Matthew Erickson, Ph.D.

Approved by:

Date: 09/26/2019

Rich Westberg

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Revision	Date	Pages/Sections Changed	Brief Description
0	09/2019	All	Original Issue

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Acronyms and Abbreviations

ALS	Australian Laboratory Services
AOP	Abnormal Operating Procedure
ASTM	ASTM International, Inc.
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 Chromatograph
IH	Industrial Hygiene
IP	Ionization Potential
MDL	Method Detection Limit
ML	Mobile Laboratory (Mobile Vapor Monitoring Laboratory)
MSA	Mission Support Alliance, LLC
ND	Non-detect
NDMA	N-Nitrosodimethylamine
NIOSH	National Institute of Occupational Safety and Health
ppbv	parts per billion by volume
PCA	Principal Components Analysis
PMF	Positive Matrix Factorization
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
QA	Quality Assurance
QC	Quality Control
R&D	Research and Development
RL	Reporting Limit
RPD	Relative Percent Difference
SME	Subject Matter Expert

SOEN	Shift Office Event Notification
TIC	Tentatively Identified Compound
TOF-MS	Time of Flight – Mass Spectrometer
VOC	Volatile Organic Compound
WRPS	Washington River Protection Solutions, LLC

Executive Summary

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

This report of Month 7 operations spans the calendar month of March 2019.

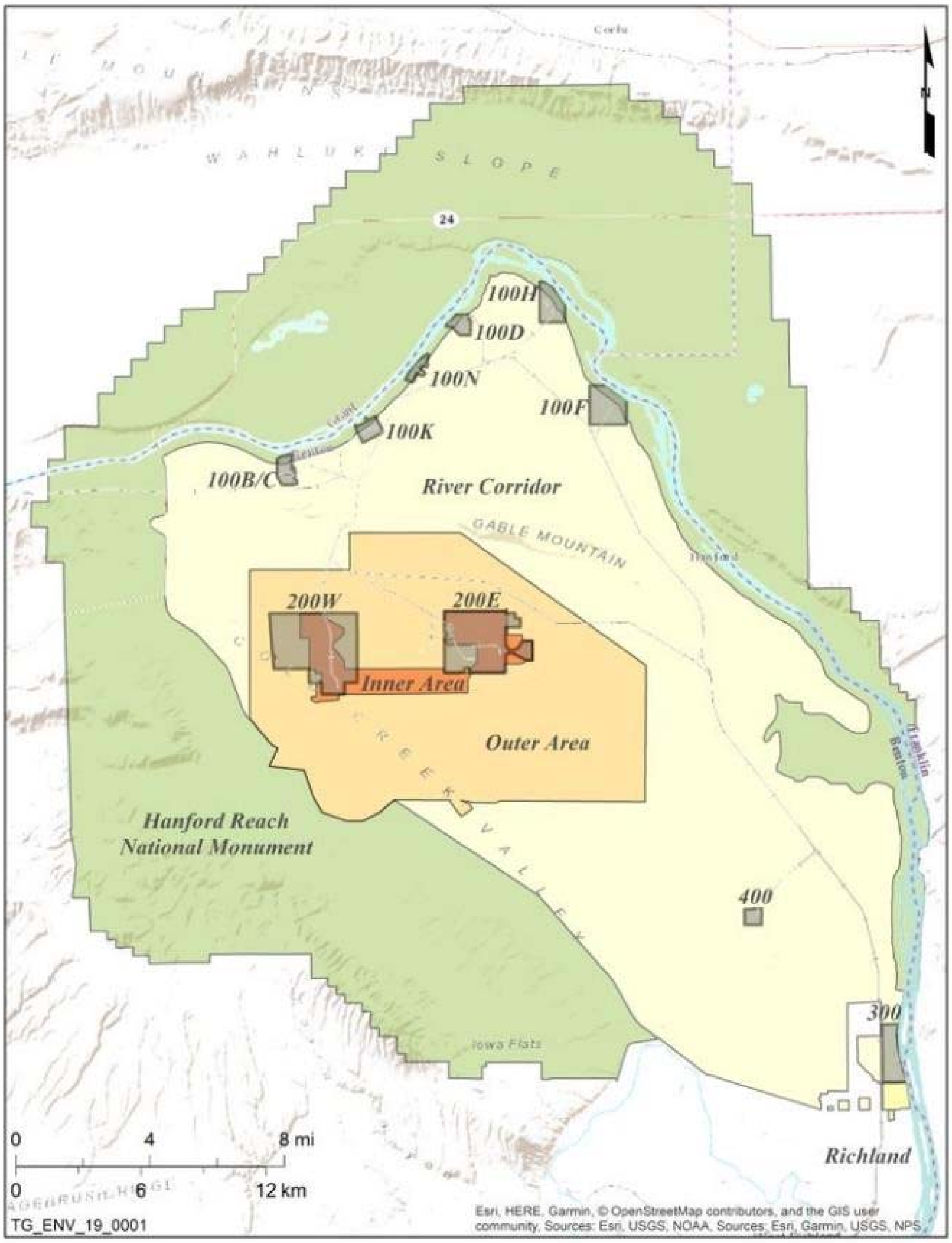
During Month 7, Mobile Laboratory operators performed maintenance, modifications, calibrations and received continuous training on the Mobile Laboratory instrumentation. Testing and verifications of the Mobile Laboratory systems occurred throughout the entire month.

Source characterization of various generators located around the 200 East Area of the Hanford Site was conducted in support of the WRPS Fugitive Emissions Team on March 28, 2019.

For the remainder of Month 7, the Mobile Laboratory performed area monitoring around the 200 East Area and 200 West Area in order to collect data on the concentrations of chemical vapors downwind of potential sources.

1.0 DESCRIPTION OF TESTS CONDUCTED

During Month 7, spanning the dates of March 1, 2019, to March 30, 2019, the Mobile Laboratory (ML) was deployed for the measurement of Volatile Organic Compounds (VOCs) after ML maintenance, modifications, operational testing, and continuous training were performed. During this period, area monitoring, and support of the fugitive emissions team were provided and conducted on the Hanford Site (Figure 1-1). Table 1-1 provides a summary of ML tests and activities conducted during Month 7.



Esri, HERE, Garmin, © OpenStreetMap contributors, and the GIS user community, Sources: Esri, USGS, NOAA, Sources: Esri, Garmin, USGS, NPS,

Figure 1-1. Hanford Site.

Table 1-1. Summary of Month 7 Testing and Operational Activities.

Week	Date	Activity
30	03/01/2019	ML Testing and Training
31	03/04/2019	ML Maintenance and Modifications
	03/05/2019	ML Training
	03/06/2019	ML Testing and Training
	03/07/2019	ML Testing and Training
	03/08/2019	ML Testing and Training
32	03/11/2019	ML Testing
	03/12/2019	ML Testing
	03/13/2019	ML Tour and Area Monitoring
	03/14/2019	ML Testing
	03/15/2019	ML Testing
33	03/18/2019	ML Testing
	03/19/2019	ML Testing
	03/20/2019	ML Testing
	03/21/2019	ML Testing
	03/22/2019	ML Testing
34	03/25/2019	ML Area Monitoring
	03/26/2019	ML Area Monitoring
	03/27/2019	ML Area Monitoring
	03/28/2019	ML Area and Fugitive Emissions Monitoring
	03/29/2019	ML Testing

This report is structured based on reporting requirements, as defined in the original statement of work (SOW 306312, “Mobile Laboratory Services and Lease”).

1.1 Description of Area Monitoring

Area monitoring conducted during March 2019 was performed when ML Operators positioned the ML downwind of ongoing Tank Farm work activities and/or any potential sources of odor. To ensure the ML was downwind of ongoing Tank Farm work, operators acquired the Hanford Daily Report at the Central Shift Office and planned the ML’s daily monitoring locations accordingly. The ML Operators would typically complete two site survey loops, around A Farm and C Farm, and monitor at least two downwind locations. Further detail is provided in Section 5.1.

1.2 Description of Fugitive Emissions Monitoring

Under the direction of Washington River Protection Solutions, LLC's (WRPS') fugitive emissions team, the ML was operated in the 200 East area of the Hanford Site on March 28, 2019, as part of an investigation of generator emissions. The ML was stationed at the northwest corner of A Tank Farm and the northwest of AY Tank Farm. Measurements were made with no issues and a multi-compound profile was produced for this analysis is detailed in Section 5.2.

1.3 Description of Testing Activities

The maintenance tasks conducted during this period were performed to support proper function of the instruments in the ML. Month 7 activities also consisted of continuous training of ML Operators through a mock deployment and Subject Matter Expert (SME) guidance, acceptance testing of ancillary instruments, sorbent system testing, and multipoint calibrations.

The purpose of this test was to supply a known concentration of VOC standard at the inlet and sample for a specific time period through the ML's sorbent system into sorbent cartridges so a percent recovery can be determined from the analytes present in the VOC standard.

2.0 MEASUREMENT SYSTEM DESIGN

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

2.1 Sampling Methods

The following sections detail the sampling methods utilized during the monitoring periods that occurred in Month 7.

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 7, 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 7. 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.

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[1] Chevrolet is a registered trademark of General Motors, LLC, Detroit, Michigan.
[2] IONICON is a registered trademark of IONICON Analytik Gesellschaft m.b.H., Innsbruck, Austria.

2.1.1.2 DAQFactory Sampling

DAQFactory®[3] is a data acquisition and automation software 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] CO_2 monitor, Picarro Ammonia Analyzer, Airmar®[5] Weather Station, and the PTR-TOF.

2.2 Instrumentation and Methods Used

The following sections provide details of the instrumentation and methods utilized during the monitoring periods that occurred in Month 7.

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.

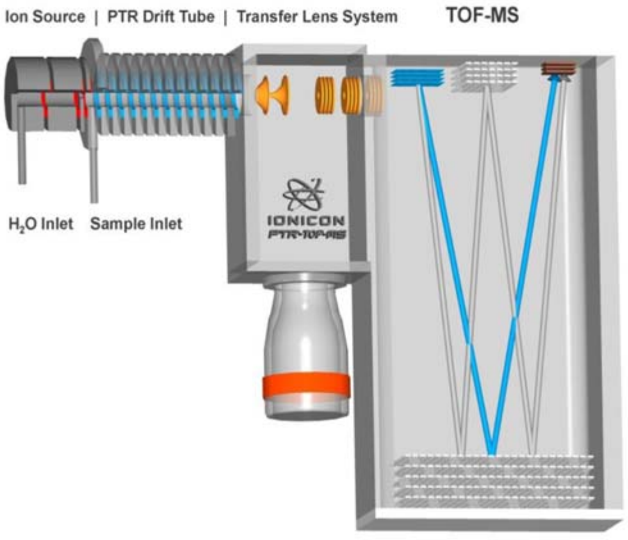

Figure 2-1. The General Configuration of an IONICON Proton Transfer Reaction – Time of Flight Instrument.

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[3] DAQFactory is a registered trademark of AzeoTech, Inc., Ashland, Oregon.
[4] LI-COR is a registered trademark of LI-COR, Inc., Lincoln, Nebraska.
[5] Airmar is a registered trademark of Airmar Technology Corporation, Milford, New Hampshire.

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

$$R + H_3O^+ \rightarrow RH^+ + H_2O \qquad \text{(R1)}$$

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

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

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

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

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

where *[AIR]* is the number density of air (molecules/cm^3) in the drift tube given the drift tube pressure (typically ~ 2.4 mbar) and temperature (typically ~ 50°C).

The Proton Transfer Reaction – Mass Spectrometer (PTR-MS) technology has been used in numerous applications around the world with hundreds of peer-reviewed publications appearing in the literature over the past 20 years. Even though the technology is widely used in the research arena and has proven to be indispensable for many applications, there is no standard method among the United States regulatory agencies such as the U.S. Environmental Protection Agency, American Society 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.

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[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.

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 March 2019 was accomplished by the kinetic approach.

2.2.2 Carbon Dioxide Monitor

Carbon dioxide is not a COPC; however, monitoring CO_2 is necessary for correlation of vapor signals to combustion processes or other sources. There were numerous combustion sources near the sampling sites during March 2019 including diesel and gas generators, all-terrain vehicles with no catalytic converters, and diesel and gasoline vehicles. These contribute VOCs to the vapor burden and are readily observed by the PTR-MS. It is necessary to distinguish these VOCs from tank farm related emissions resulting from normal work-related activities.

The CO_2 monitor used in the TerraGraphics ML was the LI-COR Model 840A. The Li840A is an absolute, non-dispersive infrared gas analyzer based upon a single path, dual wavelength infrared detection system. It is a low-maintenance, high performance monitoring solution that gives accurate, stable readings over a wide range of environmental conditions. It has a range of 0-20,000 ppm (0-2%), low power consumption (4W after power-up), and 1-second signal averaging to allow for real-time source apportionment (i.e., monitoring vehicle exhaust or other combustion sources on the fly). The instrument operates on a gas flow of less than 1 liter per minute.

It is interfaced to the ML's internal gas manifold at the same location as the PTR-MS sampling port to ensure that both instruments are simultaneously measuring the same source. The data from the CO_2 monitor are used to predict when VOC measurements from the PTR-MS come from combustion sources.

The CO_2 monitor used during March 2019 was operated using a factory calibration. Periodic checks of the unit were made with zero air and ambient background air [ambient atmospheric CO_2 levels are approximately 400 parts per million by volume (ppmv)], and a certified reference standard to ensure continued system operation. The system has a continuous direct readout which can be displayed on the DAQFactory monitor in real time to aid in real-time decision making by the field analysts.

2.2.3 Ammonia Monitor

Ammonia is a compound on the COPC list of particular importance. It is believed to be associated with all high-level waste storage tanks on the Hanford Site. The global average background for ammonia is between 5-7 parts per billion by volume (ppbv). Previous studies of ammonia levels on the Hanford Site indicate the expected measurement range should be in the low ppbv range. Although relatively easy to measure at the parts per million by volume (ppmv) level, its measurement at the low ppbv level with high temporal resolution is not trivial. The purpose of measuring trace levels of NH_3 is the correlation of vapor data from the PTR-MS to actual tank emissions. A measured vapor plume containing elevated COPCs with the same time correlation as an ammonia plume is reasonable evidence of a tank emission.

The ammonia monitor used was a Picarro model G2103 that is capable of measuring NH_3 with parts per trillion by volume (pptv) sensitivity. It is a sophisticated time-based measurement system that uses a laser to quantify spectral features of gas phase molecules in an optical cavity. It is based on cavity ring down spectroscopy. Gas phase spectroscopy measurements are subject to temperature and pressure fluctuations. The Picarro system features a ± 0.005°C temperature stability and ± 0.0002 atm pressure stability to ensure low noise and high accuracy measurements. Sample flow rate to the instrument was provided by an external pump at 0.8 liters per minute at 760 Torr.

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

2.2.4 Weather Station

The weather station used in the ML is an Airmar 200WX-IPx7 with a control unit mounted in the server cabinet and the transducer mounted on the sampling mast located above the roof of the ML. 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

Although the 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 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 Compound (TIC).

During Month 7, the sampling system within the ML was tested and verified using a Carbotrap®[8]-300 and Thermosorb®[9](n) cartridge that was analyzed by Australian Laboratory Services (ALS) Environmental. The findings from this test are discussed in Section 5.4.3.

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

3.0 CALIBRATION METHODS AND CALIBRATION GASES USED

Table 3-1, shown below, highlights the type, identification number and expiration date for each gas standard cylinder employed by the ML for calibration and testing purposes during Month 7.

Table 3-1. Calibrated Gases in Use During Month 7.

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, Mobile Laboratory personnel operate under Report No. 66409-RPT-004, *Mobile Laboratory Operational Procedure*, which states that at least once during the scheduled shift, ML Operators shall perform a user-initiated zero-air and span check on the LI-COR, Picarro, and PTR-MS instruments. If a zero-air or span check fails, the ML Operators are instructed to inform the WRPS Project Manager, TerraGraphics Senior Scientist/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 sensitivity check. Zero-air checks ensure no contamination or interferences have affected the instrument’s readings.

Tables 3-2 through 3-7 display the zero-air and span checks performed during Month 7. For the zero-air and span checks performed on the PTR-MS the trace for toluene (m/z 93) is recorded.

Table 3-2. Zero-air Checks for the LI-COR CO_2 Monitor.

Date	Time	Instrument Check	Observed Result (ppmv)	Expected Result (ppmv)	Pass/Fail
03/13/2019	06:27	Zero	1.471	<50	Pass
03/25/2019	05:52	Zero	0.8	<50	Pass
03/26/2019	05:43	Zero	1.4	<50	Pass
03/27/2019	05:37	Zero	1.3	<50	Pass
03/28/2019	06:14	Zero	1.5	<50	Pass

Table 3-3. Span Checks for the LI-COR CO_2 Monitor.

Date	Time	Instrument Check	Observed Result (ppbv)	Expected Result (ppbv)	% Difference	Acceptance Criteria (%)	Pass/Fail
03/13/2019	06:30	Span	340	384.8	11.6	20	Pass
03/25/2019	05:52	Span	348	384.6	9.4	20	Pass
03/26/2019	05:43	Span	364	385	5.5	20	Pass
03/27/2019	05:37	Span	366	384	4.6	20	Pass
03/28/2019	06:14	Span	367	385.1	4.7	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
03/13/2019	06:40	Zero	0.11	<0.5	Pass
03/25/2019	06:30	Zero	0.08	<0.5	Pass
03/26/2019	05:55	Zero	0.08	<0.5	Pass
03/27/2019	05:50	Zero	0.08	<0.5	Pass
03/28/2019	06:19	Zero	0.08	<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
03/13/2019	07:00	Span	9.4	10.8	12.9	30	Pass
03/25/2019	06:30	Span	9.3	10.8	13.9	30	Pass
03/26/2019	06:05	Span	9.6	10.8	11	30	Pass
03/27/2019	06:00	Span	9.5	10.8	12	30	Pass
03/28/2019	06:19	Span	9.5	10.8	12	30	Pass

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

Date	Time	Instrument Check	Observed Result (ppbv)	Expected Result (ppbv)	Pass/Fail
03/13/2019	06:12	Zero	5	<20	Pass
03/25/2019	06:31	Zero	4.6	<20	Pass
03/26/2019	05:25	Zero	5.2	<20	Pass
03/27/2019	05:17	Zero	5.9	<20	Pass
03/28/2019	06:18	Zero	5.8	<20	Pass

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

Date	Time	Instrument Check	Observed Result (ppbv)	Expected Result (ppbv)	% Difference	Acceptance Criteria (%)	Pass/Fail
03/13/2019	06:26	Span	3667	3250	12.8	20	Pass
03/25/2019	06:31	Span	3600	3250	10.8	20	Pass
03/26/2019	05:37	Span	3620	3250	10	20	Pass
03/27/2019	05:31	Span	3626	3250	11.5	20	Pass
03/28/2019	06:18	Span	3672	3250	13	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 CO_2 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 (± 20%). The measurement accuracy of a properly calibrated instrument listed in the LI-COR factory specifications is ±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 (± 20%). The measurement accuracy of a calibrated instrument listed in the Picarro factory specifications is ±5% of reading.

4.1.4 Weather Station

The Airmar 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.*

4.2 Method Detection Limit Study

No MDLs were calculated during Month 7.

5.0 TEST RESULTS

This section details the testing and maintenance tasks performed during this month's activities.

Table 5-1. Mobile Laboratory Testing and Maintenance Activities.

Week	Date	Description	Activities/Observations
30	03/01/2019	ML Testing and Operator Training	Attempted Calibration and ML Operator's Read/Self-studied data processing related procedures
31	03/04/2019	ML Maintenance, Modifications and Training	Installation of Mass Flow Controllers and Software Tutorial Training for Igor Pro
	03/05/2019	ML Training	Toluene Training and Mock Deployment
	03/06/2019	ML Testing and Training	Transmission Efficiency Testing
	03/07/2019	ML Testing and Training	35' Heated Line Testing
	03/08/2019	ML Testing and Training	Carbotrap-300 Sorbent Testing
32	03/11/2019	ML Testing	208' Heated Line Testing
	03/12/2019	ML Testing	Ethyl Benzene Fragmentation Testing
	03/13/2019	ML Tour and Monitoring	ML Capabilities Tour and 200E Area Monitoring
	03/14/2019	ML Testing	DAQFactory Communication Testing and System Dilution Testing
	03/15/2019	ML Testing	Mass Flow Controller Acceptance Testing and Sample Dilution Testing
33	03/18/2019	ML Testing	Mass Flow Controller Acceptance Testing and Sample Dilution Testing
	03/19/2019	ML Testing	35' Heated Line System Dilution Testing
	03/20/2019	ML Maintenance and Testing	Tire Pressure verified at Les Schwab®[10], Washed Exterior of ML, and 208' Heated Line System Dilution Testing
	03/21/2019	ML Maintenance and Testing	Winter Tire Removal, 208' Heated Line Testing
	03/22/2019	ML Testing	Multi-point Calibration and Sample Line Testing
34	03/25/2019	ML Area Monitoring	Area Monitoring: A Farms
	03/26/2019	ML Area Monitoring	Area Monitoring: A Farms
	03/27/2019	ML Area Monitoring	Area Monitoring: A Farms
	03/28/2019	ML Area Monitoring	Fugitive Emissions: Diesel Generators
	03/29/2019	ML Testing	Thermosorb-N Sorbent Testing

5.1 Area Monitoring

During Month 7, the ML performed three days of area monitoring around the 200 East Area and 200 West Area of the Hanford Site. Area monitoring typically consists of the ML performing site survey loops around A Farm and C Farm, while attempting to remain downwind of any work activities occurring within those tank farms.

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[10] Les Schwab is a registered trademark of Les Schwab Warehouse Center, Inc., Bend, Oregon.

5.1.1 Discussion of Activities and Observations – Area Monitoring

Area monitoring was performed by the ML on March 13, 2019, and March 25, 2019, through March 26, 2019, in and around 200E primarily around A Farm with some sampling around C Farm. These included stationary measurements with the ML positioned downwind of potential odor sources including discharge from sewage trucks, septic tanks, cooking with a smoker, AX and AP stacks etc. Operators checked the Hanford Daily Report and conferred with appropriate Hanford staff so the ML could be positioned downwind in positions likely to monitor emissions from current site activities. More specific details will be given for individual monitoring days below.

5.1.2 Summary of Plume Fingerprinting Approach and Motivation for Future Statistical Analysis

An effort is underway to provide more detailed chemical analysis and interpretation of ML data in terms of the sources present on the Hanford Site especially as related to the presence of COPCs. The data on transient plumes detected by the ML in site monitoring during March 2019 have been analyzed for fingerprints of individual plumes and events observed during both stationary and mobile sampling of Hanford Site activities. The goal is to assess the fingerprints for possible statistical analysis in the future that can potentially distinguish specific sources from each other and from area and regional backgrounds and allow more targeted measurements of worker exposure to COPCs generated on the Hanford Site. This approach has been used successfully in studies of atmospheric chemistry for apportionment of chemical species from specific sources and locations.

The initial evaluation of plume fingerprints presented here focuses on PTR-MS measurements with an eye toward parameters characterizing individual plumes that will be explained and demonstrated below. Wind speed and direction are not included in this initial evaluation though they can easily be added to actual statistical computations. Plume fingerprints from March 13, 2019, will be examined and discussed in some detail in order to establish the basic methodology while the fingerprints from plumes observed on March 25, 2019, through March 28, 2019, will be presented and discussed more briefly in the figure captions. The goal is to provide an overview of the variety of fingerprints observed and motivate the potential use of statistical methods to classify fingerprint types and correlate them with sources. The requirement for this type of approach will be demonstrated by the large variety of plume fingerprints that follow. Implementation of advanced statistical methods, like principal components analysis (PCA) and positive matrix factorization (PMF), have the potential to improve results and can be explored in the future if desired.

5.1.3 Identification of Vapor Sources and Quantitative Analysis of Vapor Composition – Area Monitoring

5.1.3.1 March 13, 2019, Summary of Activities

The ML personnel arrived at the TerraGraphics warehouse at 05:45 on March 13, 2019, to prepare the ML for deployment to the Hanford Site. The Quality Assurance (QA)/Quality Control (QC) zero-air/span checks were performed on the LI-COR CO_2 monitor, the Picarro NH_3

analyzer, and the PTR-MS beginning at 05:58. The ML arrived at the A/AX parking lot, in the 200E Area, at 07:05. Mr. Mike Zabel and Ms. Jill Johnston, WRPS' Industrial Hygiene (IH) representatives, arrived at 08:21, for a tour and observation of the ML capabilities. The tour ended at 09:28 and ML Operators transitioned into mobile monitoring around the A Farm complexes within the 200E area. At 10:00, the ML parked downwind from AP Stack before performing another site survey loop of A Farms. Area monitoring was completed by 12:30. Operators returned their radio and checked out with the Central Shift Manager. The ML arrived back at the TerraGraphics warehouse at 13:30. Figure 5-1 shows the stationary monitoring locations on March 13, 2019.

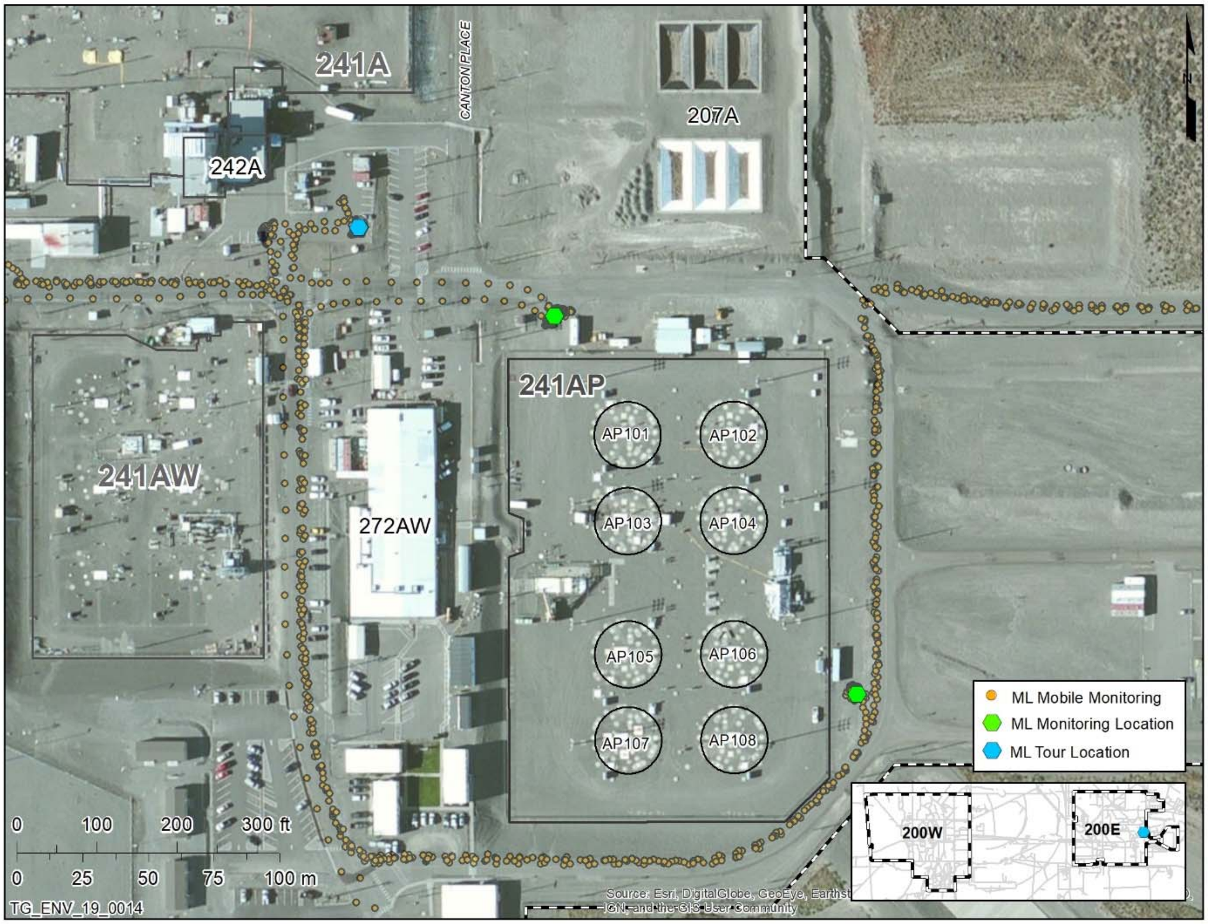

Figure 5-1. Location of the Mobile Laboratory for the Duration of the Monitoring Period.

Figure 5-2 shows a plume observed upon exiting the A/AX parking lot. For this initial study, plumes were identified in the data by an increase of benzene, CO_2, or both in the time trace of the data. Improvements in data analysis and plume identification are being developed and implemented to detect plumes based on multi-species composition. In this example, plumes appeared simultaneously in both the CO_2 and benzene signals and are labeled as CO_2/benzene plumes for the purposes of their initial plume evaluation.

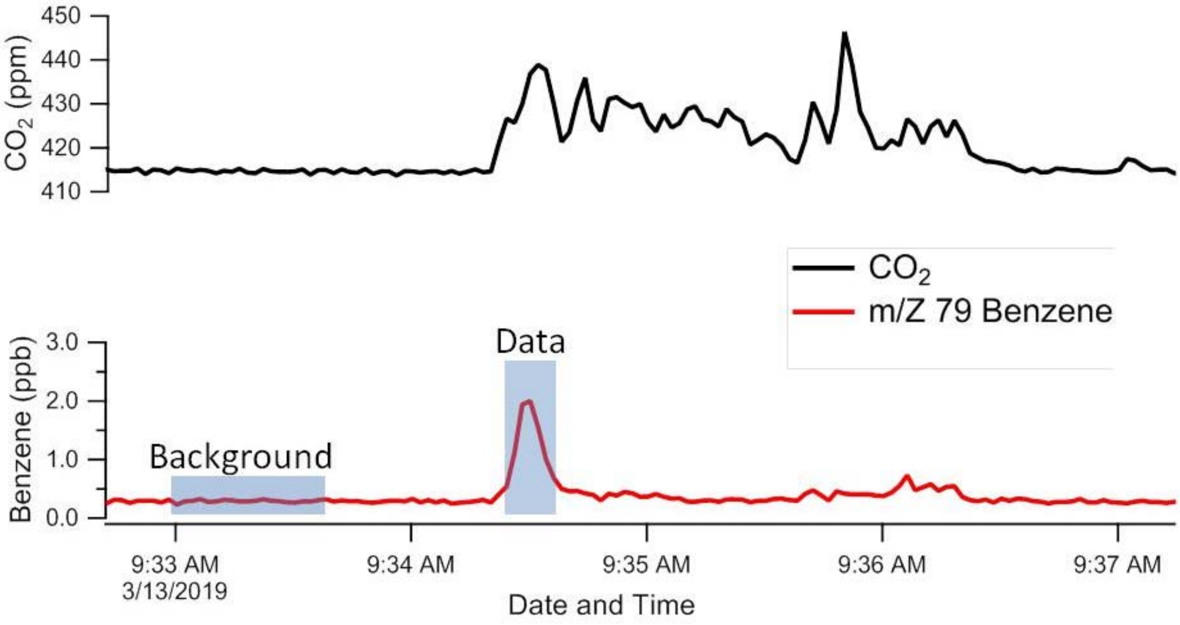

Figure 5-2. March 13, 2019, Leaving A/AX Parking Lot Simultaneous CO_2 and Benzene Plume.

All reports from 53005-81-RPT-019, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 1*, to present have provided details regarding the manner in which plume fingerprints are derived. Briefly, a beginning and an ending point is identified for the data from a given plume and a closely adjacent area before or after the plume is identified as the background as shown by the blue shaded areas in Figure 5-2 above. The average for the background is determined and subtracted from each point during the plume and the total integrated concentration for each m/z value during the plume is then calculated. The fingerprint is generated by only considering species with an average concentration above a value that can be adjusted and that contribute more than a percentage of the total to the plume that is also adjustable. The cut-off values used for all results presented here were 0.05 ppbv and 0.5 percent. The result is a fingerprint for the plume as displayed in Figure 5-3 for the same CO_2/benzene plume depicted in Figure 5-2.

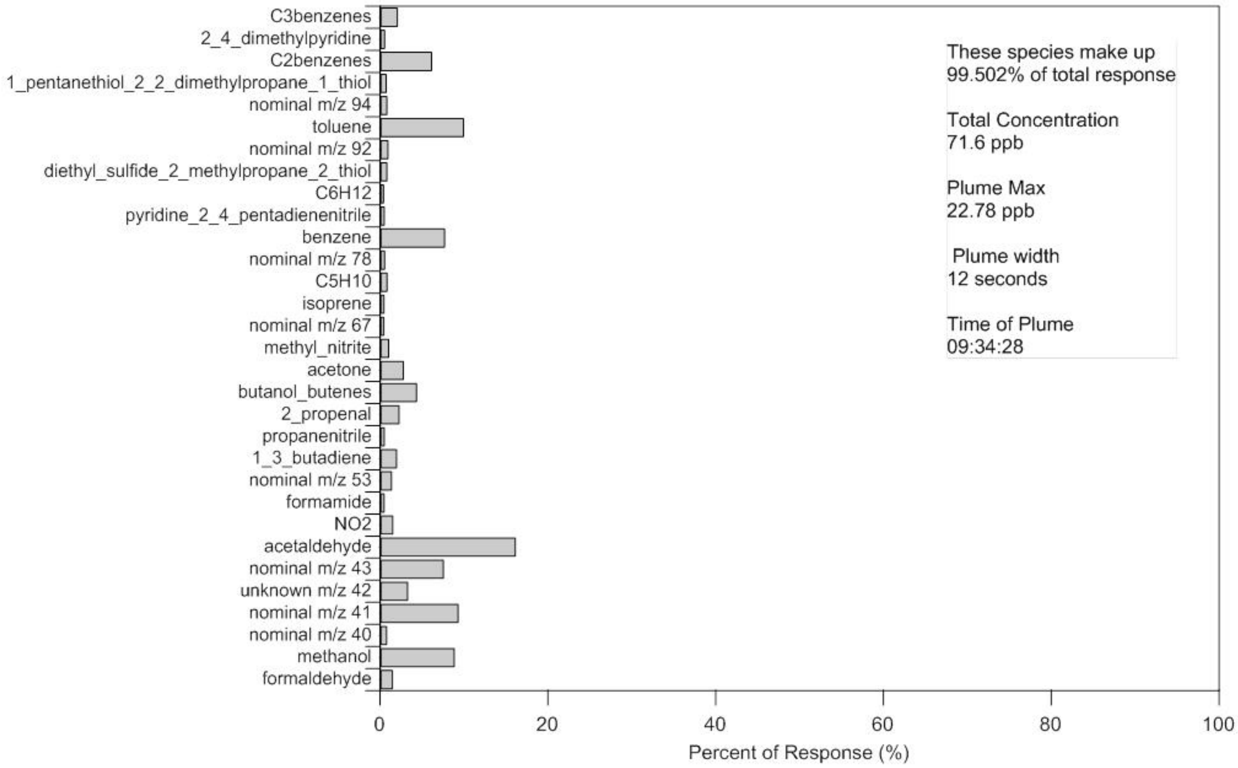

Figure 5-3. Fingerprint for March 13, 2019, Leaving A/AX Parking Lot Plume Displayed in Figure 5-2.

