PTR-MS MOBILE LABORATORY VAPOR MONITORING MONTHLY REPORT – MONTH 3

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Table of Contents

Appendices

Figures

Tables

Acronyms and Abbreviations

ALS	Australian Laboratory Services
ANOVA	Analysis of Variance
AOP	Abnormal Operating Procedure
ASTM	ASTM International
COPC	Chemical of Potential Concern
DNPH	Dinitrophenylhydrazine
DR	Deficiency Report
FY	Fiscal Year
GC/MS	Gas Chromatograph – Mass Spectrometer
HPLC	High Performance Liquid Chromatograph
MBK	2-hexanone
MDL	Method Detection Limit
ML	Mobile Laboratory (Mobile Vapor Monitoring Laboratory)
NDEA	N- Nitrosodiethylamine
NDMA	N-Nitrosodimethylamine
NEMA	N-Nitrosomethylethylamine
NIOSH	National Institute for Occupational Safety and Health
NMOR	N-Nitrosomorpholine
OEL	Occupational Exposure Limit
PM	Project Manager
ppbv	parts per billion by volume
ppmv	parts per million by volume
pptv	parts per trillion by volume
PTR-MS	Proton Transfer Reaction – Mass Spectrometer
PTR-TOF	Proton Transfer Reaction – Time of Flight
QAR	Quality Assurance Representative
RL	Reporting Limit
RPD	Relative Percent Difference
SME	Subject Matter Expert
TIC	Tentatively Identified Compound
UPS	Uninterruptible Power Supply
VOC	Volatile Organic Compound
WRPS	Washington River Protection Solutions, LLC

Executive Summary

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

During Month 3, running from October 1, 2018, through November 7, 2018, the Mobile Laboratory performed maintenance tasks and modifications to the Mobile Laboratory in preparation for the background study. Testing and verifications of the Mobile Laboratory systems occurred during the two weeks prior to the background sampling study. The Mobile Laboratory also participated in source characterization of the septic tanks located near 242-A Evaporator on the Hanford Site in support of the Fugitive Emissions Team.

For the majority of Month 3, the Mobile Laboratory was used for the measurement of volatile organic compounds during a field campaign spanning 24 days of sampling during a background sampling study that focused on sixteen chemicals of potential concern, including nitrosamines, furans, and ammonia.

The background study occurred from October 15, 2018, to November 7, 2018. It included six sites with four repeated visits to each site, on a rotating basis. The technical basis for this study is the same as the previous background studies performed by RJ Lee Group, Inc. Five sampling locations were chosen within the secured Hanford area and one site within the City of Kennewick to represent a site with heavy traffic and mixed commercial use.

1.0 DESCRIPTION OF TESTS CONDUCTED

During Month 3, spanning the dates of October 1, 2018, to November 7, 2018, the Mobile Laboratory (ML) was deployed for the measurement of Volatile Organic Compounds (VOCs) after ML maintenance, modification, and operational testing were performed. During this period, two testing campaigns were conducted on the Hanford Site (Figure 1-1). These tests detailed in Section 5.0 included a septic analysis and a background study. Table 1-1 provides a summary of tests and activities conducted during Month 3.

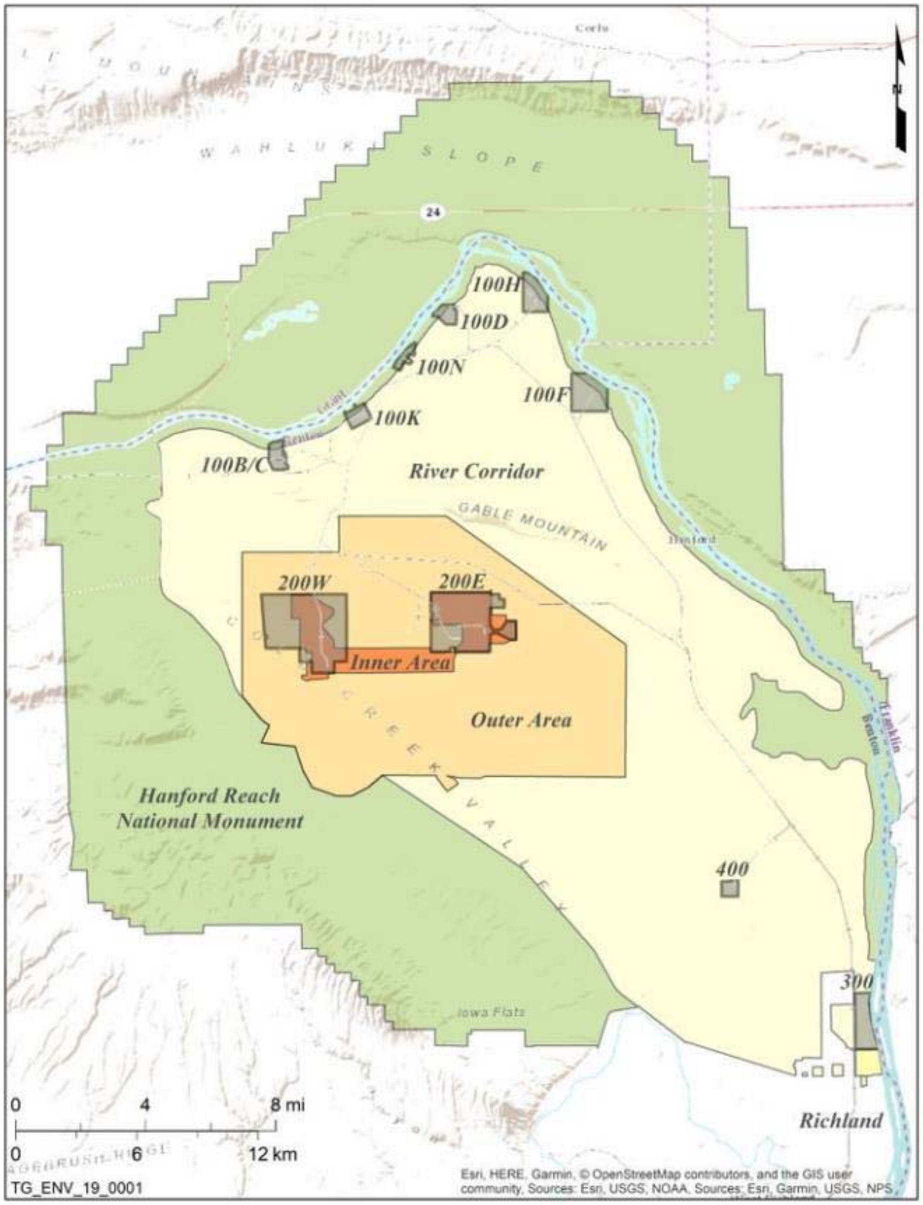

Figure 1-1. Hanford Site.

Table 1-1. Summary of Month 3 Testing and Operational Activities.

Week	Date	Activity
9	10/01/2018	Laboratory Maintenance
	10/02/2018	Laboratory Modifications
	10/03/2018	Laboratory Maintenance
	10/04/2018	Laboratory Maintenance and Modifications
	10/05/2018	Laboratory Testing
10	10/08/2018	Laboratory Modifications & Testing
	10/09/2018	Laboratory Maintenance
	10/10/2018	Characterization of Septic Tanks
	10/11/2018	Stationary Monitoring and Testing
	10/12/2018	Laboratory Modifications and Testing
11	10/15/2018	Site 1 (Stationary Monitoring)
	10/16/2018	Site 2 (Stationary Monitoring)
	10/17/2018	Site 3 (Stationary Monitoring)
	10/18/2018	Site 4 (Stationary Monitoring)
	10/19/2018	Site 5 (Stationary Monitoring)
	10/20/2018	Site 6 (Stationary Monitoring)
12	10/21/2018	Site 1 (Stationary Monitoring)
	10/22/2018	Site 2 (Stationary Monitoring)
	10/23/2018	Site 3 (Stationary Monitoring)
	10/24/2018	Site 4 (Stationary Monitoring)
	10/25/2018	Site 5 (Stationary Monitoring)
	10/26/2018	Site 6 (Stationary Monitoring)
	10/27/2018	Site 1 (Stationary Monitoring))
13	10/28/2018	Site 2 (Stationary Monitoring)
	10/29/2018	Site 3 (Stationary Monitoring)
	10/30/2018	Site 4 (Stationary Monitoring)
	10/31/2018	Site 5 (Stationary Monitoring)
	11/01/2018	Site 6 (Stationary Monitoring)
	11/02/2018	Site 1 (Stationary Monitoring)
	11/03/2018	Site 2 (Stationary Monitoring)
14	11/04/2018	Site 3 (Stationary Monitoring)
	11/05/2018	Site 4 (Stationary Monitoring)
	11/06/2018	Site 5 (Stationary Monitoring)
	11/07/2018	Site 6 (Stationary Monitoring)
	11/08/2018	Site 3 (Stationary Monitoring)
	11/09/2018	Site 6 (Stationary Monitoring)

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

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

1.1 Description of Septic Analysis

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 October 10, 2018, as part of a short-term investigation of septic odors. The ML was stationed at the southwest corner of AP Tank Farm, downwind of a septic tank and drain field to the north of the farm. Measurements were made with no issues and a multi-compound profile was produced for this analysis which is detailed in Section 5.1.

1.2 Description of Background Study

The field campaign, referred to as the background study, was performed in accordance with 66409-RPT-007, *Mobile Laboratory Operational Project Test Plan FY2019* (Test Plan). The study included 24 days of sampling at six pre-determined sampling sites four days each on a revolving schedule. This study is a continuation of Fiscal Year (FY)17 sampling activities where samples were taken over a six-week period encompassing six sites of interest with repeated visits to each location throughout the test period. The goal of the background study is to provide a comprehensive spatial and temporal study of chemicals of potential concern (COPCs) background concentrations both on and off the Hanford Site.

The sampling locations chosen for this study were the following:

- **Site 1:** Hanford Central Plateau northwest of the 200W Tank Farms, chosen as an upwind location from the central Hanford Plateau.
- **Site 2:** Southern end of the 200W Tank Farms.
- **Site 3:** Near the Corner of 4th and Buffalo; west of the 242-A Evaporator. This site is historically known for the occurrence of several Abnormal Operating Procedure (AOP)-015 Events.
- **Site 4:** Downwind of the AN Tank Farm.
- **Site 5**: Southwest of the Waste Treatment Plant.
- **Site 6:** Near the intersection of US-395 and Clearwater Avenue in Kennewick, WA. This site represents heavy traffic and mixed commercial activity.

The background study focused on sixteen compounds from the Hanford COPC list; four nitrosamines, fourteen furans, and ammonia. Additional details regarding the nature, results, and conclusion of this study are provided in Section 5.2. An assessment of study completeness along with an assessment of ML measurements to confirmatory sample measurements are also provided.

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 3.

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 3, 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 3. When deployed for septic tank monitoring, the ML used both the mast and the side port to perform air sampling. The mast was utilized for sampling for the duration of the background study sampling.

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

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

2.1.1.1 Proton Transfer Reaction – Mass Spectrometer Sampling

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

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

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

2.1.1.2 DAQFactory Sampling

DAQFactory®[3] is a data acquisition and automation software from AzeoTech that allows users to design custom applications with control and automatic output settings. In the ML, DAQFactory controls the sampling system through valves and flow controllers for the LI-COR®[4] CO_2 monitor, Picarro Ammonia Analyzer, Airmar®[5] Weather Station, and the PTR-TOF.

2.2 Instrumentation and Methods Used

The following sections detail the instrumentation and methods used while collecting data in the ML during Month 3.

2.2.1 Proton Transfer Reaction – Mass Spectrometer

Measurements performed by the ML during Month 3 utilized the IONICON PTR-TOF 6000 X2 system. The mass resolution of the PTR-TOF 6000 is sufficient to resolve 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.

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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.

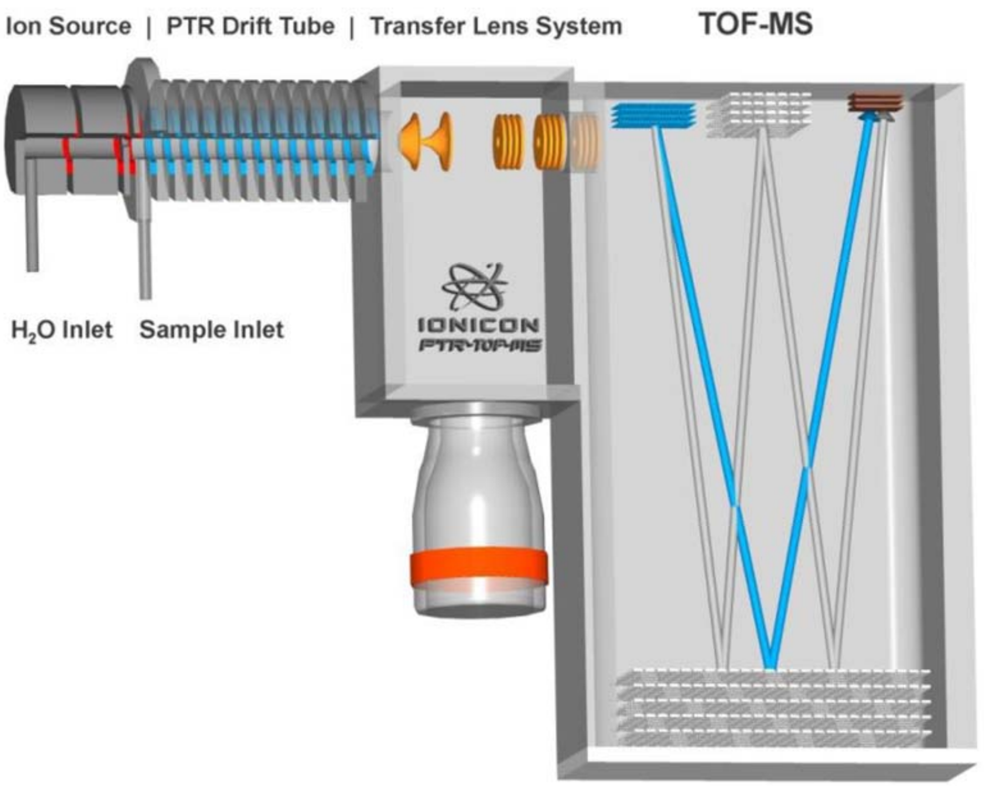

Figure 2-1. The General Configuration of an IONICON Proton Transfer Reaction – Time of Flight Instrument.

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

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

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. 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, ASTM International (ASTM)®[6], and National Institute for Occupational Safety and Health (NIOSH)®[7]. The end user of the technology is expected to provide the "best practice" in its use by adhering to established operational parameters governed by the scope of the project and the nature of the sample(s) to be measured.

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

2.2.2 Carbon Dioxide Monitor

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

The CO_2 monitor used in the ML was the LI-COR Model 850A. The Li-850A is an absolute, non-dispersive infrared gas analyzer based upon a single path, dual wavelength infrared detection system. It is a low-maintenance, high performance monitoring solution that gives accurate, stable readings over a wide range of environmental conditions. It has a range of 0-20,000 ppmv (0-2%), low power consumption (4W after power-up), and 1-second signal averaging to allow for real-time source apportionment (i.e., monitoring vehicle exhaust or other combustion sources on-the-fly). The instrument operates on a gas flow of less than 1 liter per minute.

It is interfaced to the ML's internal gas manifold at the same location as the PTR-MS sampling port to ensure that both instruments are simultaneously measuring the same source. The data

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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.

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 the background study and sewer sampling was operated using a factory calibration. Periodic checks of the unit were made with zero-air and ambient background air (ambient atmospheric CO_2 levels are approximately 400 ppm), and a certified reference standard to ensure continued system operation. The system has a continuous direct readout which can be displayed on the DAQFactory monitor in real time to aid in real-time decision making by the field analysts.

2.2.3 Ammonia Monitor

Ammonia is a compound on the COPC list of particular importance. It is believed to be associated with all high-level waste storage tanks on the Hanford Site. The global average background for ammonia is between 5-7 parts per million by volume (ppbv). 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 ± 0.005ºC temperature stability and ± 0.0002 atm pressure stability to ensure low noise and high accuracy measurements. Sample flow rate to the instrument was provided by an external pump at 0.8 liters per minute at 760 Torr.

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

2.2.4 Weather Station

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

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

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

2.3 Confirmatory Measurements

Although PTR-MS has exceptional response time, sensitivity, and is an excellent instrument for quantification, it suffers from the inability to make qualitative determinations of complex samples. Alternate analytical methods can provide important supporting evidence of the qualitative assignments made while interpreting the PTR-MS data as well as quantification validation of some COPCs. The Gas Chromatograph – Mass Spectrometer (GC/MS), High Performance Liquid Chromatograph (HPLC)/MS/MS, HPLC and GC methods used to support and confirm PTR-MS were performed using well-established methodology by accredited laboratories. Within the context of this study, the three confirmatory methods that were utilized were NIOSH Method 2522, "Nitrosamines," modified; EPA TO-17, "Volatile Organic Compounds," modified; and EPA TO-11A, "Toxic Organic Compounds."

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.

The confirmatory sampling strategy and analyte list for this background study was designed with several objectives in mind.

1. The chemical is generally present in high enough concentrations in the background studies to be detected, under reasonable sampling times, by the confirmatory methods.
2. Chemical is in the calibration list for at least one of the confirmatory methods.
3. Chemical is quantified by PTR-MS and if possible, a COPC.

Commercially available traditional laboratory analytical techniques do not analyze for a large number of the 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 by Tentatively Identified Compound (TIC).

The frequency and duration of the sampling was designed to produce duplicates for each method utilized for each of the six background sites. For this reason, both accuracy and precision data can be evaluated. Also, one blank per ten samples analyzed was performed.

By the very nature of the experiment, the concentrations measured during the background study are very low, and in most cases, below the reporting limits (RLs) or detection limits. The list analyzed, utilizing three analytical methods and covering a broad range of analytes, was chosen to accomplish the objectives above.

Since limited information can be gathered from results that are less than the laboratory and PTR-MS reporting limits, sampling times and volumes were chosen based on the laboratory detection limit and the estimated background concentration determined from previous studies.

It should be emphasized that any results reported below laboratory or PTR-MS RLs or TICs must be considered qualitative.

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 purposes during Month 3.

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

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	160-401265983-1	02/28/2019

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 a study 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, *Mobile Laboratory Operational Procedure*.

4.1.2 Carbon Dioxide Monitor

The LI-COR Li850A 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 is listed in the LI-COR factory specifications as ±3% of reading.

4.1.3 Ammonia Monitor

The Picarro G2103 Ammonia Monitor had no specific errors associated 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

In order to gain insight into the limits of detection of the PTR-TOF 6000 X2, all zero-air checks run on the instrument from October 25, 2018, to November 7, 2018, were analyzed. A total of 15 zero-air checks were run during this time period. Each zero-air check consisted of roughly 100 data points, taken at 2 Hz. This period in particular was chosen because it takes into account improvements to performance and instrument tuning achieved as a result of the findings of Deficiency Report (DR)-018-009, where high instrument background signals were observed at a variety of m/z. From October 25, 2018, onwards, the tuning of the instrument was improved, causing a marked decrease in signal noise, and thus variance, in the zero-air checks. This, in turn, reduces the detection and RLs. Overall, roughly an 80 – 90% reduction in RLs was achieved compared to the previous study conducted in Fiscal Year (FY)18. The lower RLs improve confidence that even very low counts of signal can be detected at any given m/z.

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

$$\mu = \frac{\sum_{i=1}^{n} x_i}{n}$$

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

Next, a grand mean of the mean values for each zero-air check for each compound was calculated by taking the mean of the 15 individual means calculated in the previous step.

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

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

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

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

These combined standard deviations were then multiplied by the 2-tailed Student's t-value for 14 degrees of freedom at 95% CI, i.e., 2.15. This provided the MDLs for each compound detected by the PTR-TOF 6000 X2. As a conservative approach, an additional factor of 3 was then applied to the MDLs to obtain the RLs. Calculated MDLs and RLs for each COPC and odor compound are shown in the table below.

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

COPC Name	OEL (ppbv)	MDL (ppbv)	RL (ppbv)
formaldehyde	300	0.035	0.105
methanol	200000	0.051	0.152
acetonitrile	20000	0.004	0.013
acetaldehyde	25000	0.035	0.106
ethylamine	5000	0.004	0.011
1,3-butadiene	1000	0.010	0.031
propanenitrile	6000	0.005	0.015
2-propenal	100	0.025	0.075
1-butanol + butenes	20000	0.011	0.034
methyl isocyanate	20	0.005	0.016
methyl nitrite	100	0.004	0.013
furan	1	0.004	0.012
butanenitrile	8000	0.003	0.008
but-3-en-2-one + 2,3-dihydrofuran + 2,5-dihydrofuran	200, 1, 1	0.003	0.009
butanal	25000	0.005	0.016
NDMA	0.3	0.004	0.013
benzene	500	0.018	0.053
2,4-pentadienenitrile + pyridine	300, 1000	0.005	0.014
2-methylene butanenitrile	300	0.002	0.007
2-methylfuran	1	0.003	0.010
pentanenitrile	6000	0.002	0.007
3-methyl-3-buten-2-one + 2-methyl-2-butenal	20, 30	0.004	0.011
NEMA	0.3	0.003	0.008
2,5-dimethylfuran	1	0.003	0.009
hexanenitrile	6000	0.002	0.005
2-hexanone (MBK)	5000	0.004	0.011
NDEA	0.1	0.002	0.007
butyl nitrite + 2-nitro-2-methylpropane	100, 300	0.003	0.010
2,4-dimethylpyridine	500	0.003	0.008
2-propylfuran + 2-ethyl-5-methylfuran	1, 1	0.002	0.007
heptanenitrile	6000	0.002	0.005
4-methyl-2-hexanone	500	0.003	0.008

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

COPC Name	OEL (ppbv)	MDL (ppbv)	RL (ppbv)
NMOR	0.6	0.002	0.007
butyl nitrate	8000	0.002	0.005
2-ethyl-2-hexenal + 4-(1-methylpropyl)-2,3-dihydrofuran+ 3-(1,1-dimethylethyl)-2,3-dihydrofuran	100, 1, 1	0.002	0.006
6-methyl-2-heptanone	8000	0.002	0.006
2-pentylfuran	1	0.002	0.007
biphenyl	200	0.002	0.007
2-heptylfuran	1	0.004	0.011
1,4-butanediol dinitrate	50	0.004	0.011
2-octylfuran	1	0.001	0.004
1,2,3-propanetriol 1,3-dinitrate	50	0.003	0.010
PCB	1000	0.004	0.011
6-(2-furanyl)-6-methyl-2-heptanone	1	0.001	0.003
furfural acetophenone	1	0.003	0.008

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

Odor Name	MDL (ppbv)	RL (ppbv)
methyl mercaptan	0.007	0.020
dimethyl sulfide; ethanethiol	0.005	0.014
allyl mercaptan	0.008	0.023
1-propanethiol; Isopropyl mercaptan	0.006	0.018
2-butene-1-thiol	0.005	0.014
Diethyl Sulfide; 2-methylpropane-2-thiol	0.031	0.094
thiopropanal sulfuroxide	0.008	0.024
dimethyl disulfide	0.006	0.017
1-pentanethiol; 2,2-dimethylpropane-1-thiol	0.005	0.016
benzenethiol	0.004	0.012
diallyl sulfide	0.003	0.009
methyl propyl disulfide	0.005	0.015
methylbenzenethiol	0.003	0.010
dimethyl trisulfide	0.003	0.009
(1-oxoethyl) thiophene	0.009	0.028
(1-oxopropyl) thiophene	0.004	0.012
dipropyl disulfide	0.003	0.008
methyl propyl trisulfide	0.004	0.012
dimethyl tetrasulfide	0.002	0.005
dipropyl trisulfide	0.003	0.008
diphenyl sulfide	0.002	0.006

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

Measured values below the RL but above the MDL are an estimate only. Values below the MDL should be treated with care as they have no quantitative significance.