Additional values were displayed on the fingerprint graph to aid in plume characterization along with the percentage of the plume represented by the species in the fingerprint. These are the sum of integrated background subtracted concentrations of all species in the fingerprint to characterize the size of the plume, the maximum value and the width in time. Together these give another measure of the plume, and the time the maximum of the plume was observed for future comparison with other measurements made by the ML. The fingerprint of this plume is similar to previous observations of emissions from gasoline engines which is not surprising given that it was observed upon leaving a parking lot.

Figure 5-4 shows a different type of plume. It is characterized only by CO_2 though it closely follows the CO_2/benzene plume shown in Figure 5-2.

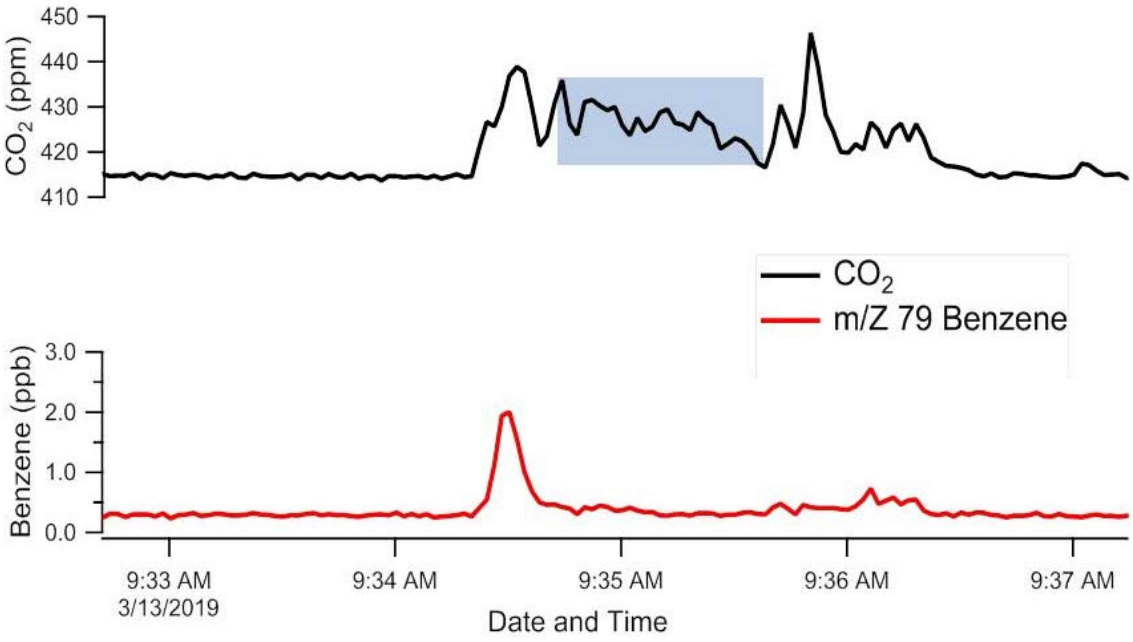

Figure 5-4. March 13, 2019, Plume Characterized by Long Tail of CO_2 from Previous CO_2/Benzene Plume.

The plume in Figure 5-4 was averaged over the area indicated by the blue box with background subtraction as usual. Although it follows a brief exhaust emission plume, the composition of the fingerprint is quite different as shown in Figure 5-5.

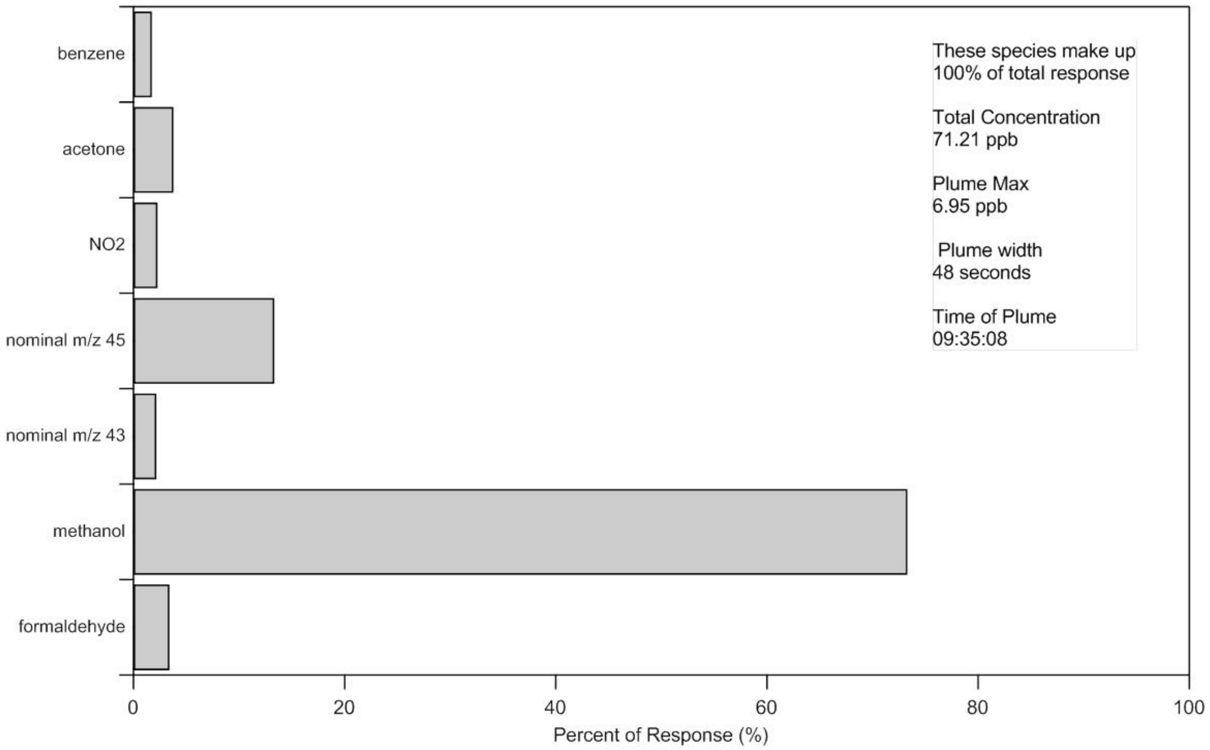

Figure 5-5. March 13, 2019, Fingerprint for Long Tail on Previous Plume Characterized by CO_2.

The obvious primary component of this plume is methanol in sharp contrast with the emission plume immediately preceding it. This example illustrates the rich variety of plume behavior that statistical analysis including wind speed and direction and other parameters apart from the PTR-MS signals (such as CO_2) may help delineate.

Another recent development is the definitive assignment of nominal m/z 46 to NO_2^+ resulting from charge transfer ionization of NO_2 by O_2^+ and further discussion is included in Section 5.2 This was confirmed both by the exact mass assignment resulting from the mass defect inherent in NO_2^+ and the fact that there is a non-zero background at the same exact mass corresponding to NO_2^+ formed in the ion source. Values of the charge transfer rate constant for formation of NO_2^+ by O_2^+ charge transfer are being researched to further confirm this assignment and the PTR-MS will then be calibrated for NO_2 measurements using a standard. This will serve as an extremely useful indicator of NO_2 from exhaust and other plumes and frequently is the primary species as shown in Figure 5-6 in a CO_2/benzene plume downwind from AP Stack.

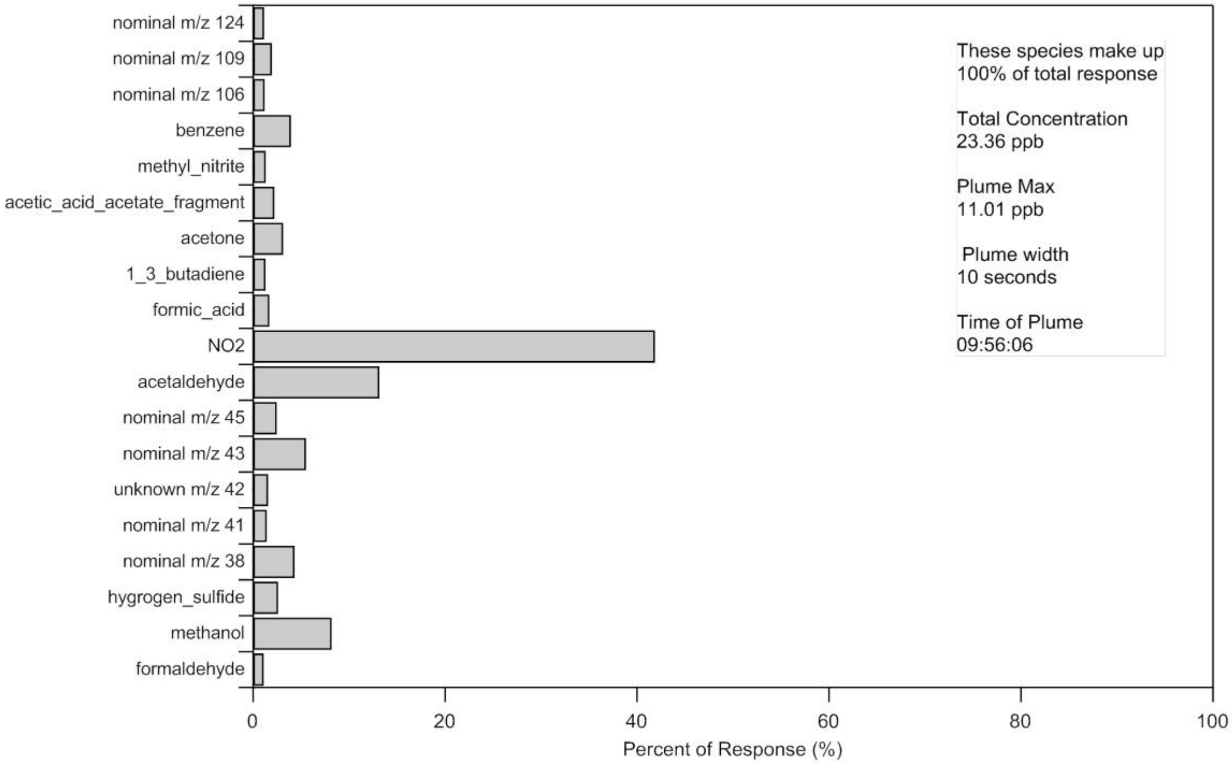

Figure 5-6. March 13, 2019, CO_2/Benzene Plume Observed Downwind of AP Stack Dominated by NO_2.

In addition to the dominant contribution of NO_2 as described above, contributions are observed from methanol, hydrogen sulfide, acetaldehyde, acetone, benzene and a smaller contribution from methyl nitrite in another fairly unique fingerprint that would lend itself to statistical analysis.

At 10:30, the ML began A Corridor loops. In Figures 5-7 through 5-9, plumes are observed with four different looking fingerprints all based on plumes located from the CO_2 time trace.

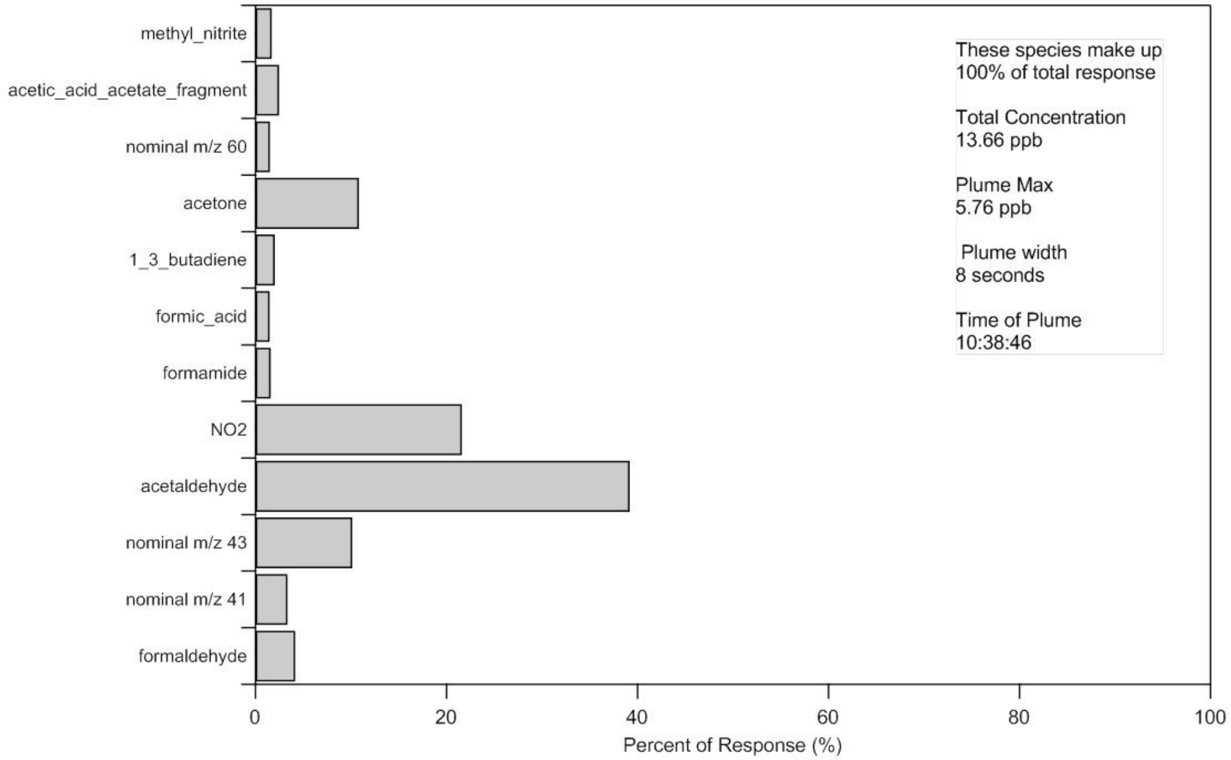

Figure 5-7. March 13, 2019, Plume from A Corridor Loop Dominated by Acetaldehyde, NO_2, and Acetone.

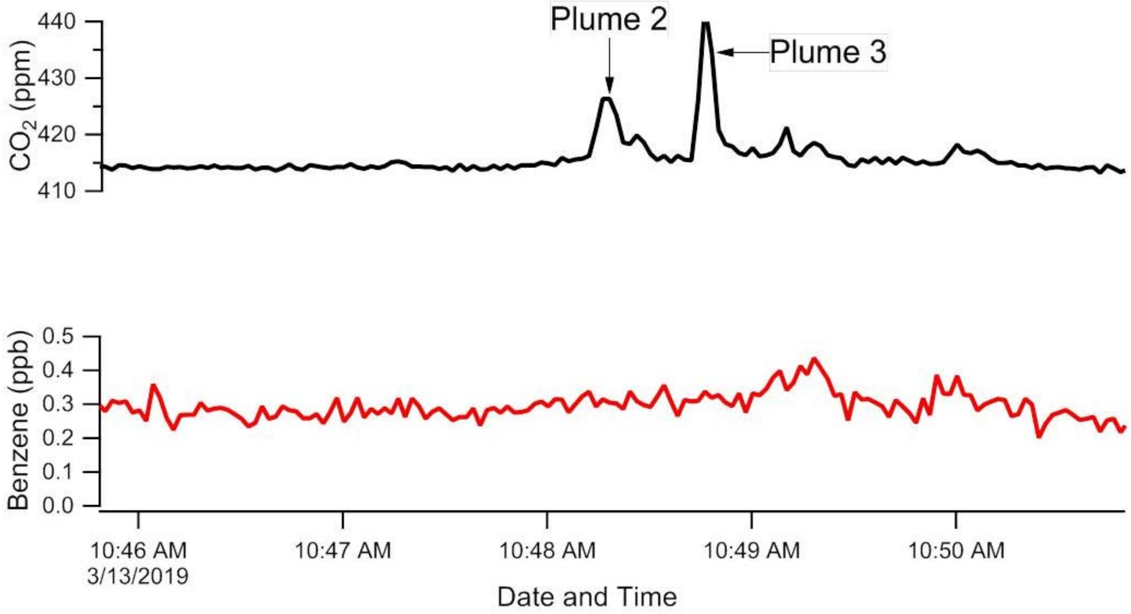

Figure 5-8. March 13, 2019, Leaving A/AX Parking Lot Time Trace of Two Sequential Plumes Indicated only by CO_2 Signal.

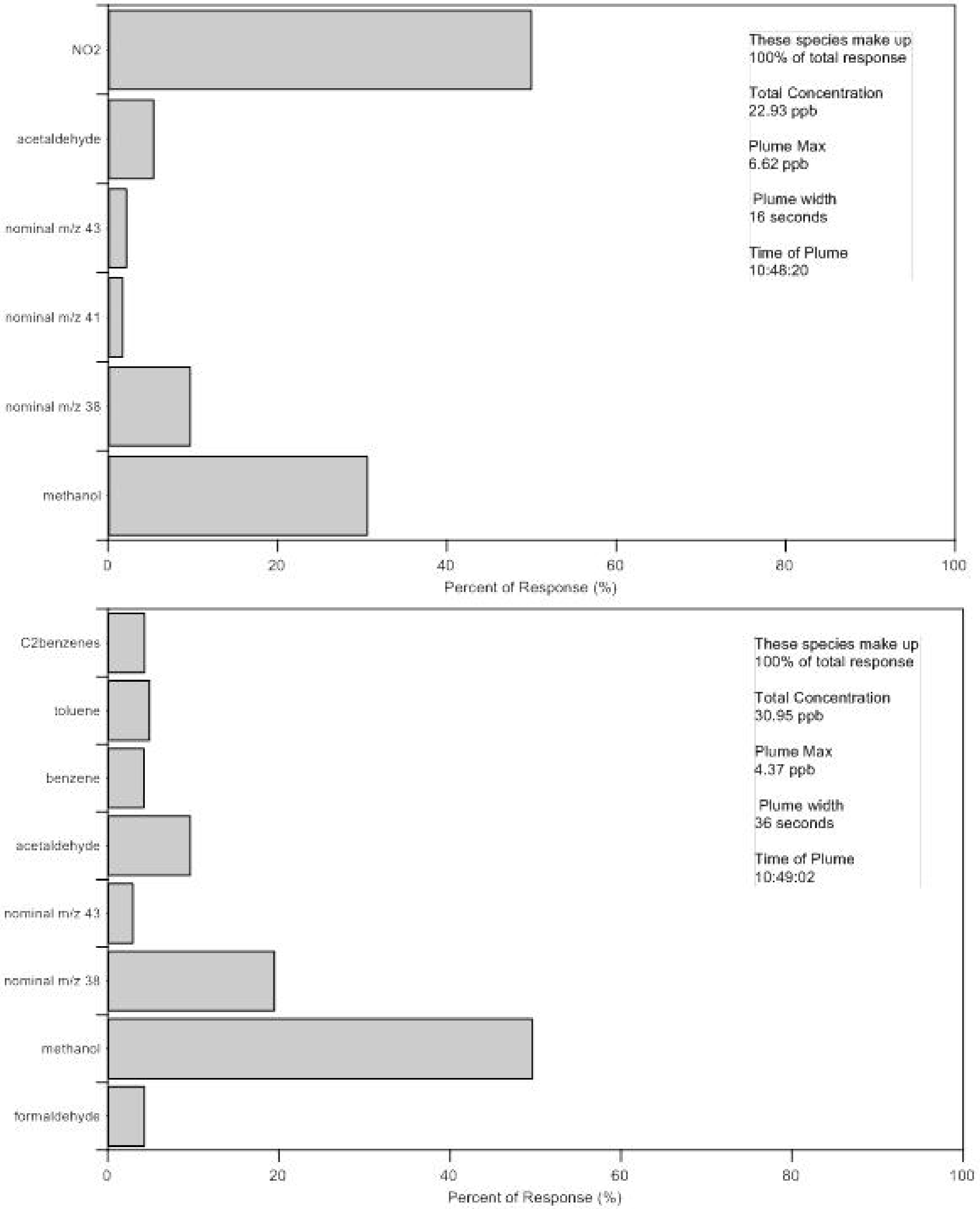

Figure 5-9. March 13, 2019, Fingerprints of the Two Sequential Plumes Shown in Figure 5-8 Indicating very Different Compositions.

Figure 5-8 shows the time trace of two plumes very close together in time present only in the CO_2 trace and not benzene. Figure 5-9 shows the fingerprints of both of these plumes. Although they both have a large contribution from methanol, the largest component of Plume 2 is NO_2 with some acetaldehyde. The plume 3 fingerprint shows no NO_2 but does have acetaldehyde and also benzene, toluene and C_2-benzenes. All components are found in engine emissions but despite the proximity in time, the substantial difference in these fingerprints suggests that they may be from different sources. Since the ML was moving, GPS location and wind speed and direction might add information in source and location when analyzed statistically. Again, the primary purpose in examining these plumes is to survey the range of fingerprints observed at the Hanford Site by the ML and assess these data for suitability of further statistical analyses to better ascertain location and nature of sources.

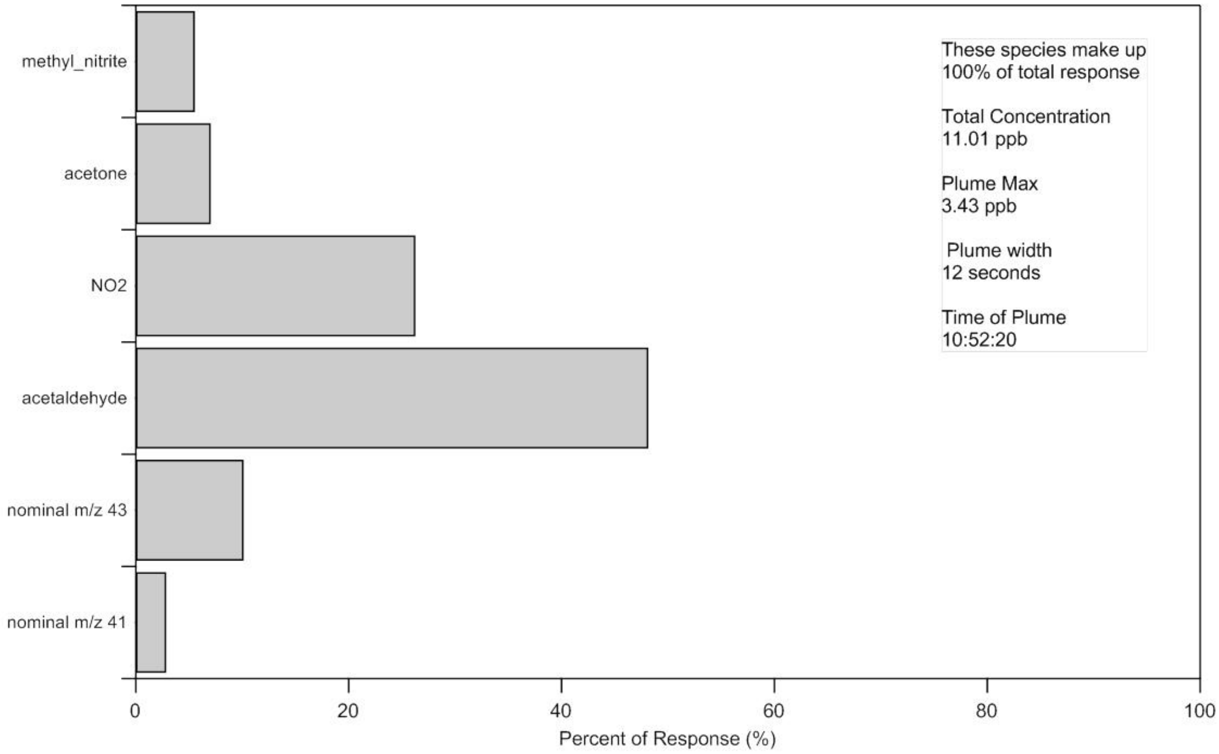

Figure 5-10. March 13, 2019, Plume from A Corridor Loop Dominated by Acetaldehyde and NO_2 but with Acetone and Methyl Nitrite Contribution.

These four plumes all have different types of signatures with components from engine emission plumes but also possible contributions from other sources. It is apparent that the signatures of the wide variety of plumes cannot be easily determined by inspection, further supporting the concept of using statistical methods with additional parameters to unravel contributions from various sources.

One additional interesting plume was observed on March 13, 2019, clearly generated by a Gator™[11] that the ML staff reported as having emitted a strong odor as it drove by. The fingerprint is shown in Figure 5-11.

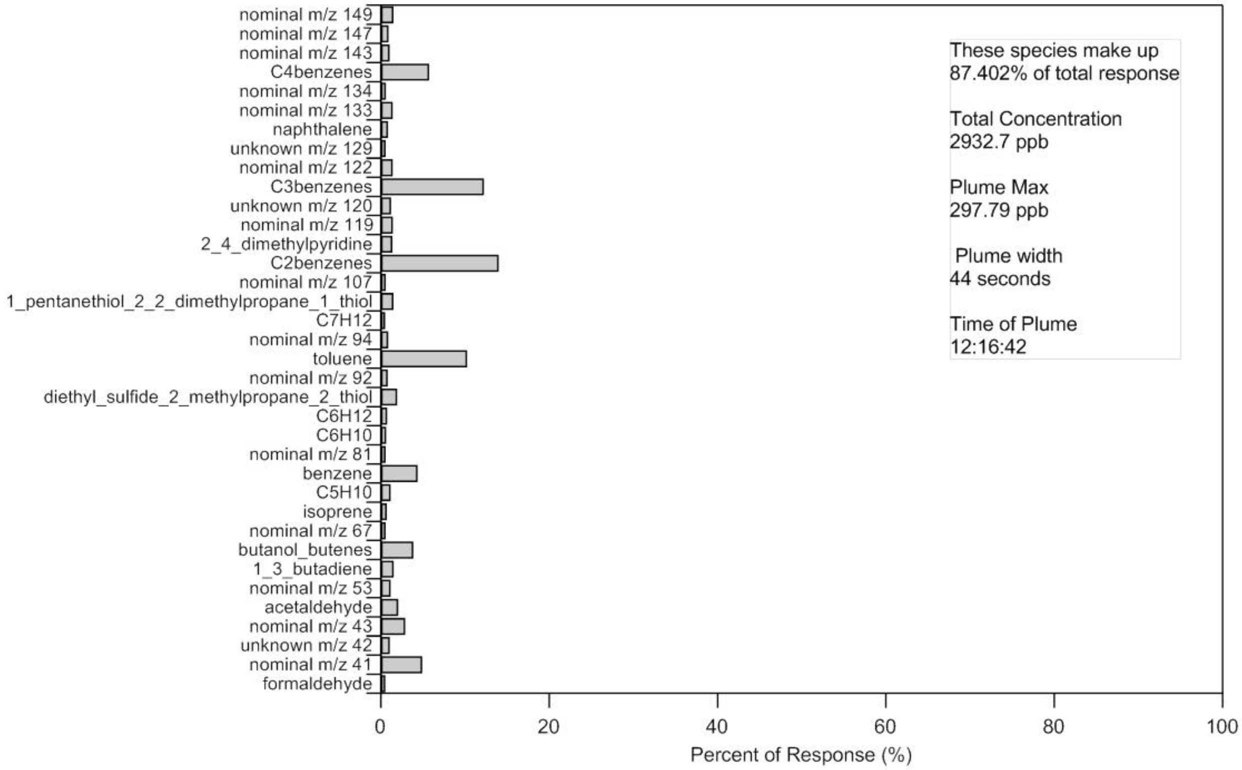

Figure 5-11. March 13, 2019, Fingerprint of Emissions from Gator Detectable by Odor as it Drove past the Mobile Laboratory.

This is clearly a large concentration plume that contains components characteristic of gasoline engine emissions. The relative abundance of components is somewhat unique with C_2- and C_3-benzenes being the largest components and a significant contribution from C_4-benzenes as well. This fingerprint is diagnostic of an engine in a very poor state of tune that contains atypical levels of unburned fuel in the exhaust. It demonstrates the power of fingerprint identification to identify and diagnose sources.

5.1.3.2 March 25, 2019, Summary of Activities

On March 25, 2019, the ML arrived on the Hanford Site and ML personnel checked in with the Central Shift Office (CSO) at 06:23. The ML Operators began mobile monitoring of A Farms at 06:36. The ML monitored in the area of the septic tanks located near the 242A Evaporator from 07:03 to 08:02. At 08:31, the ML was parked on the northeastern side of AP Farm until 09:46. After performing a site survey loop of A Farms, the ML was parked on the southeastern corner of the septic tanks.

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[11] Gator is a trademark of Deere & Company, Moline, Illinois.

After another site survey loop, the ML was parked on the northeastern corner of AP Farm downwind of a porta-potty. At 12:28, the ML relocated to the southeastern corner of 241-AW, when a Shift Office Event Notification (SOEN) alert notified operators that odors had been reported in 2715 AW. Mr. Eugene Morrey of WRPS was called at 12:30 for the location of 2715 AW. At 12:33, the ML was parked downwind of 2715 AW. At 13:38, the odors reported surveyed below background levels and access was restored to the structure. The ML Operators checked out with the CSO at 14:00 and departed the site.

Figures 5-12 through 5-16 show the variety of plume composition observed during mobile monitoring of A Farm loops from 06:36 to 07:03.

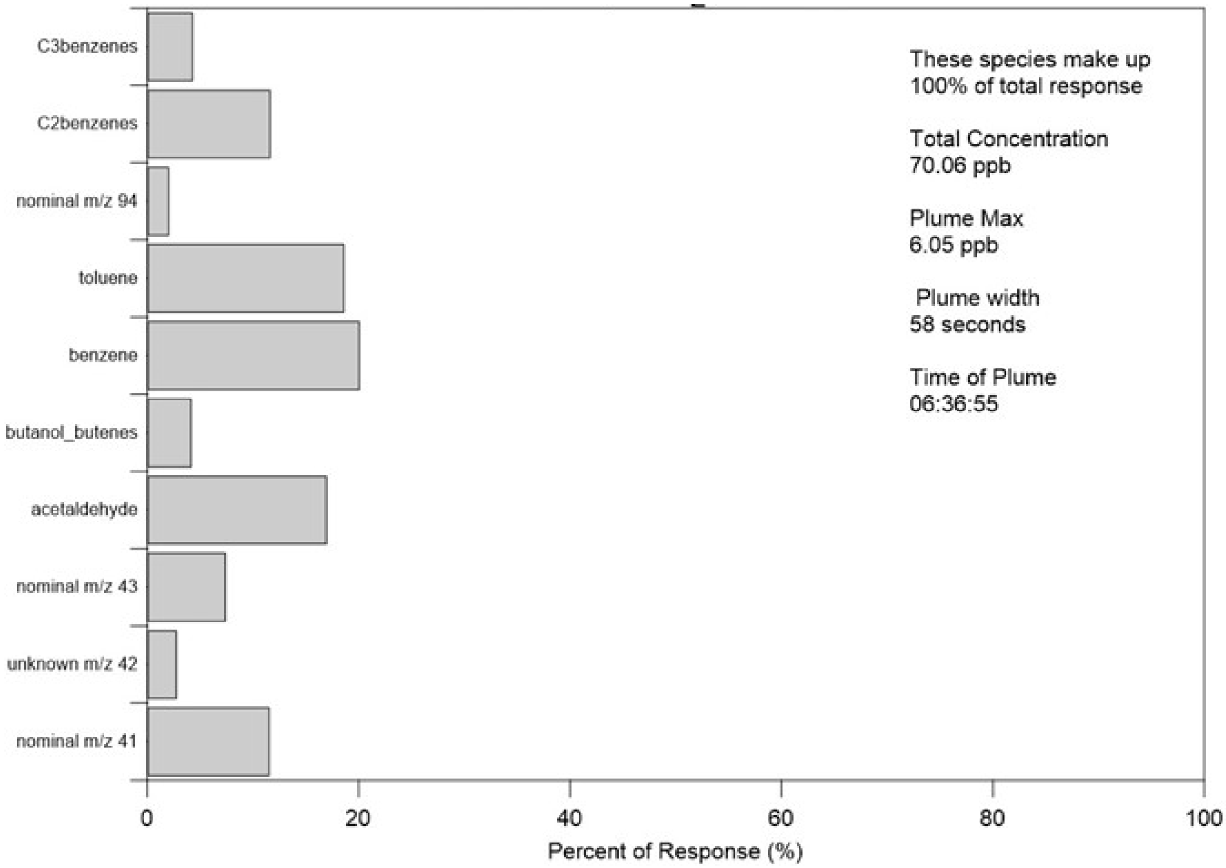

Figure 5-12. March 13, 2019, A Farm Loops Benzene/CO_2 Plume Indicative of Gasoline Engine Emissions.

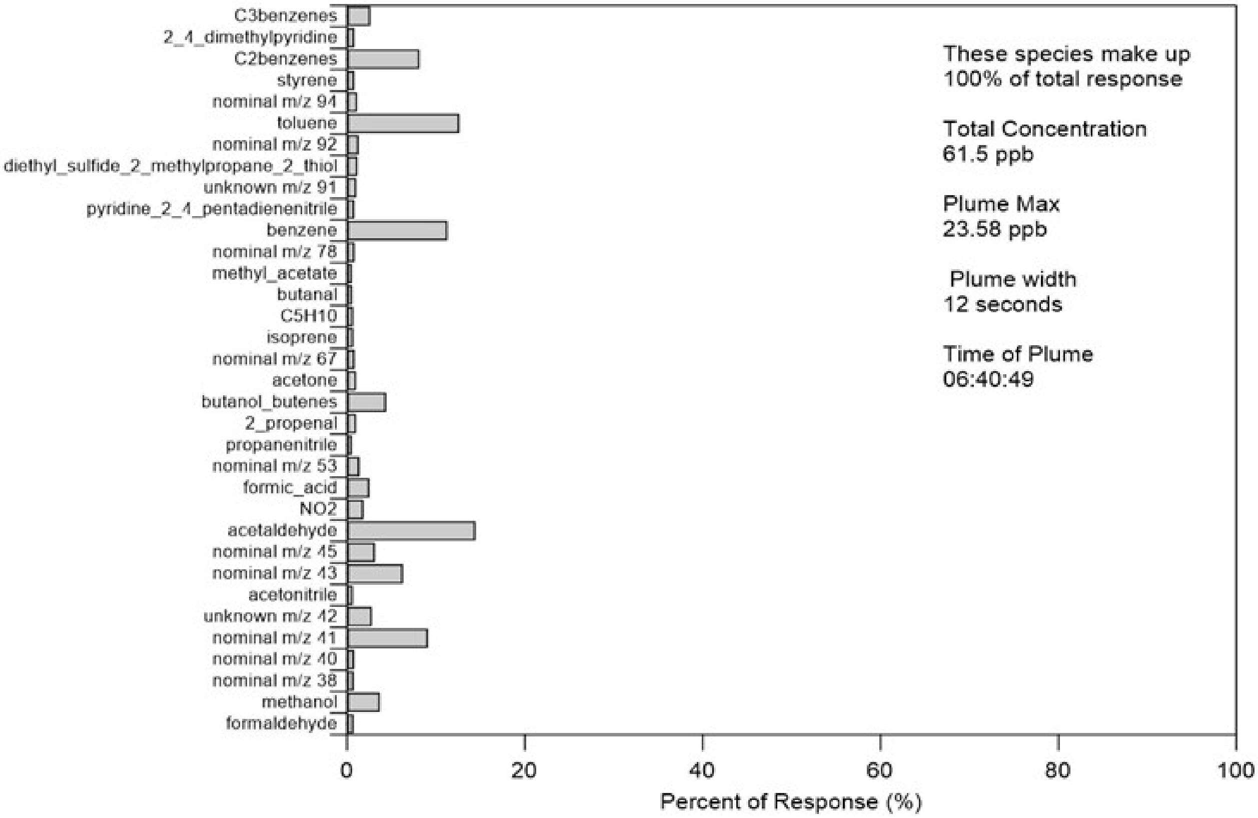

Figure 5-13. March 25, 2019, A Farm Loops Benzene/CO_2 Plume with Components from Gasoline Engine Emissions with Additional Contributions from Butenes and/or Butanol.

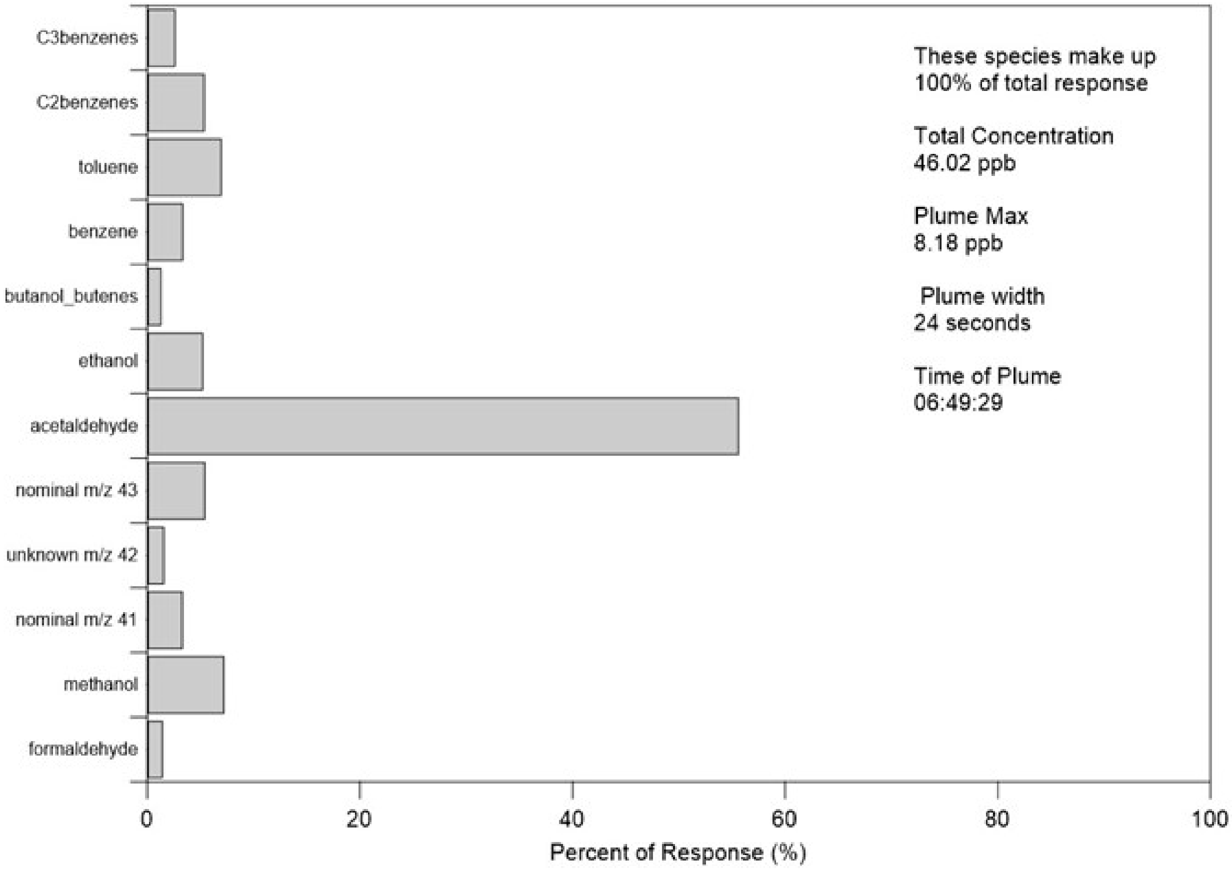

Figure 5-14. March 25, 2019, A Farm Loops Benzene Plume Composed Primarily of Acetaldehyde Indicative of Diesel Emissions.

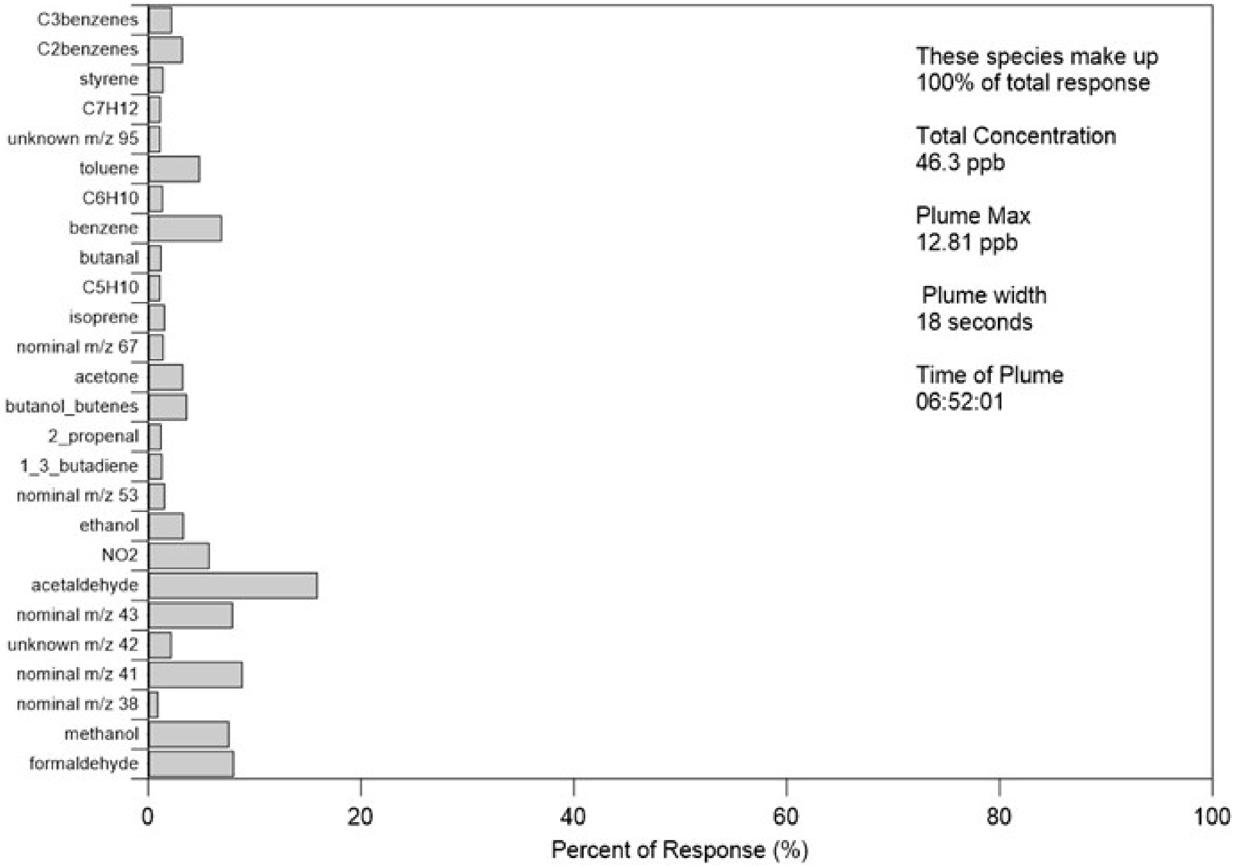

Figure 5-15. March 25, 2019, A Farm Loops Benzene/CO_2 Plume with Emission Markers and Several Additional Species.

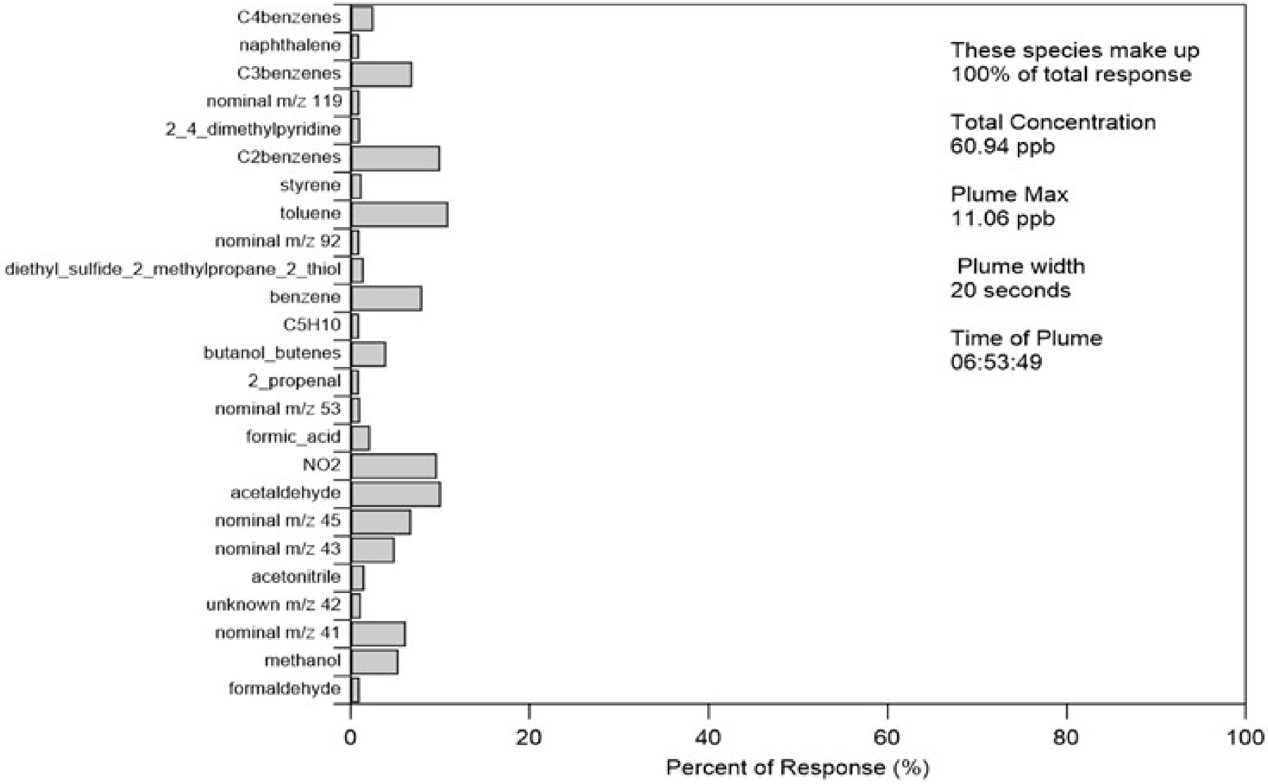

Figure 5-16. March 25, 2019, A Farm Loops Benzene/CO_2 Plume with a Different Distribution of Emission Markers with Contributions from Additional Species Including a Thiol Compound.

Figures 5-17 and 5-18 show fingerprints of plumes observed while the ML was parked near septic tanks. These show a great deal of variability although the ML was stationary.

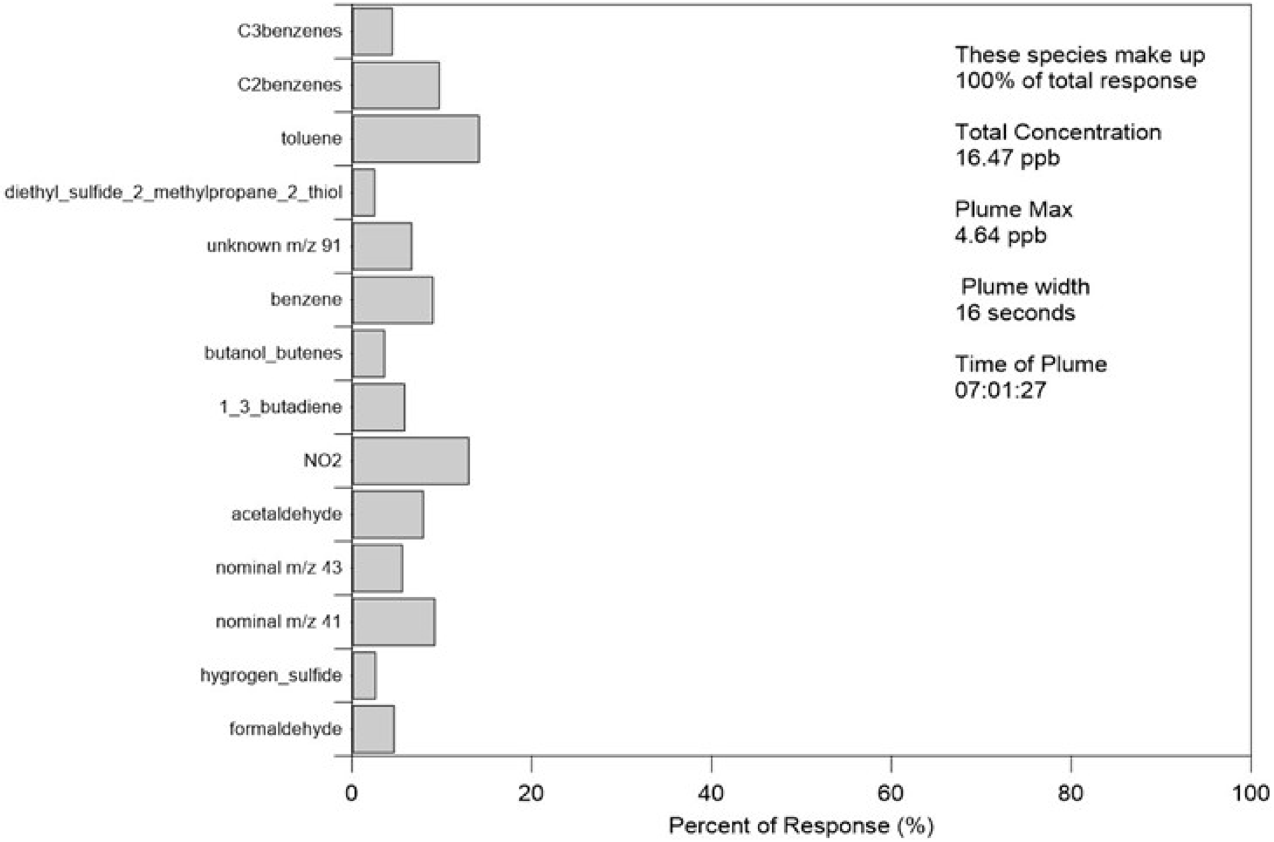

Figure 5-17. March 25, 2019, Benzene Plume near Septic Tank.

In Figure 5-17, note contributions from hydrogen sulfide and diethyl sulfide 2-methylpropane thiol, fugitive emission markers. The unknown m/z 91 is present as well.

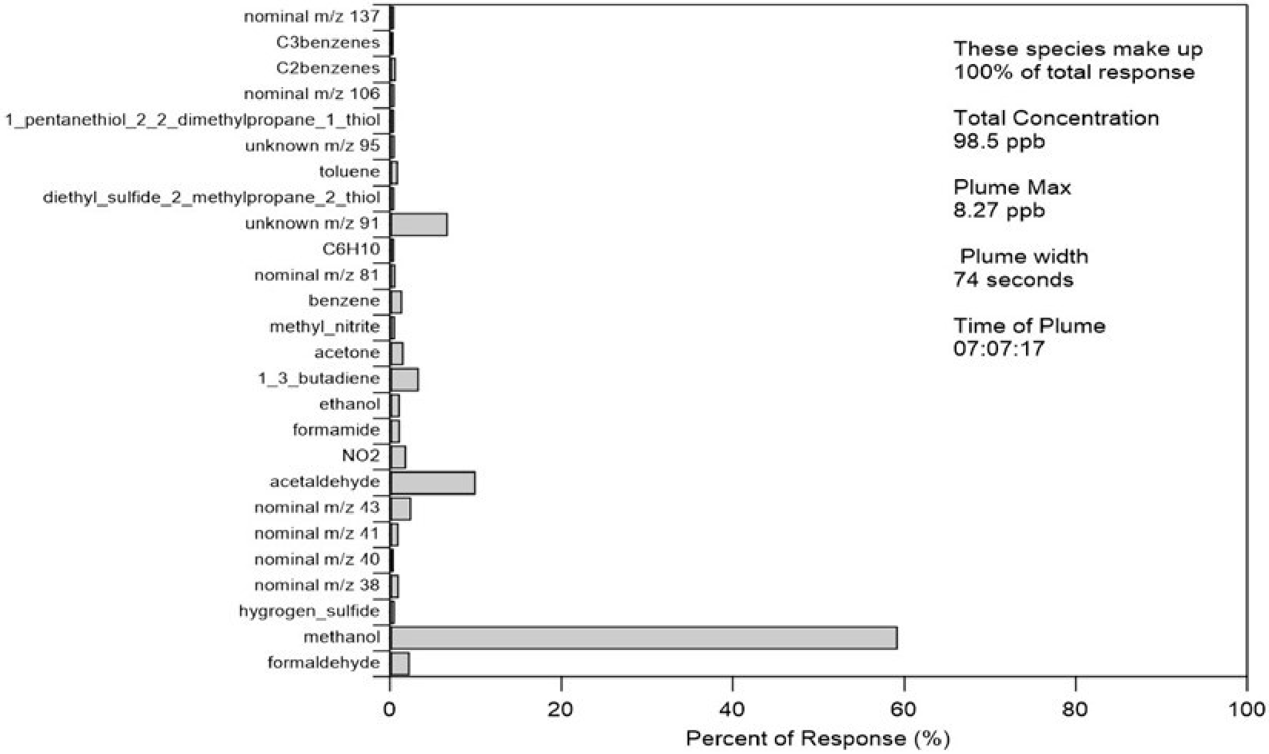

Figure 5-18. March 25, 2019, Plume from Septic Tank Composed Primarily of Methanol with Small Contributions from Hydrogen Sulfide, Diethyl Sulfide 2-methylpropane Thiol, and m/z 91.

Figures 5-19 through 5-21 show the only significant plumes observed over the next few hours which occurred during A Farm loops.

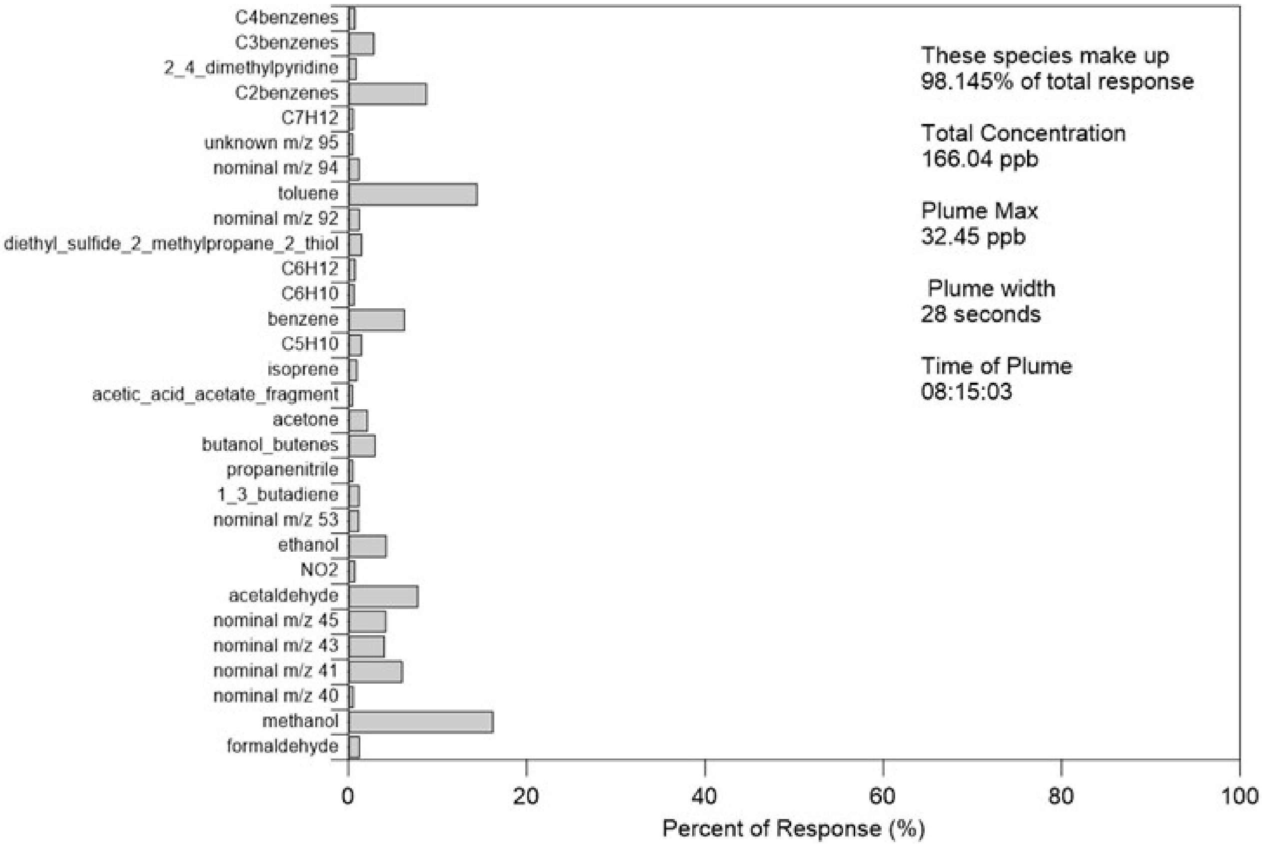

Figure 5-19. March 25, 2019, Benzene/CO_2 Plume from Gas Truck and Generator Emissions.

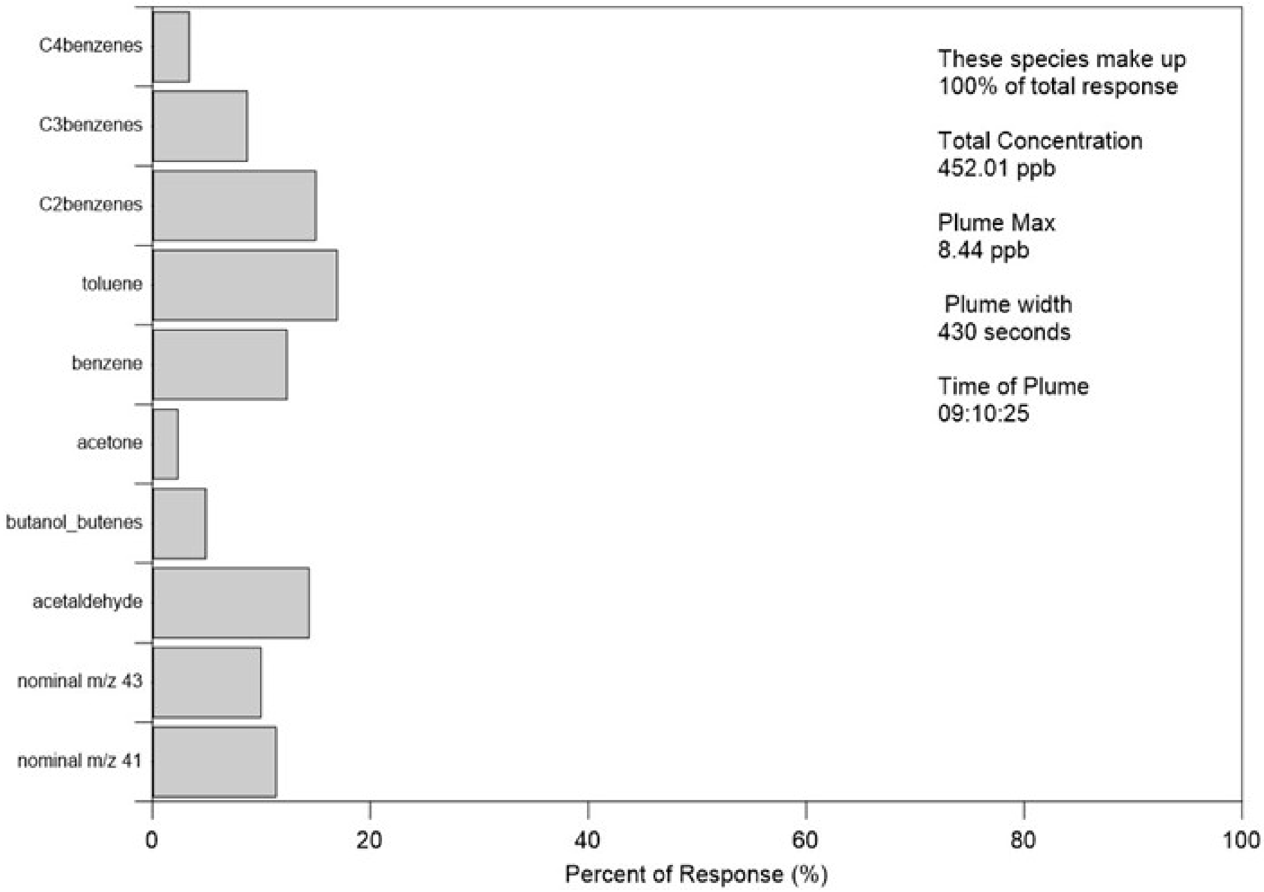

Figure 5-20. March 25, 2019, Benzene Plume Indicative of Gasoline Engine Emissions.

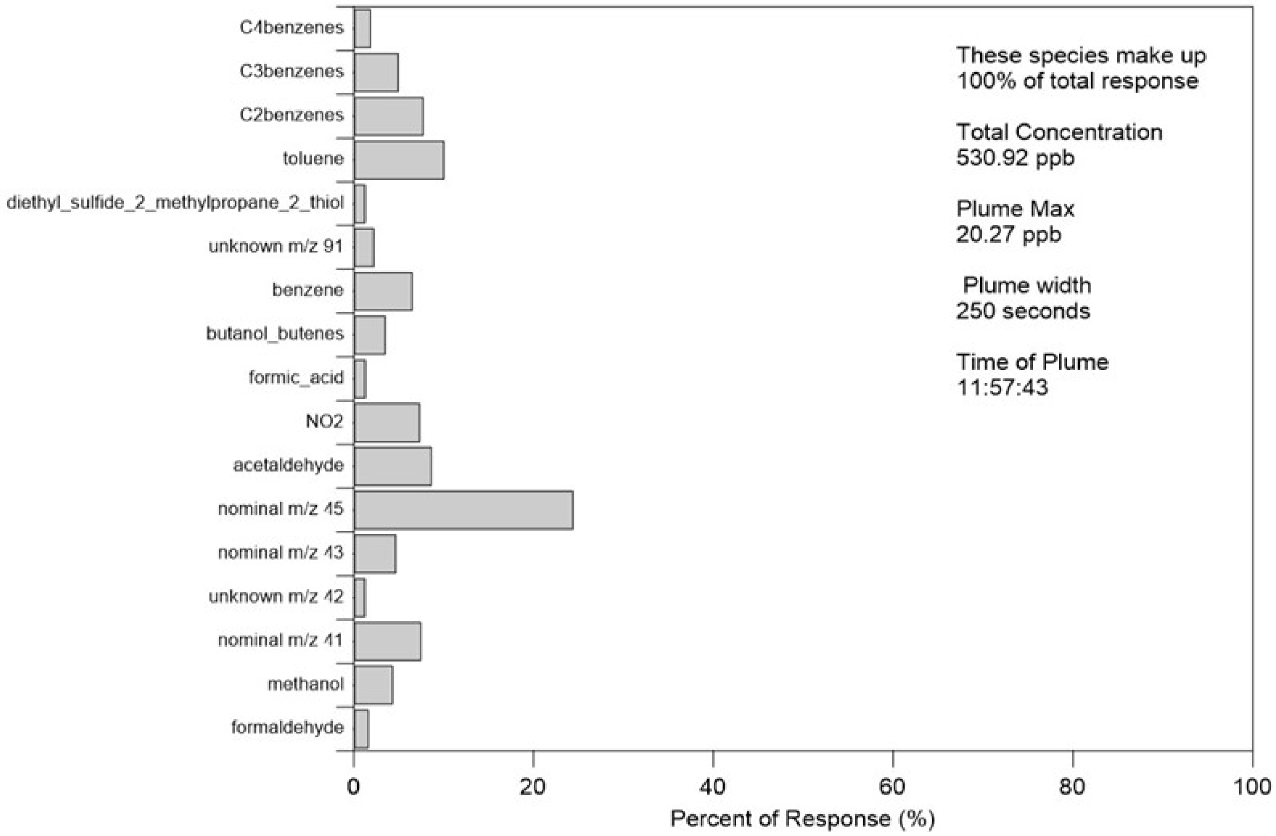

Figure 5-21. March 25, 2019, Benzene CO_2 Plume with Engine Emission Markers in a Different Distribution with Contributions from Possible Fugitive Emission Markers.

Two more significant plumes were observed on March 25, 2019, one downwind of a porta-potty and another downwind of 2715 AW where odors had been detected.

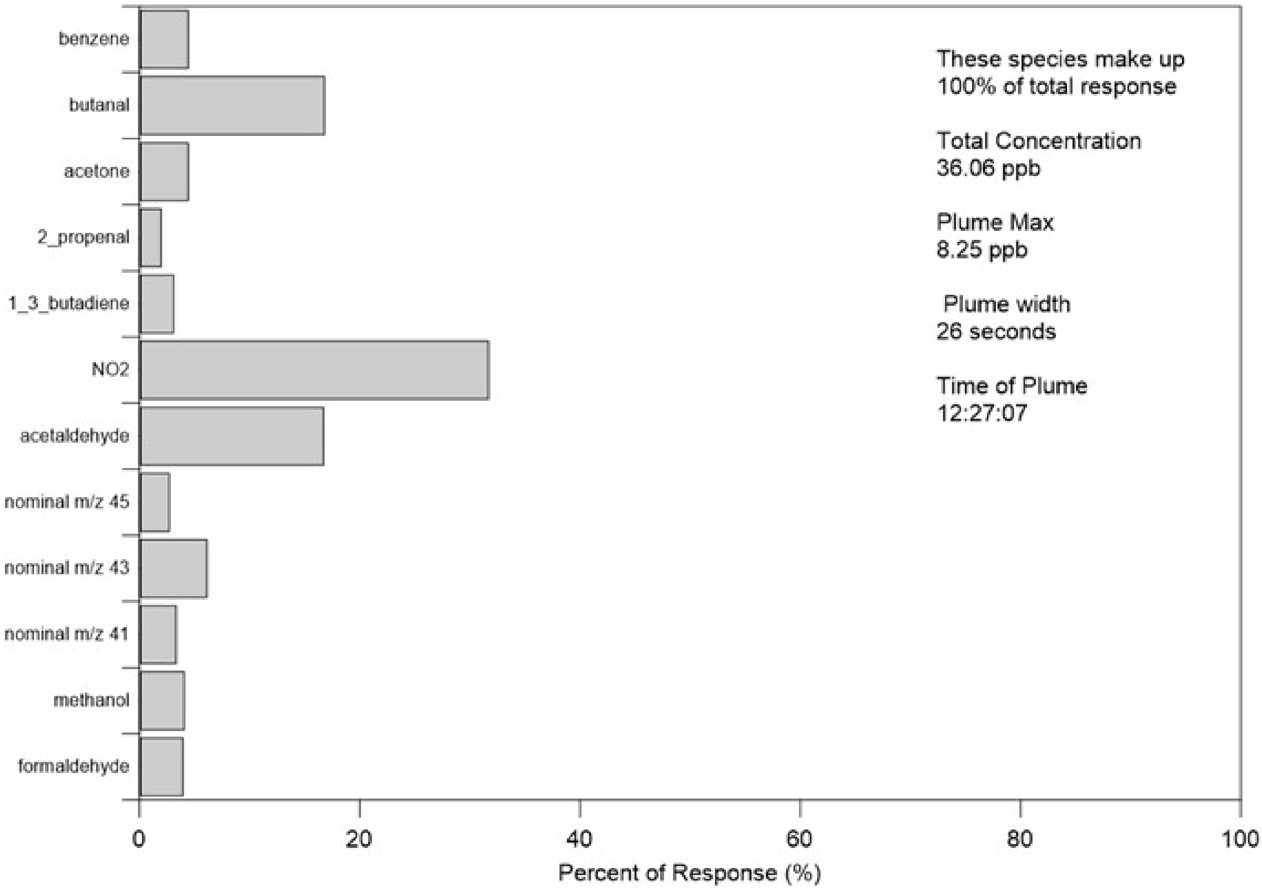

Figure 5-22. March 25, 2019, Plume Downwind of Porta-Potty Consisting Mainly of NO_2 with Contributions from Acetaldehyde, Butanal, and Propenal.