5.0 TEST RESULTS

Planned preventative and corrective maintenance was performed on the ML during the first two weeks of October 2018 and are presented in Table 5-1. During this period, the ML was used in a fugitive emission investigation for septic analysis at the direction of WRPS. Directly following the septic analysis, the ML executed the third leg of a four-part background study. Results of the septic analysis and the background study are presented in the following sections.

Table 5-1. Mobile Laboratory Maintenance Activities.

Week	Date	Activity
9	10/01/2018	ML taken to McCurley®[8] Integrity Dealership for maintenance
	10/02/2018	ML modifications
	10/03/2018	ML taken to Cummins®[9] for generator maintenance
	10/04/2018	ML modifications and maintenance
	10/05/2018	ML site walk-through
10	10/08/2018	ML modifications and testing
	10/09/2018	ML maintenance
	10/10/2018	Area monitoring-septic tanks
	10/11/2018	Stationary monitoring and testing - background study training
	10/12/2018	ML modifications and testing

5.1 Septic Analysis

On October 10, 2018, the ML was deployed under the direction of WRPS fugitive emissions program, to monitor septic tank emissions in the 200 East area of the Hanford Site.

5.1.1 Discussion of Test Activities and Observations – Septic

WRPS' fugitive emissions team hypothesized that the septic plumes travel downwind, and this results in the workers smelling an unknown substance. The team also suggested that heavier components of the septic vapor profile remain low to the ground allowing them to travel greater distances, undergo less dilution, and potentially accumulate in lower elevations. The objective was to track the septic plume downwind and monitor within a potential septic plume accumulation point.

5.1.2 Identification of Vapor Sources and Quantitative Analysis of Vapor Composition – Septic

From 10:02 until 10:42, the ML sampled from the 35' heated side port line at variable distances from the septic emissions. Figure 5-1 is a time series of methyl mercaptan during this time. As

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[8] McCurley is a registered trademark of McCurley Integrity Dealerships, LLC, Tri-Cities, Washington.
[9] Cummins is a registered trademark of Cummins, Inc., Columbus, Indiana.

reported in 53005-81-RPT-027, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 2*, methyl mercaptan is an indicator of septic emissions. The objective during this time was to characterize the septic source before tracking it downwind. From 10:02 until 10:23, the ML was sampling approximately 2' off the ground slightly downwind of the septic tank. Between 10:23 and 10:34, the inlet was moved to multiple locations trying to find an optimal sampling location. At 10:38, the inlet was positioned 1' away from the septic tank, which resulted in a large response. The inlet was moved to approximately 4" from the source and the response increased further as expected.

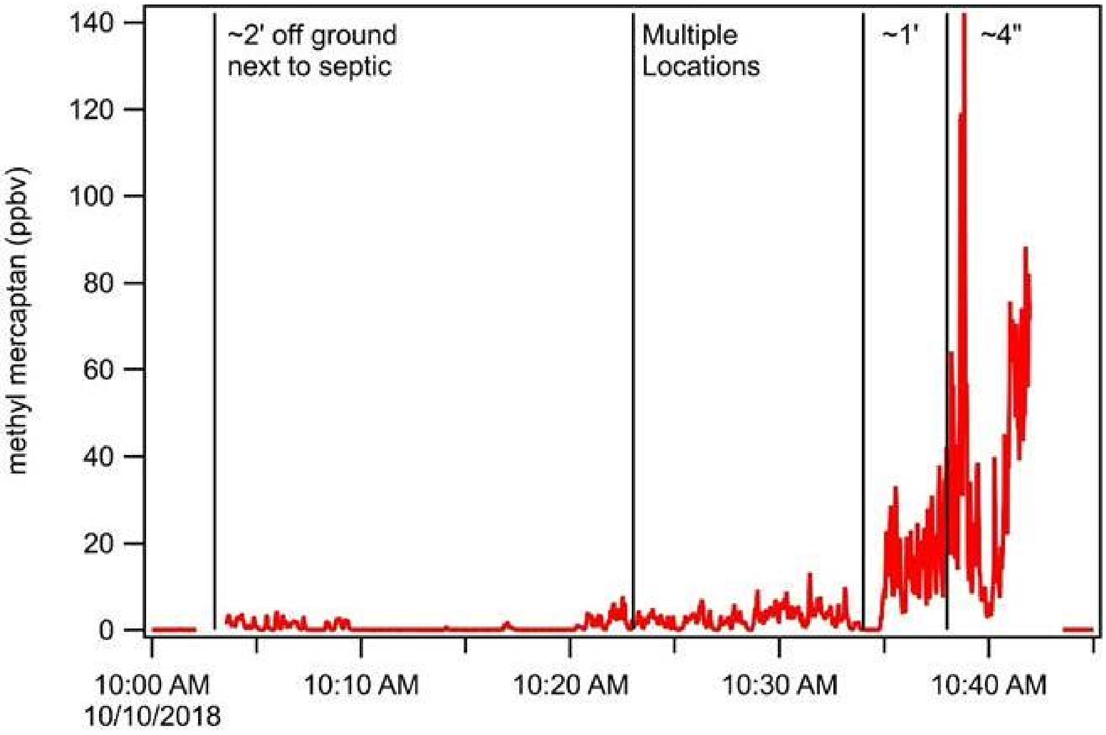


Figure 5-1. Response of Methyl Mercaptan While Sampling at Variable Distances Downwind of a Septic Tank.

5.1.3 Detailed Analysis of Test Data – Septic

A plume fingerprint was developed for the plume from 10:35 to 10:39. This was achieved using the same parameters for fingerprint analysis from 53005-81-RPT-027. To be included in the fingerprint, a species must have a concentration of at least 0.05 ppbv and contribute at least 0.5% to the total abundance of the plume. Figure 5-2 shows the resulting fingerprint for the 10:35 plume. The septic fingerprint from 53005-81-RPT-027 is included for reference.

As expected, the 10:35 fingerprint is similar to the Month 2 fingerprint. The relative abundance of the dominant species methyl mercaptan and nominal m/z 35 are different between the two fingerprints, but the ratio to one another is reasonably close with methyl mercaptan to nominal m/z 35 ratios of 0.7 and 0.6 for the 10:35 and Month 2 fingerprints, respectively. They both show comparable amounts of toluene and some slight differences in some of the nominal masses (m/z 36, 48, 50, 51). One pronounced difference is the lack of many species within the 10:35 fingerprint compared to Month 2. This is attributed to differences in the sampling strategy. Month 2 focused on tracking the plume downwind using the standard mast while the 10:35 plume was sampling directly from the source. The 10:35 fingerprint is less likely to be influenced by other sources or ambient impacts compared to the Month 2 analysis.

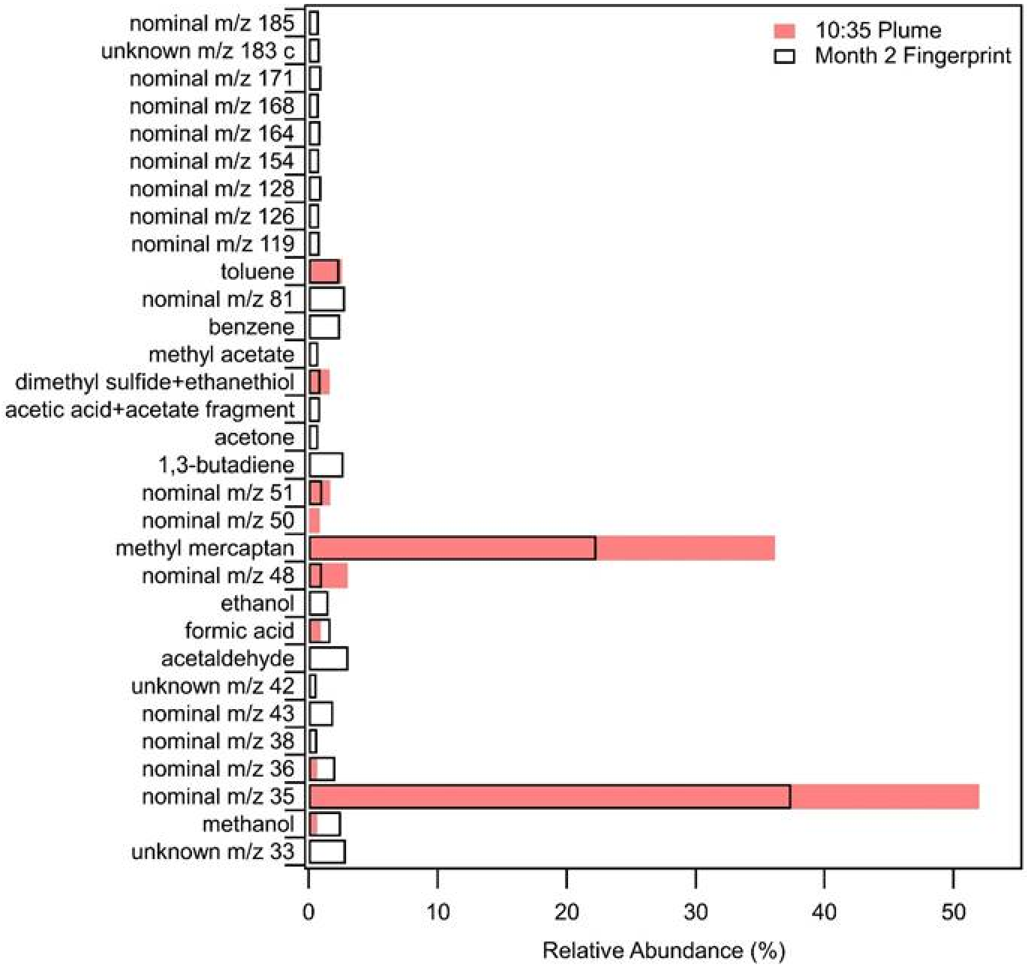


Figure 5-2. Septic Fingerprint for the Plume Beginning at 10:35 on October 10, 2018, Compared to the Septic Fingerprint Reported in Month 2.

As shown below in Figure 5-3, at 10:54, the ML was setup for side port sampling at the new location southeast of Building MO-226. The ML was parked on the north side of the road, which is at the top of a slope that extends north to AP Farm. The sample line was extended down this slope with the objective of sampling a low altitude valley that is hypothesized to be a potential accumulation area for heavier species within the septic plume. The ML and side port sampling line were moved approximately 15’ west at 11:17. The ML remained in this configuration and location until 13:03. Figure 5-3 is a map of the location of the ML and septic tanks during this time.

Figure 5-3. Location of Mobile Laboratory and Sampling Inlet Intake Downwind in Relation to the Septic Tanks from 10:54 to 13:03 on October 10, 2018.

Figure 5-4 shows the wind speed and direction during this time. For a majority of the monitoring period, the wind was from the 0 to 30 with brief periods focusing around the north. This is the general direction of the septic tank and the ML was in a reasonable position.

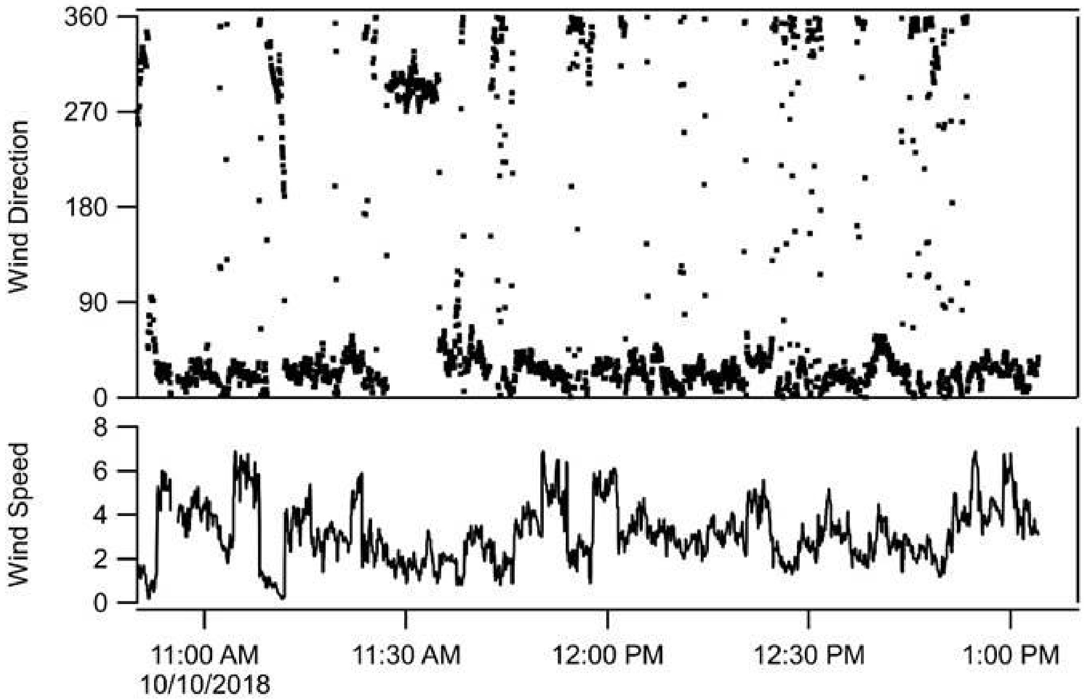


Figure 5-4. Wind Speed and Direction Between 10:54 to 13:03 on October 10, 2018.

Despite the ML being positioned downwind of the septic tanks and sampling from a low altitude area, no septic plumes were observed during this period. Figure 5-5 shows the methyl mercaptan, nominal m/z 35, and some other important species identified in exhaust. There was no response in any of the species except for toluene and benzene. Though the ML was positioned in a favorable position to track the septic plume downwind, this does not ensure that the conditions are sufficient for a plume to travel long distances along the ground. Wind speeds were sporadic varying between 1 to almost 7 meters per second with abrupt changes. In addition, there were times the wind direction was stable, but there were also abrupt changes in direction. Both of these aspects can suggest that the conditions were probably too turbulent and caused too much mixing/dilution of the plume to allow for long distance transport of the plume. To properly track this low height traveling plume, it is important to deploy during the right meteorological conditions in addition to being set up in the proper location. The most important aspect may be to monitor in more stagnant conditions with a slow and steady breeze.

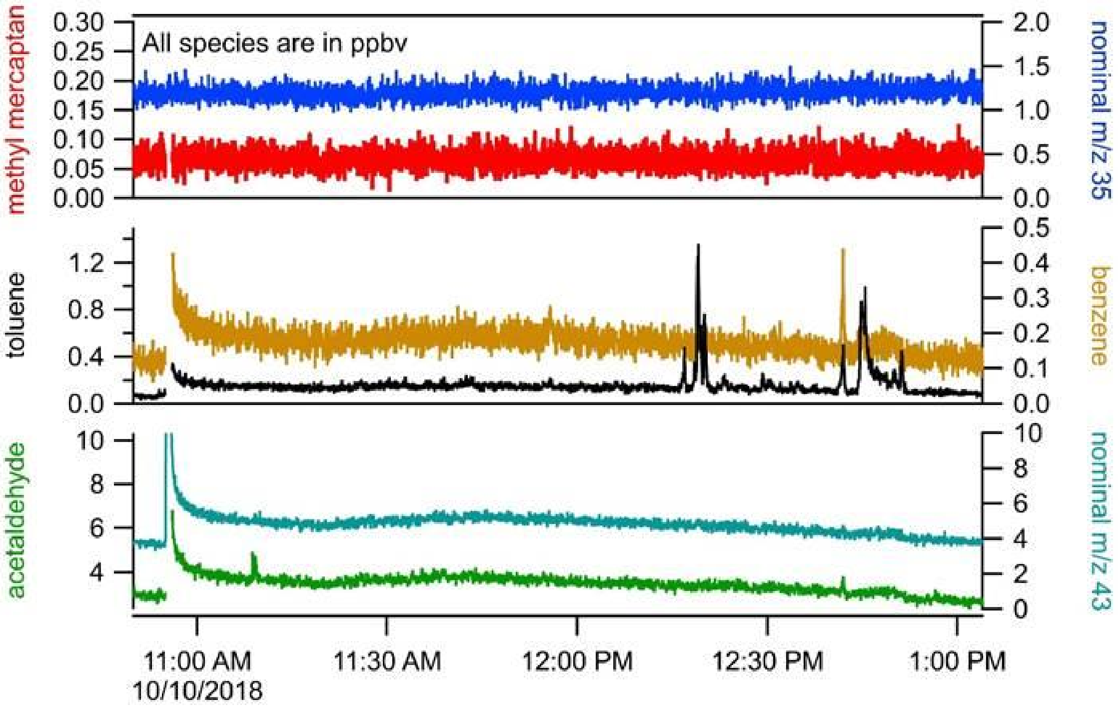


Figure 5-5. Time-series of Key Species from 10:54 to 13:03 on October 10, 2018.

Although the ML did not see septic plumes at the location, there was an interesting toluene response. Around 12:20 and again around 12:45, there were toluene plumes observed with a smaller response in benzene. All of the resolved peaks during the 12:20 plume were inspected by the Subject Matter Expert (SME) and there were only minimal responses at nominal m/z 92, nominal m/z 94, and C_2-benzenes. This plume appears to be primarily toluene and the absence of any other tracers suggests that it is not exhaust. The average wind direction during this plume was from the northeast. The ML Operators observed tank-related activity occurring in AP Farm and recorded in the logbook that workers were making a repair of a jumper on one of the tanks. This was occurring in the northeast direction and the toluene plume could be a result of the farm-related activities.

5.2 Background Study

This subsection details the fall background study conducted from October 15, 2018, through November 9, 2018. Test completeness and general observations are documented in the first subsection, followed by an analysis of background vapor composition, with a detailed assessment of the test data and confirmatory sampling measurements in the final subsection.

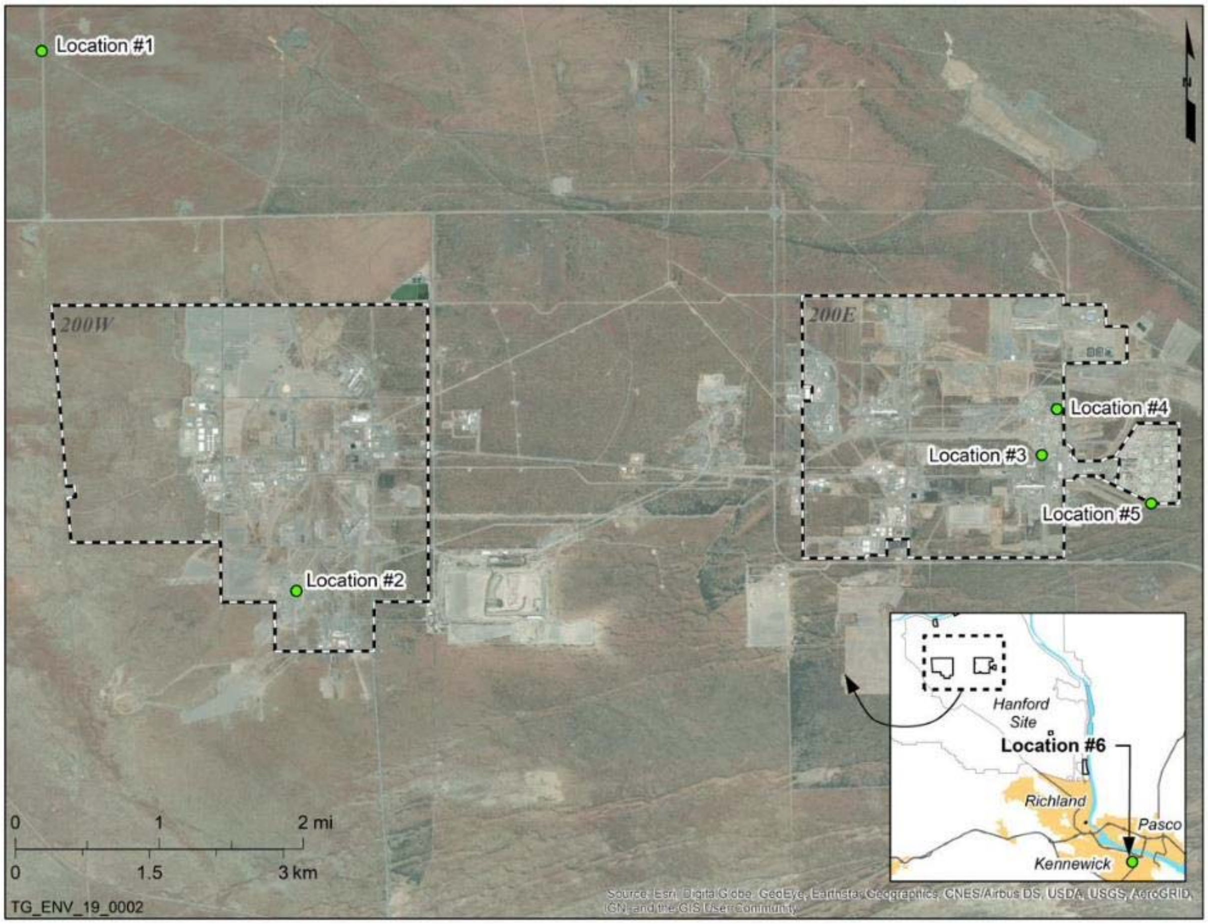
5.2.1 Discussion of Test Activities and Observations – Background

This subsection presents the fall background test activities through examination of completeness and provides validation observations through a comparison of ML data to confirmatory samples.