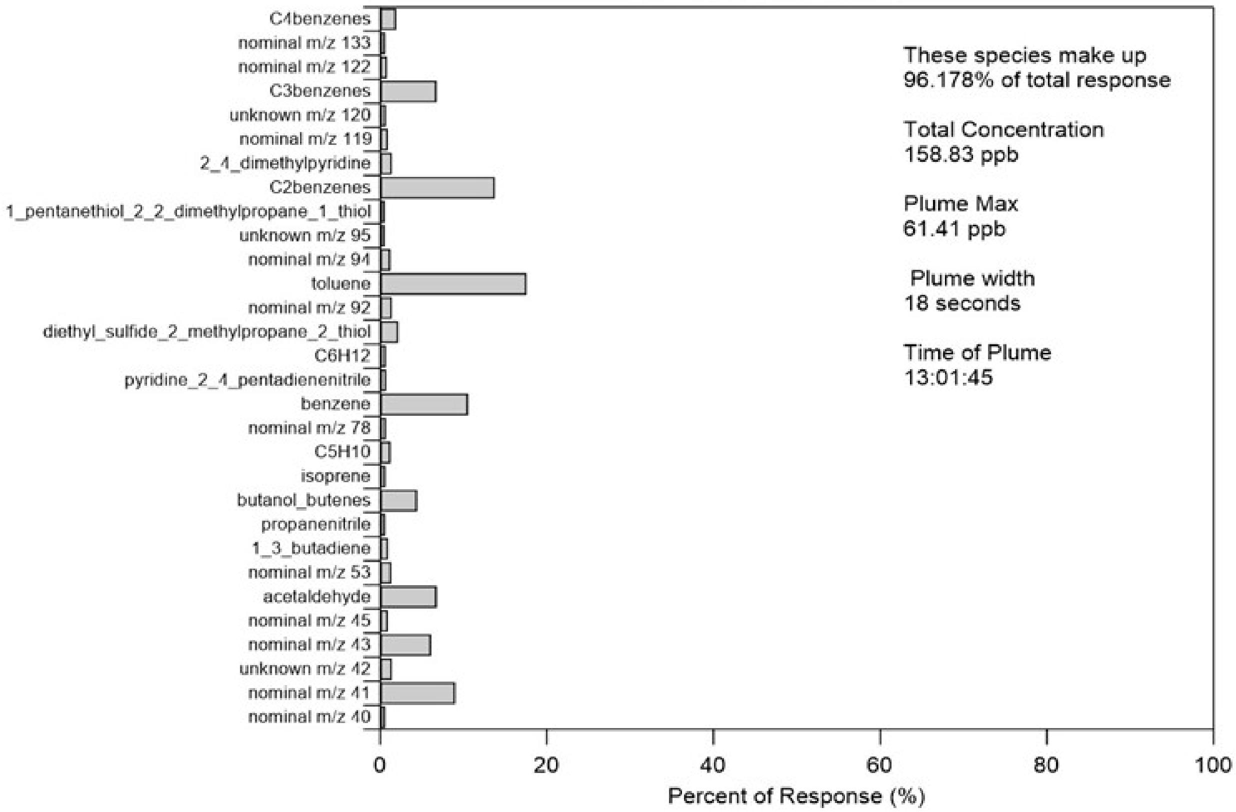

Figure 5-23. Mobile Laboratory Positioned Downwind of 2715 Where Odors had been Detected on March 25, 2019.

The fingerprint in Figure 5-23 seems to be primarily emission markers but with contributions from pyridine and thiol compounds that could result in detectable odors.

5.1.3.3 March 26, 2019, Summary of Activities

On March 26, 2019, the Operators arrived at the ML at 04:55. The QA/QC zero-air/span checks were performed on the LI-COR CO_2 monitor, the Picarro NH_3 analyzer, and the PTR-MS beginning at 05:10. The ML arrived on the Hanford Site and personnel checked in with the CSO at 06:05. The ML began mobile monitoring at 06:15. After a site survey loop, the ML parked on the southeastern corner, downwind, of the septic tanks located near the 242A Evaporator. At 07:09, Mr. Greg Hanson (TerraGraphics) and Ms. Angie Perez (WRPS) arrived for a tour of the ML. After another site survey loop, the ML parked downwind from work occurring inside of AP Farm at 08:26. At 10:50, a site survey loop was completed before the ML parked near the northeastern region of AP Farm. The ML moved west, close to the fence line between A Farm and AY Farm at 11:07.

After an hour, the ML moved from the previous location and began another A Farm survey. At 12:33, the ML parked east of AP Farm for approximately 15 minutes before relocating to the parking lot for the 242A Evaporator. At 14:15, ML Operators checked out with the CSO and departed the site. The ML arrived back at the TerraGraphics warehouse at 15:07.

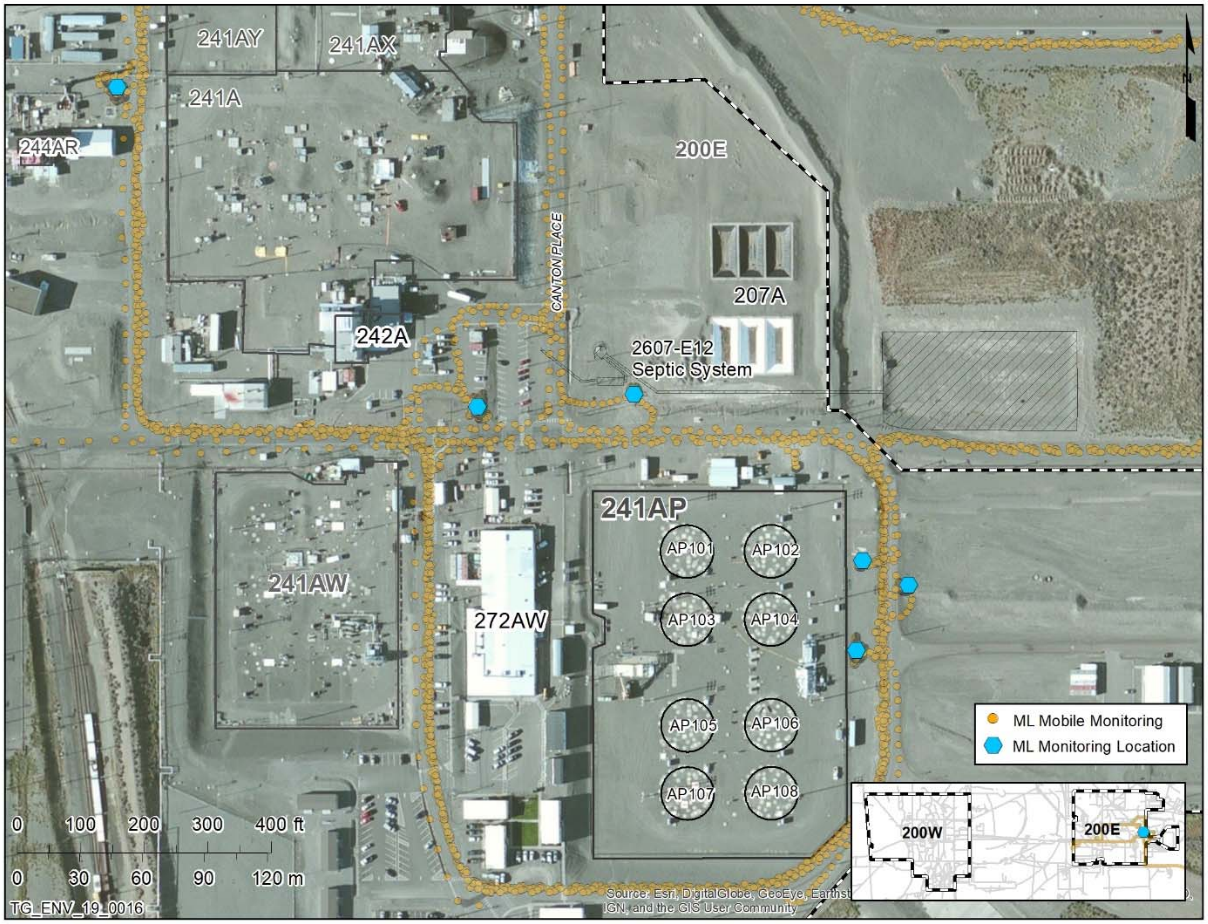

Figure 5-24. Location of Mobile Laboratory During Monitoring Period.

Figures 5-25 through 5-28 show fingerprints of plumes detected by the ML during initial 274AW area loops on March 26, 2019.

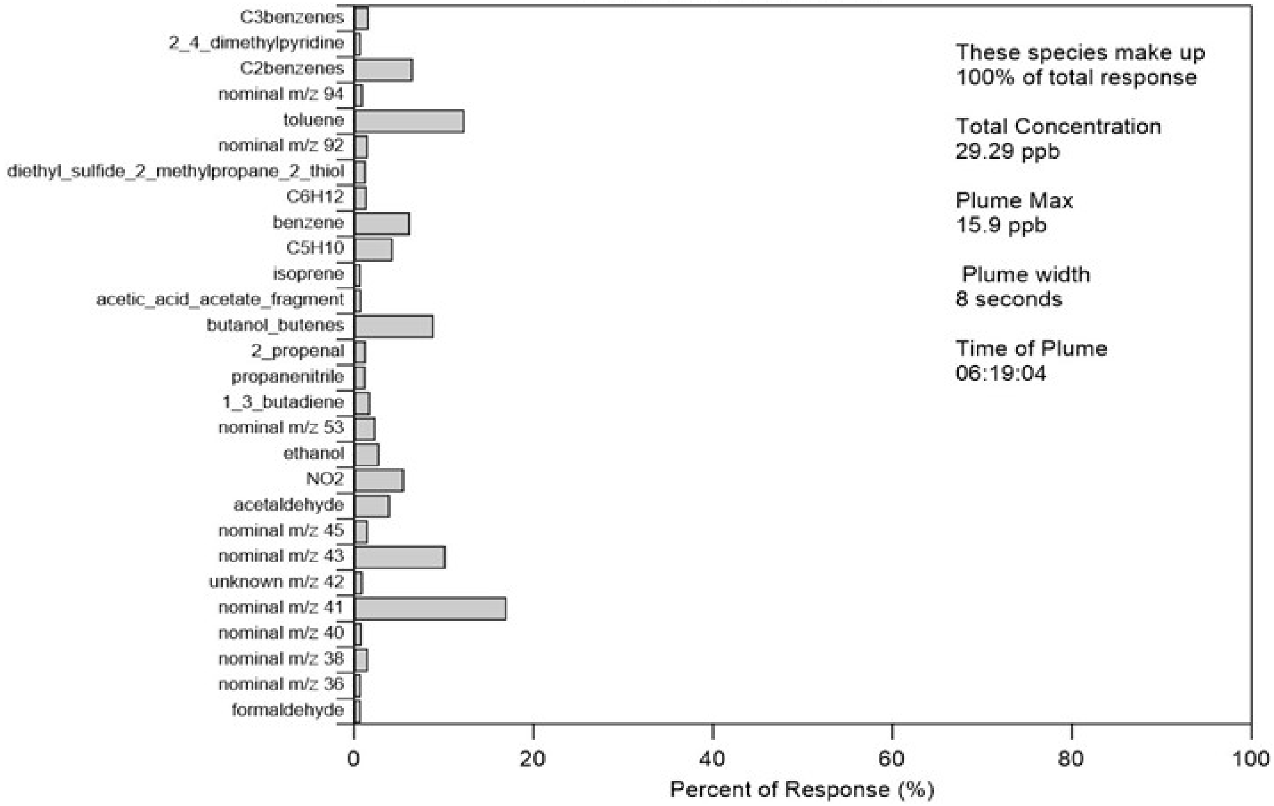

Figure 5-25. March 26, 2019, Benzene Plume Primarily Containing Emission Markers Combined with Several Other Components.

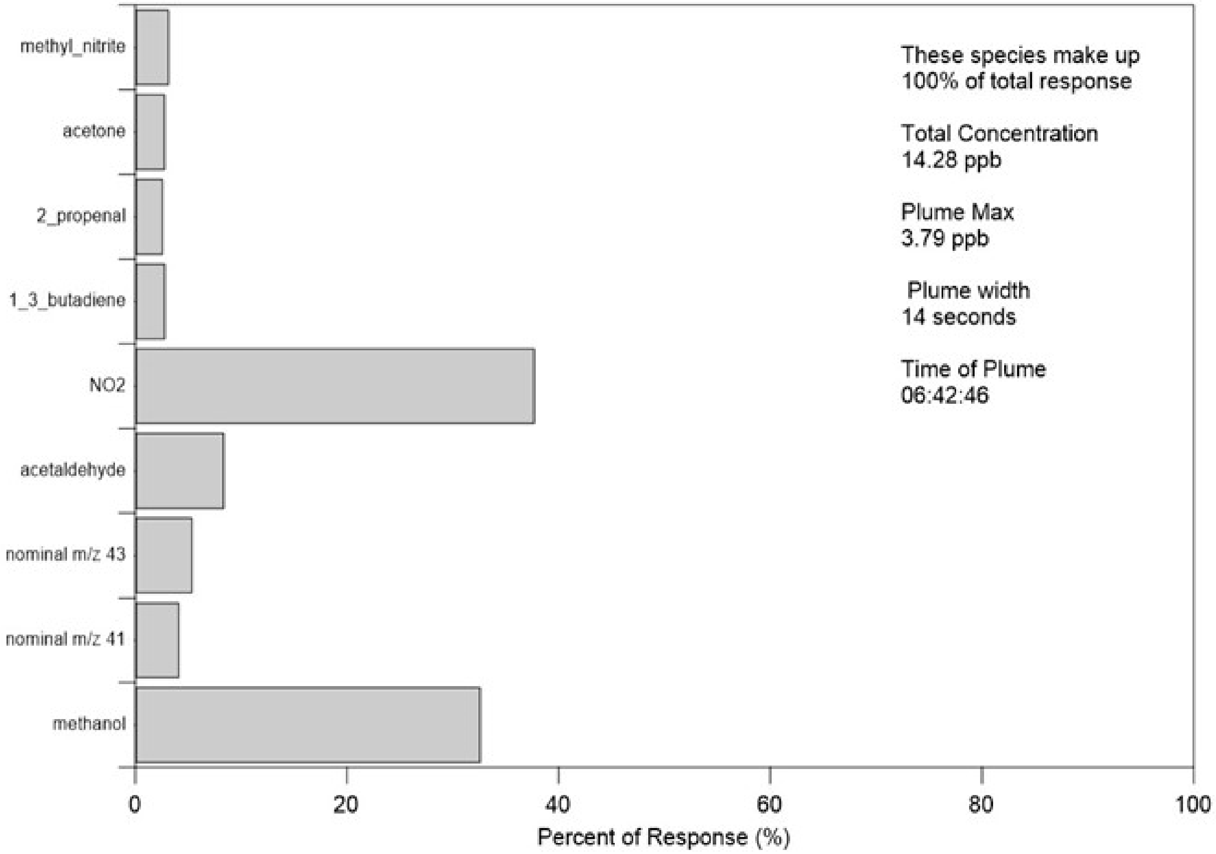

Figure 5-26. March 26, 2019, 274AW Area Loops CO_2 Atypical Plume Containing Primarily Methanol and NO_2 with Several Other Components Including Methyl Nitrite in a Unique Fingerprint.

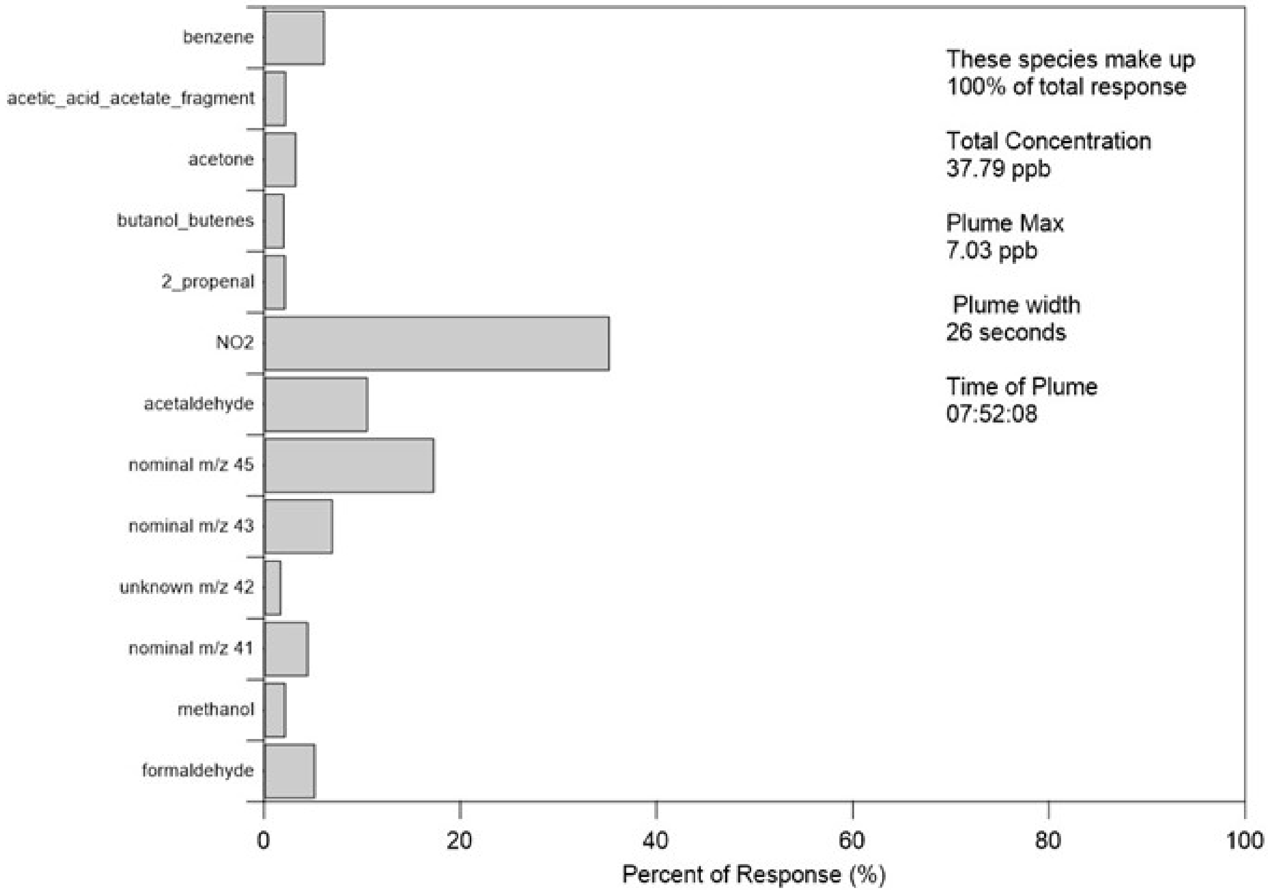

Figure 5-27. March 26, 2019, 274AW Area Loops Benzene/CO_2 Plume Primarily Composed of NO_2 with Emission and Other Components.

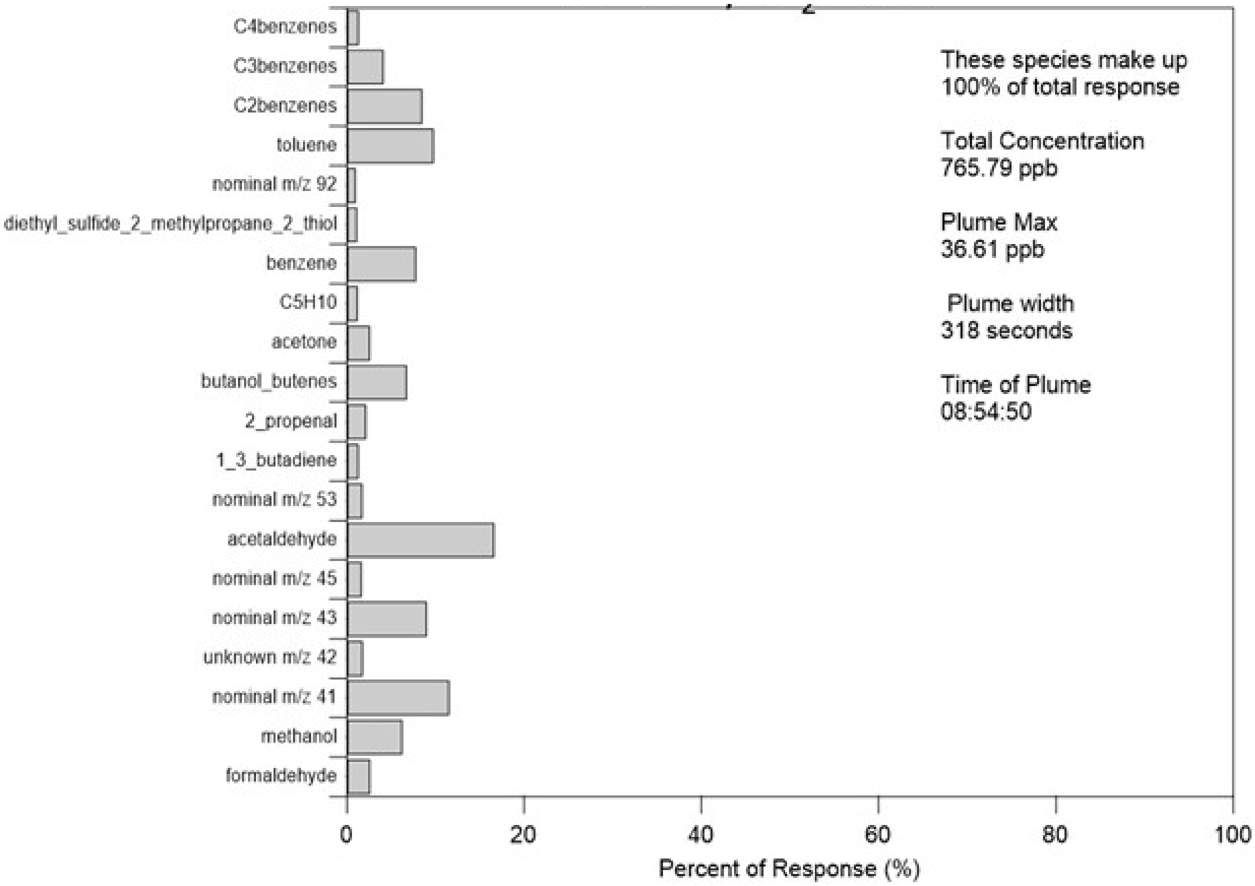

Figure 5-28. March 26, 2019, Benzene/CO_2 Plume from Mobile Laboratory Parked Downwind from AP Farm Work with Diesel Truck and a Smoker Upwind Showing Diesel Emission Markers.

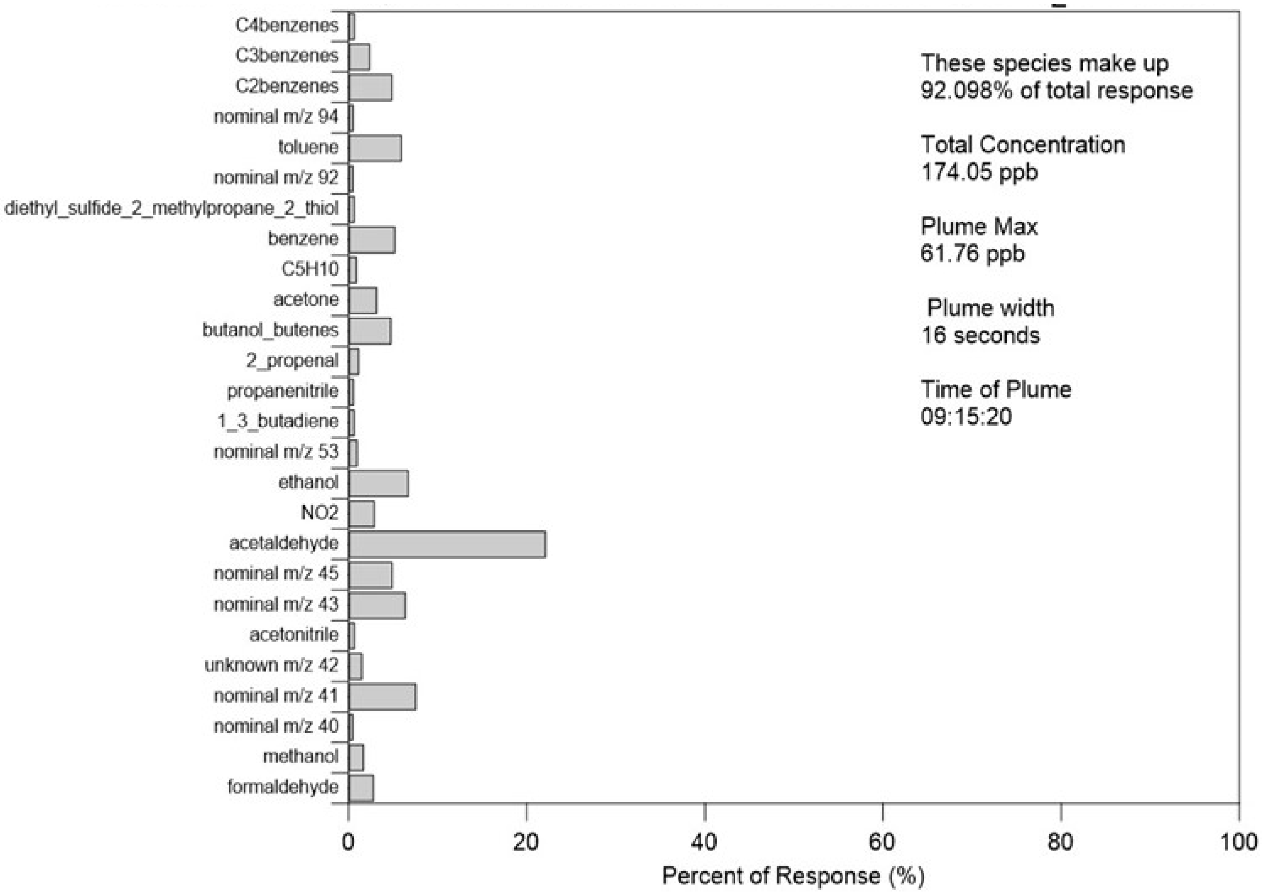

Figure 5-29. March 26, 2019, Benzene/CO_2 Plume Similar to Plume in Figure 5-28 with Truck Starting in Front of Mobile Laboratory.

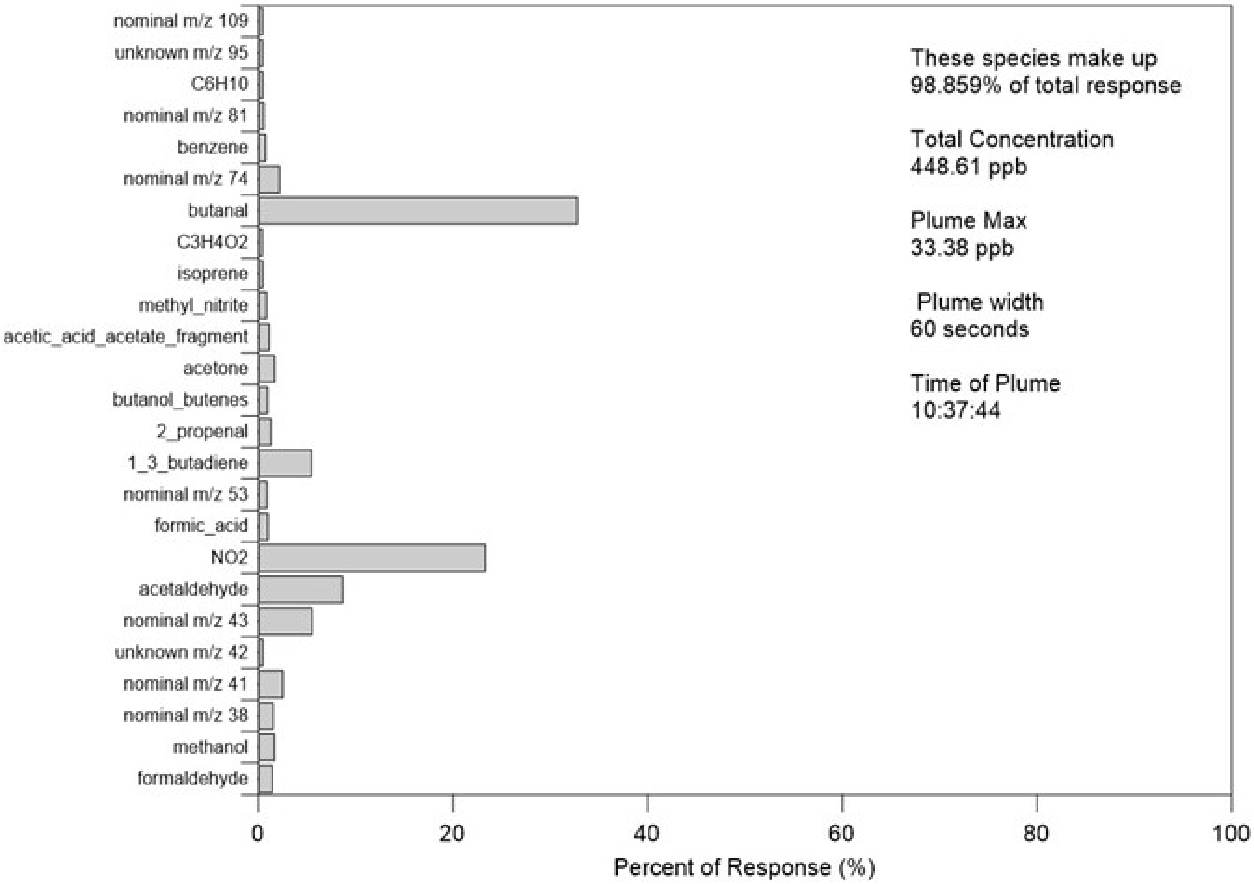

Figure 5-30. March 26, 2019, 274W Area Loops with Asphalt Odor Detectable and Containing High Contribution from Butanal.

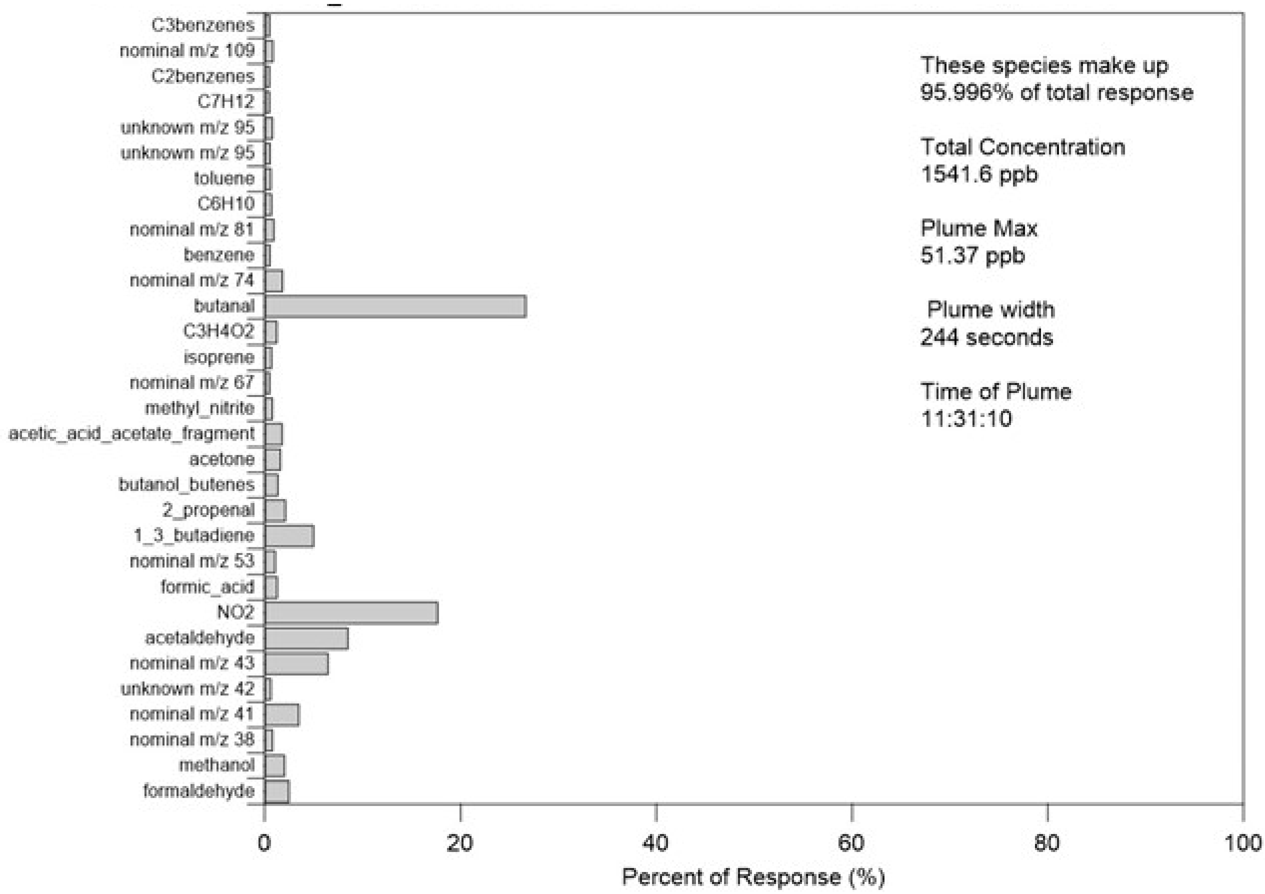

Figure 5-31. March 26, 2019, Benzene/CO_2 Plume Similar to Figure 5-30 with Asphalt Odor Present an Hour Later.

5.1.3.4 March 27, 2019, Summary of Activities

On March 27, 2019, the Operators arrived at the ML at 04:55. The QA/QC zero-air/span checks were performed on the LI-COR CO_2 monitor, the Picarro NH_3 analyzer, and the PTR-MS beginning at 05:05. The ML arrived on the Hanford Site and ML personnel checked in with the CSO at 06:15. The ML began mobile monitoring at 06:27 around A Farms. At 07:13, the ML was parked downwind of a generator fuel truck until departing to perform another A Farm survey loop. At 09:10, the ML was parked downwind of a Mission Support Alliance, LLC (MSA) water truck that was unloading its contents into a holding tank. The ML performed a site survey loop at 10:35 prior to parking south of the AP Stack. At 12:35, another site survey loop was performed until the ML was parked at the northwest corner of 241A Farm at 13:20. At 14:05, ML Operators checked out with the CSO and departed the site. The ML arrived back at the TerraGraphics warehouse at 15:00.

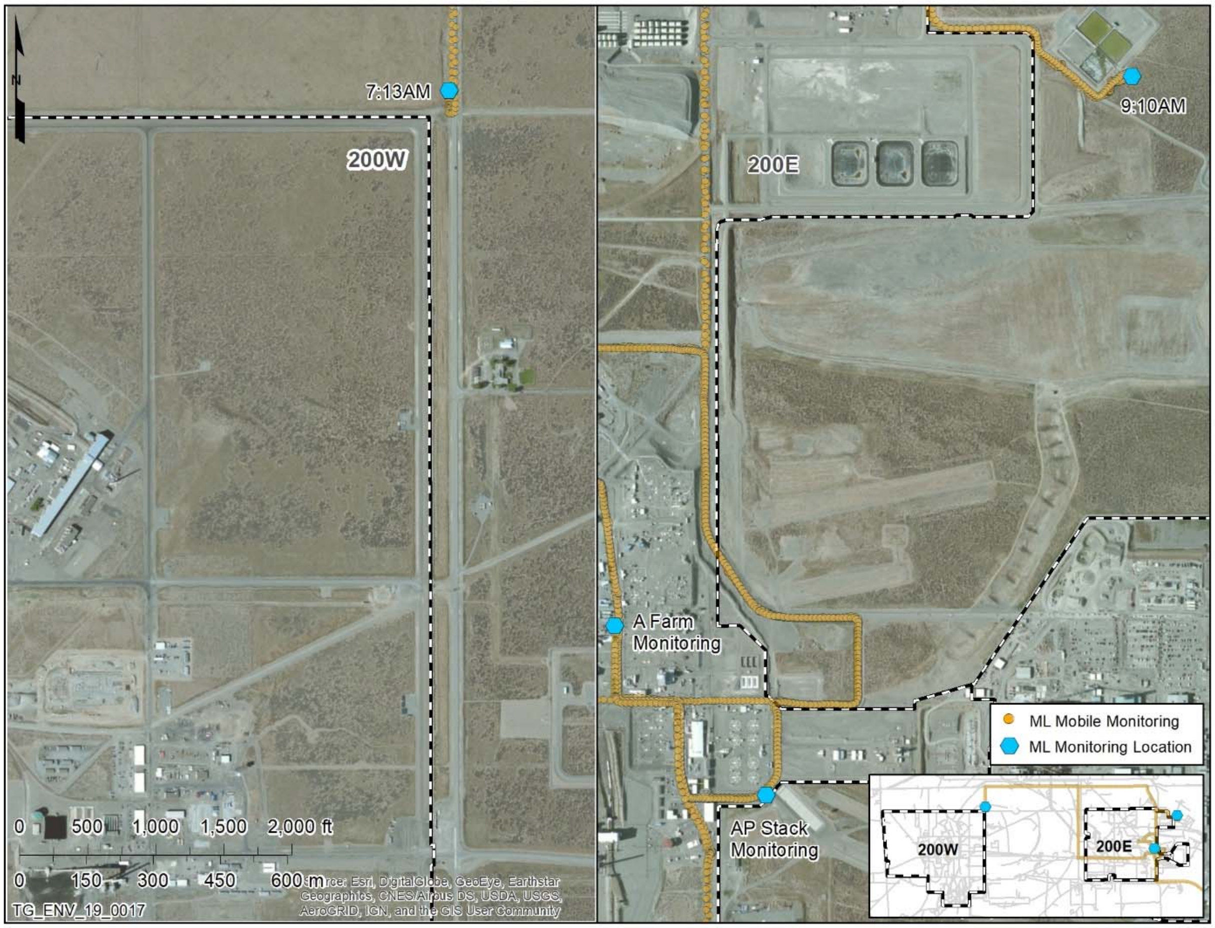

Figure 5-32. Location of the Mobile Laboratory for the Duration of the Monitoring Period.

Figures 5-33 through 5-37 show fingerprints from area loops at various times on March 27, 2019, from 07:01 – 13:19. No measurable plumes were observed while the MSA water truck was unloading its contents.

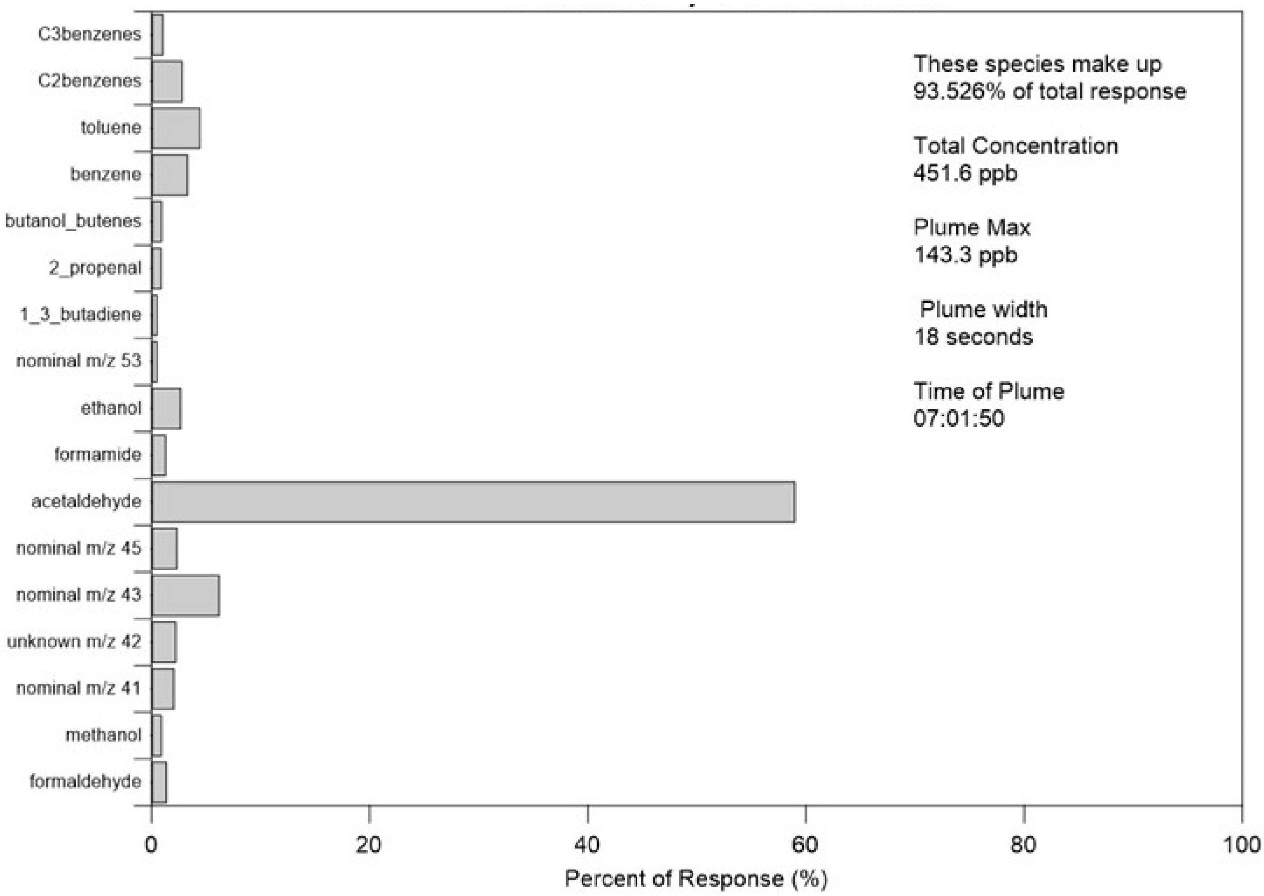

Figure 5-33. March 27, 2019, Area Loops Passing a Fuel Truck.

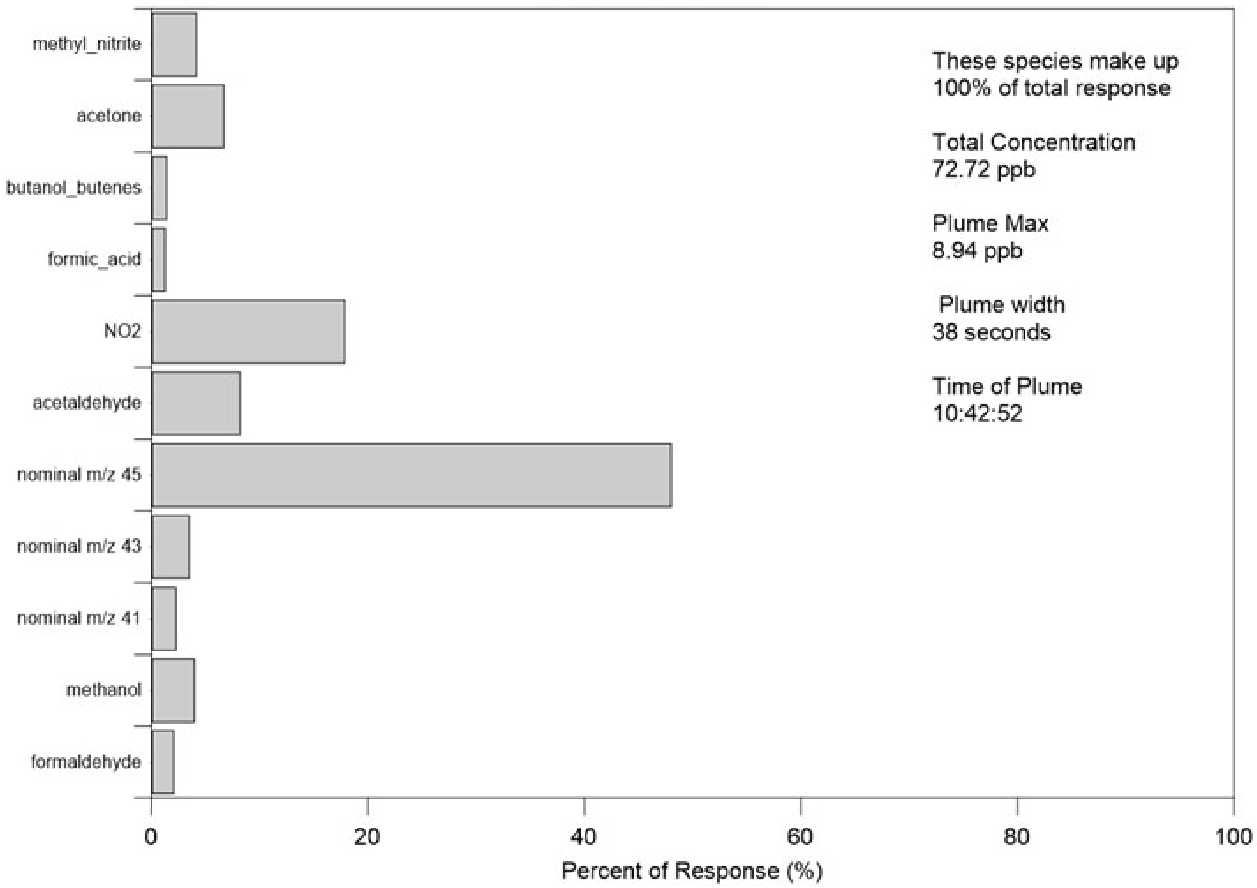

Figure 5-34. March 27, 2019, CO_2 Plume During Area Loop Later in the Morning Primarily Composed of Nominal m/z 45 and NO_2.

In Figure 5-34, acetaldehyde, acetone and methyl nitrite are also observed but no benzene, toluene or other emission markers are present.

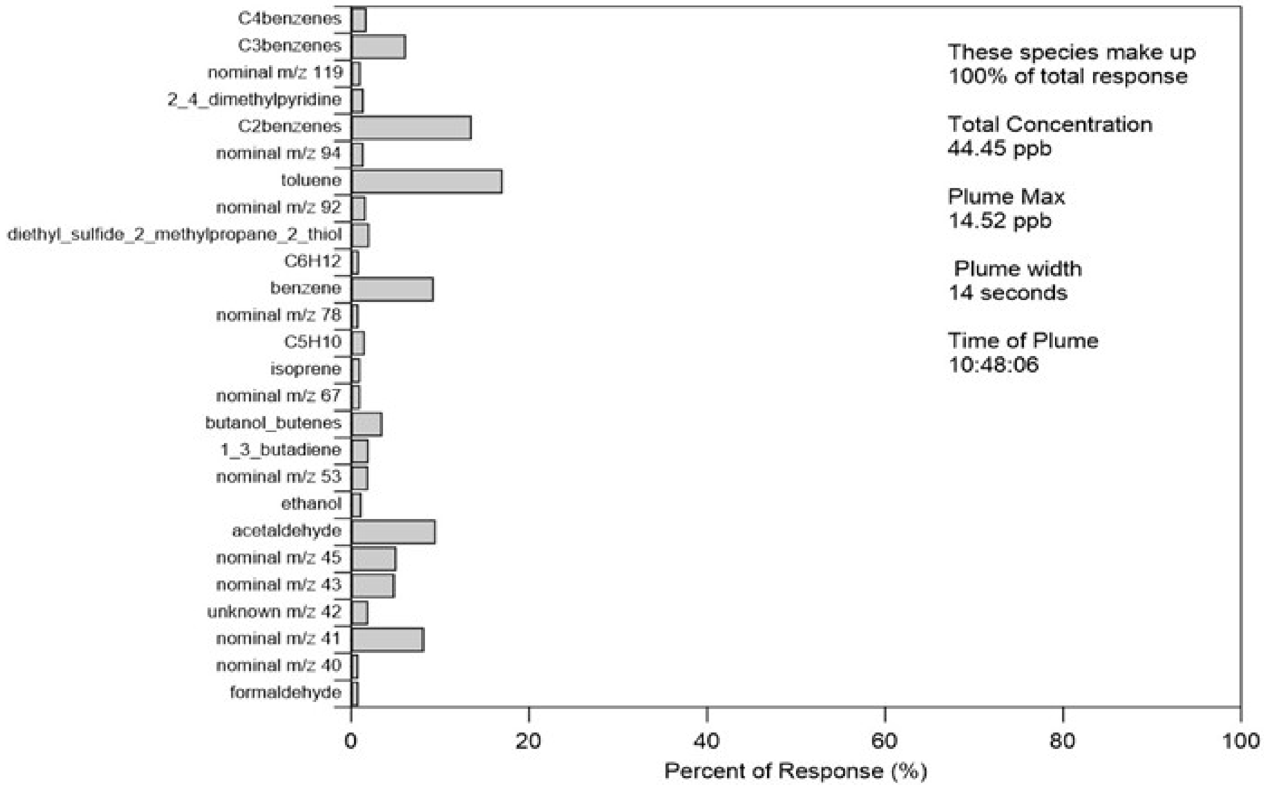

Figure 5-35. March 27, 2019, Benzene Plume with Diesel Emission Markers.

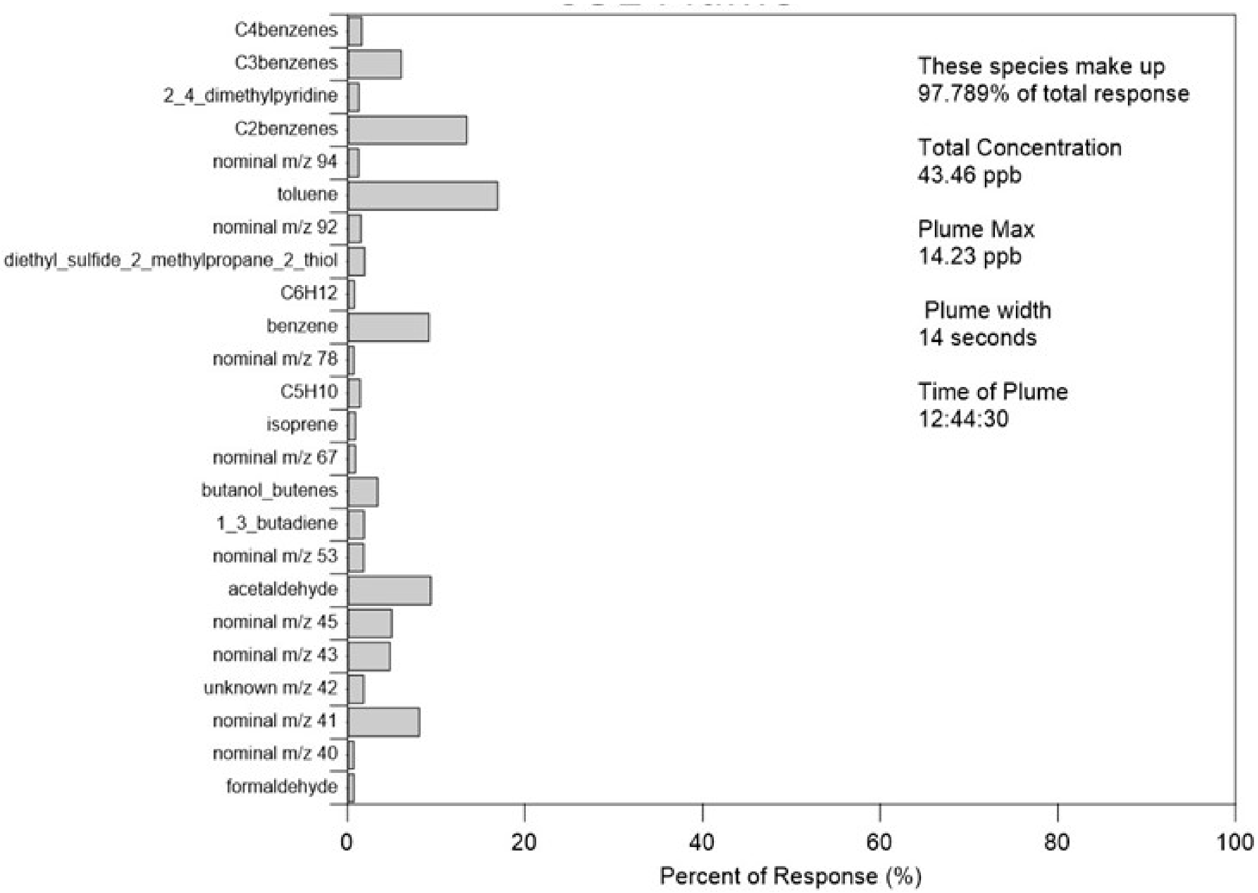

Figure 5-36. March 27, 2019, CO_2 Plume with Emission Markers Similar to that in Figure 5-35.

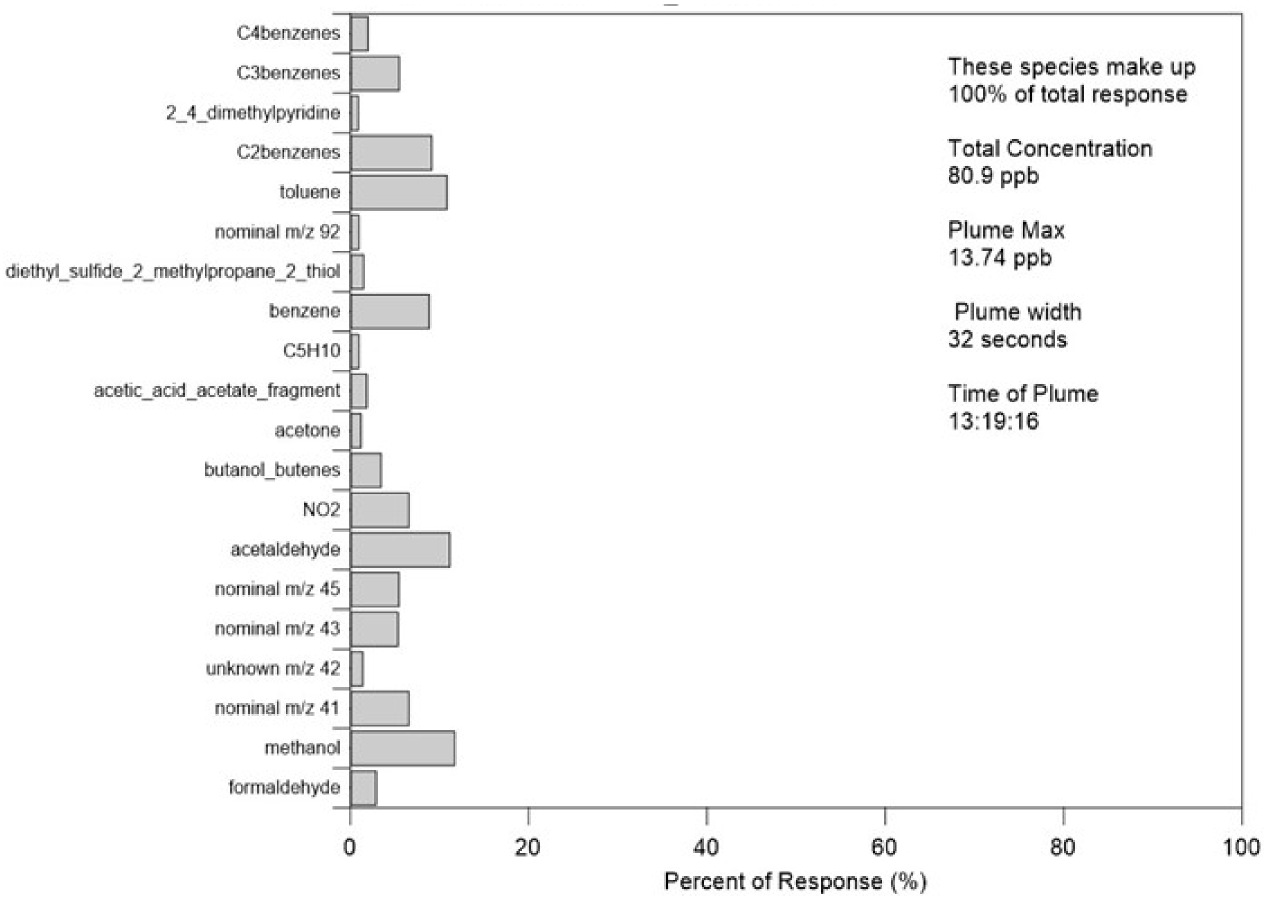

Figure 5-37. March 27, 2019, Benzene/CO_2 Plume with Similar Emission Markers but also Components from 2,4-Dimethylpyridine, Diethyl Sulfide 2-Methylpropane-2-Thiol, Butenes and Methanol.

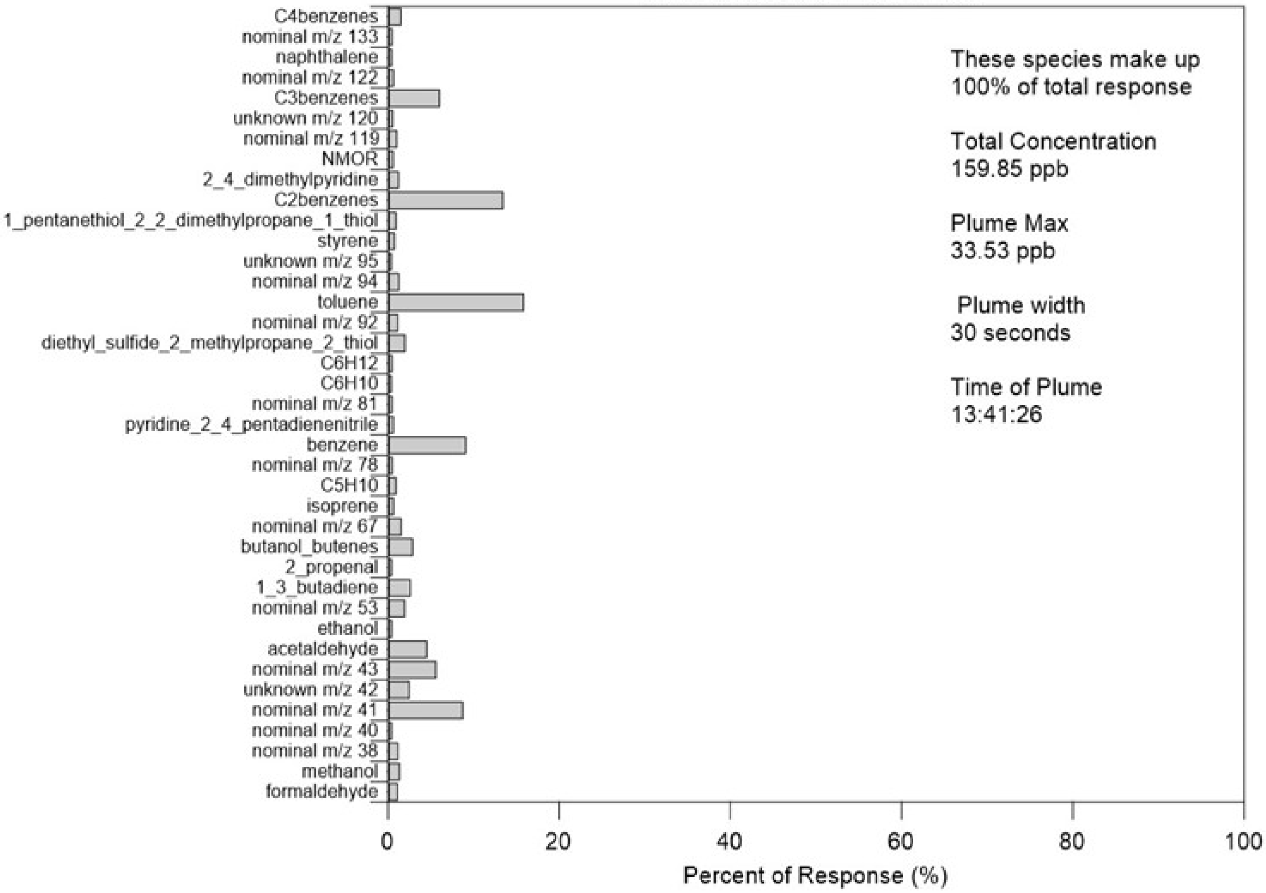

Figure 5-38. March 27, 2019, Mobile Laboratory Parked at Northwest Corner of 241A Farm. Benzene Plume Typical of Diesel Emissions.

5.1.3.5 March 28, 2019, Summary of Activities

On March 28, 2019, the Operators arrived at the ML at 05:00. The QA/QC zero-air/span checks were performed on the LI-COR CO_2 monitor, the Picarro NH_3 analyzer, and the PTR-MS beginning at 05:15. The ML arrived on the Hanford Site and ML personnel checked in with the CSO at 06:05. The ML performed a site survey loop of A Farms prior to parking southwest of the septic tanks located near the 242A Evaporator. At 07:55, the ML met the SME, Dr. Matthew Erickson, at the CSO.

At 08:48, the ML met Mr. Clark Carlson at 244AR to perform testing on diesel generators. Shortly after, the ML was parked northwest of 241-A Farm, near the farm’s entrance. The results and discussion on the testing of diesel generators is detailed in Section 5.2.

A new PTR-MS file was started for TY Farm monitoring at 11:35. Generator (ID: HO-74-4539) was plugged into storage container (CC2EG117). The side port was disconnected at 11:37, when the ML began sampling from the mast again. At 12:20, the ML was parked on the northeast side of TY/TX Farms. After approximately 20 minutes, the ML was relocated to the southeast side of the farms in an effort to remain downwind. At 14:00, ML personnel checked out with the CSO. The ML arrived at the TerraGraphics warehouse at 15:15.

Figures 5-39 through 5-45 show fingerprints from ML monitoring activities prior to measurement of the diesel generators.

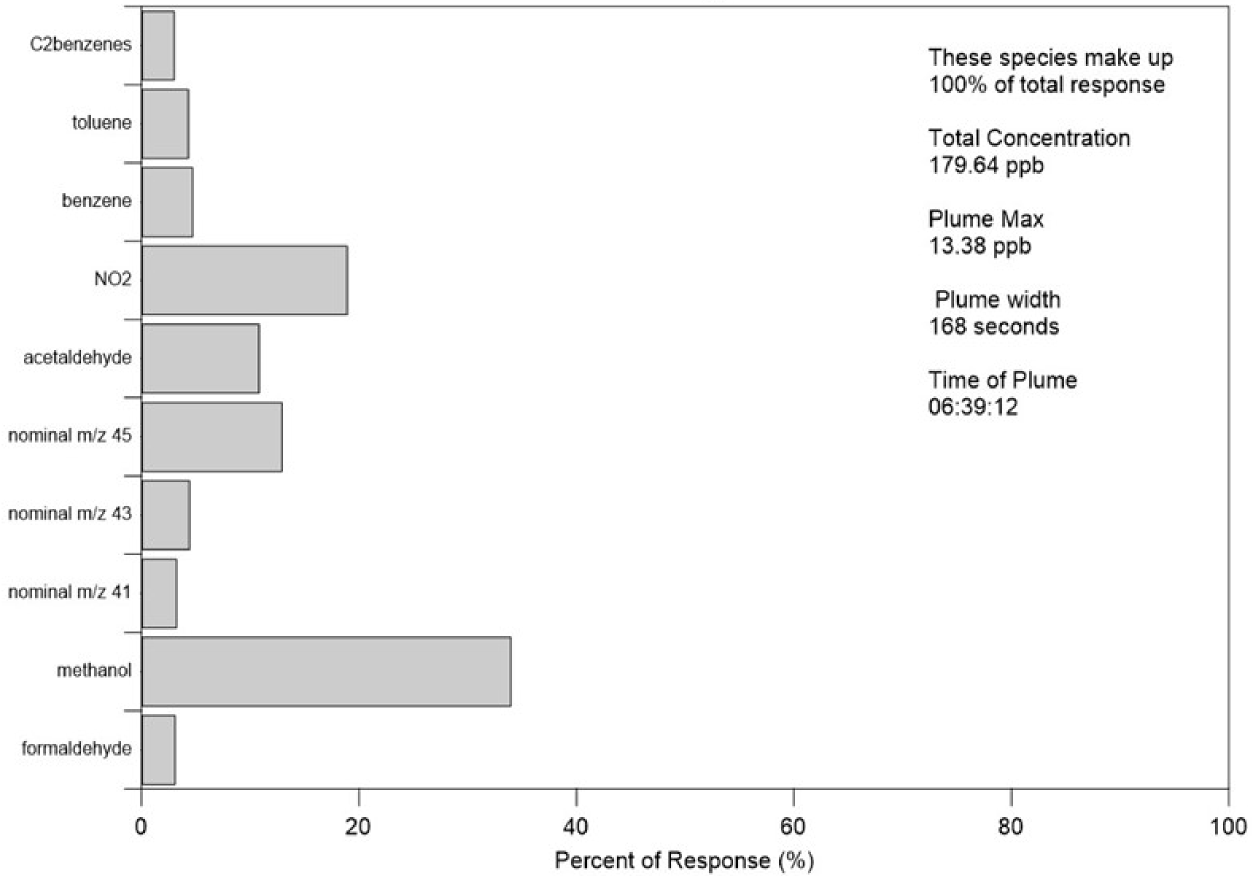

Figure 5-39. March 28, 2019, Benzene/CO_2 Plume from Site Survey Loop with some Diesel Emission Components and a Dominant Contribution from Methanol.

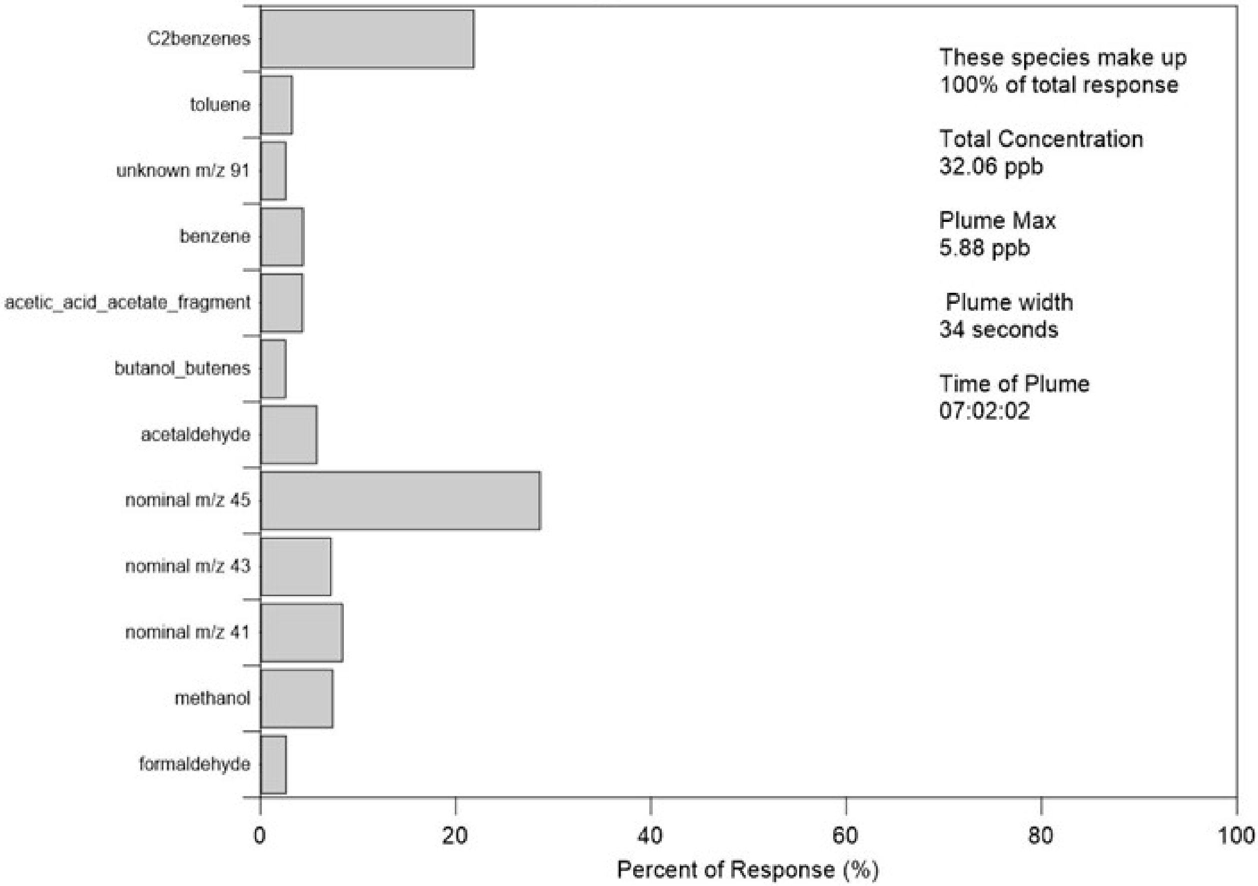

Figure 5-40. March 28, 2019, CO_2 Plume Detected while Mobile Laboratory Parked on Southwest Corner 20’ Downwind of Septic Tanks and Construction Activity.

In Figure 5-40, no major fugitive emission components are observed; the plume may be from mixed sources.

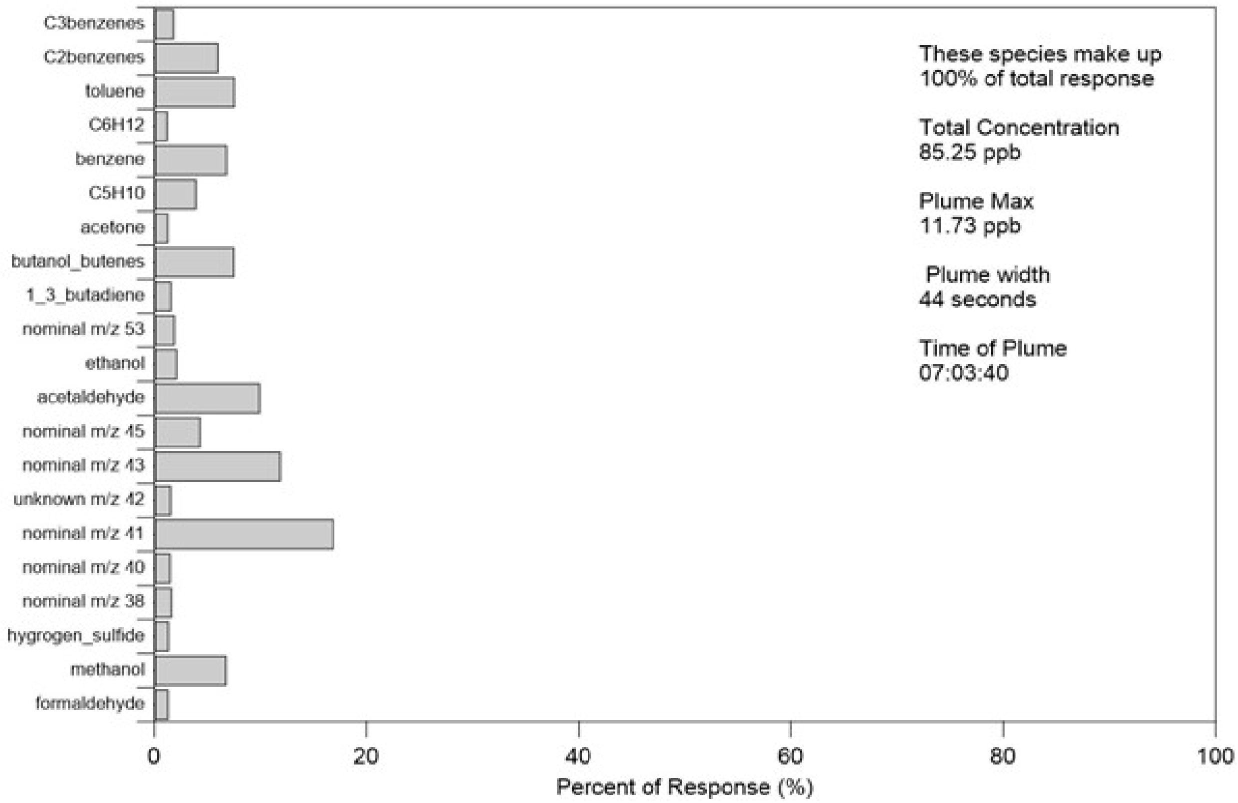

Figure 5-41. March 28, 2019, Fingerprint of Another Plume Detected by Mobile Laboratory 20’ Downwind of Septic Tanks and Construction and Activity in that Area.