5.2.1.1 Completeness of Test Activities

The Test Plan prescribes the required monitoring parameters and data collection tasks necessary to conduct the fall background study that would produce results and conclusions as part of a seasonal comprehensive background study.

From an executory perspective, the study required 24 days of sampling ambient air at six pre-determined locations on and off the Hanford Site (corresponding to locations sampled during previous segments of the study), between October 15, 2018, and November 8, 2018, for durations of 22 to 23 hours per site. Figure 5-6 shows all of the background locations. Table 5-2 shows the completed schedule of background sampling, which corresponds identically to the projected schedule from the Test Plan with one exception. The final two days of sampling at Sites 3 and 6 were carried to provide NO^+ monitoring data.



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

Figure 5-6. Fall 2018 Background Study Locations.

Table 5-2. Background Study Schedule Overview.

Start Date	Start Time	Stop Date	Stop Time	Hours	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
10/15/2018	06:59	10/16/2018	06:29	23 hr 30 min	X					
10/16/2018	07:08	10/17/2018	06:55	23 hr 47 min		X				
10/17/2018	07:20	10/18/2018	06:40	23 hr 20 min			X			
10/18/2018	06:44	10/19/2018	09:10	26 hr 26 min				X		
10/19/2018	09:20	10/20/2018	07:07	21 hr 47 min					X	
10/20/2018	07:52	10/21/2018	05:58	22 hr 6 min						X
10/21/2018	07:17	10/22/2018	07:45	24 hr 28 min	X					
10/22/2018	07:51	10/23/2018	06:31	22 hr 40 min		X				
10/23/2018	06:49	10/24/2018	06:26	23 hr 37 min			X			
10/24/2018	06:40	10/25/2018	06:18	23 hr 38 min				X		
10/25/2018	07:05	10/26/2018	13:05	30 hr					X	
10/26/2018	13:55	10/27/2018	05:35	15 hr 40 min						X
10/27/2018	06:40	10/28/2018	06:32	23 hr 52 min	X					
10/28/2018	07:11	10/29/2018	06:49	23 hr 38 min		X				
10/29/2018	07:04	10/30/2018	06:47	23 hr 43 min			X			
10/30/2018	06:57	10/31/2018	06:19	23 hr 22 min				X		
10/31/2018	06:48	11/01/2018	06:32	23 hr 44 min					X	
11/01/2018	07:20	11/02/2018	05:40	22 hr 20 min						X
11/02/2018	07:15	11/03/2018	06:41	23 hr 26 min	X					
11/03/2018	07:05	11/04/2018	07:51	24 hr 46 min		X				
11/04/2018	08:12	11/05/2018	07:28	23 hr 16 min			X			
11/05/2018	07:54	11/06/2018	07:40	23 hr 46 min				X		
11/06/2018	07:43	11/07/2018	07:21	23 hr 38 min					X	
11/07/2018	08:05	11/08/2018	07:00	23 hr 55 min						X
11/08/2018	08:23	11/09/2018	07:35	23 hr 13 min			X			
11/09/2018	08:25	11/09/2018	12:41	4 hr 16 min						X
Total					**4**	**4**	**5**	**4**	**4**	**5**

As planned, the fall background study was executed to meet the temporal requirements at the planned locations for the prescribed durations.

Detailed data collection and reporting requirements were prescribed in the Test Plan. Table 5-3 lists the required COPCs. The Test Plan required summary-level reporting of all COPCs measurable by the PTR-MS with attention on the compounds in Table 5-3 due to the difficulty of measuring them with standard analytical methods. The COPCs in Table 5-3 were successfully measured for the duration of the fall background study and summaries of those results are presented in Section 5.3, as well as other compounds detected by the PTR-MS during this campaign.

Table 5-3. List of Applicable Chemicals of Potential Concern.

COPC	OEL (ppb)
Ammonia	25000
Furan	1
But-3-en-2-one + 2,3-dihydrofuran + 2,5-dihydrofuran	200, 1, 1
NDMA	0.3
2-methylefuran	1
NEMA	0.3
2,5-dimethylfuran	1
NDEA	0.1
2-propylfuran + 2-ethyl-5-methylfuran	1
NMOR	0.6
2-ethyl-2-hexenal + 4-(1-methylpropyl)-2,3-dihydrofuran + 3-(1,1-dimethylethyl)-2,3-dihydrofuran	1
2-pentylfuran	1
2-heptylfuran	1
2-octylfuran	1
6-(2-furanyl)-6-methyl-2-heptanone	1
furfural acetophenone	1

5.2.1.2 Validation Observations from Confirmatory Samples

A standard quality control tool deployed in environmental sampling plans is the collection and analysis of split samples to validate both sample collection and analytical techniques. In lieu of using a second PTR-MS to validate ML measurements, the decision to utilize standard sampling media and standard laboratory methods for confirmation and validation of ML PTR-MS results. Three confirmatory methods were prescribed in the Test Plan and were utilized by TerraGraphics during the fall background study:

1. NIOSH Method 2522 modified (Thermosorb®[10]/N, solid sorbent tube sampling);
2. EPA TO-17 modified (Carbotrap®[11] 300, thermal desorption tube sampling); and
3. EPA TO-11A [Dinitrophenylhydrazine (DNPH) sorbent tubes].

Confirmatory measurements were required in duplicate by each analytical method at a rate of one per every ten samples with a blank collected and analyzed every 20 samples. Because of the difficulties measuring the COPC list of interest (Table 5-3), a secondary list of compounds was selected for confirmatory measurements. Confirmatory compounds along with detection and volume requirements are shown in Table 5-4.

Table 5-4. List of Compounds for Confirmatory Analysis.

Method	Species	ALS Detection Limit (ug)	Estimated Background Concentration (ug/m^3)	Mass per 1 Liter (ug/L)	Flow Rate (L/min)	Recommended Sampling Time (Minutes)
TO-17	1,3-butadiene	0.025	1.1	0.0011	0.250	45
	acetonitrile	0.025	0.08	0.00008	0.250	596
	benzene	0.025	0.32	0.00032	0.250	157
	2-hexanone	0.025	0.2	0.0002	0.250	245
	acetone	0.025	1.19	0.00119	0.250	42
	toluene	0.025	0.19	0.00019	0.250	266
	m,p-xylene	0.025	0.22	0.00022	0.250	231
	o-xylene	0.025	0.22	0.00022	0.250	231
	ethylbenzene	0.025	0.22	0.00022	0.250	231
	styrene	0.025	0.11	0.00011	0.250	470
TO-11A	acetaldehyde	0.05	0.36	0.00036	1.0	278
	butanal	0.05	0.29	0.00029	1.0	340
	2-propenal	0.05	0.23	0.00023	1.0	437
	acetone	0.05	1.15	0.00115	1.0	87
NIOSH 2522	NDEA	0.01	0.08	0.00008	1.0	240
	NDMA	0.01	0.15	0.00015	1.0	132
	NMEA	0.01	0.11	0.00011	1.0	185
	NMOR	0.01	0.05	0.00005	1.0	422

Australian Laboratory Services (ALS) was selected to perform analysis of the confirmatory samples for compounds listed in Table 5-4, with the added direction of reporting any TICs.

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[10] Thermosorb is a registered trademark of Ellutia Limited, Cambridgeshire, United Kingdom.

[11] Carbotrap is a registered trademark of Sigma-Aldrich Co., LLC, St. Louis, Missouri.

Once analyzed, these samples were compared, where possible, to the average PTR-MS signal observed over the same time period the samples were collected. Air sample collection on the alternative media occurred once daily per site. Carbotrap-300 samples were generally collected over the course of 360 minutes, while Thermosorb/N and DNPH cartridges were generally collected over the course of 180 minutes. Confirmatory samples were collected and analyzed from each of the six sites during each of the four trips to each site, equating to four confirmatory samples per site, which doubles the Test Plan requirement of two samples per site. The frequency and duration of the sampling was designed to produce duplicates for each method utilized for each of the six background sites. For this reason, both accuracy and precision data can be evaluated. Also, one blank per ten samples analyzed was performed.

By the very nature of the experiment, the concentrations measured during the background study are very low, and in most cases, below the reporting limits or MDLs. Since limited information can be gathered from results that are less than the laboratory and PTR-MS reporting limits, sampling times and volumes were chosen based on the laboratory detection limit and the estimated background concentration determined from previous studies. The chemical list was chosen based on available standard analysis, overlap with the COPC list, and the likelihood of the chemicals to be greater than the laboratory and PTR-MS RLs. Despite the limitations of the subcontract laboratory analyte list, samples were able to be analyzed for ten COPCs with full calibration, and two others using TICs. The ML data along with confirmatory sampling data are provided in Appendix A.

5.2.1.3 Comparison to Carbotrap-300 TO-17 Results

Table A-2 in Appendix A provides all Carbotrap-300 samples taken over the course of the fall background study while Table 5-5 summarizes a subset of results for confirmatory sample comparison of PTR-MS to EPA Compendium TO-17. Very little quantitative confidence can be ascribed to results below either the PTR-MS or Laboratory RL. Thus, results that are summarized here are those where the ALS result is above the RL and where the PTR-MS result is above the MDL.

The 312 analytical measurements attempted on the 26 (includes two blanks and three duplicates) Carbotrap-300 samples were sent to ALS for laboratory testing. Of the measurements made by ALS, 68% were reported as not detectable above the RL. Conversely, only 23% of the measurements made by the ML were reported as not detectable above the RL. Out of those sample locations where analytes were detected above RLs for both methods, three compounds (acetone, benzene, and toluene) were detected at frequencies and levels substantial enough to be analyzed for comparative precision. Table 5-5 shows the results of a simple precision analysis between TO-17 and PTR-MS.

Table 5-5. Precision of Proton Transfer Reaction – Mass Spectrometer and TO-17 Using Carbotrap-300.

Constituent	Number of Duplicates Evaluated	Number of Duplicate Measurements[a]	Percent Out of Limits (>20%)	Range of Out-of-Limit RPD
Benzene	26	16	62%	26 - 44%
Acetone	26	24	33%	23 - 83%
Toluene	26	12	88%	31 - 89%

a. Duplicates with both results greater than reporting limits

Compared to TO-17, the PTR-MS system in the ML has a lower threshold for detection, as represented by the difference between 68% non-detections for ALS and 23% for the ML. Due to the low abundance of many of the TO-17 compounds (Table 5-4) in the background study area, confirmation of PTR-MS results with standard sampling and analysis techniques will continue to be difficult. For the measurements made by both systems above the RLs, considering these levels are in the proximity of instrument detection limits, the precision between the methods is favorable. Adjustments in sample volume for Carbotrap-300 media may increase TO-17 sensitivity and reliability as results approach the RL for that method.

5.2.1.4 Comparison to Dinitrophenylhydrazine TO-11 Results

Table A-3 in Appendix A provides all DNPH samples taken over the course of the fall background study while Table 5-6 summarizes a subset of results for confirmatory sample comparison of PTR-MS to EPA Compendium TO-11a. Very little quantitative confidence can be ascribed to results below either the PTR-MS or Laboratory RL. Thus, results that are summarized here are those where the ALS result is above the RL and where the PTR-MS result is above the MDL. Some acetone results in Table 5-6 are included that ALS reported below their RL because acetone was also analyzed by TO-17 (Table 5-5 and Appendix A, Table A-2) and it is interesting to look at the behavior of acetone by all three methods.

The 85 analytical measurements attempted on the 17 (includes one blank and two duplicates) DNPH samples were sent to ALS for laboratory testing. Of the measurements made by ALS, 52% were reported as not detectable above the RL. Conversely, only 6% of the measurements made by the ML were reported as not detectable above the RL. Out of those sample locations where analytes were detected above RLs for both methods, two compounds (acetone and formaldehyde) were detected at frequencies and levels substantial enough to be analyzed for comparative precision. Table 5-5 shows the results of a simple precision analysis between TO-11a and PTR-MS.

Table 5-6. Precision of Proton Transfer Reaction – Mass Spectrometer and TO-11a Using LpDNPH.

Constituent	Number of Duplicates Evaluated	Number of Duplicate Measurements[a]	Percent Out of Limits (>20%)	Range of Out-of-Limit RPD
Formaldehyde	17	13	54%	22 - 174%
Acetone	17	8	87%	22 - 169%

[a] Duplicates with both results greater than reporting limits

Compared to TO-11a, the PTR-MS system in the ML has a lower threshold for detection, as represented by the difference between 52% non-detections for ALS and 6% for the ML. Due to the low abundance of many of the TO-11a compounds (Table 5-4) in the background study area, confirmation of PTR-MS results with standard sampling and analysis techniques will continue to be difficult. Because of the wide range of difference between the detectable results for the two methods, the use of DNPH and TO-11a as a confirmatory method for PTR-MS measurements should be re-evaluated. This conclusion is further supported by observations made when comparing acetone results from TO-11a to acetone results from TO-17, where TO-11a results are significantly less than TO-17. Adjustments in sample volume for DNPH media may increase TO-17 sensitivity and reliability as results approach the RL for that method.

5.2.1.5 Comparison of Thermosorb/N NIOSH 2522 Results

Table A-4 in Appendix A provides all Thermosorb/N samples taken over the course of the fall background study as confirmatory sample comparison of PTR-MS to NIOSH Method 2522. Very little quantitative confidence can be ascribed to results below either the PTR-MS or Laboratory RL. No results were reported by ALS above the RL for the four nitrosamine compounds of interest:

1. N-Nitrosodimethylamine (NDMA),
2. N- Nitrosodiethylamine (NDEA),
3. N-Nitrosomorpholine (NMOR), and
4. N-Nitrosomethylethylamine (NEMA).

The 104 analytical measurements attempted on the 26 (includes two blanks and three duplicates) Thermosorb/N samples were sent to ALS for laboratory testing. One hundred percent of the measurements made by ALS were reported as not detectable above the RL. Of the measurements made by the ML, 81% were reported as not detectable above the RL. Upon analyzing these results, it is believed that a slight positive bias has been identified in the PTR-MS results for these COPCs which caused frequent hits above the MDL but below the RL. Alternatively, there could be an unidentified interferent at very low concentrations that impacts these results in the PTR-MS, but the positive bias from the peak deconvolution process at these low concentrations seems more likely of an explanation. Because no samples produced results using both testing methods, no comparative precision analysis was performed.

An evaluation of sampling parameters that may be adjusted to the NIOSH method to achieve detectable results in the laboratory is being conducted. Adjustments in sample volume for DNPH media may increase TO-17 sensitivity and reliability as results approach the RL for that method.

5.2.2 Identification of Vapor Sources, Quantitative Analysis of Vapor Composition and Summary of Background Results

This section is typically reserved for description of and analysis of chemical makeup of observed vapor sources, emissions, or plumes. The nature of this study is to provide information as part of a comprehensive background study compositional analysis of vapors at ambient concentrations occurs as iterative steps in the four-part study. Summaries of the results for the six sampling sites are presented in the following subsection.

Total average concentrations of COPCs at each site over the course of the fall background study are listed in the following tables, along with figures depicting locations for background data collection. The values shown in the site summary tables below are based on the aggregate of all measurements taken at each individual study site across four separate monitoring days.

5.2.2.1 Summary of Site 1

The location of the ML at Site 1, which is approximately one mile northwest of the 200 West Area of the Hanford Site, is displayed in Figure 5-7. Summary statistics including compound average concentrations as well as maximum concentrations observed over the fall background study period are shown in Table 5-7.

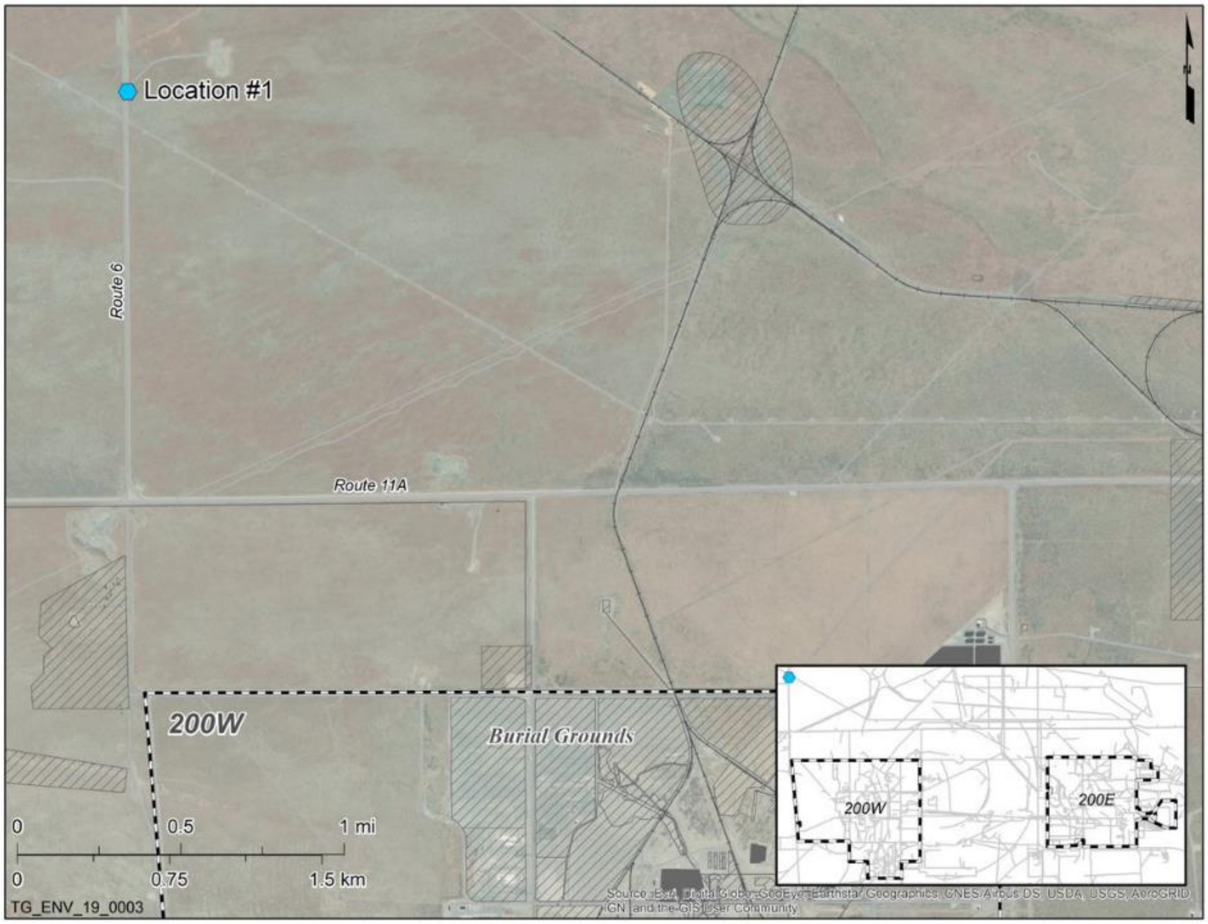

Figure 5-7. Mobile Laboratory Site 1 for the Duration of the Monitoring Period.

Table 5-7. Summary of Site 1 Proton Transfer Reaction – Mass Spectrometer Observations of Chemicals of Potential Concern. (2 Sheets)

COPC Name	OEL (ppbv)	Average (ppbv)	Max (ppbv)
ammonia	25000	4.470	14.589
formaldehyde	300	0.809	6.519
methanol	200000	6.027	31.826
acetonitrile	20000	4.900	128.336
acetaldehyde	25000	2.705	16.107
ethylamine	5000	0.016	0.109
1,3-butadiene	1000	0.125	1.468
propanenitrile	600	0.035	0.187
2-propenal	100	0.128	3.396
1-butanol; butenes	20000	0.079	0.787
methyl isocyanate	20	0.063	0.340
methyl nitrite	100	0.074	1.618
furan	1	0.030	0.302
butanenitrile	8000	0.012	0.103
but-3-en-2-one; 2,3-dihydrofuran; 2,5-dihydrofuran	200, 1, 1	0.049	0.789
butanal	25000	0.130	0.514
NDMA	0.3	0.029	0.307
benzene	500	0.109	1.740
2,4-pentadienenitrile; pyridine	300, 1000	0.028	0.144
2-methylene butanenitrile	300	0.013	0.136
2-methylfuran	1	0.030	0.412
pentanenitrile	6000	0.009	0.060
3-methyl-3-buten-2-one; 2-methyl-2-butenal	20, 30	0.030	0.313
NEMA	0.3	0.011	0.149
2,5-dimethylfuran	1	0.021	0.263
hexanenitrile	6000	0.004	0.058
2-hexanone (MBK)	5000	0.013	0.083
NDEA	0.1	0.005	0.065
butyl nitrite; 2-nitro-2-methylpropane	100, 300	0.046	0.216
2,4-dimethylpyridine	500	0.019	0.152
2-propylfuran; 2-ethyl-5-methylfuran	1	0.035	0.208
heptanenitrile	6000	0.032	0.153

Table 5-7. Summary of Site 1 Proton Transfer Reaction – Mass Spectrometer Observations of Chemicals of Potential Concern. (2 Sheets)

COPC Name	OEL (ppbv)	Average (ppbv)	Max (ppbv)
4-methyl-2-hexanone	500	0.033	0.158
NMOR	0.6	0.005	0.117
butyl nitrate	2500	0.018	0.118
2-ethyl-2-hexenal; 4-(1-methylpropyl)-2,3-dihydrofuran; 3-(1,1-dimethylethyl)-2,3-dihydrofuran	100, 1, 1	0.030	0.152
6-methyl-2-heptanone	8000	0.030	0.138
2-pentylfuran	1	0.035	0.155
biphenyl	200	0.022	0.124
2-heptylfuran	1	0.119	0.417
1,4-butanediol dinitrate	50	0.038	0.169
2-octylfuran	1	0.001	0.155
1,2,3-propanetriol 1,3-dinitrate	50	0.001	0.130
PCB	1000	0.048	0.186
6-(2-furanyl)-6-methyl-2-heptanone	1	0.023	0.123
furfural acetophenone	1	0.109	0.393

5.2.2.2 Summary of Site 2

The location of the ML at Site 2, near the S-SX Tank Farms in the 200 West Area of the Hanford Site, is displayed in Figure 5-8. Summary statistics including compound average concentrations as well as maximum concentrations observed over the fall background study period are shown in Table 5-8.