Figure 5-41 shows a combination of emission markers with a trace of hydrogen sulfide, a fugitive emission compound.

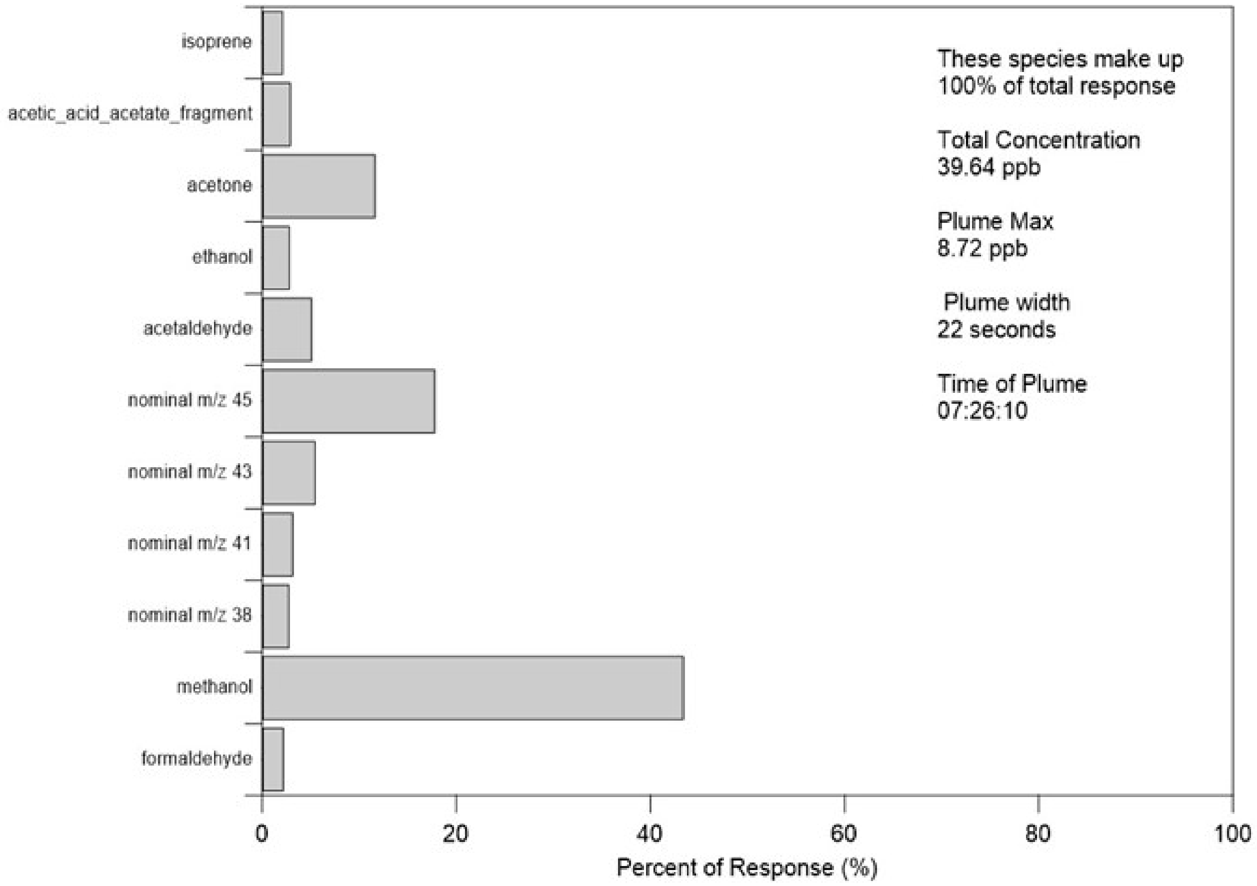

Figure 5-42. March 28, 2019, Third Plume Detected 20' Downwind of Septic Tanks and Construction Activity with a Different Fingerprint Dominated by Methanol.

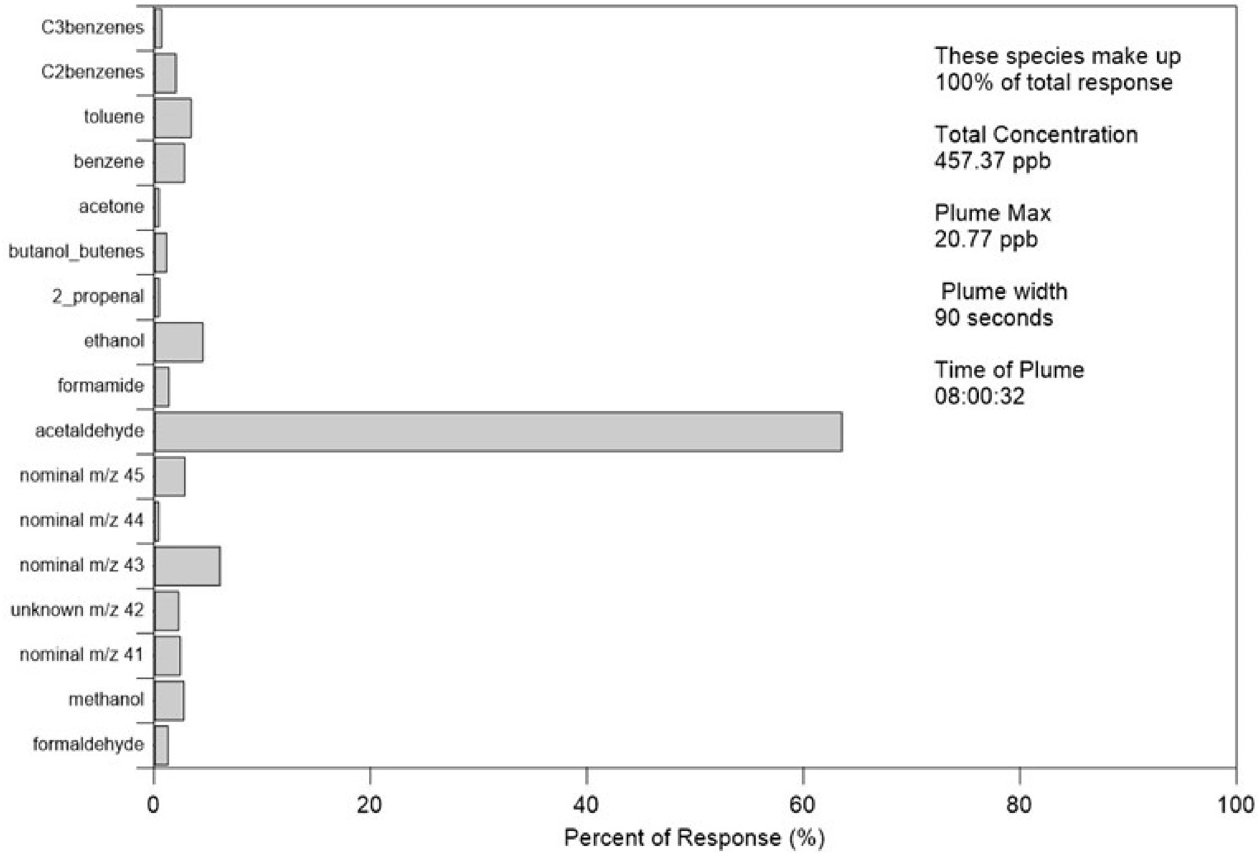

Figure 5-43. March 28, 2019, Mobile Laboratory Sampling While on Way to Meet Subject Matter Expert. Fingerprint Consistent with Diesel Emissions.

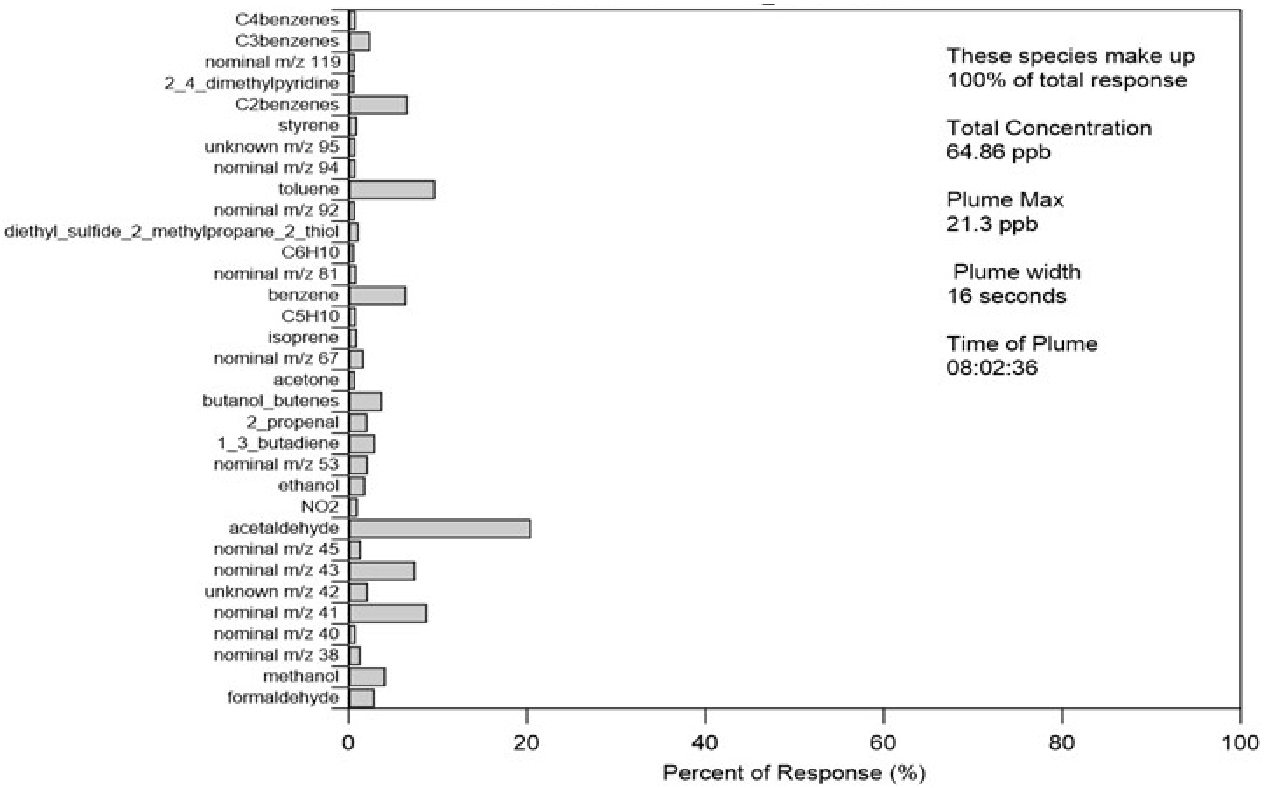

Figure 5-44. March 28, 2019, Fingerprint of Another CO_2/Benzene Plume Detected on way to Meet Subject Matter Expert. Could be a Combination of Diesel and Gasoline Engine Emissions.

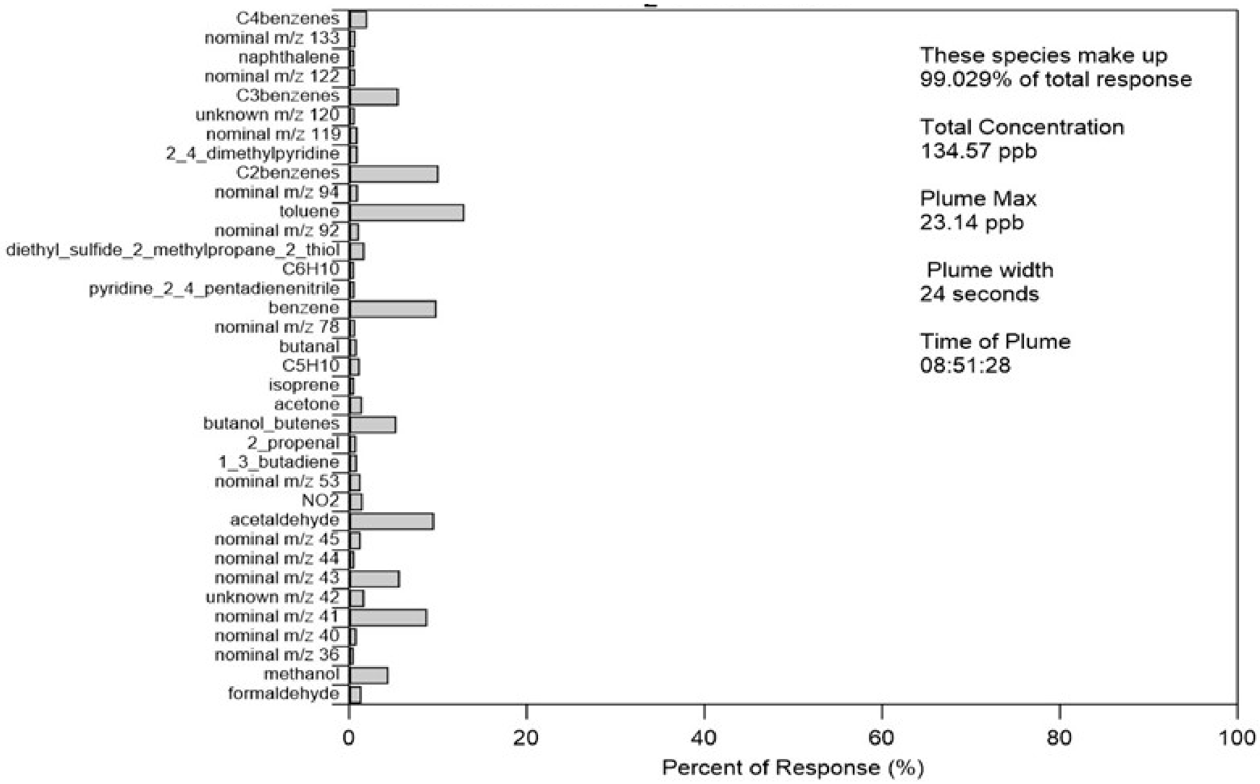

Figure 5-45. March 28, 2019, Fingerprint of CO_2/Benzene Plume Observed on way to Measure Generator Fingerprints. This Appears to be from Gasoline Engine Emissions.

The final plume fingerprint was observed when the ML was deployed at TY/TX Farm in response to a reported source emission.

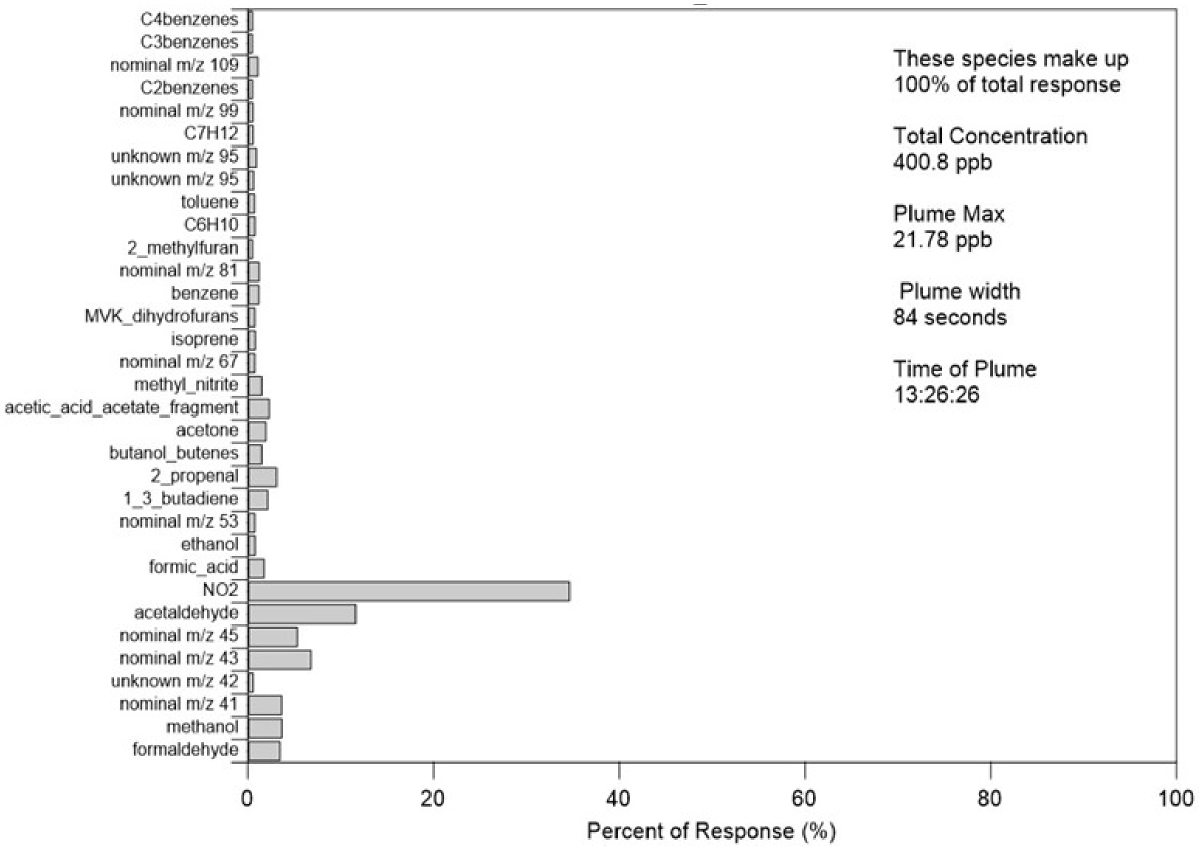

Figure 5-46. March 28, 2019, CO_2/Benzene Plume Fingerprint Downwind of TY/TX Farm in Response to Reported Source.

In Figure 5-46, the plume contained primarily NO_2 and acetaldehyde with minor contributions from a number of compounds.

5.2 Fugitive Emissions – Diesel Generator Fingerprint

As part of the ongoing mission of characterizing fugitive emission sources on site, the ML sampled the exhaust of two generators on March 28, 2019. The first generator (GEN1) was a Multiquip®[12] Diesel Powered AC Generator (model: DCA-70SSJU4I, serial: 7305248) containing a John Deere®[13] 4-cylinder engine (4045HRG92) located at near the west fence line of 241A. The second generator (GEN2) was a Terex®[14] Model AL4 (AL413-2557) diesel generator (labeled HO-74-4539) connected to container CC2E0117 located at to the west of 241AY. Locations of both generators are shown in Figure 5-47. The sampling was accomplished using the 35’ side-port sample line and positioning the inlet near the exhaust output of the generators. Sampling direct emissions in this way often leads to high concentrations; therefore, the sample dilution system was used to limit instrument saturation that can occur at high levels. Figure 5-48 shows the sample configuration for both generators.

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[12] Multiquip is a registered trademark of Multiquip, Inc., Carson, California.
[13] John Deere is a registered trademark of Deere & Company, Moline, Illinois.
[14] Terex is a registered trademark of Terex Corporation, Westport, Connecticut.

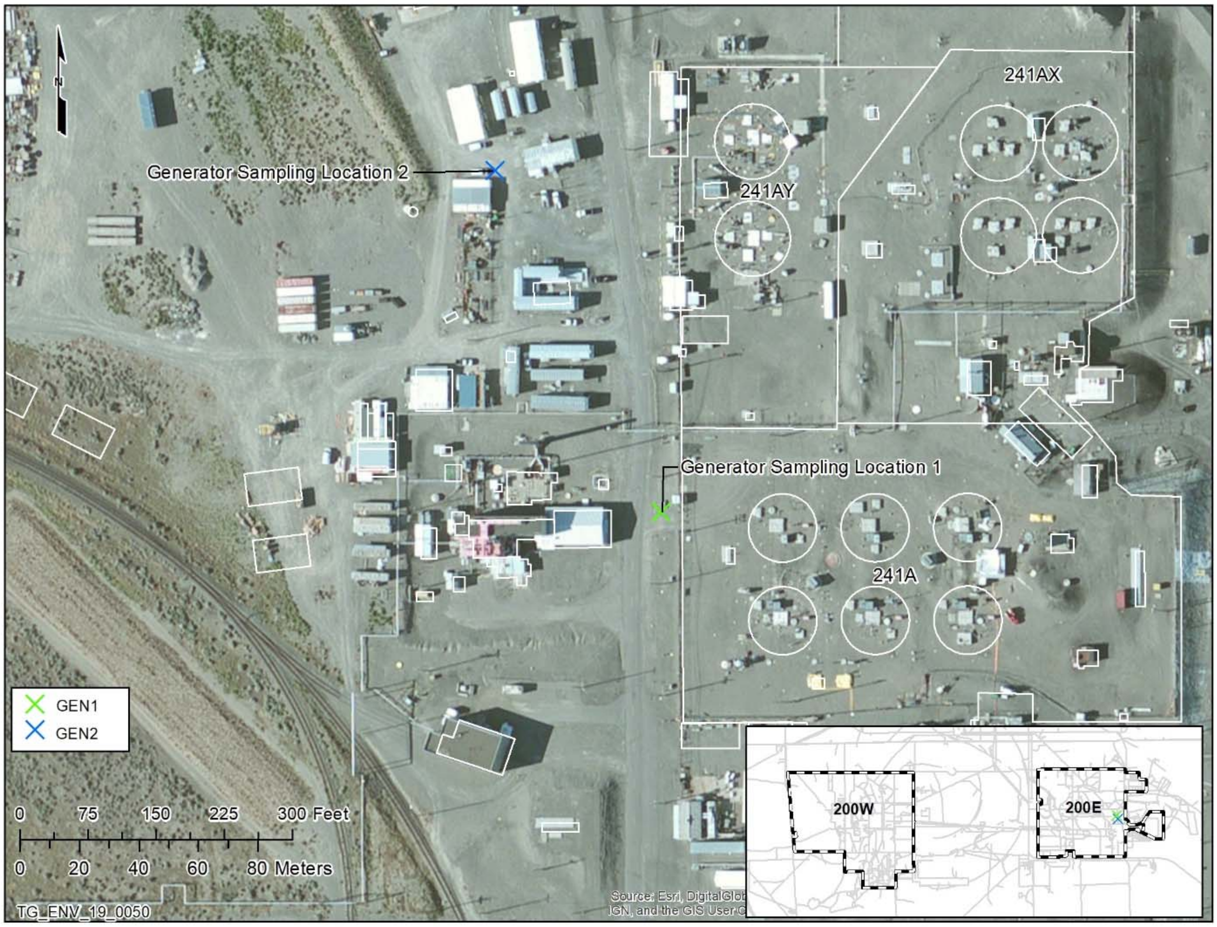

Figure 5-47. Location of Both Generators Monitored.

Figure 5-48. Sampling Configuration for GEN1 (Left) and GEN2 (Right).

Figure 5-49 shows a time-series of some species typically observed within diesel combustion engine exhaust. The GEN1 response was first observed at 09:45 and sampling continued until 10:31. In the beginning, the sample dilution flow was setup to achieve a ~tenfold dilution until

09:56 when the dilution was reduced to ~fourfold. At 10:08, this was altered once again to result in ~50% dilution. The purpose of changing the dilution flow was to begin in a setup that would prevent saturation due to high concentrations. If saturation is not observed during this initial monitoring period, the sample dilution can be reduced to increase the source signal. For GEN2, the dilution flow initially setup for the ~tenfold dilution for sampling between 10:49 and 11:09 when it was changed to ~60% dilution. The dilution shift at 11:09 shows the most drastic difference in Figure 5-49 with large step change response of all the plotted species.

Comparing these common species in diesel combustion engine exhaust highlights the similarities and differences between the generators. The acetaldehyde to formaldehyde ratios are reasonably close with GEN1 seeming to have a slightly higher ratio. The aromatics are suppressed greatly in GEN1 compared to GEN2. The acetic acid + acetate fragment is much more prominent within GEN1. There was also more CO_2 observed in GEN1. One explanation for the differences could be that GEN1 has more emission control components than GEN2 that is removing/converting select species from the exhaust stream.

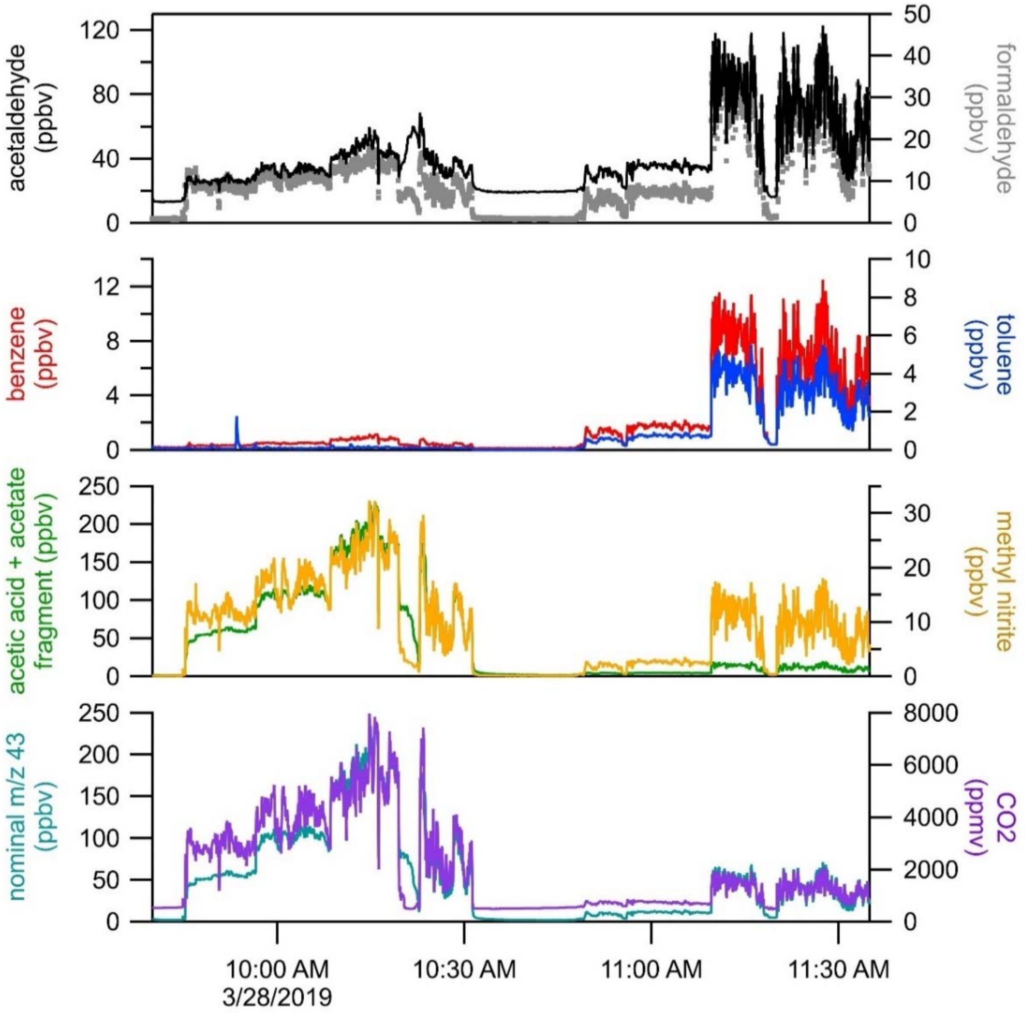

Figure 5-49. Time-series of Common Diesel Combustion Exhaust Species Observed on Generator Testing on March 28, 2019.

The data were inspected by the SME to determine the periods to be utilized for fingerprint analysis. Multiple stable periods (plumes) were selected and the average response for all masses monitored by the PTR-MS were considered. The criteria for being considered part of the fingerprint were a response of at least 0.05 ppbv and a contribution of at least 0.5% to the overall signal. These are the same criteria used for fingerprint analysis in previous reports. Figure 5-50 shows the fingerprints calculated from six plumes for GEN1 along with the average of the individual fingerprints. The 12 species shown account for ~95% of the total response for the individual plumes and the average fingerprint. Nominal m/z 43, nominal m/z 46, and the acetic acid + acetate fragment are the most prominent and account for ~72% of the average fingerprint. Nominal m/z 43 is a common fragmentation ion for many species and is generally present within complex mixtures. The nominal m/z 46 species (mass = 45.9888) is unidentified, but the mass resolution is sufficient for peak separation from formamide (mass = 46.0297) and ethylamine (mass = 46.066). Investigating the exact masses of potential hydrocarbons did not yield any that would have an exact mass near that of the nominal m/z 46 ion. The most likely candidate was NO_2^+ which has an exact mass of 45.9929. Diesel engine emissions typically contain large amounts of NOx. Within the PTR-MS, the ionization potential (IP) of NO_2 is 9.586 eV and it will undergo electron transfer with O_2^+ (IP = 12.063 eV) creating an NO_2^+ response. Formaldehyde, nominal m/z 44, acetaldehyde, formic acid, acetone, and methyl nitrite have been observed within diesel exhaust as shown in 53005-81-RPT-027, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 2*, but the presence of nominal m/z 45 and nominal m/z 99 is new. It is unknown what is responsible for the response and further investigation is required.

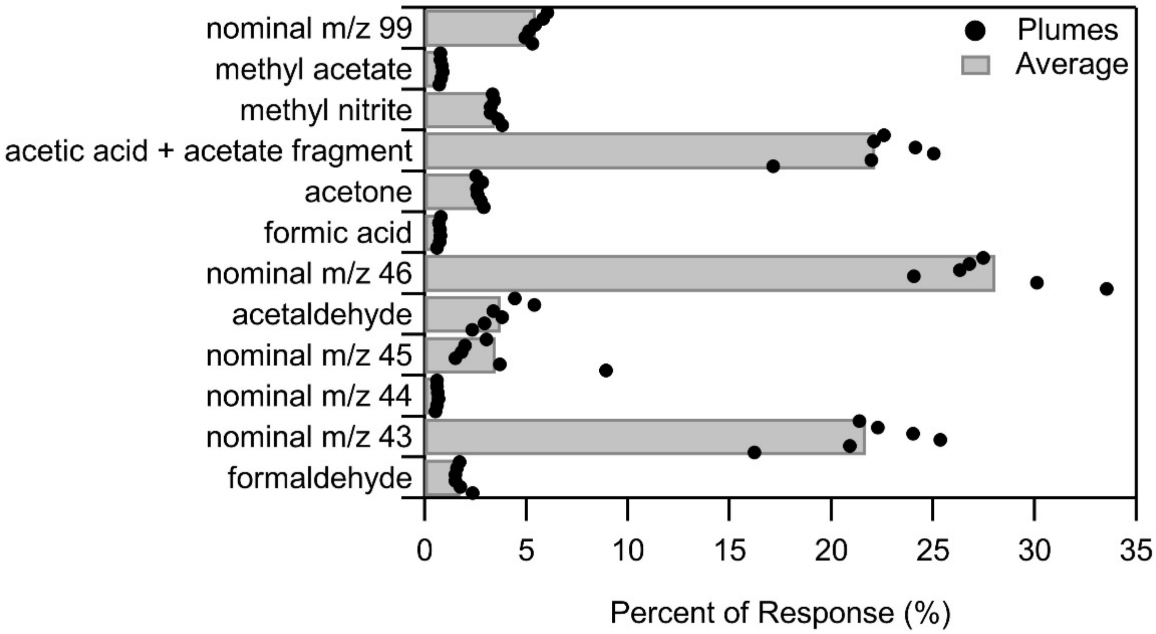

Figure 5-50. Fingerprint of the First Generator (GEN1) Sampled on March 28, 2019.

In Figure 5-51, the fingerprints are calculated from four plumes for GEN2 along with the average of the individual fingerprints. The 30 species shown in the figure make up ~83% of the total response on average, with approximately 44% of attributed to nominal m/z 46, acetaldehyde, and nominal m/z 43. In Figure 5-51, acetaldehyde and nominal m/z 43 are shown as common constituents of diesel combustion emissions, but nominal m/z 46 response tentatively attributed to NO_2 is the most prominent. As expected, formaldehyde, nominal m/z 41, acetic acid + acetate fragment, methyl nitrate, benzene, and toluene are all present within the fingerprint.

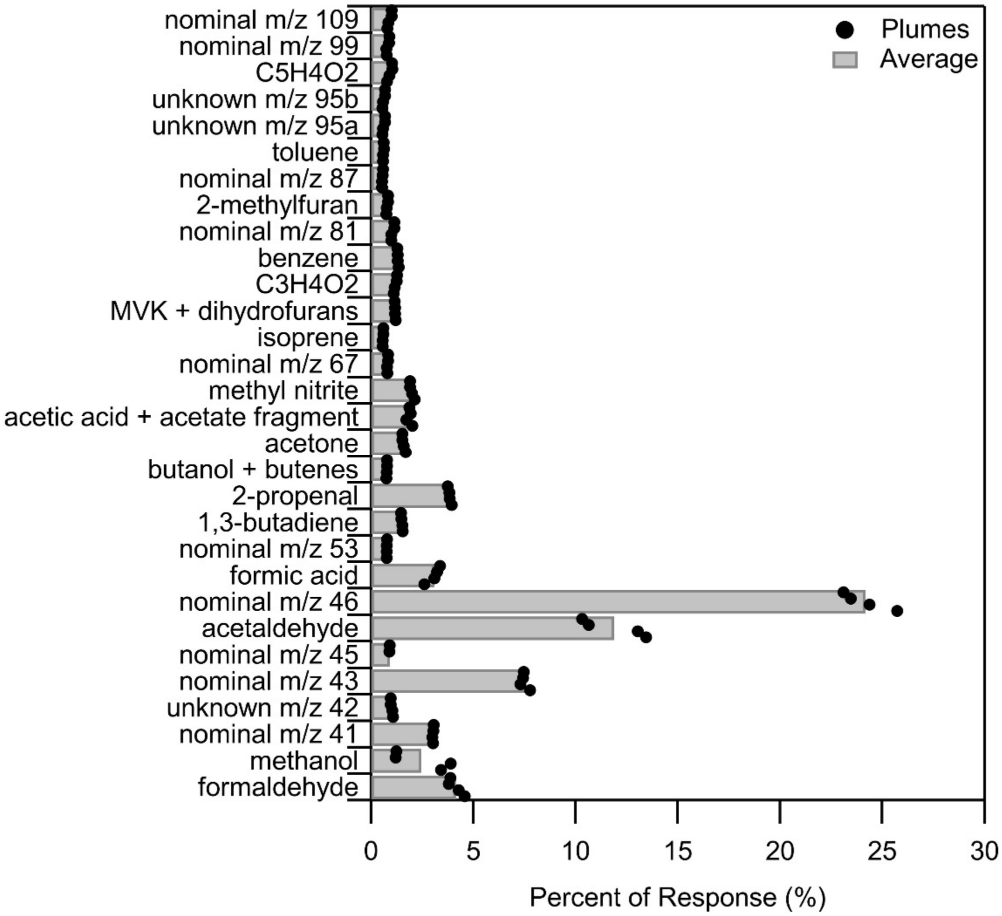

Figure 5-51. Fingerprint of the Second Generator (GEN2) Sampled on March 28, 2019.

Figure 5-52 shows the comparison between GEN1 and GEN2 fingerprints. It is important to note that the unit of measure is relative abundance, which is different than percent of response. The relative abundance is the percent of response normalized so that the total sum equals 100%. For example, it was stated that the 30 species in Figure 5-51 make up 83% of the signal, which means the summation of the percent responses will equal 83%. To get the relative abundance, this is normalized so that the summation equals 100%. This essentially considers 17% of the response to be negligible and focuses the fingerprint to just the key species. This is done to help with comparisons to past and future datasets. For comparisons, each fingerprint will have a relative abundance total of 100% which provides a standard metric for comparison.

The common dominant responses between the exhausts lies at nominal m/z 43 and nominal m/z 46. Both exhausts also showed similar responses with formaldehyde, acetone, and methyl nitrite. Acetaldehyde is common within diesel exhaust which shows up within both generators but is amplified much more in GEN2. Acetic acid + acetate fragment is the opposite with a much higher attribution within GEN1. It is also apparent that GEN2 (30 species) has much broader emissions than GEN1 (12 species) with more than twice as many species contributing to the fingerprint. This suggests that GEN1 has more efficient combustion or emission controls compared to GEN2.

For continued comparison, Figure 5-52 also shows the diesel exhaust fingerprint established in 53005-81-RPT-027. The fingerprint was derived from seven plumes originating from the ML itself. The biggest difference between Month 2 and the generators is a shift in signal to acetaldehyde versus nominal m/z 46. The Month 2 exhaust follows the more traditional understanding of diesel exhaust with large presence of aldehydes (formaldehyde, acetaldehyde) and aromatics (benzene, toluene, C_2-benzenes, C_3-benzenes, C_4-benzenes). The response of aromatics is limited to benzene and toluene in GEN2 and was negligible in GEN1. There is a good comparison with formaldehyde, acetone, and methyl nitrate between all three sources and all of them had a nominal m/z 43 response, but it is much more prominent in GEN2. Month 2 and GEN2 also had reasonable comparison with nominal m/z 41, 1,3-butadiene, and 2-propenal.

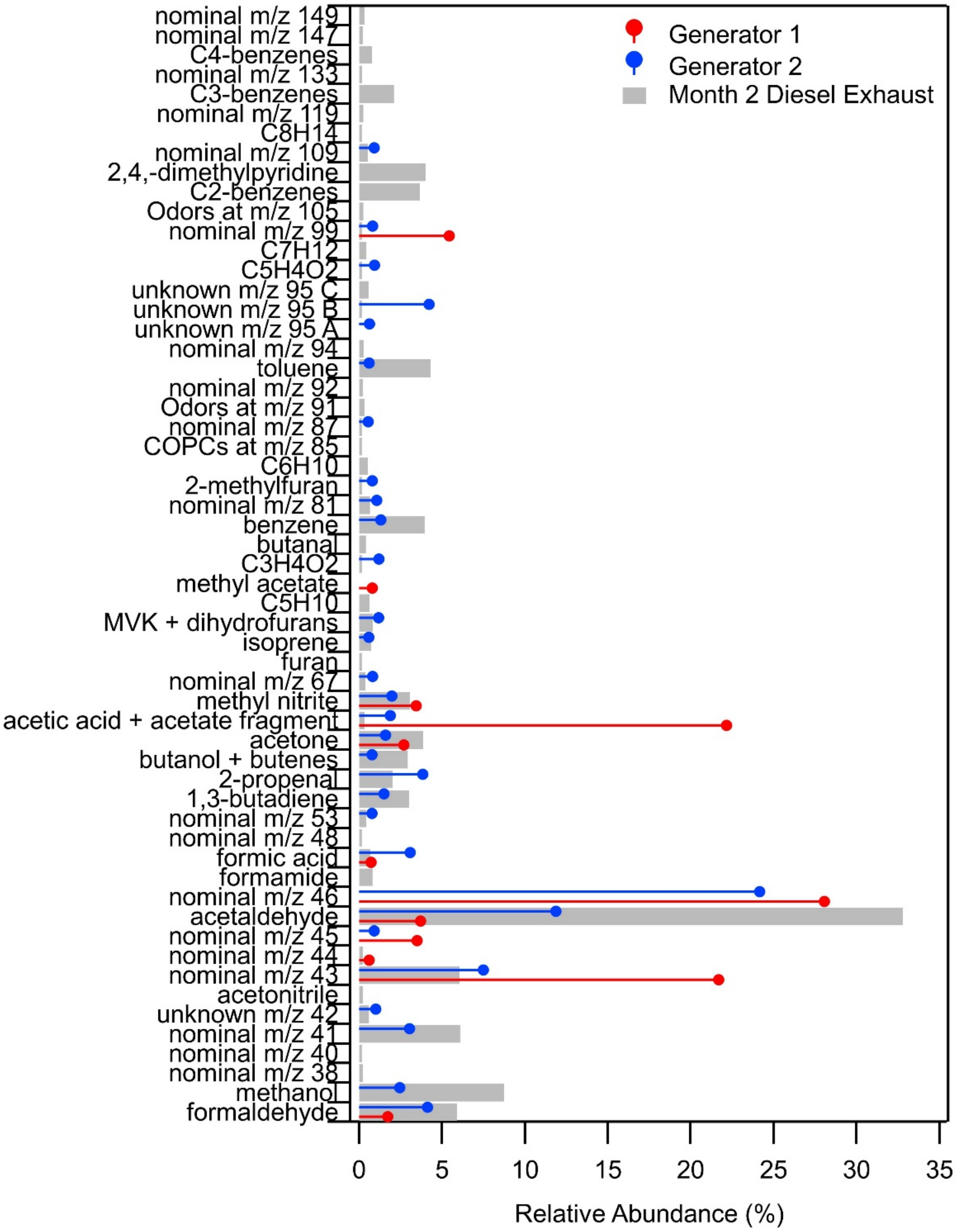

Figure 5-52. Fingerprint Comparison of the Generators Sampled on March 28, 2019, Along with the Diesel Exhaust Fingerprint from 53005-81-RPT-027.

While the presence of CO_2 does not lend to identification of the type of combustion, it does signify that combustion is the likely source. Once a fingerprint is established for a combustion source we can take CO_2 information one step further. The efficiency of burning is characterized by how much of the fuel is converted to CO_2 and H_2O with higher conversion being more efficient. The efficiency will vary between different combustion processes and even between different machines using the same process. Less efficient combustion means increased emission of VOCs that are either unburnt fuel or a byproduct of the combustion reactions. A metric for determining the combustion efficiency would be to take the ratio of CO_2 to VOCs with higher ratios meaning more efficient combustion. In addition, emission treatment processes (i.e., catalytic converters) are commonly utilized with combustion processes and will affect the CO_2 to VOC ratios. Table 5-2 shows the ratio of CO_2 to key VOCs identified within both GEN1 and GEN2 exhaust. The ratios observed in GEN1 are higher than GEN2 except for acetic acid + acetate fragment and nominal m/z 99. This suggests that GEN1 has more complete combustion and/or improved emission controls compared to GEN2.

This improves the source identification beyond just pointing towards a combustion source to suggest the efficiency of the source and potentially identify what type of generator produced the emissions. The largest differences between the two exhausts lies with formaldehyde, acetaldehyde, and formic acid with the ratios in GEN1 being more than an order of magnitude than GEN2. The CO_2:formic acid and CO_2:acetaldehyde ratios are approximately 12.6 and 11 times higher respectively in GEN1 and are the best candidates to distinguish between the two generators due to the order of magnitude differences in the CO_2 ratios. Investigation of additional generators will expand upon this analysis and will help improve and develop this comparison/identification metric further.

Table 5-2. Ratios of CO_2 to Key VOCs Within Diesel Generator Exhaust Measured on March 28, 2019.

Species	CO_2 [ppmv]/VOC [ppbv]	
	GEN1	GEN2
formaldehyde	395	53
nominal m/z 43	32	30
nominal m/z 45	268	171
acetaldehyde	198	18
nominal m/z 46	24	9
formic acid	948	75
acetone	251	138
acetic acid + acetate fragment	31	118
Methyl nitrite	196	111
nominal m/z 99	125	278

5.3 Source Characterization – Window Cleaner Solution

On March 29, 2019, a test was performed to generate a fingerprint for window cleaner solution (Stoner Invisible Glass). The cleaner is a proprietary blend; therefore, the exact contents of the cleaner are not documented but it is a blend of hydrocarbons mixed with at least 80% water and their advertisement claims the product contains no ammonia or silicone. This is part of the ongoing effort to characterize unique sources and generate fingerprints. At 13:52, the ML Operators sprayed the window cleaner on the windshield and began cleaning the window. Figure 5-7 is a times series of key species within the window cleaner emissions. The inlet mast is located just behind the vehicle cab, which results in a large response from the window cleaner.

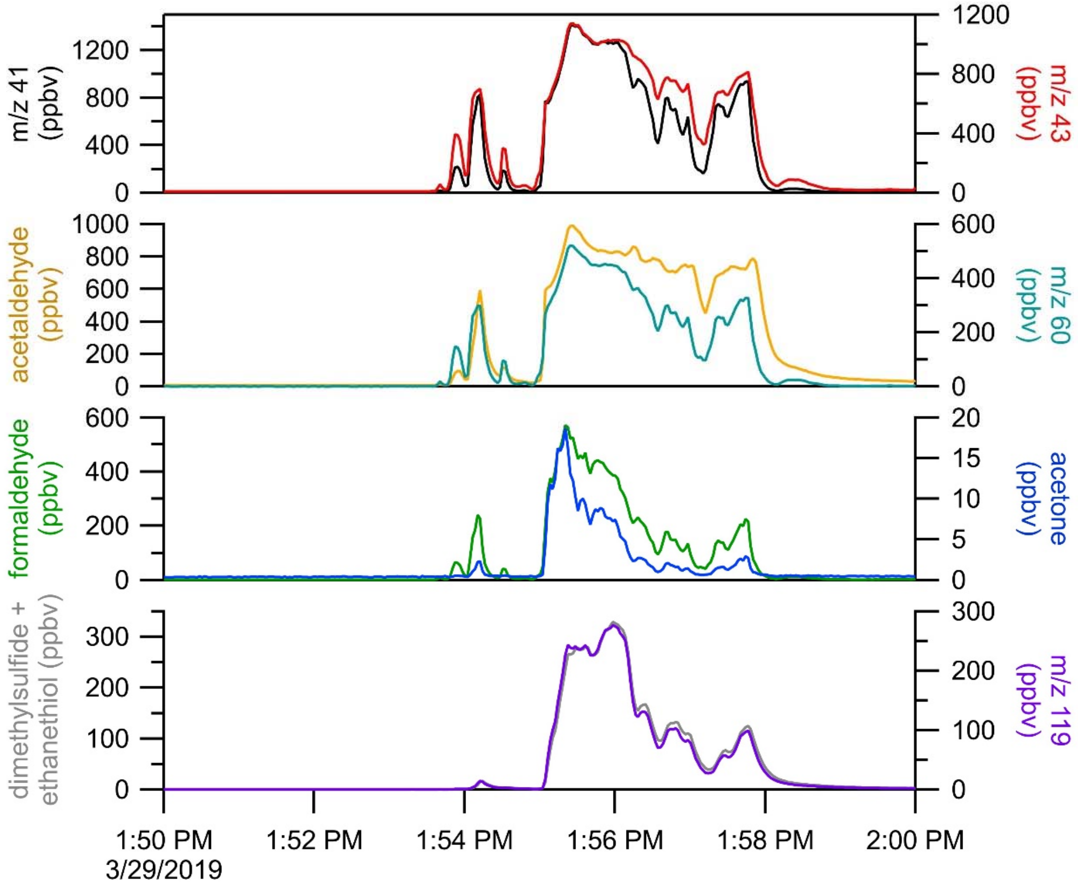

Figure 5-53. Time Series of Abundant Species Found Within the Stoner Invisible Glass Window Cleaner Solution Sampled on March 29, 2019.

Figure 5-54 shows the fingerprint of the window cleaner. The most prominent signals were nominal m/z 41, nominal m/z 43, and acetaldehyde which comprise approximately 55% of the total response. Nominal masses m/z 41 and 43 are common responses due to fragmentation, which make identification of potential species based on responses at these ions difficult and less reliable. Formaldehyde, acetone, nominal m/z 60, dimethylsulfide + ethanthiol, and nominal m/z 119 make up just under 25%. In total, these eight species account for 80% of the response. Investigation into window cleaner ingredients pointed to 2-butoxyethanol as potentially responsible for the response at nominal m/z 119. While this window cleaner is not expected to be a common source during ML monitoring, it will assist in identification of unknown plumes have influence from similar cleaning products.

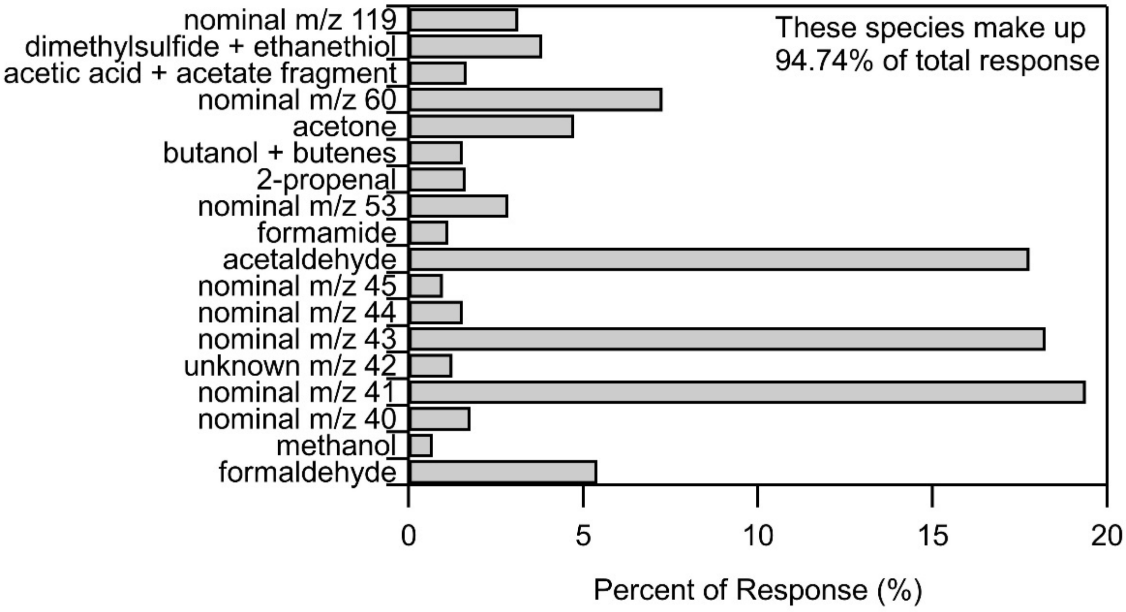

Figure 5-54. Fingerprint of the Stoner Invisible Glass Window Cleaner Solution Sampled on March 29, 2019.

5.4 Testing Activities

Testing activities occurred as part of an ongoing mission of enhancing and evolving the ML's product. Three testing activities were focused on during the span of this monthly report and they are as follows: Sample dilution, sample line characterization, and sorbent system testing. Further findings are detailed in subsequent sections.

5.4.1 Sample Dilution System Testing

The ability to quickly dilute a sample stream with an accurate ratio of zero air is important when investigating sources with high VOC content, such as direct stack or exhaust measurements. A dilution system was built using a pump pushing ambient air through a certified 5000 sccm MFC before passing the air through a charcoal scrubber to produce a stream of zero air at an accurately known flow rate. This zero air stream is tied into the main sample line and dilution can be determined knowing the total sample flow drawn by the instruments operating within the ML. The total flow drawn by the PTR-TOF, LI-COR and Picarro instruments was measured to be 1800 sccm.

5.4.1.1 Performance of the Charcoal Scrubber

A charcoal scrubber is used to produce the zero air due to the high flow rate necessary to dilute the main sample stream. Using zero air cylinders would require frequent exchange of empty cylinders with the gas vendor. A simple test to verify the performance of the charcoal scrubber was done on the afternoon of March 14, 2019. While sampling shop air through the ML mast, the PTR-TOF was switched to sampling ML air through the charcoal scrubber at 14:05. At

14:14, sampling returned to ambient shop air through the ML mast and then switched to a zero-air cylinder at 14:19 as the first step of a multipoint calibration routine. Figure 5-55 below shows the measured toluene concentration during this time where it is shown that the toluene is removed by the charcoal scrubber (between 14:05 and 14:14) to a similar extent as the concentration present in the zero air cylinder (14:19 to 14:28).

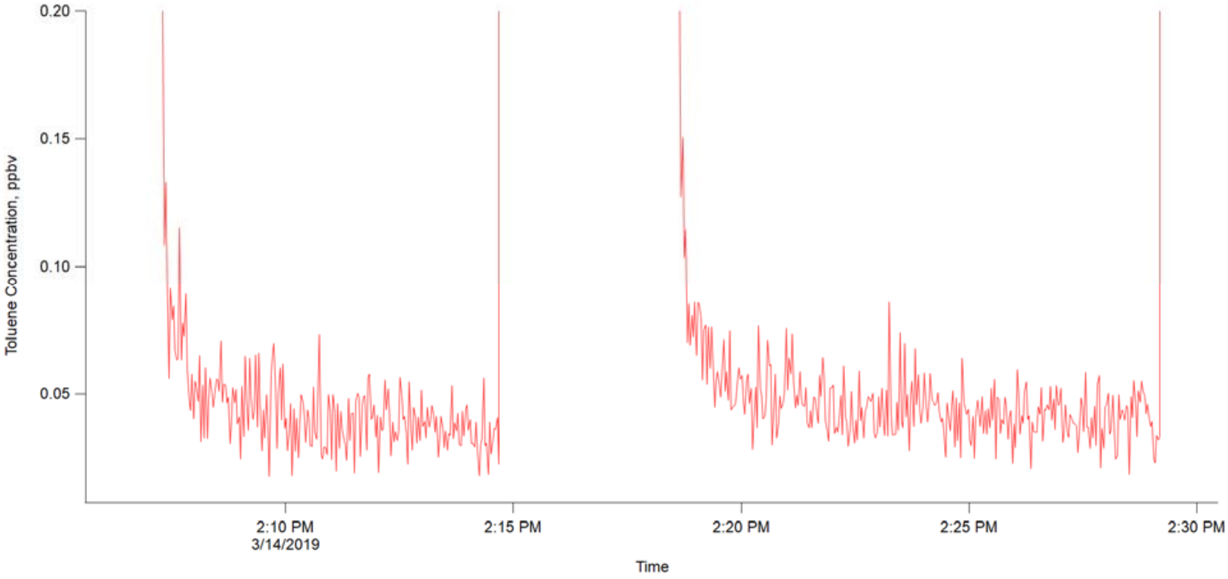

Figure 5-55. Toluene Time Series Plot Verifying the Performance of the Charcoal Scrubber.

Table 5-3 shows the measured concentration of toluene for a representative time of the charcoal scrubbed zero and the zero-air cylinder. The charcoal scrubber provides a sufficient zero-air stream to be used to dilute real samples.

Table 5-3. Toluene Concentration Comparing the Charcoal Scrubber and a Zero-Air Cylinder.

Time	Toluene Result (ppbv)	Method
14:07	0.0358	Charcoal Filter
14:18	0.0398	ZA Cylinder

5.4.1.2 Performance of the Dilution System

The performance of the dilution system was evaluated on March 15, 2019. The instruments onboard the ML were sampling a cumulative flow rate of 1800 sccm of sample. A main sample line MFC controlled the overflow volume to be 2000 sccm so the total sample flow in the main line prior to the instruments was 3800 sccm. The charcoal scrubber dilution zero air was plumbed into a tee prior to the instruments. Ambient air from the shop was sampled through the ML mast with variable dilution flows from 10:41 to 11:21 according to Table 5-4 below. Figure 5-56 shows the time series plot over the course of the experiment. The toluene concentration in the ambient shop air was observed to be 5.30 ppbv with no dilution. Assuming perfect removal of the toluene by the charcoal scrubber, the observed background concentration of 0.057 ppbv in the pure zero air dilution stream after 11:03 was used for background subtraction of all observed concentrations. The resulting estimated concentration of toluene in the ambient shop air was 5.24 ppbv prior to dilution at 10:46. The dilution ratios were used to predict the toluene concentration after dilution assuming the 5.24 ppbv toluene concentration was relatively constant inside the shop. The observed ambient toluene concentration at the end of this experiment was 5.31 ppbv, which is close enough to the assumed concentration of 5.24 ppbv to have confidence the toluene concentration in the ambient air was stable during this experiment. Percent (%) error between the observed concentration and the predicted concentration shows that the dilution system is working very well over a broad range of dilution ratios.

Table 5-4. Toluene Concentrations During Dilution System Testing.

Time	Zero Air Flow Rate (sccm)	Sample Flow Rate (sccm)	Observed Toluene Concentration (ppbv)	Predicted Toluene Concentration (ppbv)	% Error Between Observed and Predicted
10:41	0	3800	5.24	5.24	N/A
10:46	2000	1800	2.46	2.48	-0.8%
10:53	3000	800	1.09	1.10	-0.9%
10:57	3500	300	0.387	0.414	-6.5%
11:03	3800	0	0	0	N/A
11:11	1900	1900	2.56	2.62	-2.3%
11:14	0	3800	5.31	5.24	N/A

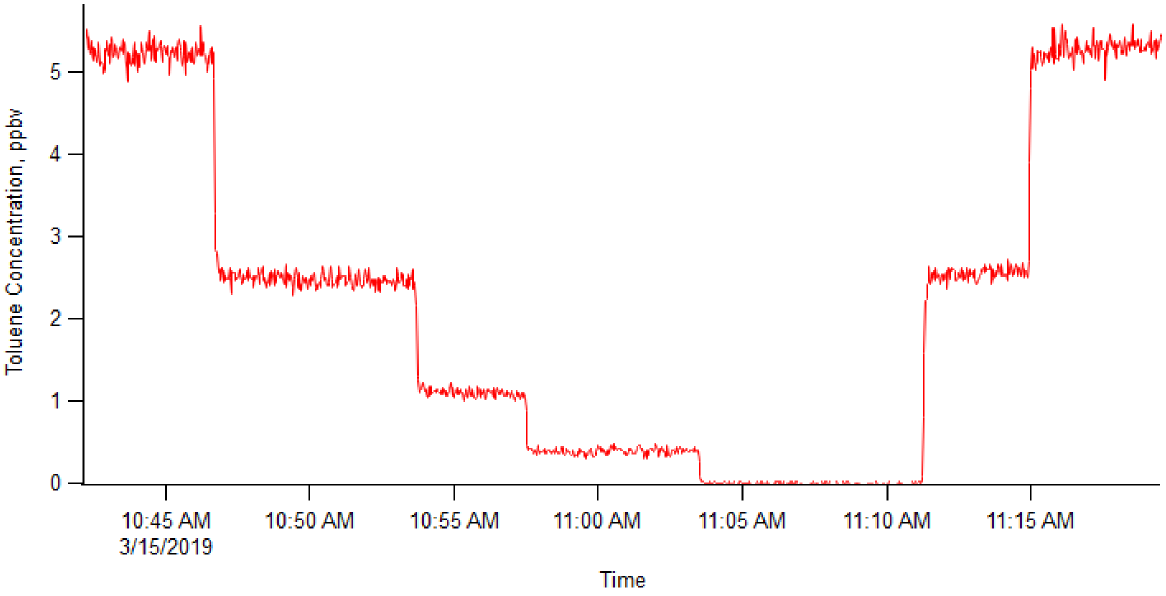

Figure 5-56. Toluene Time Series Over the Course of the Dilution System Performance Test.

The most severe dilution, from 300 sccm to 3800 (or roughly twelvefold dilution), shows the largest error at -6.5%. Perhaps the most significant source of error in determining the dilution is the estimation of the total flow sampled by the instruments. It was measured to be ~1800 sccm. Small errors in knowing this flow rate have a significant impact on the dilution calculation when diluting significantly. For example, if the actual flow sampled by the instrumentation was 1780 sccm, the predicted toluene concentration would have been 5.24 ppbv *(280 sccm/3800 sccm) = 0.387 ppbv, which is the observed toluene concentration. Considering this, it is encouraging that accuracy at the twelvefold dilution is less than 10% error.

5.4.1.3 Performance of the Dilution System with Heated Sample Lines

Multipoint dilution experiments were carried out through the 35’ and 208’ heated lines on March 19, 2019. Table 5-5 shows the results of this experiment with the 35’ heated line. The observed toluene concentrations were background corrected by 0.04 ppbv as determined by pure scrubbed zero air. The LI-COR instrument samples a variable flow depending on the pressure in the sampling system. For this reason, the total flow rate through the sample system was determined by plotting observed toluene concentration against the zero air flow rate. The intercept shows the total flow through the sampling system since any zero air flow rate equal or greater to this flow should result in pure zero air being sampled by the instrument and no ambient sample being drawn in and diluted. The total flow was then used to predict the toluene concentrations based on the dilution factor of the zero and sample flow rates. The error between the predicted and observed toluene concentration at each dilution tested was less than 1%, showing the dilution system is working well with the 35’ heated sample line. Figure 5-57 shows the time series for toluene over the course of the 35’ heated line dilution experiment.

Table 5-5. Toluene Concentrations During Dilution System Testing Down 35’ Sample Line.

Time	Zero-air Flow Rate (sccm)	Sample Flow Rate (sccm)	Observed Toluene Concentration (ppbv)	Predicted Toluene Concentration (ppbv)	% Error Between Observed and Predicted
11:50	0	3949	5.02	5.02	NA
9:59	1000	2949	3.75	3.75	0.1%
10:05	2000	1949	2.47	2.48	-0.1%
10:13	3000	949	1.21	1.21	0.6%
10:21	4000	0	0	0	NA

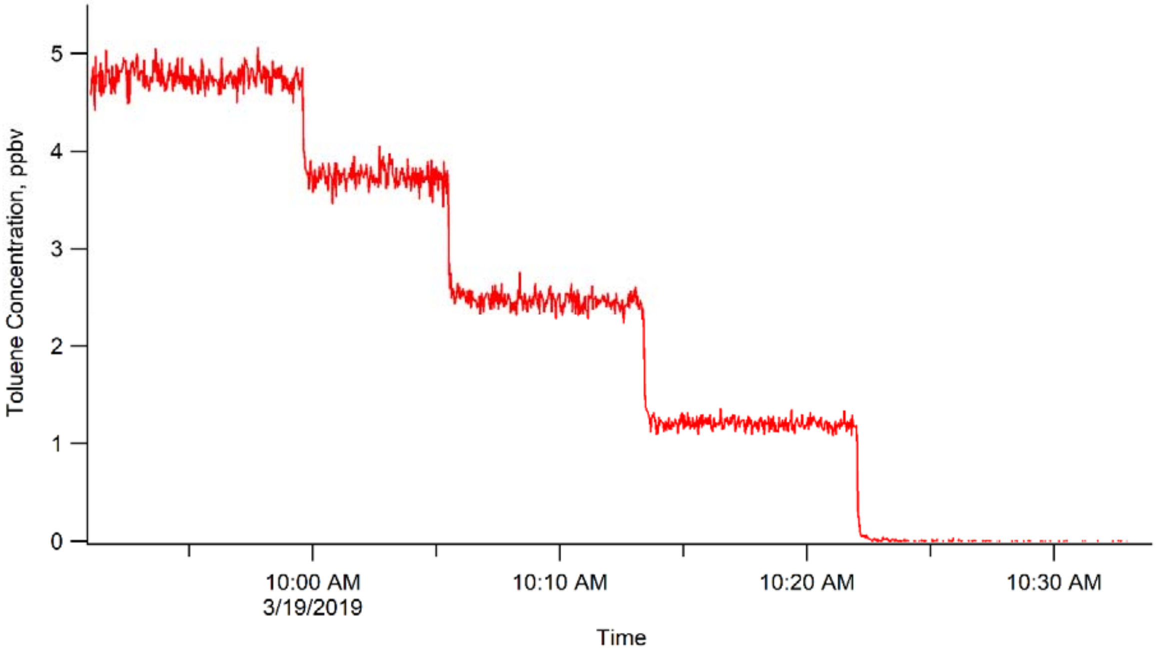

Figure 5-57. Toluene Time Series Over the Course of the Dilution System Performance Test with the 35’ Heated Line.

Table 5-6 shows the results of this experiment with the 208’ heated line. The observed toluene concentrations were background corrected by 0.26 ppbv as determined by pure scrubbed zero air. The 208’ sample line suffers a much greater pressure drop than the ML mast or 35’ heated line so the total flow drawn by the LI-COR is greatly reduced. The total flow rate through the sample system was determined by plotting observed toluene concentration against the zero-air flow rate. The intercept showed a total flow of 3310 sccm, meaning the instruments within the ML were drawing a total of 1310 sccm. The total flow was then used to predict the toluene concentrations based on the dilution factor of the zero and sample flow rates. The error between the predicted and observed toluene concentration at each dilution was more significant with the long sample line, ranging from 14.4% to -8.1%. Figure 5-58 shows the time series for toluene over the course of the 208’ heated line dilution experiment.

Table 5-6. Toluene Concentrations During Dilution System Testing Down 208’ Sample Line.

Time	Zero-Air Flow Rate (sccm)	Sample Flow Rate (sccm)	Observed Toluene Concentration (ppbv)	Predicted Toluene Concentration (ppbv)	% Error Between Observed and Predicted
13:00	0	3310	3.93	3.93	NA
13:10	1000	2310	2.52	2.74	-8.1%
13:20	2000	1310	1.52	1.56	-2.3%
13:30	3000	310	0.42	0.37	14.4%
13:40	4000	0	0	0	NA

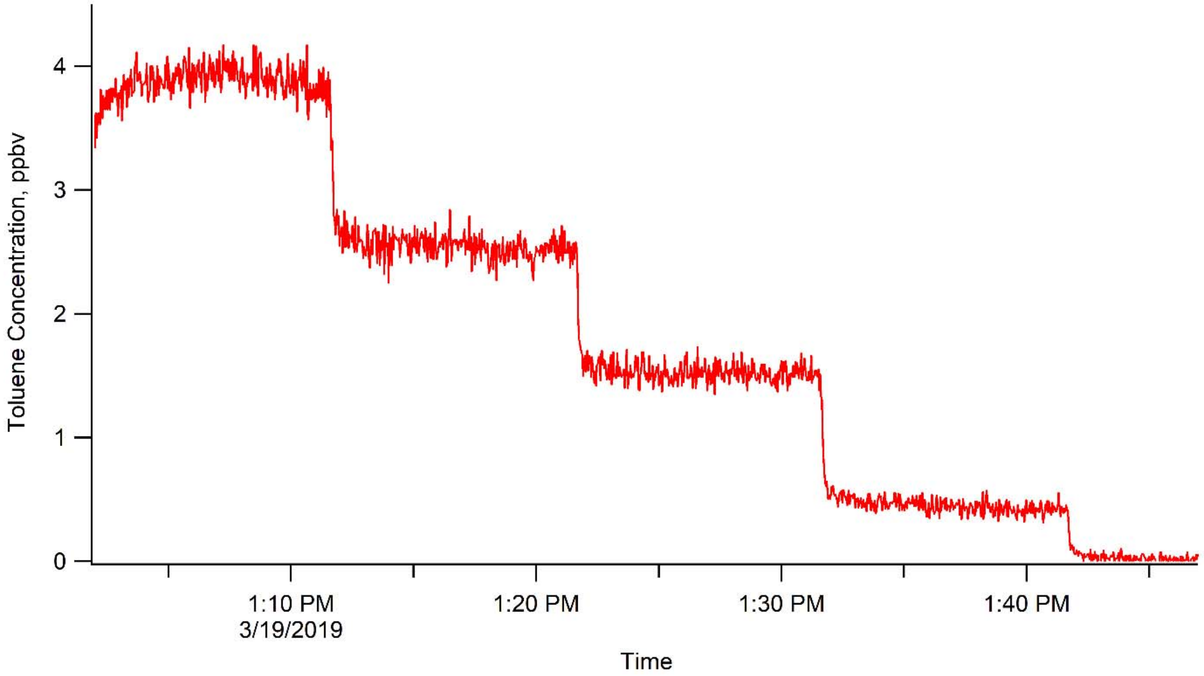

Figure 5-58. Toluene Time Series Over the Course of the Dilution System Performance Test with the 208’ Heated Line.

5.4.2 Sample Line Characterization

Injecting standards at the inlet of a sample line, referred to as a method calibration, reveals any sampling problems that cause observed concentrations to deviate from actual concentrations being sampled. Experiments were conducted using a multicomponent standard diluted to known concentrations sampled down the ML mast, the 35’ heated line, and the 208’ heated line.