Source: Esri, DigitalGlobe, GeoEye, Earthst
IGN, and the GIS User Community

Figure 5-8. Mobile Laboratory Site 2 for the Duration of the Monitoring Period.

Table 5-8. Summary of Site 2 Proton Transfer Reaction – Mass Spectrometer Observations of Chemicals of Potential Concern. (2 Sheets)

COPC Name	OEL (ppbv)	Average (ppbv)	Max (ppbv)
ammonia	25000	6.417	22.477
formaldehyde	300	0.829	9.569
methanol	200000	6.309	143.014
acetonitrile	20000	0.841	105.245
acetaldehyde	25000	2.458	30.462
ethylamine	5000	0.015	0.103
1,3-butadiene	1000	0.131	3.993
propanenitrile	600	0.035	1.864
2-propenal	100	0.139	6.926
1-butanol; butenes	20000	0.082	7.805
methyl isocyanate	20	0.052	0.496
methyl nitrite	100	0.083	3.085
furan	1	0.029	1.597
butanenitrile	8000	0.012	0.698
but-3-en-2-one; 2,3-dihydrofuran; 2,5-dihydrofuran	200, 1, 1	0.042	1.569
butanal	25000	0.133	0.708
NDMA	0.3	0.022	0.402
benzene	500	0.109	3.868
2,4-pentadienenitrile; pyridine	300, 1000	0.027	0.855
2-methylene butanenitrile	300	0.014	0.563
2-methylfuran	1	0.032	0.770
pentanenitrile	6000	0.008	0.342
3-methyl-3-buten-2-one; 2-methyl-2-butenal	20, 30	0.029	0.623
NEMA	0.3	0.011	0.209
2,5-dimethylfuran	1	0.020	0.521
hexanenitrile	6000	0.003	0.214
2-hexanone (MBK)	5000	0.012	0.131
NDEA	0.1	0.005	0.082
butyl nitrite; 2-nitro-2-methylpropane	100, 300	0.040	1.217
2,4-dimethylpyridine	500	0.013	0.303
2-propylfuran; 2-ethyl-5-methylfuran	1	0.029	0.272

Table 5-8. Summary of Site 2 Proton Transfer Reaction – Mass Spectrometer Observations of Chemicals of Potential Concern. (2 Sheets)

COPC Name	OEL (ppbv)	Average (ppbv)	Max (ppbv)
heptanenitrile	6000	0.026	0.235
4-methyl-2-hexanone	500	0.028	0.177
NMOR	0.6	0.005	0.164
butyl nitrate	2500	0.015	0.171
2-ethyl-2-hexenal; 4-(1-methylpropyl)-2,3-dihydrofuran; 3-(1,1-dimethylethyl)-2,3-dihydrofuran	100, 1, 1	0.025	0.164
6-methyl-2-heptanone	8000	0.025	0.165
2-pentylfuran	1	0.033	0.239
biphenyl	200	0.019	0.140
2-heptylfuran	1	0.097	0.530
1,4-butanediol dinitrate	50	0.031	0.204
2-octylfuran	1	0.002	0.146
1,2,3-propanetriol 1,3-dinitrate	50	0.001	0.147
PCB	1000	0.040	0.240
6-(2-furanyl)-6-methyl-2-heptanone	1	0.019	0.127
furfural acetophenone	1	0.089	0.544

5.2.2.3 Summary of Site 3

The location of the ML at Site 3, just west of the 242-A Evaporator in the 200 East area of the Hanford Site, is displayed in Figure 5-9. Summary statistics including compound average concentrations as well as maximum concentrations observed over the fall background study period are shown in Table 5-9.

Figure 5-9. Mobile Laboratory Site 3 for the Duration of the Monitoring Period.

Table 5-9. Summary of Site 4 Proton Transfer Reaction – Mass Spectrometer Observations of Chemicals of Potential Concern. (2 Sheets)

COPC Name	OEL (ppbv)	Average (ppbv)	Max (ppbv)
ammonia	25000	7.121	59.446
formaldehyde	300	0.826	3.620
methanol	200000	6.301	25.991
acetonitrile	20000	1.244	120.924
acetaldehyde	25000	2.742	47.713
ethylamine	5000	0.015	0.087
1,3-butadiene	1000	0.152	1.578
propanenitrile	600	0.040	0.706
2-propenal	100	0.145	1.886
1-butanol; butenes	20000	0.114	3.248
methyl isocyanate	20	0.074	0.365
methyl nitrite	100	0.081	0.860
furan	1	0.028	0.182
butanenitrile	8000	0.014	0.347
but-3-en-2-one; 2,3-dihydrofuran; 2,5-dihydrofuran	200, 1, 1	0.044	0.429
butanal	25000	0.165	0.573
NDMA	0.3	0.028	0.238
benzene	500	0.141	5.479
2,4-pentadienenitrile; pyridine	300, 1000	0.030	0.398
2-methylene butanenitrile	300	0.013	0.089
2-methylfuran	1	0.032	0.234
pentanenitrile	6000	0.009	0.147
3-methyl-3-buten-2-one; 2-methyl-2-butenal	20, 30	0.032	0.208
NEMA	0.3	0.013	0.167
2,5-dimethylfuran	1	0.020	0.155
hexanenitrile	6000	0.004	0.049
2-hexanone (MBK)	5000	0.014	0.096
NDEA	0.1	0.006	0.088
butyl nitrite; 2-nitro-2-methylpropane	100, 300	0.049	0.237
2,4-dimethylpyridine	500	0.017	0.738
2-propylfuran; 2-ethyl-5-methylfuran	1	0.032	0.178

Table 5-9. Summary of Site 4 Proton Transfer Reaction – Mass Spectrometer Observations of Chemicals of Potential Concern. (2 Sheets)

COPC Name	OEL (ppbv)	Average (ppbv)	Max (ppbv)
heptanenitrile	6000	0.029	0.166
4-methyl-2-hexanone	500	0.031	0.179
NMOR	0.6	0.005	0.290
butyl nitrate	2500	0.017	0.130
2-ethyl-2-hexenal; 4-(1-methylpropyl)-2,3-dihydrofuran; 3-(1,1-dimethylethyl)-2,3-dihydrofuran	100, 1, 1	0.028	0.155
6-methyl-2-heptanone	8000	0.028	0.144
2-pentylfuran	1	0.034	0.159
biphenyl	200	0.021	0.139
2-heptylfuran	1	0.105	0.441
1,4-butanediol dinitrate	50	0.034	0.204
2-octylfuran	1	0.001	0.121
1,2,3-propanetriol 1,3-dinitrate	50	0.001	0.134
PCB	1000	0.043	0.194
6-(2-furanyl)-6-methyl-2-heptanone	1	0.020	0.130
furfural acetophenone	1	0.098	0.428

5.2.2.4 Summary of Site 4

The location of the ML at Site 4, east of the AN and C Tank Farms in the 200 East area of the Hanford Site, is displayed in Figure 5-10. Summary statistics including compound average concentrations as well as maximum concentrations observed over the fall background study period are shown in Table 5-10.

Figure 5-10. Mobile Laboratory Site 4 for the Duration of the Monitoring Period.

Table 5-10. Summary of Site 4 Proton Transfer Reaction – Mass Spectrometer Observations of Chemicals of Potential Concern. (2 Sheets)

COPC Name	OEL (ppbv)	Average (ppbv)	Max (ppbv)
ammonia	25000	7.332	93.356
formaldehyde	300	0.741	4.331
methanol	200000	5.891	170.061
acetonitrile	20000	1.301	124.642
acetaldehyde	25000	2.600	49.246
ethylamine	5000	0.015	0.092
1,3-butadiene	1000	0.131	1.634
propanenitrile	600	0.036	0.413
2-propenal	100	0.131	3.198
1-butanol; butenes	20000	0.091	2.897
methyl isocyanate	20	0.096	0.577
methyl nitrite	100	0.077	1.349
furan	1	0.026	0.314
butanenitrile	8000	0.012	0.131
but-3-en-2-one; 2,3-dihydrofuran; 2,5-dihydrofuran	200, 1, 1	0.042	0.695
butanal	25000	0.158	2.973
NDMA	0.3	0.023	0.196
benzene	500	0.120	4.544
2,4-pentadienenitrile; pyridine	300, 1000	0.028	0.371
2-methylene butanenitrile	300	0.011	0.108
2-methylfuran	1	0.030	0.398
pentanenitrile	6000	0.009	0.075
3-methyl-3-buten-2-one; 2-methyl-2-butenal	20, 30	0.029	0.323
NEMA	0.3	0.011	0.123
2,5-dimethylfuran	1	0.019	0.254
hexanenitrile	6000	0.004	0.055
2-hexanone (MBK)	5000	0.012	0.127
NDEA	0.1	0.004	0.064
butyl nitrite; 2-nitro-2-methylpropane	100, 300	0.031	0.475
2,4-dimethylpyridine	500	0.012	0.452
2-propylfuran; 2-ethyl-5-methylfuran	1	0.023	0.285
heptanenitrile	6000	0.020	0.254

Table 5-10. Summary of Site 4 Proton Transfer Reaction – Mass Spectrometer Observations of Chemicals of Potential Concern. (2 Sheets)

COPC Name	OEL (ppbv)	Average (ppbv)	Max (ppbv)
4-methyl-2-hexanone	500	0.022	0.279
NMOR	0.6	0.004	0.101
butyl nitrate	2500	0.012	0.196
2-ethyl-2-hexenal; 4-(1-methylpropyl)-2,3-dihydrofuran; 3-(1,1-dimethylethyl)-2,3-dihydrofuran	100, 1, 1	0.020	0.250
6-methyl-2-heptanone	8000	0.020	0.262
2-pentylfuran	1	0.025	0.254
biphenyl	200	0.015	0.265
2-heptylfuran	1	0.072	1.145
1,4-butanediol dinitrate	50	0.024	0.462
2-octylfuran	1	0.001	0.150
1,2,3-propanetriol 1,3-dinitrate	50	0.001	0.119
PCB	1000	0.030	0.468
6-(2-furanyl)-6-methyl-2-heptanone	1	0.014	0.282
furfural acetophenone	1	0.067	1.254

5.2.2.5 Summary of Site 5

The location of the ML at Site 5, south of the Waste Treatment Plant in the 200 East area of the Hanford Site, is displayed in Figure 5-11. Summary statistics including compound average concentrations as well as maximum concentrations observed over the fall background study period are shown in Table 5-11.

Figure 5-11. Mobile Laboratory Site 5 for the Duration of the Monitoring Period.

Table 5-11. Summary of Site 5 Proton Transfer Reaction – Mass Spectrometer Observations of Chemicals of Potential Concern. (2 Sheets)

COPC Name	OEL (ppbv)	Average (ppbv)	Max (ppbv)
ammonia	25000	9.025	105.025
formaldehyde	300	0.720	27.280
methanol	200000	7.564	923.333
acetonitrile	20000	1.724	23.613
acetaldehyde	25000	2.685	27.946
ethylamine	5000	0.014	0.083
1,3-butadiene	1000	0.163	3.467
propanenitrile	600	0.041	0.947
2-propenal	100	0.165	6.204
1-butanol; butenes	20000	0.117	5.775
methyl isocyanate	20	0.109	0.565
methyl nitrite	100	0.085	2.492
furan	1	0.036	0.511
butanenitrile	8000	0.015	0.397
but-3-en-2-one; 2,3-dihydrofuran; 2,5-dihydrofuran	200, 1, 1	0.067	1.419
butanal	25000	0.200	6.061
NDMA	0.3	0.028	0.214
benzene	500	0.149	7.627
2,4-pentadienenitrile; pyridine	300, 1000	0.035	0.629
2-methylene butanenitrile	300	0.019	0.151
2-methylfuran	1	0.040	0.708
pentanenitrile	6000	0.011	0.148
3-methyl-3-buten-2-one; 2-methyl-2-butenal	20, 30	0.039	0.615
NEMA	0.3	0.012	0.154
2,5-dimethylfuran	1	0.032	0.431
hexanenitrile	6000	0.004	0.067
2-hexanone (MBK)	5000	0.015	1.171
NDEA	0.1	0.004	0.059
butyl nitrite; 2-nitro-2-methylpropane	100, 300	0.032	0.567
2,4-dimethylpyridine	500	0.020	1.067
2-propylfuran; 2-ethyl-5-methylfuran	1	0.027	0.194
heptanenitrile	6000	0.015	0.135

Table 5-11. Summary of Site 5 Proton Transfer Reaction – Mass Spectrometer Observations of Chemicals of Potential Concern. (2 Sheets)

COPC Name	OEL (ppbv)	Average (ppbv)	Max (ppbv)
4-methyl-2-hexanone	500	0.020	0.453
NMOR	0.6	0.005	0.398
butyl nitrate	2500	0.009	0.107
2-ethyl-2-hexenal; 4-(1-methylpropyl)-2,3-dihydrofuran; 3-(1,1-dimethylethyl)-2,3-dihydrofuran	100, 1, 1	0.018	0.133
6-methyl-2-heptanone	8000	0.018	0.131
2-pentylfuran	1	0.031	0.128
biphenyl	200	0.012	0.109
2-heptylfuran	1	0.060	0.359
1,4-butanediol dinitrate	50	0.018	0.149
2-octylfuran	1	0.001	0.098
1,2,3-propanetriol 1,3-dinitrate	50	0.001	0.111
PCB	1000	0.024	0.175
6-(2-furanyl)-6-methyl-2-heptanone	1	0.011	0.105
furfural acetophenone	1	0.051	0.330

5.2.2.6 Summary of Site 6

The location of the ML at Site 6, an urban location in Kennewick, WA at the corner of Clearwater avenue and U.S. highway 395, is displayed in Figure 5-12. Summary statistics including compound average concentrations as well as maximum concentrations observed over the fall background study period are shown in Table 5-12.

Figure 5-12. Mobile Laboratory Site 6 for the Duration of the Monitoring Period.

Table 5-12. Summary of Site 6 Proton Transfer Reaction – Mass Spectrometer Observations for Chemicals of Potential Concern. (2 Sheets)

COPC Name	OEL (ppbv)	Average (ppbv)	Max (ppbv)
ammonia	25000	12.485	50.305
formaldehyde	300	0.979	12.556
methanol	200000	7.656	321.696
acetonitrile	20000	0.612	191.592
acetaldehyde	25000	5.413	76.282
ethylamine	5000	0.016	0.101
1,3-butadiene	1000	0.270	16.829
propanenitrile	600	0.080	8.205
2-propenal	100	0.266	10.050
1-butanol; butenes	20000	0.339	62.521
methyl isocyanate	20	0.119	0.609
methyl nitrite	100	0.115	1.753
furan	1	0.061	0.675
butanenitrile	8000	0.030	3.584
but-3-en-2-one; 2,3-dihydrofuran; 2,5-dihydrofuran	200, 1, 1	0.060	1.350
butanal	25000	0.195	1.463
NDMA	0.3	0.043	0.511
benzene	500	0.370	42.829
2,4-pentadienenitrile; pyridine	300, 1000	0.049	2.437
2-methylene butanenitrile	300	0.021	0.318
2-methylfuran	1	0.061	0.528
pentanenitrile	6000	0.015	1.186
3-methyl-3-buten-2-one; 2-methyl-2-butenal	20, 30	0.047	0.663
NEMA	0.3	0.015	0.191
2,5-dimethylfuran	1	0.034	0.304
hexanenitrile	6000	0.006	0.503
2-hexanone (MBK)	5000	0.019	0.424
NDEA	0.1	0.004	0.075
butyl nitrite; 2-nitro-2-methylpropane	100, 300	0.035	0.277
2,4-dimethylpyridine	500	0.043	9.759
2-propylfuran; 2-ethyl-5-methylfuran	1	0.030	0.203
heptanenitrile	6000	0.017	0.232

Table 5-12. Summary of Site 6 Proton Transfer Reaction – Mass Spectrometer Observations for Chemicals of Potential Concern. (2 Sheets)

COPC Name	OEL (ppbv)	Average (ppbv)	Max (ppbv)
4-methyl-2-hexanone	500	0.022	0.694
NMOR	0.6	0.009	0.637
butyl nitrate	2500	0.010	0.113
2-ethyl-2-hexenal; 4-(1-methylpropyl)-2,3-dihydrofuran; 3-(1,1-dimethylethyl)-2,3-dihydrofuran	100, 1, 1	0.020	0.145
6-methyl-2-heptanone	8000	0.019	0.134
2-pentylfuran	1	0.027	0.144
biphenyl	200	0.014	0.110
2-heptylfuran	1	0.059	0.351
1,4-butanediol dinitrate	50	0.019	0.142
2-octylfuran	1	0.002	0.127
1,2,3-propanetriol 1,3-dinitrate	50	0.001	0.120
PCB	1000	0.024	0.155
6-(2-furanyl)-6-methyl-2-heptanone	1	0.011	0.101
furfural acetophenone	1	0.053	0.329

5.2.3 Detailed Analysis of Test Data – Background

The data collected during the Fall FY18 background study were used to draw comparisons between the following:

- Fall FY18 Background Study Data and co-collected confirmatory samples on alternative media;
- Data collected at differing sites; and
- Fall FY18 Background Study Data, Spring FY18 Background Study Data and FY17 Background Study Data.

5.2.3.1 Site Comparisons

In order to obtain an estimate of the true background concentration of COPCs at each study site, each data set was visually scanned for the longest continuous period of time with few or no signal spikes above the noise. An average was taken for this time period, which varied depending on monitoring location and other environmental factors, for each day of the background study. These averages were then sorted by study site (four data points per site) and averaged again to produce a single average and standard deviation value for each study site, per COPC.

The purpose of using this method was to attempt to disregard all short-duration local sources that could skew the estimate of the background concentration. This ensures that the comparison between site averages is truly a meaningful like-for-like comparison of bulk background concentrations that is not heavily biased towards local emissions, which, in many cases, are likely to be vehicle exhaust.

During the course of the study, the resolution of DR18-009 caused a significant decrease in background signal observed at nearly every mass of interest. After performing the site comparison analysis using every day of data gathered in the study, it was observed that many sites had disproportionately large error bars, caused by the decrease in perceived signal at low concentrations (i.e., at the background) after the tuning performed on October 24, 2018. While the data generated before the tuning still holds merit for examining plumes and signal hits above the noise, the background signal observed prior to October 24, 2018, in its current form, is incomparable to the background signal observed for the remainder of the study.

To this end, this analysis was performed only on the days of the study that took place after the instrument tuning described in DR18-009. Thus, each study site average only consists of either two or three data points, as opposed to the originally intended four. This ensures not only a better comparison between sites, but between days at a given site as well. While it would be expected to observe differences in concentration between dates at the same study site, the high standard deviation produced by the full dataset (in many cases exceeding the study site's average) could only be attributed to the change in tuning. The dates examined in this analysis range from October 26, 2018, to November 7, 2018.

Generally speaking, averages obtained at Site 6 were higher than the other sites for all analytes. It also appears that Site 4 produced the lowest averages on the whole, as opposed to the typical assumption that Site 1 would be the lowest. However, it is important to reiterate that the average concentrations obtained by examining the background from each dataset are extremely low, often times near the instrument's limits of detection. None of the averages, barring ammonia, exceed 0.05 ppbv (i.e., 50 pptv).

Examining ammonia specifically, the highest average concentration obtained was while monitoring at Site 6, which was expected. Site 1 produced the lowest average ammonia concentration. Sites 2 through 4 seem to be relatively equal in terms of average ammonia concentration.

Another general trend noted in this analysis is the fact that many averages at Site 1 actually exceed the averages obtained at Sites 2 through 5, i.e., the other study locations on the Hanford Site. This held true for many analytes, including but not limited to NEMA, 2,5-dimethylfuran, the combined 2-propylfuran + 2-ethyl-5-methylfuran signal, 2-pentylfuran, and 2-heptylfuran.

These site averages and relative standard deviations are shown below in Table 5-13. Bar plots for all COPCs detected by PTR-MS showing averages by site with error bars showing the relative standard deviation are located in Appendix B.

Table 5-13. Averages and Relative Standard Deviations by Study Site for Background Study Chemicals of Potential Concern.

Analyte	Site 1		Site 2		Site 3		Site 4		Site 5		Site 6	
	Avg. (ppbv)	**RSD (%)**	**Avg. (ppbv)**	**RSD (%)**	**Avg. (ppbv)**	**RSD (%)**	**Avg. (ppbv)**	**RSD (%)**	**Avg. (ppbv)**	**RSD (%)**	**Avg. (ppbv)**	**RSD (%)**
ammonia	3.914	13.1	5.561	48.7	5.900	56.6	6.010	57.0	5.824	62.2	9.751	53.0
furan	0.021	2.6	0.023	28.6	0.016	22.3	0.019	51.9	0.019	45.5	0.044	50.0
but-3-en-2-one + 2,3-dihydrofuran + 2,5-dihydrofuran	0.028	28.5	0.018	7.1	0.020	24.4	0.022	56.3	0.031	80.5	0.038	39.5
NDMA	0.013	23.8	0.011	27.9	0.010	0.2	0.014	39.1	0.013	37.8	0.028	56.9
2-methylfuran	0.021	30.2	0.018	19.1	0.017	27.7	0.017	45.9	0.020	60.7	0.043	59.4
NEMA	0.009	47.6	0.006	8.4	0.005	9.5	0.007	51.9	0.007	58.5	0.012	43.1
2,5-dimethylfuran	0.016	39.6	0.011	11.1	0.011	25.0	0.010	40.2	0.014	68.9	0.025	41.4
NDEA	0.002	16.8	0.002	0.9	0.002	9.5	0.002	44.6	0.002	35.3	0.003	23.7
2-propylfuran + 2-ethyl-5-methylfuran	0.010	26.5	0.007	16.6	0.006	25.0	0.005	35.4	0.007	68.2	0.017	45.8
NMOR	0.002	20.8	0.002	17.1	0.002	24.0	0.002	49.5	0.002	54.1	0.005	61.3
2-ethyl-2-hexenal + 4-(1-methylpropyl)-2,3-dihydrofuran + 3-(1,1-dimethylethyl)-2,3-dihydrofuran	0.004	38.1	0.003	4.7	0.003	25.3	0.003	38.2	0.003	50.7	0.007	45.7
2-pentylfuran	0.014	66.2	0.011	22.6	0.009	42.6	0.008	64.3	0.010	72.0	0.015	31.2
2-heptylfuran	0.012	40.1	0.010	13.6	0.009	36.9	0.008	34.0	0.010	64.9	0.016	42.5
2-octylfuran	0.001	12.0	0.001	17.4	0.001	27.4	0.001	32.2	0.001	53.1	0.001	40.4
6-(2-furanyl)-6-methyl-2-heptanone	0.001	1.3	0.001	33.3	0.001	39.1	0.001	46.5	0.001	61.4	0.002	63.1
furfural acetophenone	0.006	3.7	0.007	17.4	0.006	36.3	0.006	38.2	0.007	58.9	0.011	52.4

5.2.4 Comparisons to Fiscal Year 18 Spring Study and Fiscal Year 17 Study

During the course of the study, the resolution of DR18-009 caused a significant decrease in background signal observed at nearly every mass of interest. After performing the FY comparison analysis using every day of data gathered in the study, it was observed that many sites in the FY19 dataset had disproportionately large error bars, caused by the decrease in perceived signal at low concentrations (i.e., at the background) after the tuning performed on October 24, 2018. While the data generated before the tuning still holds merit for examining plumes and signal hits above the noise, the background signal observed prior to October 24, 2018, is incomparable to the background signal observed for the remainder of the study.

To this end, each FY19 study site average only consists of either two or three data points, as opposed to the originally intended four. This ensures not only a better comparison between fiscal years, but between days at a given site as well. While it would be expected to observe differences in concentration between dates at the same study site, the high standard deviation produced by the full FY19 dataset (in many cases exceeding the study site's average) could only be attributed to the change in tuning.

Overall, the average concentrations encountered were comparable to the previous study conducted in Spring FY18. In most cases, the error bars for FY18 and FY19 seem to overlap. The NDEA averages continue to be higher than encountered during the FY17 Summer study. In general, though, the outlier still appears to be the data collected in Summer FY17 during extreme wildfire conditions. The glaring exception to this trend is the increased NDEA averages observed during FY18 and FY19, an increase over the averages observed during the FY17 study. The trend of seeing higher averages at Site 6 seems to be magnified in FY19, with many Site 6 averages exceeding those encountered during the FY18 Spring study.

When making general comparisons about average concentrations, it seems apparent that Sites 1, 2, and 3, where it can be expected that the variance would be less, are in relative agreement between FY18 and FY19. It would be expected for the FY17 data to compare less favorably to the other two datasets due to the already stated fact that it is believed that wildfire smoke significantly impacted the results.

Generally speaking, the trend of seeing higher average concentrations at Site 6 is reinforced by the FY19 data. The Site 6 averages also have generally larger error bars than other sites, a direct representation of the higher standard deviation of the background at that site. This would be expected due to the higher variability of local emitters when located next to a busy freeway intersection. In addition, higher average concentrations were observed at site 6 during the fall FY19 study. This could possibly be attributed to the lower temperatures causing decreased mixing and a lower boundary layer, keeping higher concentration plumes from dispersing and mixing. Once again, the average concentrations obtained by examining the background from each dataset are extremely low, often times near the instrument's limits of detection. None of the averages, barring ammonia, exceed 0.3 ppbv (i.e., 300 pptv). Ammonia's background has also stayed relatively consistent across studies and sites, rarely exceeding 10 ppbv except in the case of Site 6 in FY17. This discrepancy can be explained by the increased expected variance at Site 6 due to urban influences.

The FY17, FY18, and FY19 averages are compared below in Figures 5-13 through Figure 5-28, showing bar plots with error bars showing the relative standard deviation for each of the 16 COPCs of interest for the Background Study. All comparisons will be more useful after completing additional background studies at different times of the year. The bar plots for the remaining COPCs detected by PTR-MS are located in Appendix C.

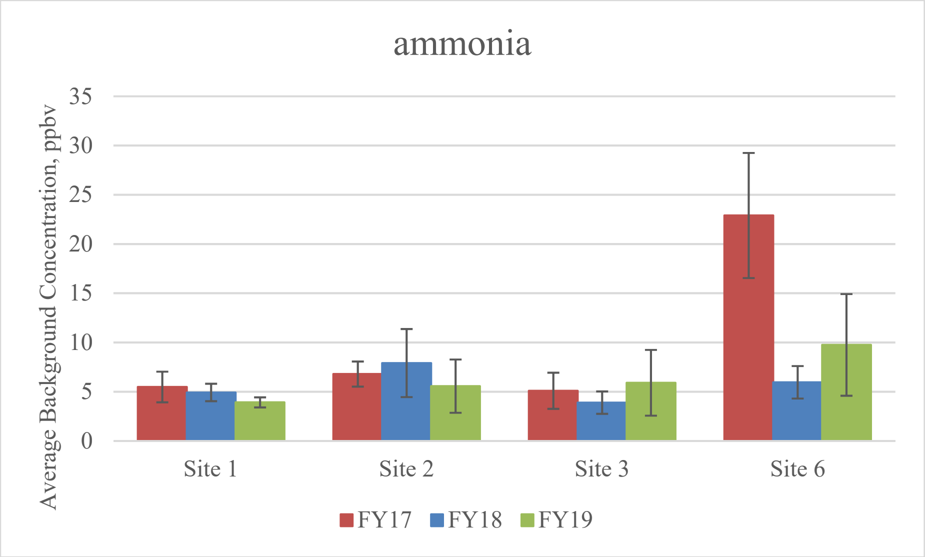

Figure 5-13. Comparison Between FY17, FY18, and Fall FY19 Ammonia.

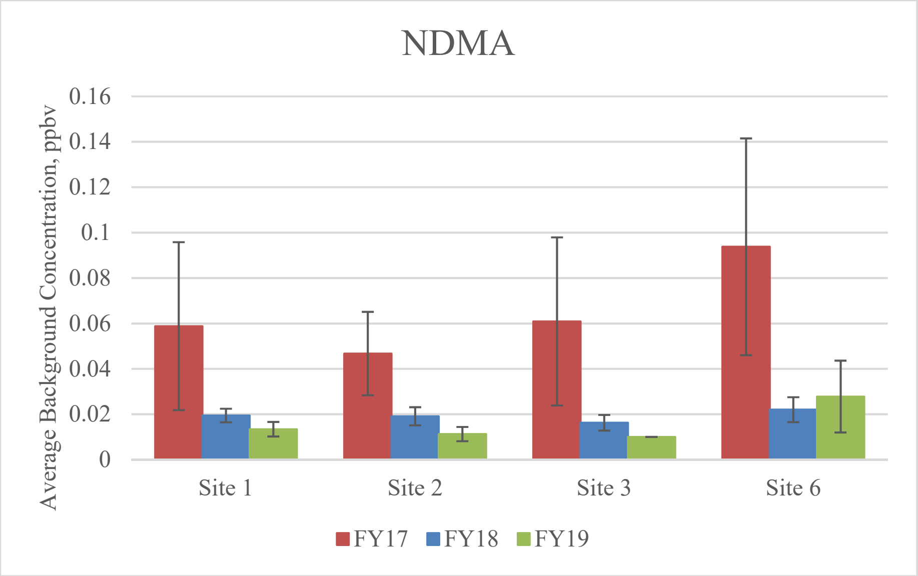

Figure 5-14. Comparison Between FY17, FY18, and Fall FY19 NDMA.

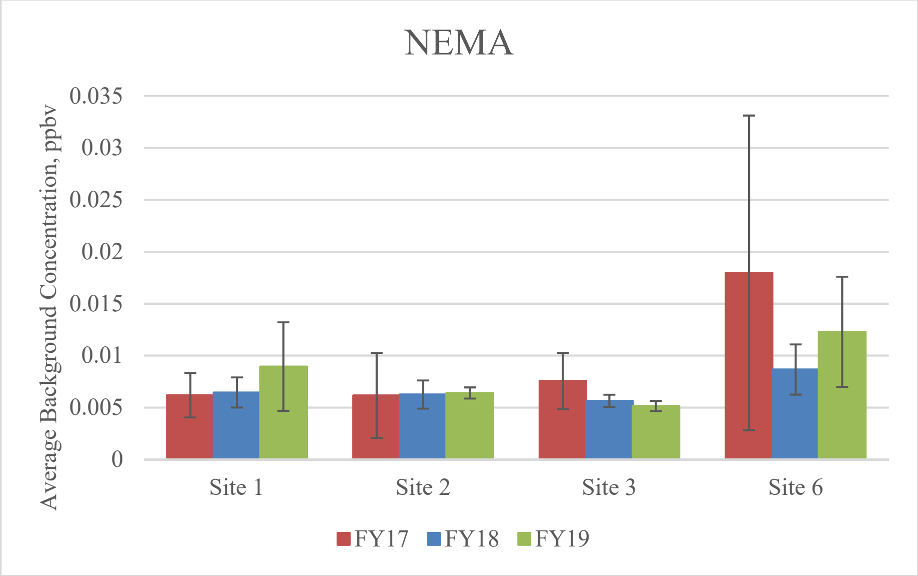

Figure 5-15. Comparison Between FY17, FY18, and Fall FY19 NEMA.

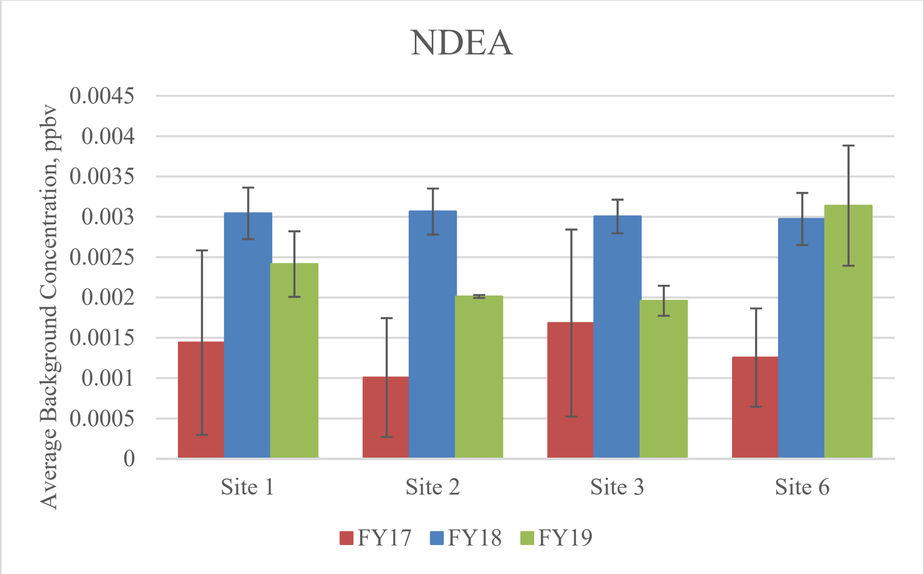

Figure 5-16. Comparison Between FY17, FY18, and Fall FY19 NDEA.

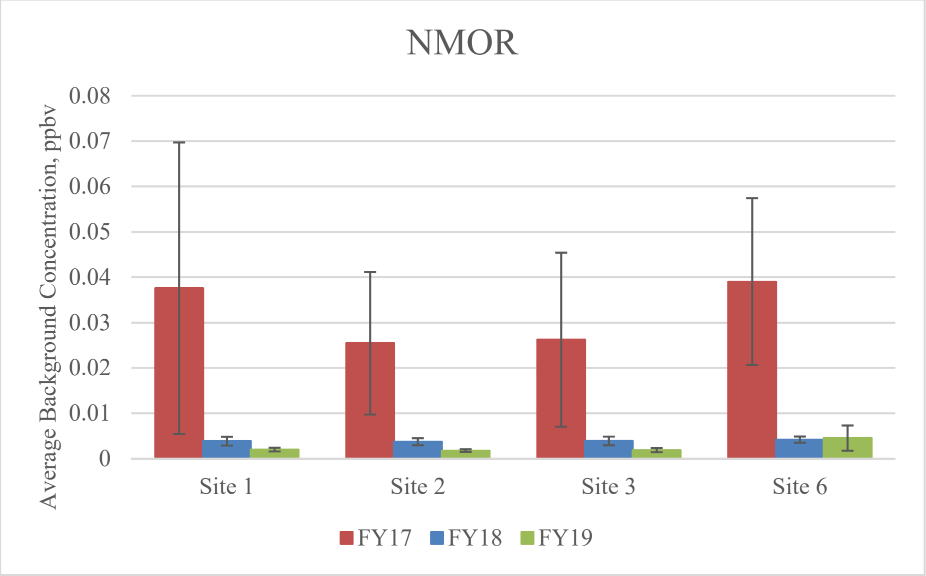

Figure 5-17. Comparison Between FY17, FY18, and Fall FY19 NMOR.

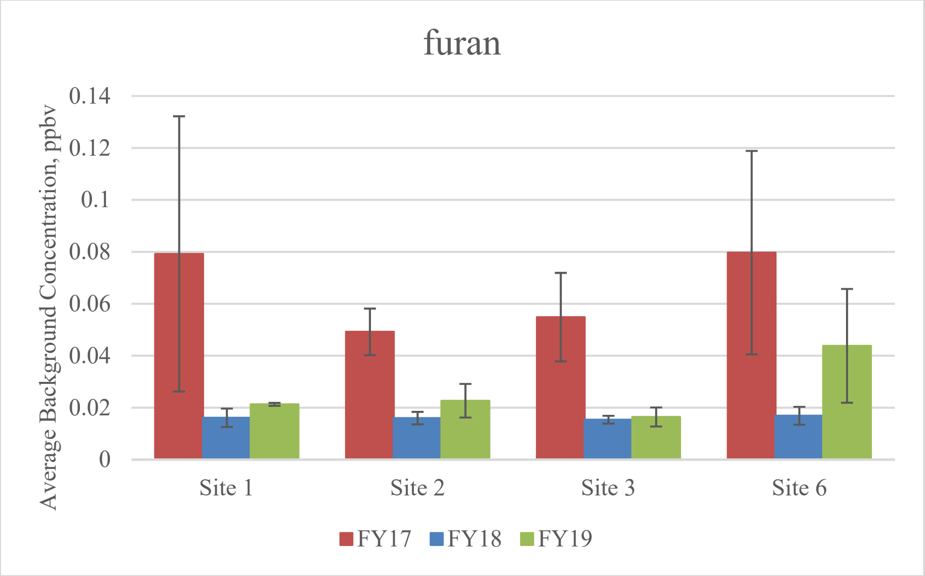

Figure 5-18. Comparison Between FY17, FY18, and Fall FY19 Furan.

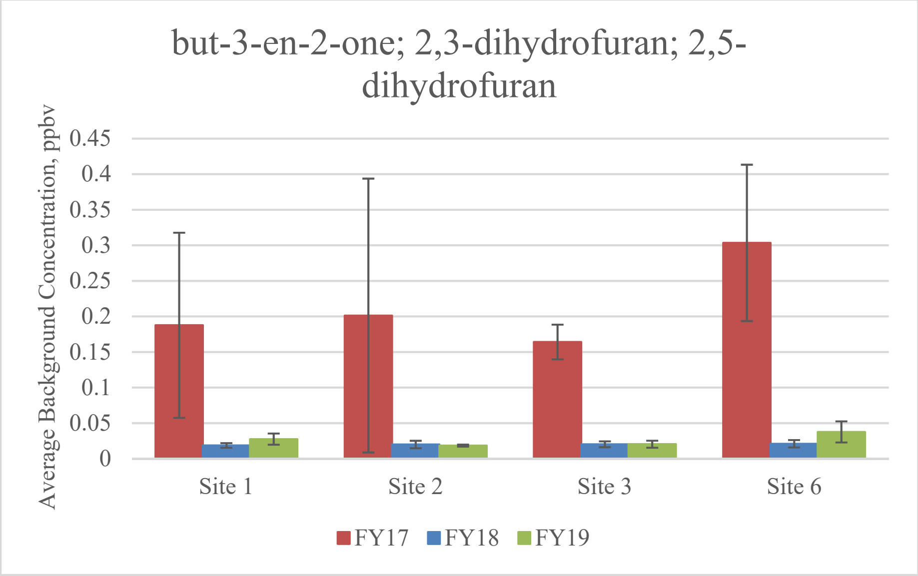

Figure 5-19. Comparison Between FY17, FY18, and Fall FY19 but-3-en-2-one, 2,3-dihydrofuran, and 2,5-dihydrofuran.

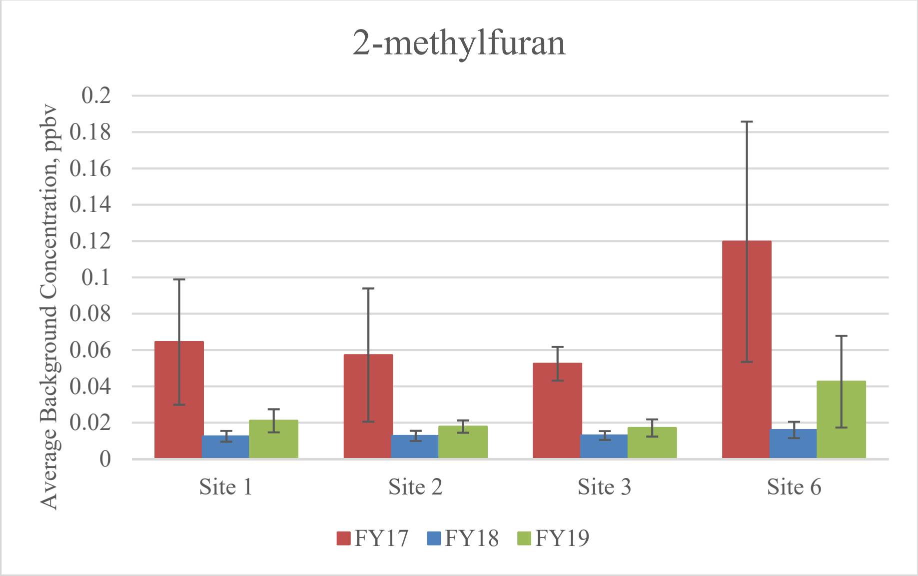

Figure 5-20. Comparison Between FY17, FY18, and Fall FY19 2-methylfuran.

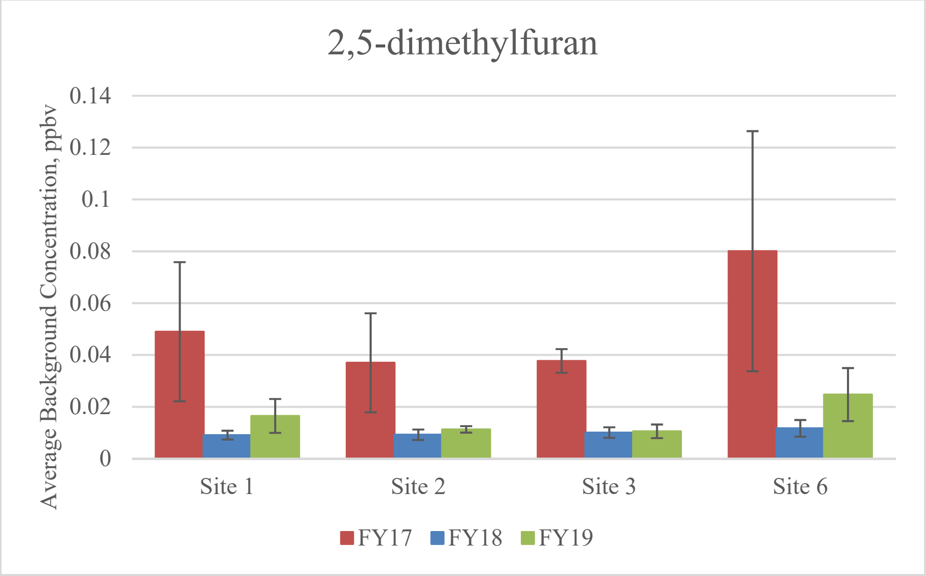

Figure 5-21. Comparison Between FY17, FY18, and Fall FY19 2,5-dimethylfuran.

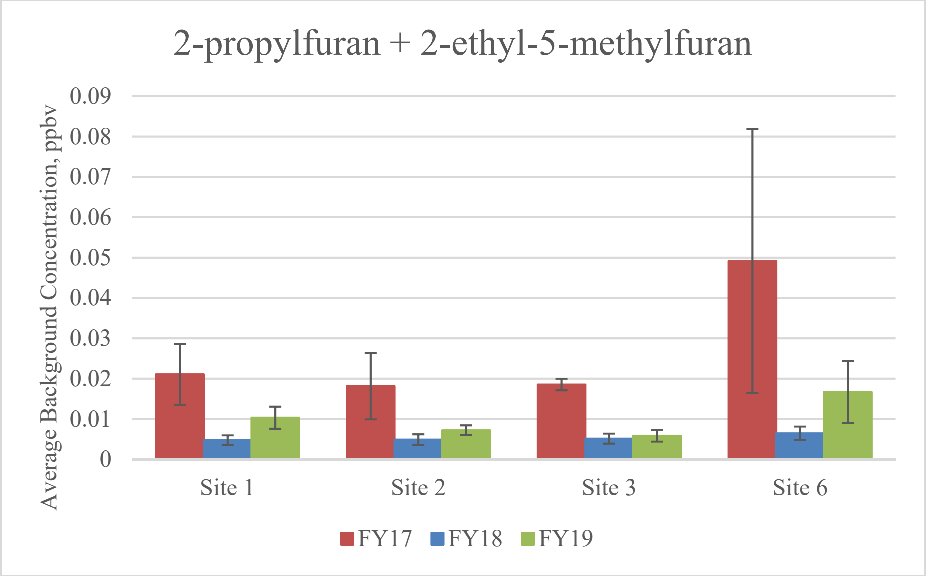

Figure 5-22. Comparison Between FY17, FY18, and Fall FY19 2-propylfuran and 2-ethyl-5-methylfuran.