5.4.2.1 Mast Sample Line Characterization

Several different dilutions of a multicomponent standard were sampled at the inlet of the ML mast on March 6, 2019. Figure 5-59 (a) through (g) shows correlation plots between the observed concentrations of seven species and the predicted concentration after applying the dilution factor to the standard concentrations. The slope of each plot shows that six compounds are underestimated while toluene is slightly overestimated. All observed concentrations fall within 30% of the expected concentration suggesting no major line loss in the sampling system. All are also very linear suggesting that varying concentration does not impact transport through the sample line. Figure 5-59 (h) shows the time series for all seven species during the multistep dilution experiment. Zero-air was being sampled at 10:11 to purge the sample lines. At 11:00, a flow of 20 sccm of the Research and Development (R&D) standard (roughly 500 ppbv in each compound) was injected into the zero-air flow of 3000 sccm. At 11:51, the standard flow was increased to 80 sccm, then lowered to 60 sccm at 12:12, lowered to 40 sccm at 12:38, lowered to 20 sccm at 12:57, and finally no standard flow (all zero-air) at 13:17. The increase in standard concentration at 11:51 shows that the C_4-benzene ion signal takes time to reach equilibrium with the walls of the sample line. C_3-benzenes show this behavior too but to a lesser degree. The C_4-benzenes required approximately 8 minutes to achieve 95% of the final stable concentration while the C_3-benzenes required 3 minutes to achieve 95% of the stable concentration. Each of the other compounds achieved equilibrium with the sample line walls in a reasonable amount of time. Overall, the observed errors for all seven compounds fall in an acceptable range which demonstrates reliable sampling through the ML mast.

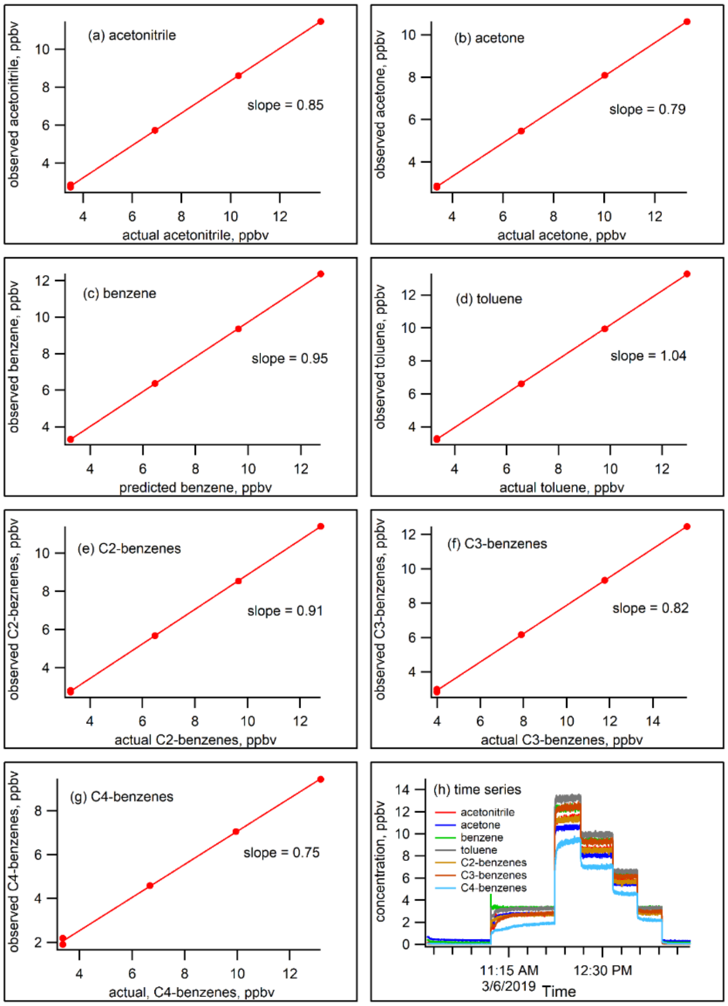

Figure 5-59. [(a) Through (h)] Method Calibration of Seven Compounds in a Standard Sampled Through the Mobile Laboratory Mast.

5.4.2.2 35’ Heated Sample Line Characterization

Two method calibration experiments were performed through the 35’ sample line on March 7, 2019. The first experiment was done with the sample line at ambient temperature while the second was done with the line heated to 60˚C. Figure 5-60 (a) through (g) shows correlation plots between the observed and predicted concentrations for seven compounds in the standard with the 35’ sample line at ambient temperature. Similar to the method calibration through the ML mast, all observed concentrations fall within 30% of the expected value and the linearity of the different dilutions suggests concentration plays no role in line loss effects. Figure 5-60 (h) shows the time series for all seven species during the multistep experiment. The zero-air flow rate was 2000 sccm for this experiment. A standard flow of 80 sccm was started at 11:31 before decreasing to 60 sccm at 12:05, down to 40 sccm at 12:30, 20 sccm at 12:55, and finally only zero air was sampled after 13:21. Similar to the ML mast, the larger compounds require more time to condition the sample lines and provide a constant measurement.

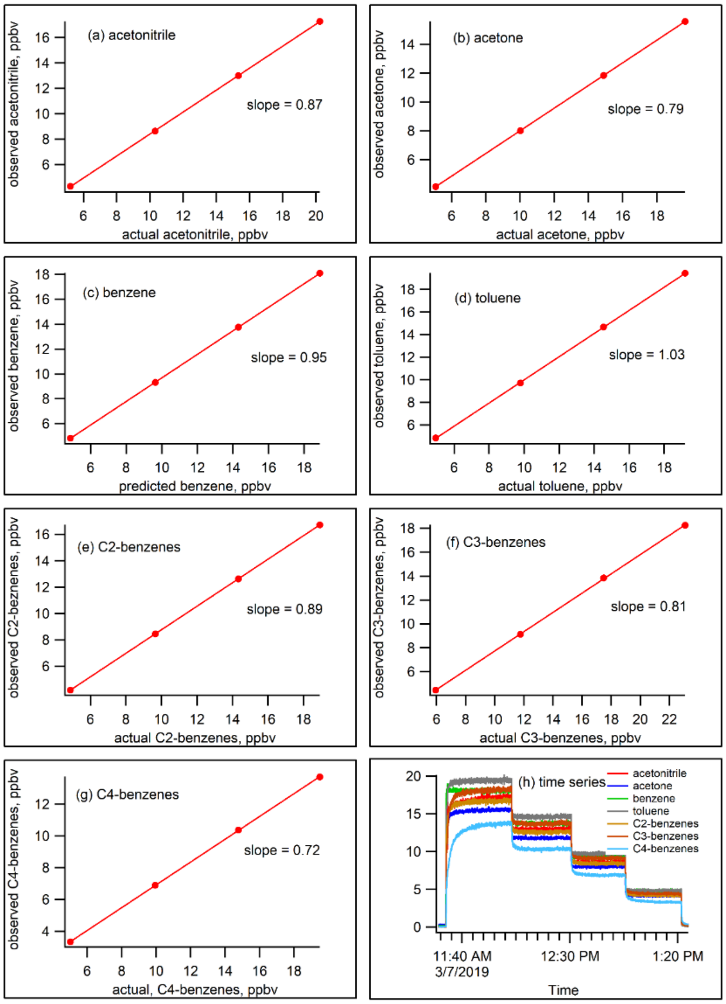

Figure 5-60. [(a) Through (h)] Method Calibration of Seven Compounds in a Standard Sampled Through an Unheated 35' Sample Line.

The heater on the 35' sample line was turned on and allowed to reach a stable temperature of 60˚C. Another multistep experiment was performed starting with a flow of 2000 sccm of zero air at 14:48. At 14:50, the standard flow rate was increased to 80 sccm. The standard flow was decreased to 60 sccm at 15:05, to 40 sccm at 15:20, to 20 sccm at 15:35, and turned off at 15:50 (pure zero air flowing). Figure 5-61 (a) through (g) shows correlation plots between the observed and predicted concentrations for seven compounds in the standard with the 35' sample line at 60˚C. Similar to the method calibration experiments sampled through the unheated line and the ML mast, all observed concentrations fall within 30% of the expected value and the linearity of the different dilutions suggests concentration plays no role in line loss effects. Figure 5-61 (h) shows the time series for all seven species during the multistep experiment. The results are very similar to that of the unheated line except the line conditioning time is slightly shorter in the case of the sample line being heated. The time required to achieve 95% of the equilibrium value of C_4-benzenes is approximately 8 minutes in the 60˚C line compared to approximately 11 minutes in the ambient temperature sample line.

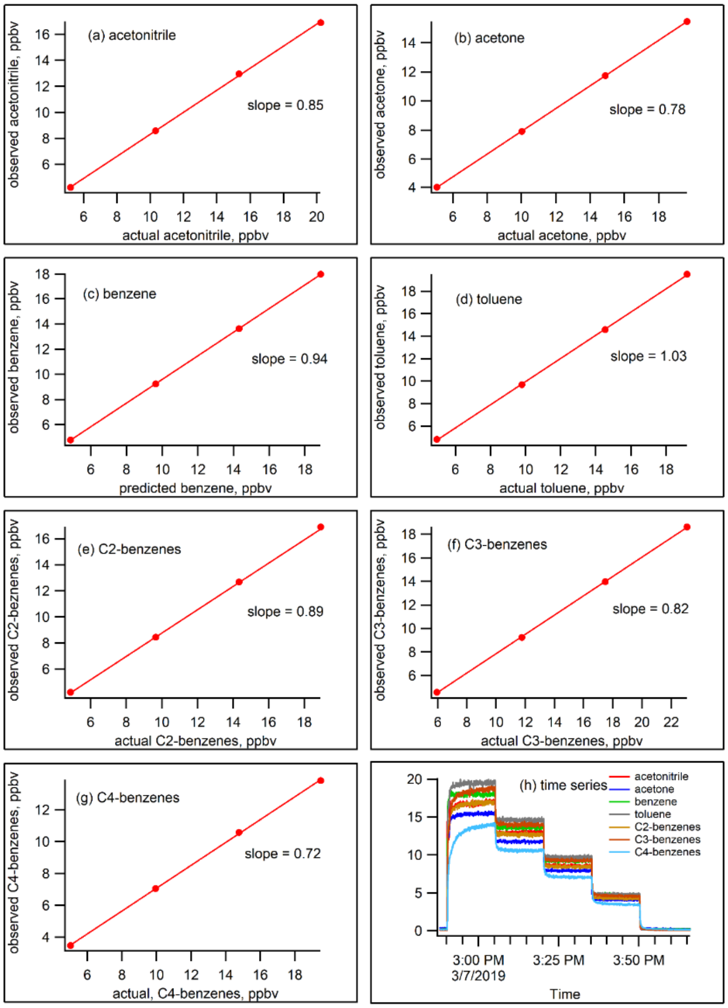

Figure 5-61. [(a) Through (h)] Method Calibration of Seven Compounds in a Standard Sampled Through a Heated 35' Sample Line.

5.4.2.3 208' Heated Sample Line Characterization

A series of tests on the 208' heated sample line was conducted on March 11, 2019; March 20, 2019; March 21, 2019; and March 22, 2019. Four 52' sections of heated sample line are connected in series to achieve a heated line of this length. These sections were installed on March 11, 2019, for leak testing and verification of the heater system to achieve a stable line temperature of 60˚C. On March 20, 2019, and March 21, 2019, experiments were done to demonstrate the use of the longer heated lines by doing basic operational tests using one 52' section. The full method calibration experiment down the full length of 208' at 60˚C was performed on March 22, 2019. The sample line was flushed out with zero air prior to the experiment although background concentration of acetone was still relatively high (9.04 ppbv).

The multistep method calibration started with a flow of 80 sccm of the R&D standard into a flow of 2000 sccm zero air at 13:00. The flow of the R&D standard decreased to 60 sccm at 13:30, decreased to 40 sccm at 13:50, decreased to 20 sccm at 14:10, and was turned off (pure zero air) at 14:30. All data in this experiment was background subtracted using the zero air measurements after 14:30 to remove the elevated background observed in the long heated line. Figure 5-62 (a) through (g) shows correlation plots between the observed and predicted concentrations for seven compounds in the standard with the 208' sample line at 60˚C.

The accuracy of some compounds have improved compared to the method calibrations performed on the ML mast and 35' sample line while the larger compounds have a slightly higher error. This is likely due to an adjustment of the PTR-TOF tuning that occurred between these experiments and not related to the performance of the sample line itself. The results are broadly quite similar. It is worth noting that the C_4-benzene quantification is 31% lower than predicted, falling outside of the desired error range of +/- 30%. The C_4-benzene quantification was low by 25% to 28% on method calibration experiments on the ML mast and shorter heated inlet, which is relatively similar in error magnitude. The linearity of the different dilutions suggests concentration plays no role in line loss effects. Figure 5-62 (h) shows the time series for all seven species during the multistep experiment. There is a delay of approximately 45 seconds from the time the sample is introduced at the inlet until it appears at the PTR-TOF. This agrees with theoretical calculations for the velocity of sample flow through the 208' inlet line. Line conditioning time is higher for the 208' inlet line compared to the shorter 35' heated inlet and ML mast. It takes approximately 20 minutes for the C_4-benzene concentration to achieve 95% of its steady state concentration. The long-heated line demonstrated temperature stability, sufficient flow to feed all instrumentation onboard the ML, and acceptable time response and line conditioning time.

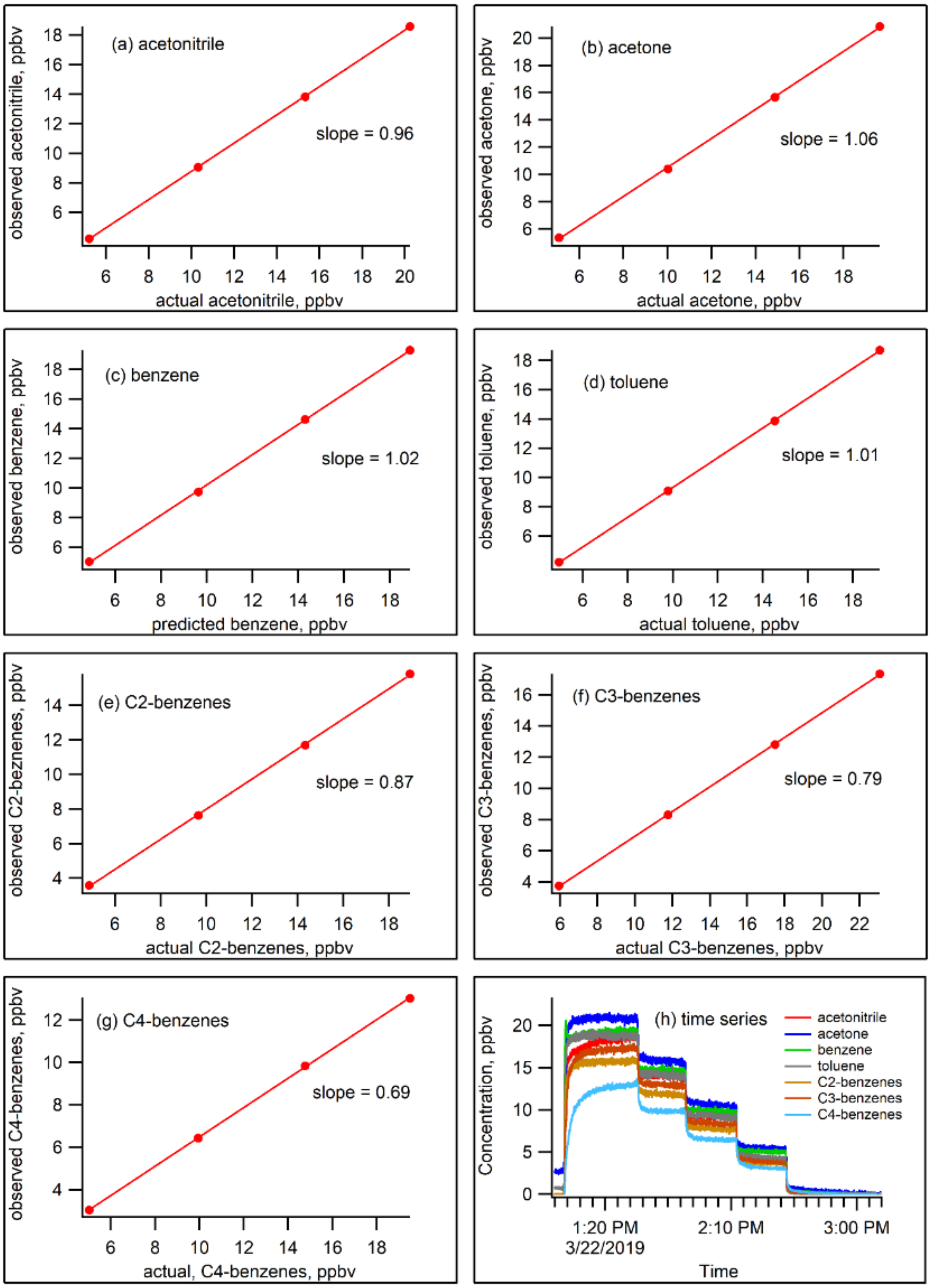

Figure 5-62. [(a) Through (h)] Method Calibration of Seven Compounds in a Standard Sampled Through a Heated 208' Sample Line.

5.4.2.4 Sample Line Characterization Overview

The method calibration experiments on the ML mast, 35’ heated line, and the 208’ heated line all show accurate results for a number of compounds. Table 5-7 shows the ratio of observed to actual concentrations for each of the seven compounds in each multistep experiment presented in the previous sections. The relative error is quite similar over the course of many days and spanning tuning adjustments of the instrument. In each instance, the largest compounds have longer line conditioning times, which is to be expected. Some very polar compounds, such as ammonia, would be expected to suffer very long line conditioning times but were not included in this study.

Efforts should be made to better understand the elevated background observed for all species in the 208’ heated inlet line. While this method calibration experiment demonstrates that background correction is effective when an elevated background is observed, it may be possible to minimize the background prior to deployment. Possible solutions may result from heating and flushing the new sample lines with zero air or by wrapping the lines to prevent the possibility of contaminants transporting through the wall of the tubing.

Table 5-7. Ratio of Observed to Actual Concentrations Across all Method Calibration Experiments in Section 5.3.2.

	ML Mast	35’ Inlet Unheated	35’ Inlet Heated	208’ Inlet Heated
Acetonitrile	0.85	0.87	0.85	0.96
Acetone	0.79	0.79	0.78	1.06
Benzene	0.95	0.95	0.94	1.02
Toluene	1.04	1.03	1.03	1.01
C_2-benzenes	0.91	0.89	0.89	0.87
C_3-benzenes	0.82	0.81	0.82	0.79
C_4-benzenes	0.75	0.72	0.72	0.69

5.4.3 Sorbent System

During testing activities performed during Month 7, efforts were made to collect Carbotrap and Thermosorb sorbent samples using a known quantity of analyte, using certified standard cylinders. The purpose of these tests was to add an additional layer of evaluation to sorbent results comparisons. While previously, sorbents had been taken using the ML sampling system during routine monitoring for the purpose of comparison between the sorbent method and the PTR-MS results, this method lacks a solid point of reference to understand what the “expected” concentration present in ambient air ought to be. Thus, while agreement (i.e., precision) between methods could be tested, their overall accuracy to the air mass being measured was left in question.

Carbotraps are evaluated at ALS by EPA TO-17 VOC analysis and Thermosorbs are evaluated by NIOSH 2522 nitrosamine analysis. To test these laboratory methods, the R&D standard cylinder (a multi-component mix containing a range of compounds detectable by TO-17) and a standard cylinder containing only NDMA were respectively used to provide an “answer key” with which to compare both laboratory analytical methods to PTR-MS. Using the ML sampling and dilution system, the cylinders were separately sampled onto duplicate sorbent media as well as through the PTR-MS. The PTR-MS data were processed at the TerraGraphics office while the sorbents were sent to ALS for EPA TO-17 and NIOSH 2522 analysis. The reproducibility of the reporting laboratory’s analysis using both methods was tested by comparing the results of the duplicate samples. Furthermore, upon obtaining both methods’ results, their percent recovery of the original sample were both compared to determine which is the most accurate to the original cylinder’s concentration. Table 5-8 below details the sorbent samples collected during Month 7.

Table 5-8. Sorbent Samples Collected During Month 7.

Sorbent Type	Sorbent ID#	Date Collected	Cylinder Sampled	Cylinder ID#
Carbotrap	A052439	03/08/2019	R&D	160-401265983-1
Carbotrap	A052433	03/08/2019	R&D	160-401265983-1
Thermosorb	EL33313	03/29/2019	NDMA	CC496322
Thermosorb	EL33302	03/29/2019	NDMA	CC496322

5.4.3.1 Carbotrap Comparison

Using the ML’s sampling and dilution system, a consistent and measurable flow of R&D standard cylinder was sampled through both duplicate Carbotraps and the PTR-MS. Table 5-9 below details the results of the test performed on March 8, 2019.

Table 5-9. Reproducibility and Recovery of Analytes from a Volatile Organic Compound Standard Cylinder, by Duplicate Carbotrap TO-17 Analysis and Proton Transfer Reaction – Mass Spectrometer.

Analyte	Carbotrap TO-17 RPD	Carbotrap TO-17 %REC	PTR-MS %REC
1,3,5-trimethyl benzene	12	204	74
acetone	9	956	79
benzene	0	154	100
methyl ethyl ketone	0	100	70
p-xylene	11	220	84
toluene	11	199	97

For the purpose of comparison, the two duplicate sorbent results were averaged together when calculating percent recovery of the original sample. In addition, this test only focuses on the compounds detectable by both TO-17 and PTR-MS present in the standard cylinder being sampled.

The reproducibility of the Carbotraps was, as expected, fairly low (0 – 12%). This metric can be understood as a percent difference calculation, where the absolute difference between the two duplicate samples was normalized to the average of the two samples, per analyte. Thus, low values are desirable. In effect, these results indicate that the reporting laboratory and the ML sampling system itself were fairly consistent in their analysis methods and ML sample dilution methods, respectively.

The percent recovery of the original standard calculated for the Carbotraps as reported by ALS yielded interesting results. Many of the analytes showed close to a 200% recovery of the standard cylinder, i.e., the results as reported by ALS were roughly twice as high as the calculated expected result using the standard cylinder concentration, dilution, and duration of sampling. Methyl ethyl ketone recovery came out to be almost exactly 100% of the original sample. The biggest outlier result was the unaccountably high acetone result as reported by ALS, calculated to be nearly 1000% or ten times that of the original acetone present in the cylinder.

The percent recoveries calculated for PTR-MS all fall within 70% – 100% of the calculated expected value. This result is partially driven by PTR-MS transmission efficiency tuning using this cylinder in other tests, allowing the PTR-MS to more accurately reflect the contents of the standard. Additionally, the analytes being investigated are all shown to be detectable by PTR-MS, especially when sampled in simpler matrices at higher concentration like standard cylinders, as opposed to trace amounts in ambient air. A few caveats related to isobaric interferences should be mentioned, however. For example, any isomers of 1,3,5-trimethylbenzene (such as any C_3-benzene) would produce the same signal at m/z 121 in the PTR-MS. Also, the difference between ortho-, para-, and meta-xylene would be indistinguishable on PTR-MS. The successes of PTR-MS when analyzing compounds of this nature come down to the composition of the standard cylinder and choosing a mixture which does not contain compounds of identical empirical formulas, and therefore molecular weight.

In review, the duplicate sorbents drawn on March 8, 2019, had good agreement in their reproducibility. This speaks well of both the sampling system used to draw the sorbents and the consistency of the analytical technique employed by ALS. The calculated PTR recoveries help to validate the assumption that the PTR reports within ±30% of the expected concentration of an analyte. However, the generally double recoveries obtained by comparing the ALS results to the expected result indicate some sort of systematic bias in the analysis of the results. This is especially true with the inexplicably high acetone found in the ALS results. Upon reviewing with the ML SME, there was found to be no plausible way to systematically introduce acetone as a contaminant to the sorbents at that magnitude while collecting the samples. The acetone source would have to be very pure and introduced in relatively large quantities to exceed the amount of acetone delivered by the cylinder. Furthermore, acetone as a solvent is not present in the ML or the shop during testing or routine operations. This opens up the possibility that the samples were contaminated in transit to or at the analytical laboratory.

5.4.3.2 Thermosorb Comparison

Using the ML's sampling and dilution system, a consistent and measurable flow of NDMA standard cylinder was sampled through both duplicate Thermosorbs and the PTR-MS. Table 5-10 below details the results of the test performed on March 29, 2019.

Table 5-10. Reproducibility and Recovery of Analytes from an NDMA Standard Cylinder, by Duplicate Thermosorb NIOSH 2522 Analysis and Proton Transfer Reaction – Mass Spectrometer.

Analyte	Thermosorb NIOSH 2522 RPD	Thermosorb NIOSH 2522 %REC	PTR-MS %REC
n-nitrosodimethylamine (NDMA)	N/A	0.87	169

A reproducibility could not be calculated for the Thermosorb results as ALS reported a non-detect (ND) on sample EL33302. Sample EL33313 was reported to have a result of 17 ng of NDMA. Based on the concentration of the standard cylinder, the configuration of the sampling and dilution system, and sampling duration, the sorbent cartridge was expected to have collected 1955 ng of NDMA. Thus, the one ALS result that produced a result above the detection limit only achieved a 0.87% recovery of the original sample.

The PTR-MS achieved a recovery of 169%. This means that the PTR-MS over-estimated the NDMA concentration by over two-thirds of the expected result. While the ML can be confident in accurately qualitatively identifying NDMA, this result represents room for improvement in the ML’s ability to accurately quantify the ambient NDMA concentration. Typically, NDMA concentration is converted from instrument counts using a kinetic approximation method, wherein the effective rate constant of ionization is estimated. Further efforts to improve the quantitative result of NDMA could be achieved through the application of calibration factors during data analysis at the TerraGraphics office, especially with access to a pure NDMA standard. Seeing as absolute quantification of NDMA is viewed as supremely desirable to the client, it is recommended to use the NDMA standard cylinder to accurately calibrate the PTR for NDMA.

6.0 QUALITY ASSESSMENT

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

During the March 1, 2019, to March 31, 2019, period, there were no DRs documented.

7.0 CONCLUSION

In Section 5.1, analysis was performed utilizing the fingerprint tool on all 5 days of area monitoring in March 2019. This identified a variety of unique plumes that could be attributed to vehicle exhaust, generator exhaust, Gator exhaust, septic tank emissions, asphalt, and some unidentified sources. No plumes with considerable levels of COPCs were detected or identified and the composition of the observed plumes were similar to those analyzed in previous reports. There were some unique plumes containing higher levels of butanal on March 25, 2019, and March 26, 2019, and multiple plumes throughout all the days with either a strong NO_2 or acetaldehyde response. Continual observation and analysis of all types of plumes increases understanding of already known sources and strengthens the knowledge and ability to identify unknown sources. The number of plumes analyzed demonstrates the wide variety of sources and the variability of composition even within similar sources. While this analytical effort was extensive and addressed all the important plumes occurring during these observations, it takes considerable effort to do this through visual inspection of the data. Future analysis will incorporate the fingerprint information to generate tools that enhance the ability to identify and analyze plumes more efficiently.

Analysis of the composition of two diesel generators was detailed in Section 5.2. Diesel generators are a common emission source onsite and sampling within the exhaust plume provides the best dataset for determining the actual composition. The fingerprints showed that nominal m/z 46 was the primary constituent and has been attributed to NO_2, which is a known component of diesel combustion. In addition, the typical combustion engine species were found with contributions from formaldehyde, nominal m/z 43, and acetaldehyde. There were also some large differences between the two generators with GEN2 having higher acetaldehyde and containing a wider variety of species and GEN1 having a higher response in nominal m/z 43 and acetic acid + acetate fragment. There were also come differences in the ratio of CO_2 to VOCs that could relate to the combustion efficiency or emission controls of the generator with higher ratios suggesting more complete combustion. Overall, GEN1 had a higher combustion efficiency and/or emission controls than GEN2.

There was additional source characterization to determine the composition of windshield cleaner. While not a major source, there is enough vehicle traffic performing a variety of duties that makes monitoring of a windshield cleaner possible. The ML is often cleaned using Stoner Invisible Glass®[15] and was found to contain formaldehyde, acetaldehyde, acetone, and dimethyl sulfide + ethanethiol. There was also response at nominal m/z 41, nominal m/z 43, and nominal m/z 60, but the species responsible for the response is unknown.

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[15] Invisible Glass is a registered trademark of Stoner, Incorporated, Quarryville, Pennsylvania.

There have been ongoing efforts to characterize the efficacy of the ML sampling system in its multiple sampling configurations (mast, 35' inlet, 208' inlet). This includes performance analysis of the newly-developed sample dilution system used to sample from sources with high VOC composition. This system dilutes the sample in real-time to manageable levels by introducing a controlled amount of charcoal-filtered zero-air to the sample line. All three sampling configurations were tested and were shown to perform well in each scenario. The highest differences between measured and expected toluene concentration were within 15% for the 208' heated line, within 7% when sampling through the mast, and showing differences less than 1% when sampling through the 35' heated line.

In addition to testing the sample dilution system, all three sample lines were tested with a multipoint calibration using a multi-component VOC standard. Measurements were within 30% of expected for all analyzed components except for C_4-benzenes within the 208' line. This showed good sample recovery and minimal analyte loss for all the sampling configurations. Larger species need additional time to condition within the sample line especially for the 208' line. Polar compounds not tested would be expected to have long conditioning times as well. There is an elevated background when sampling through the 208' line and further testing could help in understanding the source and potential solutions.

To compare the PTR-MS to other analytical methods, two Carbotraps and two Thermosorbs were set up to sample a known mixture of VOCs simultaneously with the PTR-MS. While sampling the Carbotraps in duplicate, the PTR-MS had percent recoveries ranging from 74% to 100% showing good performance within expected ranges. The Carbotraps had good agreement between one another within 12% relative percent difference (RPD) showing precision with ALS and the ability of the ML dilution system to produce consistent concentrations. However, the percent recovery as reported by ALS was around 200% for most analytes except acetone, which suggests there may be a systematic bias in their analysis method. The acetone was 956% recovery and there is not a sufficiently high concentration source that could produce acetone at those levels within the ML sampling setup. It is potentially a contaminant introduced in sample handling from time of collection through ALS analysis. For the two Thermosorbs, the PTR-MS had 169% recovery which shows an overestimation by the PTR-MS. The ALS results showed inconsistency with one Thermosorb result resulting in a non-detect and the other resulting in a less than 1% recovery. This shows complications of sampling NDMA with either method, but the PTR-MS results provided a more reasonable result. Further testing to understand NDMA could improve the accuracy of NDMA measurements with the PTR-MS.

8.0 REFERENCES

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REVIEW COMMENT RECORD (RCR)

Project Number/Title.: 53005-81, Data Analysis for the Proton Transfer Reaction – Mass Spectrometer Mobile Laboratory		Page: 1 of 1
Document Number(s)/Title(s): 53005-81-RPT-059, PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report -Month 7	Reviewer(s): Eugene Morrey	Date: September 11, 2019

DISPOSITION CONCURRENCE/COMPLETION

Reviewer Concurrence (Print & Sign): Eugene Morrey	Date:	Author/Originator Completion (Print & Sign): Kimberly Boone Kimberly Boone	Date: 9/24/2019

Item No.:	Page/Section No.:	Reviewer Comments: (Provide Basis and Recommended Action)	Reviewer Initials:	Disposition: (Provide Justification if NOT Accepted)	Status:
1	Pg. 9, 3rd para., 1st sentence	Add space after (n)	EM	Complete. -KDB	Complete
2	Pg. 10, Table 3-1	Per expiration dates in Table 3-1, several of the calibration gases expired previous to or during the test period. I don't see this addressed in the report.	EM	These calibration gases were not used for the duration of Month 7. Looking into the possibility of getting these recertified before using for testing. -KDB	Complete
3	Pg. 11, Table 3-5	Which mass unit or compound is being reported in Tables 3-4 and 3-5 for observed and expected results?	EM	For the PTR-MS we use the trace for toluene to track the zero-air and span checks. This has been added to the report. -KDB	Complete
4	Pg. 51, Figure 5-37	The thiols seem to be present a lot in emissions plumes. I wonder if they are possibly misidentified as thiols or would we expect thiols in emissions?	EM	We do see the presence of thiols in some petroleum-based fuels, so this is not unusual to see in exhaust plumes. -KDB	Complete
5	Pg. 62, Figure 5-49	It would be nice to label Gen 1 and Gen 2 data in the figure.	EM	The Gen 1 and Gen 2 are time-stamped and separated by a gap in signal, captured by two separate plumes, and explained in the text. -KDB	Complete

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REVIEW COMMENT RECORD (RCR)

Project Number/Title.: 53005-81, Data Analysis for the Proton Transfer Reaction – Mass Spectrometer Mobile Laboratory		Page: 1 of 2
Document Number(s)/Title(s): 53005-81-RPT-059, PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report -Month 7	Reviewer(s): George Weeks	Date: August 27, 2019

DISPOSITION CONCURRENCE/COMPLETION

Reviewer Concurrence (Print & Sign): George Weeks	Date:	Author/Originator Completion (Print & Sign): Kimberly Boone Kimberly Boone	Date: 9/16/2019

Item No.:	Page/Section No.:	Reviewer Comments: (Provide Basis and Recommended Action)	Reviewer Initials:	Disposition: (Provide Justification if NOT Accepted)	Status:
1	Pg. 16, Section 2.1.1.2, 1st sentence	Change to “software system.”	GEW	Accepted. RLF	Complete
2	Pg. 18, Section 2.2.2, 2nd sentence	Change “are” to “were.”	GEW	Accepted. RLF	Complete
3	Pg. 20, Para. 2, 2nd sentence	Delete “of.”	GEW	Accepted. RLF	Complete
4	Pg. 21, Table 3-1	Look like R&D, Furan, N-Nitrosodimethylamine, and 1,3-butadiene look like they all have already expired or expired during the sampling period. This is a significant QA failure if ture.	GEW	We are currently investigating the possibilities of getting these tanks recertified. However, the gas cylinders in question are not used for reporting purposes. They have only been used for testing in concurrence with VOC cylinder. -KDB	Complete
5	Pg. 24, Section 4.1.1	Yes, but what was the uncertainty of each measurement and how was it determined? Biased? Random error?	GEW	The uncertainty has not been calculated, as it was not defined to do so in the scope of work. However, this can be readdressed upon request in new scope of work/new contract. -KDB	Complete

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REVIEW COMMENT RECORD (RCR)

Project Number/Title.: 53005-81, Data Analysis for the Proton Transfer Reaction – Mass Spectrometer Mobile Laboratory		Page: 2 of 2
Document Number(s)/Title(s): 53005-81-RPT-059, PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report -Month 7	Reviewer(s): George Weeks	Date: August 27, 2019

6	Pg. 24, Section 4.1.2, Last sentence	Did you determine the actual uncertainty?	GEW	See Item No. 5	Complete
7	Pg. 24, Section 4.1.3, Last Sentence	Did you determine the actual uncertainty?	GEW	See Item No. 5	Complete
8	Pg. 26, Section 5.1.1, 1st sentence	Change “in” to “around.” The ML didn’t enter either the A or C Farm.	GEW	Accepted. RLF	Complete
9	Pg. 75, Para. 1, 1st sentence	Change “units” to “unit of measure is.”	GEW	Accepted. RLF	Complete
10	Pg. 78, Para. 1, 2nd sentence	Higher or Lower	GEW	GEN 1 higher than GEN 2, as stated. - KDB	Complete
11	Pg. 97, Section 7.2	Remove Section 7.2.	GEW	Accepted. RLF	Complete