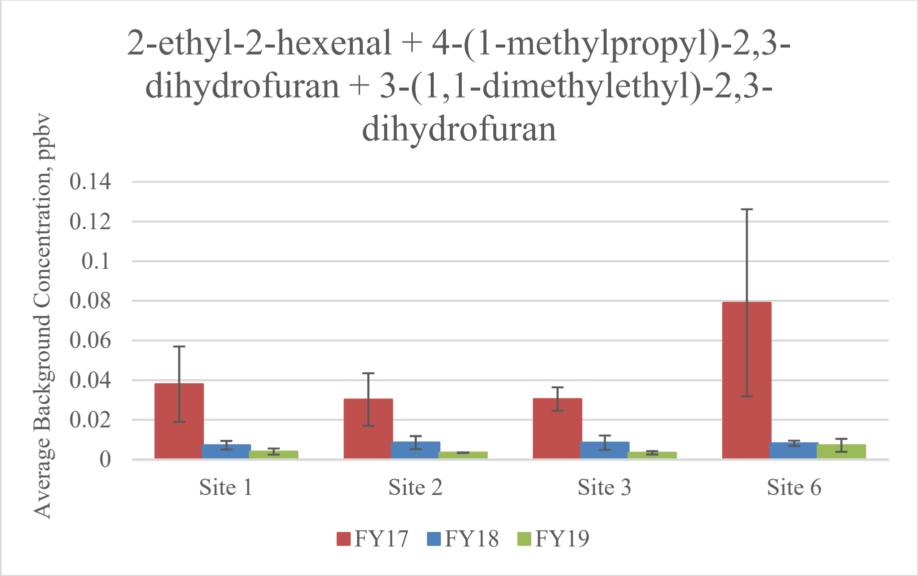

Figure 5-23. Comparison Between FY17, FY18, and Fall FY19 2-ethyl-2-hexenal, 4-(1-methylpropyl)-2,3-dihydrofuran, and 3-(1,1-dimethylethyl)-2,3-dihydrofuran.

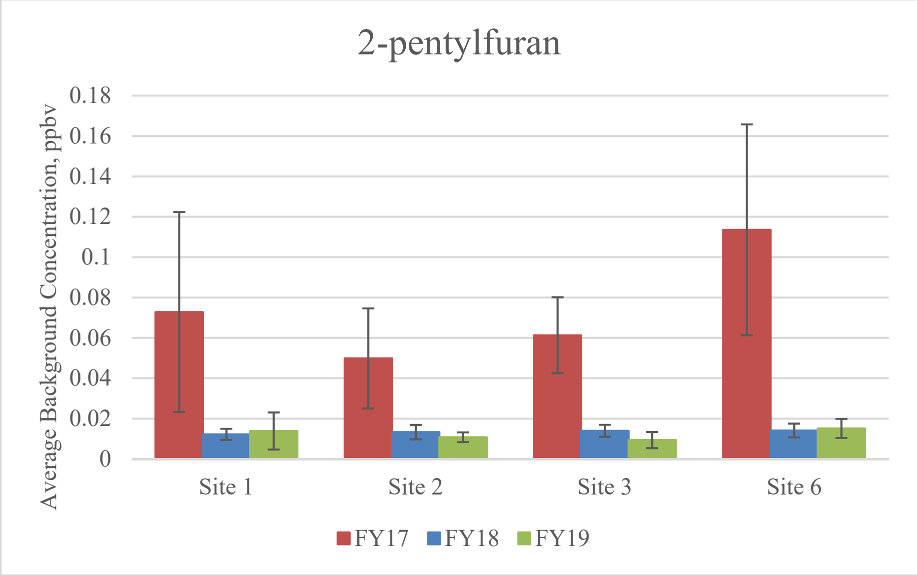

Figure 5-24. Comparison Between FY17, FY18, and Fall FY19 2-pentylfuran.

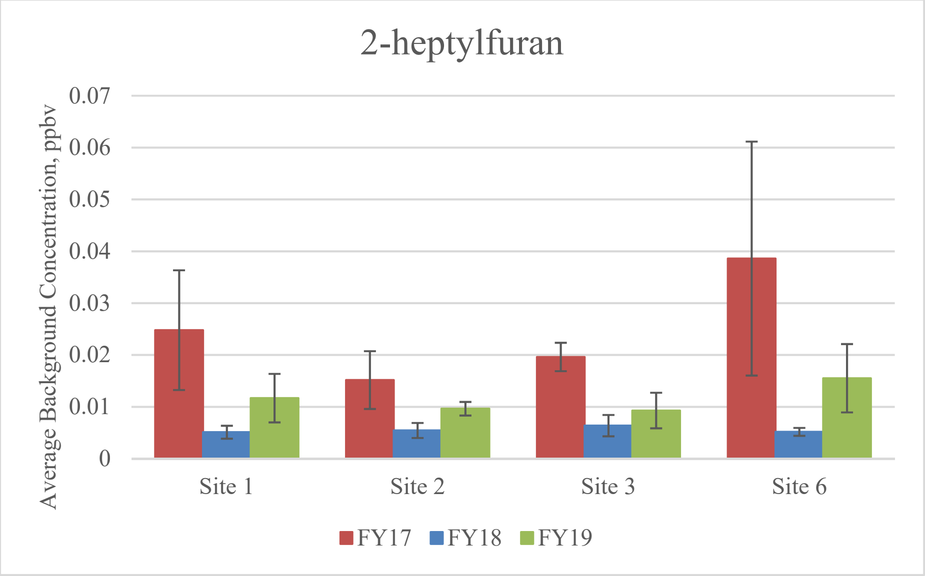

Figure 5-25. Comparison Between FY17, FY18, and Fall FY19 2-heptylfuran.

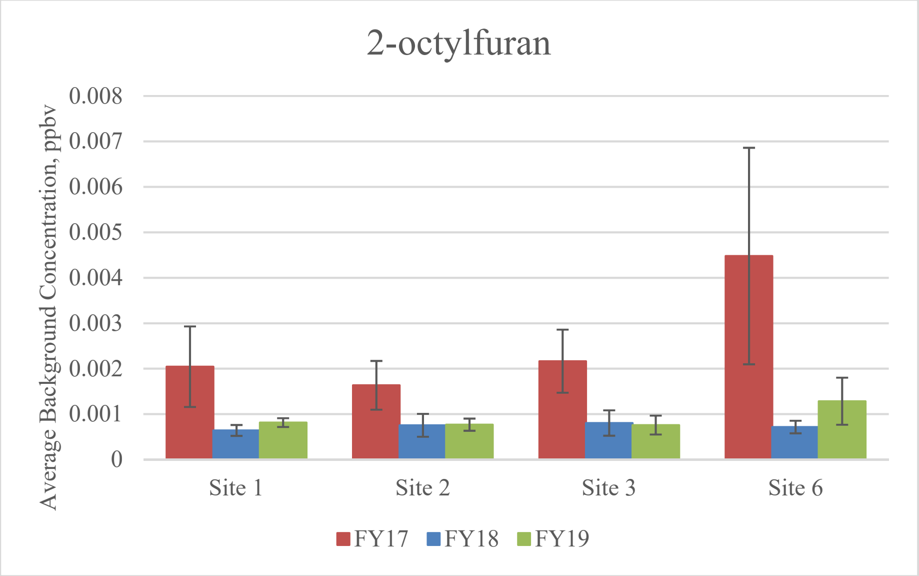

Figure 5-26. Comparison Between FY17, FY18, and Fall FY19 2-octylfuran.

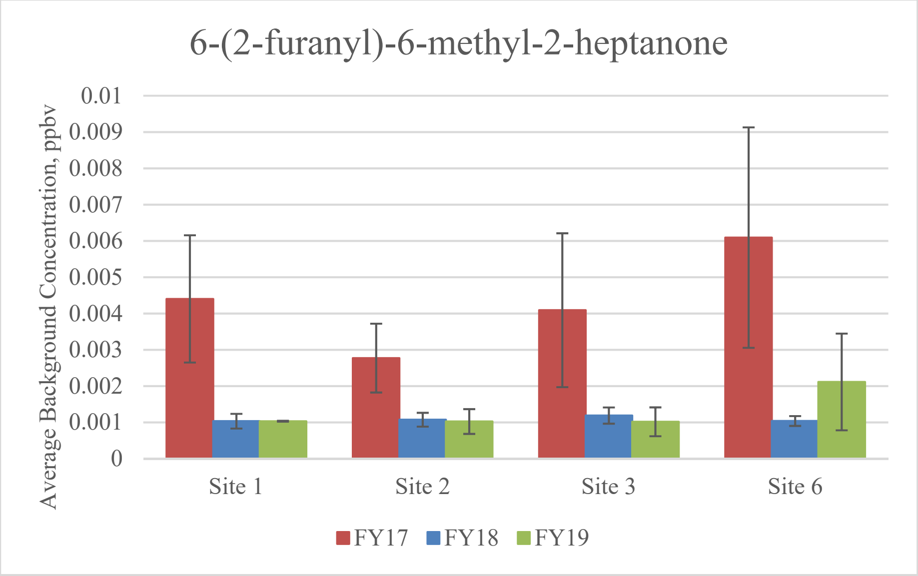

Figure 5-27. Comparison Between FY17, FY18, and Fall FY19 6-(2-furanyl)-6-methyl-2-heptanone.

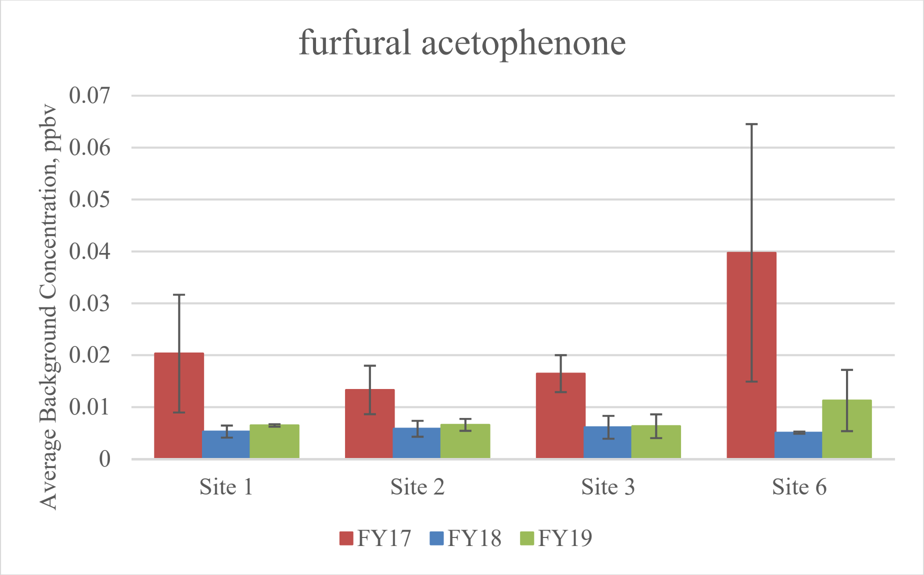

Figure 5-28. Comparison Between FY17, FY18, and Fall FY19 Furfural Acetophenone.

5.2.5 Background Study Statistical Analysis and Conclusions

To assess differences between sampling locations an analysis of variance (ANOVA) is typically performed. However, for an ANOVA to be valid, the variances in each population must be similar. Figure 5-29 plots the hourly averages and medians for furan measured at each of the six study sites. As can be clearly seen in this figure, the data variance is quite different at each site. As expected, the Bartlett test indicated a significant difference in these variances. As a result, a regular ANOVA test will be suspect.

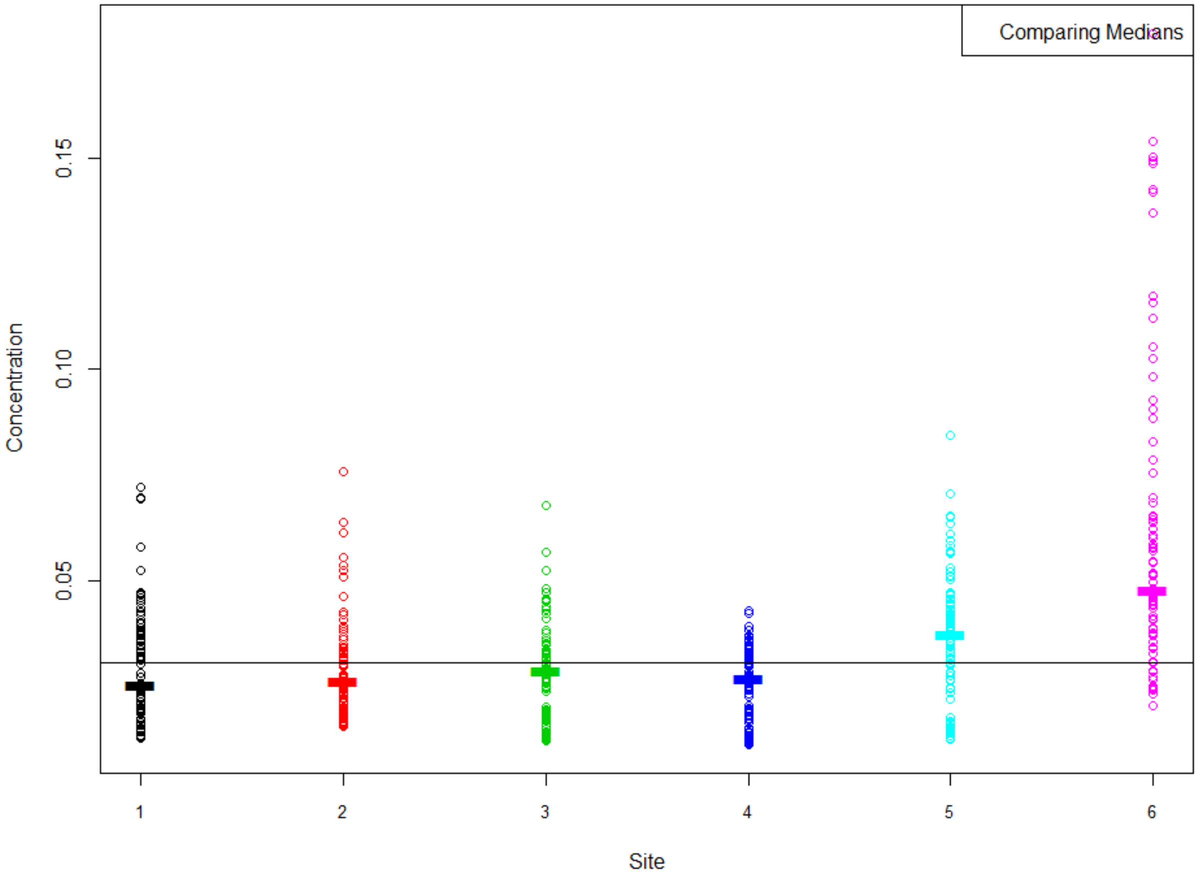

Figure 5-29. Dissimilar Variances in Hourly Average Furan Concentrations (ppbv) by Sites.

Since the variances are statistically different, a Kruskal-Wallis test is a more reliable way to determine whether a significant difference exists between background concentrations at the different test sites. A pairwise Dunn's test was also performed to assess statistical differences between pairs of sites for each chemical compound. The results of the Kruskal Wallis and Dunn's pairwise comparison tests are presented in this section for the combined furans.

Combined furans were selected for statistical analysis instead of individual furans to streamline reporting and summarize the combined effects of furan exposure. Furans that are confidently measured by the PTR-MS were included in the combined furan analysis as follows:

- Furan,
- 2-methylfuran,
- 2,5-dimethylfuran,
- 2-propylfuran, and
- 2-ethyl-5-methylfuran

4-(1-methylpropyl)-2,3-dihydrofuran and 3-(1,1-dimethylethyl)-2,3-dihydrofuran were not included in the combined furan analysis since they are not separable from 2-ethyl-2-hexenal by the PTR-MS. Including this combined PTR-MS result would potentially report higher than actual combined furan results. Since 2-ethyl-2-hexanal has an OEL which is 100 times greater than the furans, including this compound in the combined furan results would not allow comparison to the furan OEL. For consistency with prior background studies 2-pentylfuran, 3-(2-furanyl)-1-phenyl-2-propen-1-one, 2-heptylfuran, 2-octylfuran, and 6-(2-furanyl)-6methyl-2-heptanone were not included in the combined furan analysis as they were not included in prior studies. The PTR-MS TOF 4000 used in the spring and summer background studies did not have sufficient mass resolution to resolve interferences with these compounds.

In addition to the Kruskal Wallis and Dunn's tests, an additional statistical analysis was performed to assess potential linear correlations between furan concentrations and environmental factors including smoke and wind. A significant correlation exists between furans and smoke, but an inverse correlation exists between furans and wind speed. A statistical analysis was not performed for diurnal effects. The data are plotted for visualization instead.

5.2.5.1 Site Comparisons

The p-value is defined as the probability of obtaining a result equal to or "more extreme" than what was actually observed, when the null hypothesis is true. In this case, the null hypothesis is that "there is no difference between the vapor concentrations at each of the sites." If a 95% confidence limit is established, the null Hypothesis must be rejected when the p-value is less than 0.05. The Kruskal-Wallis test produced a p-value of 5.759e-10, which clearly indicates that there are significant differences in concentrations between the different sites as shown below.

non-parametric tests

```
        Kruskal-Wallis rank sum test

data:  Combined Furans by Site
Kruskal-Wallis chi-squared = 51.862, df = 5, p-value = 5.759e-10
```

By visual inspection, Figure 5-30 shows that the sites with the highest furan concentration are associated with the sites with the highest ammonia concentration [Site 5 (WTP) and Site 6 (395 and Clearwater)]. The most notable observation from the data is that all sites had extremely low furan concentrations. Hourly averaged furan concentrations at all sites were less than 20% of the OEL, and the median hourly average furan concentration for each site was less than 5% of the OEL (see Figure 5-29). Similarly, all hourly averaged combined furan concentrations at all sites were less than 55% of the OEL (see Figure 5-30).

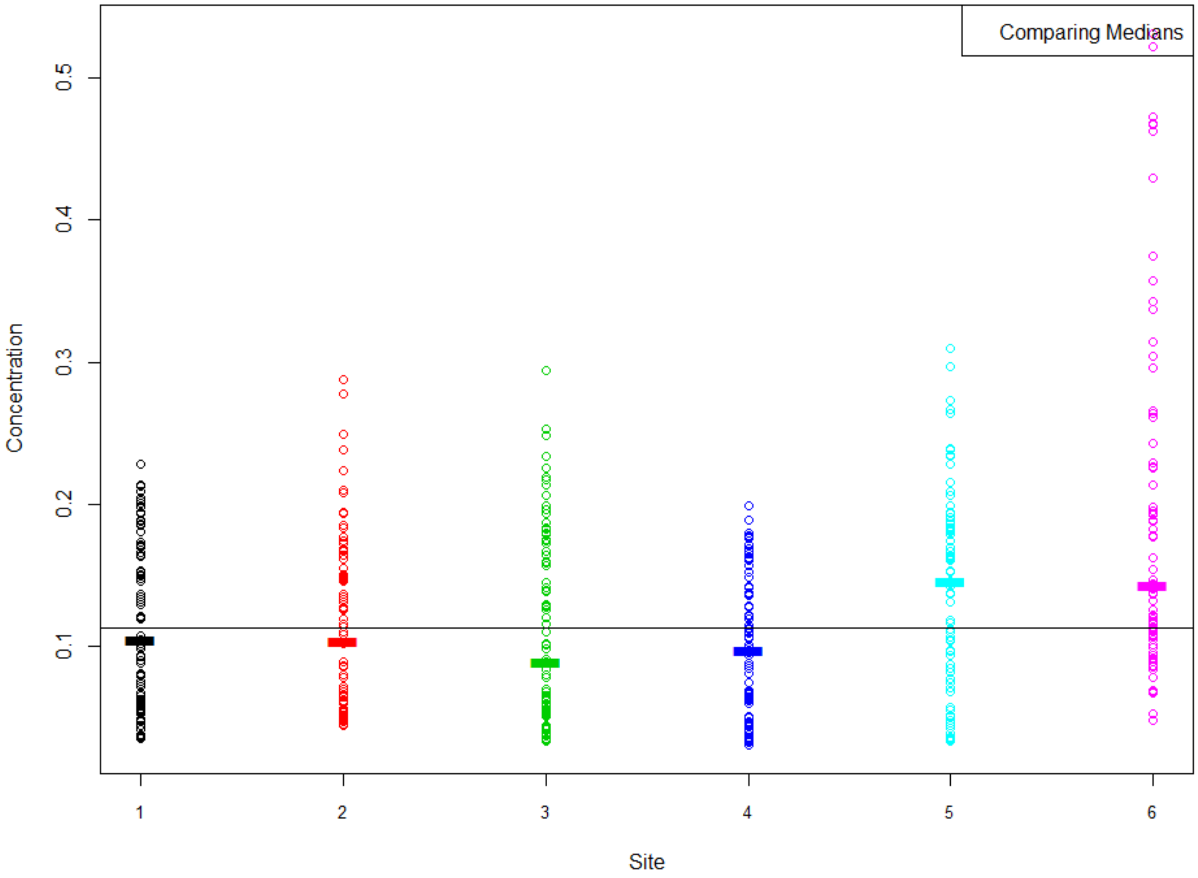

Figure 5-30. Median of Hourly Averages of Combined Furan Concentrations (ppbv) by Site.

The pairwise Dunn's Test results for the combined furan signals measured during the background study are shown in Table 5-14. This test was run for each pair of study sites to test the null hypothesis that there is no significant difference between them. For each intersection of study site columns and rows, a calculated p-value is shown. P-values highlighted in yellow denoted pairs of study sites where the null hypothesis was rejected; i.e., with 95% confidence there is a significant difference between the sites (p-values < 0.05). The significance of site comparisons become more apparent when addressing the Dunn's pairwise comparison result, as follows:

- Site 1 (remote and upwind), Site 2 (SY Farm), Site 3 (4th and Buffalo), and Site 4 (AN Farm) are not statistically different from each other, indicating that the tank farm sites (2, 3, and 4) are similar to the pristine upwind location (Site 1); and
- Sites 5 (WTP) and 6 (Hwy 395 and Clearwater) are statistically higher in furan concentration than the tank farm sites (2, 3, and 4), suggesting that the tank farm sites may generally have lower furan concentrations than typical commercial or industrial sites.

It should be noted that although these values may be statistically interesting in postulating the source of the ultra-trace furans, they are not significant from an Industrial Hygiene or Operations perspective.

Table 5-14. Dunn's Pairwise Comparison of the Combined Furans by Site (Holm-Šidák).

	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
Site 1 (Remote and upwind)						
Site 2 (SY Farm)	0.3491					
Site 3 (4th & Buffalo)	0.3763	0.4242				
Site 4 (AN Farm)	0.1053	0.4086	0.4481			
Site 5 (WTP)	0.1132	0.0153	0.0092	0.0001		
Site 6 (395 & Clearwater)	0.0002	0.0000	0.0000	0.0000	0.1140	
P-values highlighted in yellow denote pairs of study sites where the null hypothesis was rejected; i.e., with 95% confidence there is a significant difference between the sites (p-values <0.05).						

Site statistical comparisons for nitrosamines are not provided in this report due to unknown contributions from interfering chemicals. Past background studies with the PTR-MS TOF 4000 indicated significant contributions from interfering compounds particularly during smoke days. The PTR-MS TOF 6000 used in this background study may have reduced the contribution from interfering compounds, but to what extent is unknown.

5.2.5.2 Ammonia as an Indicator of Tank Vapors

Trace quantities of ammonia are a potential indicator of tank vapors in the surrounding atmosphere. Ammonia is a major constituent of the headspace vapors in all Hanford waste storage tanks. A positive correlation of a Hanford Tank Farm COPC profile to an ammonia profile may provide a link to a waste tank emission. Additionally, elevated ammonia levels around the tank farms may be an indication of tank vapor emissions. Figure 5-31 provides a summary of hourly average ammonia concentrations by site, with the median value for each site shown as a black solid line. First it should be noted that the ammonia concentrations for all sites are extremely low (three orders of magnitude below its OEL and well below what might be considered a leading indicator action level). Ammonia concentrations for three sites [Site 1 (remote and upwind), Site 2 (SY Farm) and Site 3 (4th and Buffalo)] were consistent with global atmospheric averages (0.3 – 6 ppbv, https://www.atsdr.cdc.gov/toxprofiles/tp126-c2.pdf). The three other sites [Site 4 (AN Farm), Site 5 (WTP), and Site 6 (395 and Clearwater)] had ammonia concentrations higher than the global atmospheric average. Although these values may be statistically interesting in postulating the source of the ammonia, they are not significant from an Industrial Hygiene or Operations perspective.

Table 5-15 indicates that Sites 5 and 6 are statistically similar to each other and statistically different than the rest (Site 1, Site 2, Site 3 and Site 4). Site 6 is off-site and logically not due to tank waste vapors. Sites 5 is downwind of the A-Tank Farm complex. If the ammonia from Site 5 was from the tank waste, it should be accompanied by elevated furan levels, which it was. Therefore, it is possible that the elevated ammonia and furan at Site 5 are due to tank emissions.

It is more likely, however, that the elevated ammonia and furan concentrations at Site 5 are due to construction-related activities at the WTP since they are accompanied by combustion markers (see Combustion Marker section below). The low ammonia concentrations for all tank farm sites (near global average) support a conclusion that the observed furan concentrations around the tank farms are not due to the tank waste, but rather to vehicle traffic, diesel generators and fugitive emissions. Further, the furan and ammonia levels at the tank farm and remote downwind monitoring locations indicate that current vapor control strategies are working (i.e., vapor control zones, stacks and stack extensions).

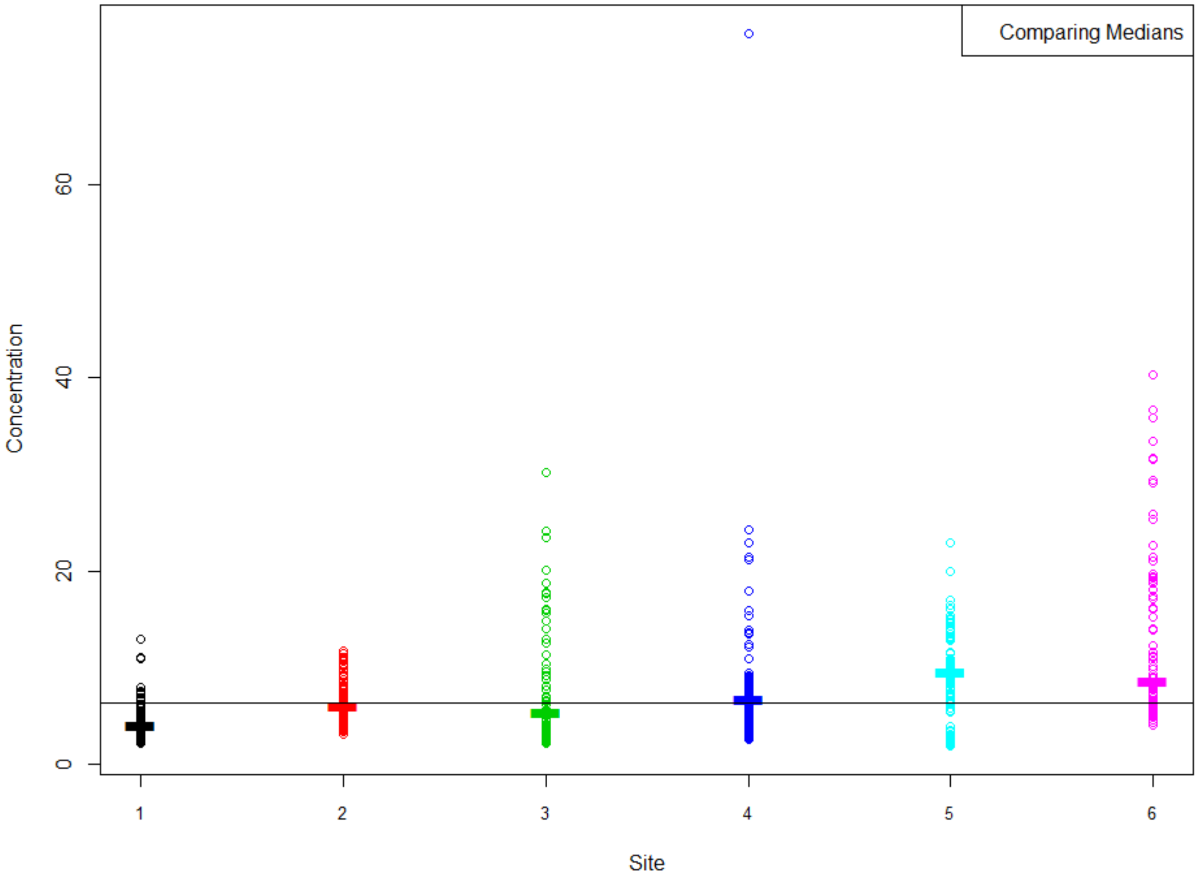

Figure 5-31. Hourly Average Ammonia Concentrations (ppbv) by Site.

Table 5-15. Dunn's Pairwise Comparison of Ammonia by Site (Holm-Šidák).

	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
Site 1 (Remote and Upwind)						
Site 2 (SY Farm)	0.0000					
Site 3 (4th & Buffalo)	0.0015	0.2028				
Site 4 (AN Farm)	0.0000	0.2360	0.0972			
Site 5 (WTP)	0.0000	0.0023	0.0000	0.0210		
Site 6 (395 & Clearwater)	0.0000	0.0000	0.0000	0.0001	0.1277	

P-values highlighted in yellow denote pairs of study sites where the null hypothesis was rejected; i.e., with 95% confidence there is a significant difference between the sites (p-values <0.05).

5.2.5.3 Correlation with Smoke

In order to assess the correlation between smoke and furan concentrations, particulate matter data of less than 2.5 micron were obtained from a public sampling location in Kennewick, WA (on the roof of Tri-Tech) managed by Washington State Department of Ecology. Particulate matter of less than 2.5 microns is typical of smoke found at a long distance from its source. There was some evidence of smoke observed during the study.

Figure 5-32 shows a time series plot of combined furan concentration on the right axis and particulate matter concentrations less than 2.5 microns on the left axis. The linear correlation coefficient was calculated to be 0.6279 indicating a relatively strong correlation between the combined furan signal and smoke. The smoke can be said to account for 62.8% of the furan variability. This is not surprising, since furans are produced during combustion. There were six smoke days during the FY19 Fall background study as defined in the FY17 Summer background study (>15 µg/m^3).

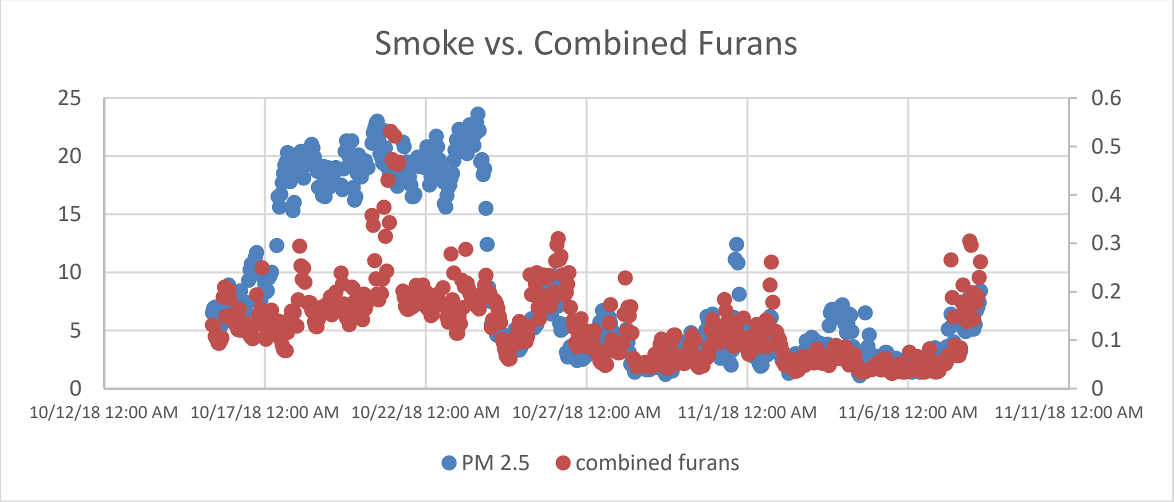

Figure 5-32. Time Series Plot of Combined Furan Concentrations (ppbv) for all Sites Versus Smoke (µgm^3).

5.2.5.4 Diurnal Variations

Figure 5-33 is a plot of the combined furan signal broken into one-hour averages for the entire background study. The dots represent each average taken at a given hour. The thick colored bars represent the median of each of those sets of averages. The black line represents the overall median for combined furans throughout the entire data set. This plot shows very little diurnal variation in the combined furan concentrations; with minor increases in the morning and evening hours. The median hourly averages were well below 10% of the OEL. From an operational perspective, there is no significant increase in vapor hazard between day versus night given the trace concentrations.

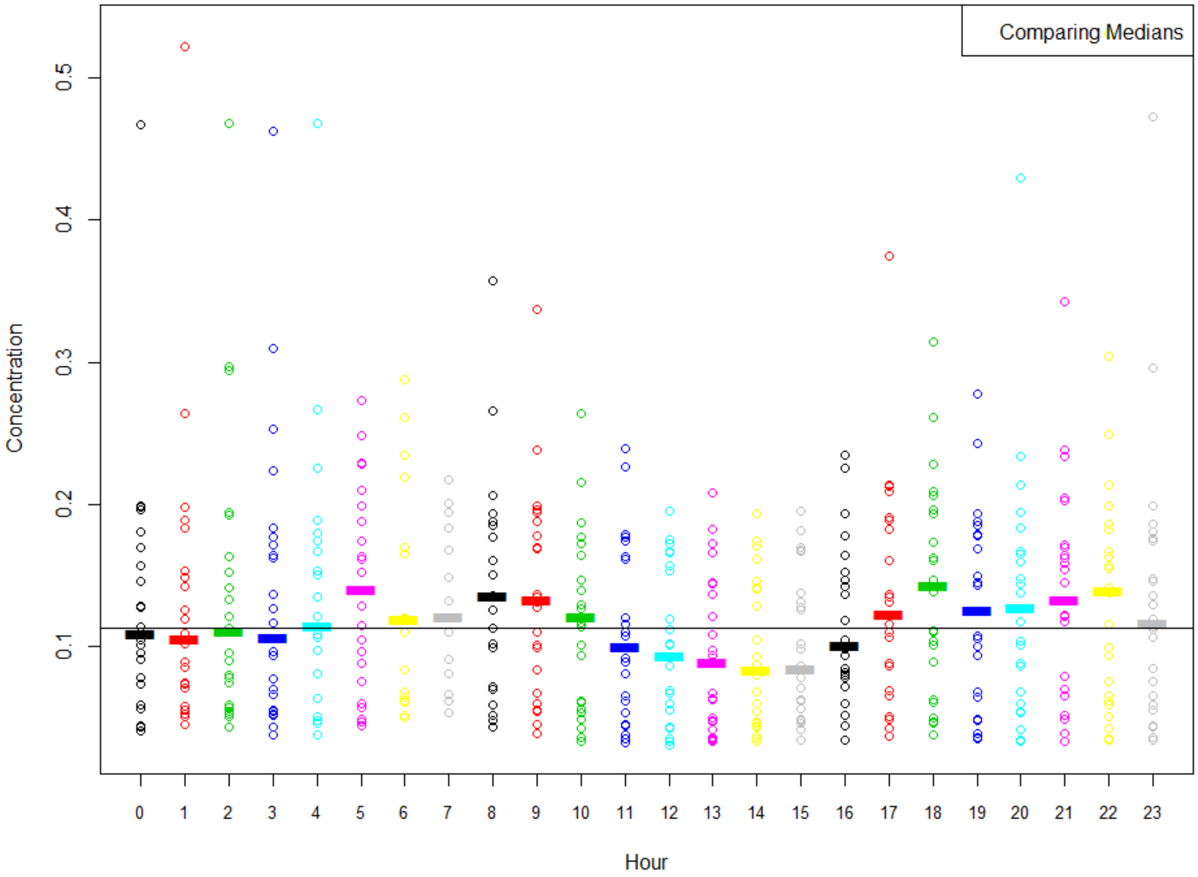

Figure 5-33. Diurnal Effects for Combined Furans (ppbv).

Figure 5-34 is a plot of the carbon dioxide signal broken into one-hour averages for the entire background study. The dots represent each average taken at a given hour; the thick colored bars represent the median of each of those sets of averages. The black line represents the overall median for carbon dioxide throughout the entire data set. This plot shows a maximum CO_2 concentration around 08:00 to 09:00 decreasing to a minimum during the afternoon and evening. The cause of the variation is not known, but may be partially due to the accumulation of CO_2 in the morning hours until the boundary layer breaks up.

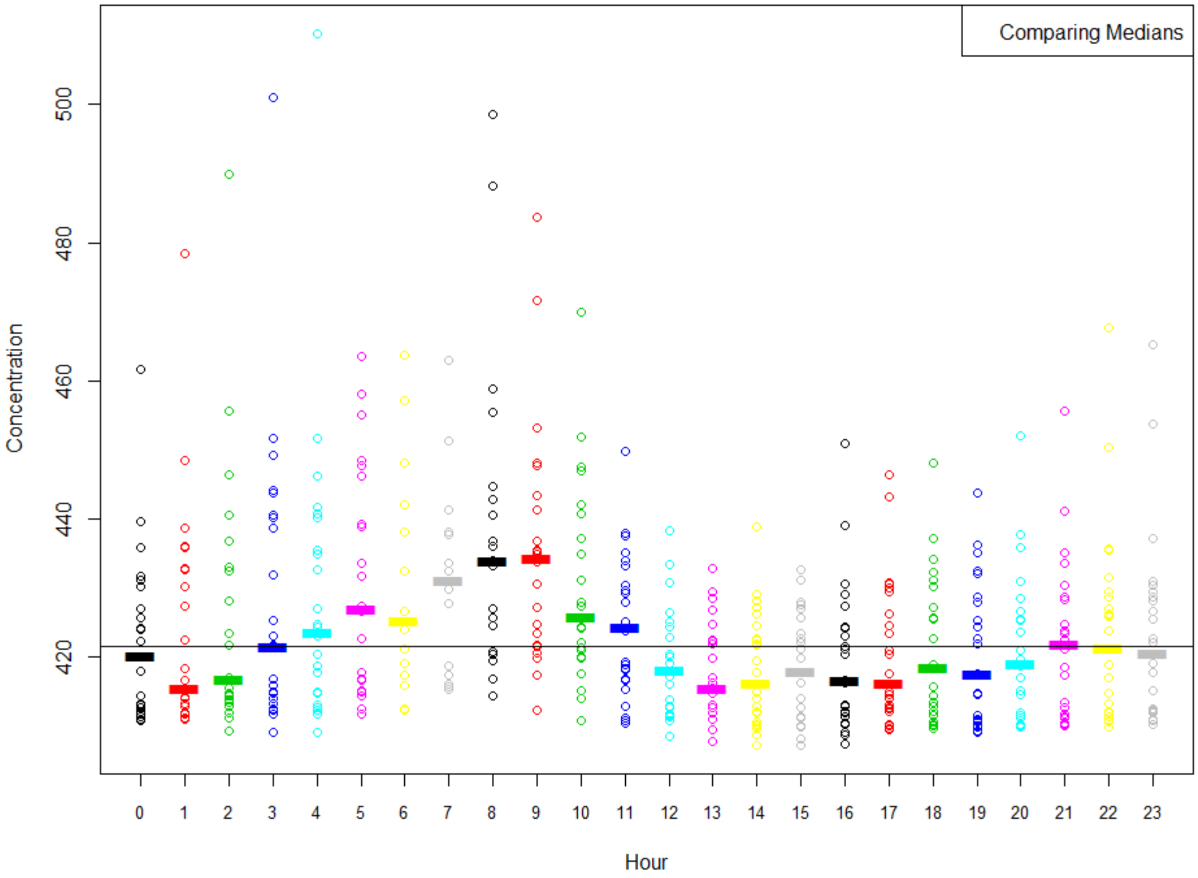

Figure 5-34. Diurnal Effects for CO_2 (ppm).

Figure 5-35 is a plot of the ammonia signal broken into one-hour averages for the entire background study. The dots represent each average taken at a given hour. The thick colored bars represent the median of each of those sets of averages. The black line represents the overall median for ammonia throughout the entire data set. This plot shows an increase in ammonia at 07:00, decaying to a baseline level over the next ten hours.

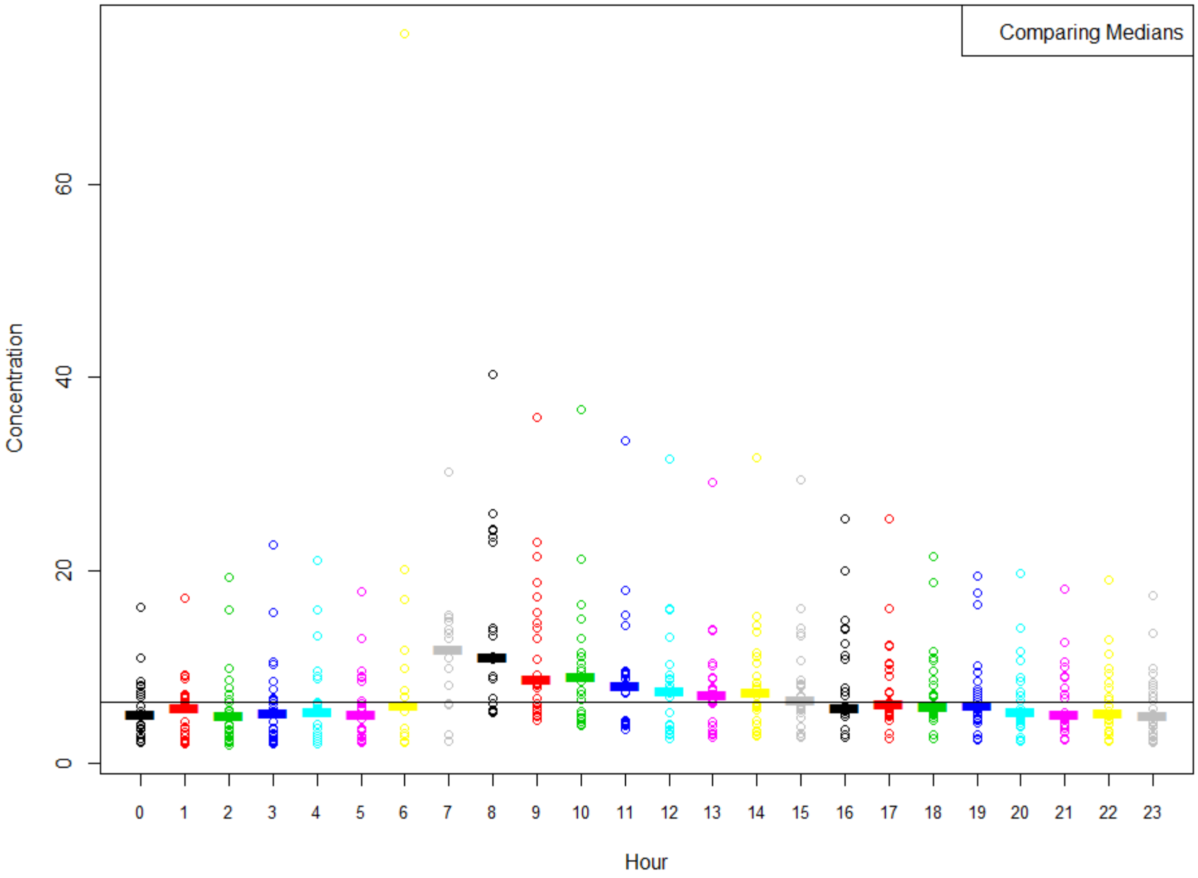

Figure 5-35. Diurnal Variation for Ammonia (ppbv).

5.2.6 Combustion Markers

Several PTR-MS analytes are generated as a result of combustion and can be used to help identify the source of other trace analytes (e.g., furans) also generated during combustion. Ethylamine is a good indicator of diesel combustion. While benzene and toluene are good indicators of gasoline combustion., carbon dioxide is a good indicator for all combustion sources.

Figure 5-36 provides a summary of hourly average CO_2 concentrations by site, with the median value for each site shown as a solid colored line. The dots represent each average taken at a given hour. The thick colored bars represent the median of each of those sets pf averages. The black line represents the overall media for CO_2 throughout the entire data set. This plot shows two sites with above average concentrations of CO_2 [Site 5 (WTP) and Site 6 (395 and Clearwater)], with Site 6 being significantly higher than Site 5. This is consistent with the amount of traffic moving through the corner of 395 and Clearwater. Statistically, Sites 1, 2, 3, and 4 are not significantly different and are all at or below the median level.

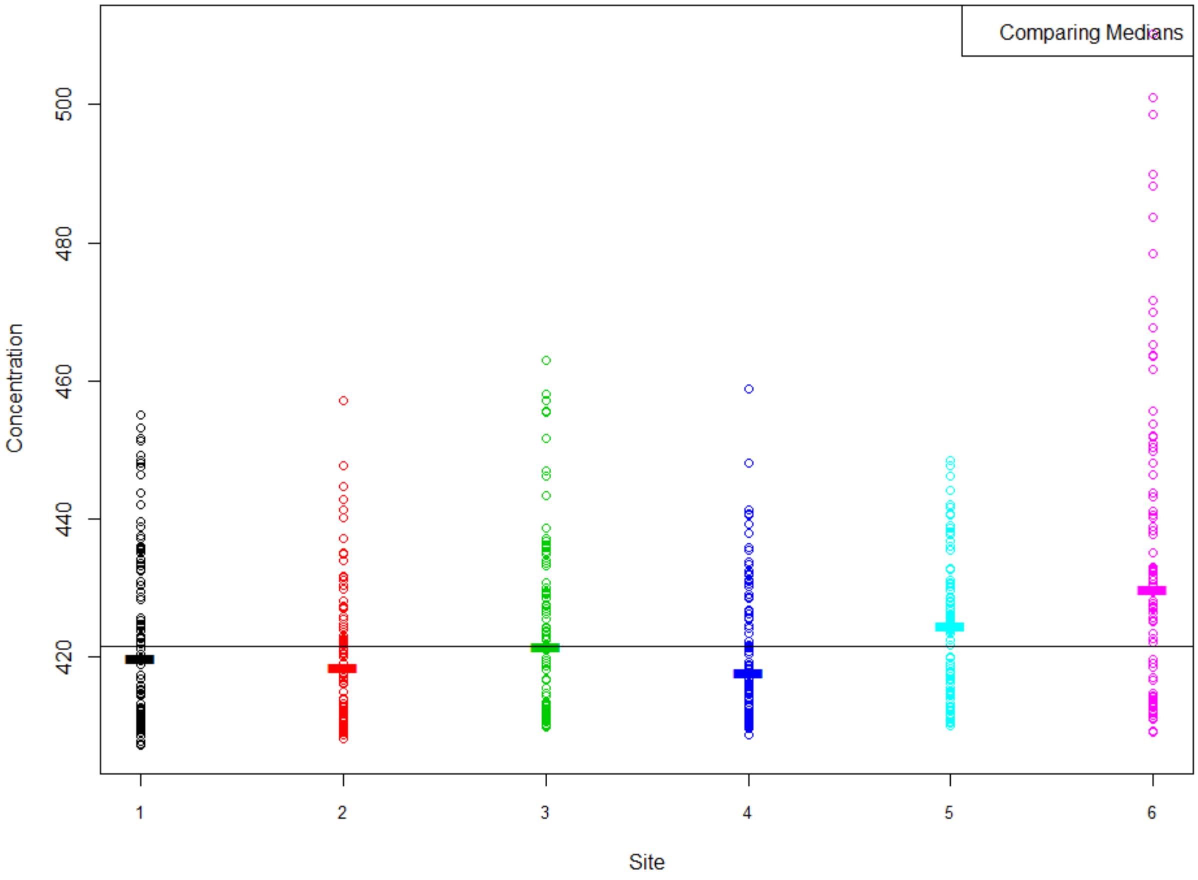

Figure 5-36. CO_2 Concentrations (ppm) at Each Sampling Site.

6.0 QUALITY ASSESSMENT

During the October 1, 2018, through November 7, 2018, monitoring campaign, quality control procedures were followed by the TerraGraphics Vapor Team: Data Collection and Data Processing. Data were collected and quality documents according to Procedure 66409-RPT-004. All data were accepted, processed, and reported according to Procedure 17124-DOE-HS-102, “Mobile Laboratory Data Processing – Analysis.” All exceptions have been noted and any potential quality-affecting issues were resolved prior to report or are noted in this report. All potential quality-affecting deviations have been captured in DRs and are summarized below with some interpretation.

During the October 1, 2018, to November 7, 2018, monitoring campaign, there were four (4) DRs. DR18-008 documents an issue discovered on October 18, 2018, from switching between H_3O^+ and NO^+ modes on the PTR-MS. DR18-009 records the high background signal observed on the PTR-TOF for all ions above m/z 100. DR18-010 documents the lack of notification to WRPS by TerraGraphics when average concentrations of NDEA exceeded the Occupational Exposure Limit (OEL) due to an elevated baseline. DR18-011 notes a power loss in the ML on November 8, 2018, to November 9, 2018, from a drain on the Uninterruptible Power Supply (UPS) backup system.

6.1 Lessons Learned – DR18-008

On October 18, 2018, an issue was discovered during data processing regarding the switching between H_3O^+ and NO^+ modes on the PTR-MS. Around the time that the PTR-MS switched modes, a high peak was forming at acetonitrile (m/z 42), interfering with the instrument’s chemistry. The WRPS Project Manager (PM) was informed on October 18, 2018, of the chemistry interference and it was decided to halt switching to NO^+ mode until this issue was investigated and resolved.

Through investigation by the SME, it was determined that the issue was caused by the LpDNPH S10 sample tubes. When the S10 tubes were connected to the sample lines there was a contaminate that off-gassed, saturating the sample lines. To resolve this, LpDNPH tubes were moved to an independent sample inlet, as captured in Revision 7 of 66409-RPT-004.

6.2 Lessons Learned – DR18-009

During data processing, it was discovered that there was a high background signal for all ions above m/z 100 detected by the PTR-TOF. The issue was determined to be present in all datasets collected from October 15, 2018, to October 24, 2018. The TerraGraphics PM and SME, and IONICON, the PTR manufacturer, were notified. On October 24, 2018, the IONICON support team suggested specific tuning of the PTR settings. The high background immediately resolved after tuning the instrument’s parameters as suggested.

Future datasets will be assessed for high background signals and the SME will periodically observe the PTR during data collection to ensure IONICON’s suggestion is a long-term solution. Field technicians will also be trained to identify this behavior and notify the SME once observed.

6.3 Lessons Learned – DR18-010

Apparent average concentrations of NDEA that exceeded the OEL were reported for 53005-81-RPT-014, *Weekly Report for Week 6 (September 10, 2018 – September 15, 2018)*; 53005-81-RPT-016, *Weekly Report for Week 7 (September 17, 2018 – September 22, 2018)*; and 53005-81-RPT-017, *Weekly Report for Week 8 (September 24, 2018 – September 27, 2018)*. These potential OEL breaches were not immediately brought to the client's attention. The source of the elevated NDEA baseline was addressed and corrected through DR18-008. This DR focuses on the lack of notification of the OEL breaches to WRPS by the TerraGraphics Data Processing and Reporting Team.

After identification and correction of the high background issue in DR18-008, further clarification of reporting preferences by the client have been explained. Going forward, all reports will have a 50% OEL line and 100% OEL line printed on the time series plots for COPCs where that line does not expand the Y axis of the plot. The data processing procedure was also revised to include steps, in two separate areas, for data analysts to verify the daily average concentrations of COPCs do not exceed 50% of the OEL and if so, to notify the TerraGraphics PM as soon as possible after the data have been processed.

6.4 Lessons Learned – DR18-011

On November 8, 2018, cold weather prompted the heating system inside the ML to operate longer than anticipated. The power usage was high, causing a drain on the UPS battery backup system. The generator was unable to keep up with power demands and the UPS system connected to the LI-COR, Picarro, and PTR was unable to charge, resulting in a shutdown.

On November 15, 2018, the SME broadened the UPS sensitivity to the "Fair" power quality. With the temperature continuing to decrease in the winter months, the TerraGraphics Vapor Team and Quality Assurance Representative (QAR) will continue to monitor the power supply.

6.5 Lessons Learned – DR19-003

Per 66409-RPT-004, Section 4.6, "Alternative Media Sampling," specifically Thermosorb, the configuration to sample line was incorrect. During the development of the Operational Procedure, the orientation was not specified correctly. Therefore, following the procedure resulted in the incorrect installation of the Thermosorb tubes. The consequence of sampling in this orientation is the possibility of getting false positives. The presence of amines and NOx can lead to generation of nitrosamines within the sorbent. Proper orientation of the Thermosorb directs the sample air through an amine trap first and then to the nitrosamine trap. This removes the amines and eliminates the chance of them generating a false positive. To date, no false positives have occurred because none of the Thermosorb results from ALS have been above their reported detection limit.

66409-RPT-004 will be revised (Revision 11) to reflect the correct installation process. Further training on the correct orientation of the Thermosorbs, additional labeling of the sampling system to avoid confusion, and changing of the procedure to the correct installation process will be completed.

6.6 Overall Assessment of Data Quality and Quality Assurance Recommendations

All operational anomalies and exceptions of potential negative impact on data quality were documented, addressed, and corrected using root cause analysis. Data presented in this report have passed acceptance criteria.

7.0 CONCLUSION AND RECOMMENDATIONS

The ML was deployed on October 10, 2018, to track and monitor septic plume transport to a potential lower elevation accumulation area. Initially, the ML characterized the septic emissions and the resulting fingerprint compared well with previous observations with the composition dominated by methyl mercaptan and hydrogen sulfide. When the ML relocated to southeast of Building MO-226 and was sampling from the lower elevation accumulation area, no septic tracers were observed. The only observation of note was a toluene plume that is suspected to be related to AP Farm related activities.

The three types of confirmatory samples collected at each of the sites lends a good comparison between the PTR-MS and traditional methods. By nature of monitoring the ambient background concentrations during this study, many species analyzed by ALS were reported as not detectable. For the TO-17 method, ALS reported 68% of the measurements as not detectable while the ML only had 23% of measurements during those times as non-detects. Acetone, benzene, and toluene had the best comparison and detection frequencies to allow for further analysis. The relative percent difference (RPD) values for these three species with the TO-17 analysis had maximums below 100%, which shows reasonable comparison between this method and the PTR-MS. The TO-11A analysis by ALS reported 52% as not detectable while the PTR-MS only reported 6%. Formaldehyde and acetone were the only species observed enough to warrant further analysis and had RPD value maximums to nearly 180%. Comparing the acetone results between the TO-17 and TO-11A, the TO-17 yielded a better comparison. Given this, use of DNPH for TO-11A analysis needs to be reassessed. For the NIOSH 2522 analysis, ALS reported 100% of the measurements as not detectable and the PTR-MS reported 81%. Given the high level of non-detects there was not enough data for further comparison analysis.

The site comparison generally showed higher concentrations for all analytes at Site 6 and generally the lowest concentrations at Site 4. Ammonia is a notable exception with the lowest concentrations at Site 1, but the highest were still observed at Site 6. It is expected that Site 6 would see the highest concentration since it is an urban location and has a larger number and variety of sources. However, Site 1 was expected to be the lowest since it is in the most remote location, but the averages for many species were above those observed at Sites 1 through 5. It is important to note that the concentrations observed were often near the instrument detection limit; therefore, even though Site 1 averages are higher than others, the levels observed are still small.

This study compared well with FY18 results; however, the FY17 results were higher due to wildfires. Sites 1, 2, and 3 compare well between this study and FY19. Both studies show the highest concentrations at Site 6 with this study shows higher concentrations than FY18. This could be attributed to different meteorological conditions reducing the dilution and mixing when comparing this study’s data during the fall to the FY18 data collected during the spring.

8.0 REFERENCES

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APPENDIX A

COMPARISON OF PTR-MS TO CONFIRMATORY SAMPLES

The table below shows comparison between Carbotrap-300 sorbent samples as analyzed by TO-17 modified and average PTR data taken over the corresponding time period as the sample was drawn. Reporting limits for TO-17 modified analysis were provided by ALS. Reporting limits for PTR were calculated using a Method Detection Limit Study, as described in Section 4.2. Note that the RLs calculated in this report apply to all data taken after October 25, 2018. Data prior to October 25, 2018, used the RLs calculated in 53005-81-RPT-019, *PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report – Month 1*. Cells shaded in orange represent values that fall below their respective RLs. Cells shaded in yellow represent a TIC as identified by ALS, and as such represent a more qualitative result. Cells shaded in red represent no TIC detected by ALS in the sorbent sample.

Table A-1. Key.

🟨	Tentatively Identified Compound (TIC)
▨	Between RL and MDL
🟧	Non-Detect (ND)
🟥	ND of a TIC

Table A-2. Comparison of TO-17 Results to Proton Transfer Reaction – Mass Spectrometer for Selected Analytes. (3 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	Relative % difference
10/15/2018	Site 1	Carbotrap-300	benzene	0.083	0.25	0.117	0.112	4.367
			acetone	0.112	0.251	1.433	1.799	-22.649
			toluene	0.071	0.111	0.147	0.064	78.673
10/16/2018	Site 2	Carbotrap-300	benzene	0.084	0.25	0.201	0.099	68
			acetone	0.113	0.251	1.714	2.039	-17.319
			toluene	0.071	0.111	0.54	0.041	171.773
10/17/2018	Site 3	Carbotrap-300	benzene	0.084	0.25	0.192	0.172	10.989
			acetone	0.114	0.251	2.18	2.893	-28.110
			toluene	0.072	0.111	0.172	0.105	48.375
10/18/2018	Site 4	Carbotrap-300	benzene	0.084	0.25	0.209	0.166	22.933
			acetone	0.114	0.251	3.542	3.389	4.415
			toluene	0.072	0.111	0.152	0.092	49.180
10/20/2018	Site 6	Carbotrap-300	benzene	0.082	0.25	0.528	0.482	9.109
			acetone	0.111	0.251	4.437	4.418	0.429
			toluene	0.07	0.111	1.203	0.683	55.143
10/20/2018	Site 6 (Duplicate)	Carbotrap-300	benzene	0.083	0.25	0.529	0.482	9.298
			acetone	0.111	0.251	4.446	4.418	0.632
			toluene	0.07	0.111	1.205	0.683	55.297

Table A-2. Comparison of TO-17 Results to Proton Transfer Reaction – Mass Spectrometer for Selected Analytes. (3 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	Relative % difference
10/20/2018	Site 6 (Blank)	Carbotrap-300	benzene	N/A	0.25	ND	N/A	N/A
			acetone	N/A	0.251	N/A	N/A	N/A
			toluene	N/A	0.111	ND	N/A	N/A
10/21/2018	Site 1	Carbotrap-300	benzene	0.084	0.25	0.205	0.148	32.295
			acetone	0.113	0.251	2.886	3.436	-17.400
			toluene	0.071	0.111	0.114	0.085	29.146
10/22/2018	Site 2	Carbotrap-300	benzene	0.085	0.25	0.176	0.163	7.670
			acetone	0.114	0.251	2.779	3.366	-19.105
			toluene	0.072	0.111	0.181	0.122	38.944
10/23/2018	Site 3	Carbotrap-300	benzene	0.084	0.25	0.206	0.181	12.920
			acetone	0.114	0.251	3.678	3.693	-0.407
			toluene	0.072	0.111	0.258	0.161	46.301
10/24/2018	Site 4	Carbotrap-300	benzene	0.084	0.25	ND	0.13	N/A
			acetone	0.113	0.251	0.949	2.291	-82.840
			toluene	0.071	0.111	ND	0.179	N/A
10/25/2018	Site 5	Carbotrap-300	benzene	0.083	0.053	0.149	0.169	-12.579
			acetone	0.111	0.038	2.227	2.692	-18.906
			toluene	0.07	0.016	1.32	0.97	30.568
10/26/2018	Site 6	Carbotrap-300	benzene	0.085	0.053	0.2	0.163	20.386
			acetone	0.114	0.038	1.141	3.366	-98.735
			toluene	0.072	0.016	0.345	0.122	95.503
10/26/2018	Site 6 (Duplicate)	Carbotrap-300	benzene	0.085	0.053	0.2	0.188	6.186
			acetone	0.114	0.038	1.229	1.467	-17.656
			toluene	0.072	0.016	0.281	0.234	18.252
10/27/2018	Site 1 (Blank)	Carbotrap-300	benzene	N/A	0.053	ND	N/A	N/A
			acetone	N/A	0.038	ND	N/A	N/A
			toluene	N/A	0.016	ND	N/A	N/A
10/28/2018	Site 2	Carbotrap-300	benzene	0.084	0.053	0.084	0.094	-11.236
			acetone	0.112	0.038	1.079	1.292	-17.967
			toluene	0.071	0.016	ND	0.114	N/A
10/30/2018	Site 4	Carbotrap-300	benzene	0.083	0.053	0.096	0.093	3.175
			acetone	0.111	0.038	0.846	0.855	-1.058
			toluene	0.07	0.016	0.081	0.076	6.369

Table A-2. Comparison of TO-17 Results to Proton Transfer Reaction – Mass Spectrometer for Selected Analytes. (3 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	Relative % difference
10/31/2018	Site 5	Carbotrap-300	benzene	0.083	0.053	0.229	0.163	33.673
			acetone	0.112	0.038	1.609	1.491	7.613
			toluene	0.07	0.016	0.592	0.234	86.683
11/1/2018	Site 6	Carbotrap-300	benzene	0.084	0.053	0.331	0.224	38.559
			acetone	0.114	0.038	0.772	0.846	-9.1471
			toluene	0.072	0.016	0.658	0.253	88.913
11/2/2018	Site 1	Carbotrap-300	benzene	0.085	0.053	0.096	0.066	37.037
			acetone	0.115	0.038	0.781	0.925	-16.882
			toluene	0.072	0.016	ND	0.025	N/A
11/3/2018	Site 2	Carbotrap-300	benzene	0.083	0.053	0.11	0.082	29.167
			acetone	0.112	0.038	0.493	0.79	-46.298
			toluene	0.071	0.016	ND	0.032	N/A
11/4/2018	Site 3	Carbotrap-300	benzene	0.086	0.053	0.113	0.078	36.649
			acetone	0.115	0.038	0.646	0.858	-28.191
			toluene	0.073	0.016	ND	0.03	N/A
11/5/2018	Site 4	Carbotrap-300	benzene	0.084	0.053	0.118	0.081	37.186
			acetone	0.113	0.038	0.498	0.691	-32.464
			toluene	0.071	0.016	ND	0.031	N/A
11/6/2018	Site 5	Carbotrap-300	benzene	0.083	0.053	0.127	0.081	44.231
			acetone	0.112	0.038	0.436	0.604	-32.308
			toluene	0.071	0.016	ND	0.029	N/A
11/7/2018	Site 6	Carbotrap-300	benzene	0.082	0.053	0.489	0.351	32.857
			acetone	0.11	0.038	1.228	1.156	6.040
			toluene	0.069	0.016	0.94	0.434	73.654
11/7/2018	Site 6 (Duplicate)	Carbotrap-300	benzene	0.082	0.053	0.457	0.351	26.238
			acetone	0.11	0.038	1.273	1.156	9.634
			toluene	0.069	0.016	0.941	0.434	73.745

Table A-3. Comparison of TO-17 Results to Proton Transfer Reaction – Mass Spectrometer. (13 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	% diff
10/15/2018	Site 1	Carbotrap-300	1,3-butadiene	0.120	0.236	ND	0.123	N/A
			acetonitrile	TIC	0.077	5.639	8.817	56
			benzene	0.083	0.250	0.117	0.112	-4
			2-hexanone	0.065	0.100	ND	0.013	N/A
			acetone	0.112	0.251	1.433	1.799	26
			toluene	0.071	0.111	0.147	0.064	-56
			m,p-xylene	0.061	0.178	0.066	0.036	N/A
			o-xylene	0.061		ND		
			ethylbenzene	0.061		0.086		
			styrene	0.062	0.306	ND	0.008	-87
			furan	TIC	0.071	N/A	0.021	N/A
			isoprene	TIC	0.143	N/A	0.045	N/A
10/16/2018	Site 2	Carbotrap-300	1,3-butadiene	0.121	0.236	ND	0.109	N/A
			acetonitrile	TIC	0.077	N/A	0.725	N/A
			benzene	0.084	0.250	0.201	0.099	-51
			2-hexanone	0.065	0.100	ND	0.010	N/A
			acetone	0.113	0.251	1.714	2.039	19
			toluene	0.071	0.111	0.540	0.041	-92
			m,p-xylene	0.062	0.178	0.321	0.024	-96
			o-xylene	0.062		0.123		
			ethylbenzene	0.062		0.091		
			styrene	0.063	0.306	ND	0.008	N/A
			furan	TIC	0.071	N/A	0.022	N/A
			isoprene	TIC	0.143	N/A	0.039	N/A

Table A-3. Comparison of TO-17 Results to Proton Transfer Reaction – Mass Spectrometer. (13 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	% diff
10/17/2018	Site 3	Carbotrap-300	1,3-butadiene	0.122	0.236	ND	0.143	N/A
			acetonitrile	TIC	0.077	4.240	2.224	-48
			benzene	0.084	0.250	0.192	0.172	-11
			2-hexanone	0.066	0.100	ND	0.013	N/A
			acetone	0.114	0.251	2.180	2.893	33
			toluene	0.072	0.111	0.172	0.105	-39
			m,p-xylene	0.062	0.178	ND	0.046	N/A
			o-xylene	0.062		ND		
			ethylbenzene	0.062		ND		
			styrene	0.063	0.306	ND	0.009	N/A
			furan	TIC	0.071	N/A	0.027	N/A
			isoprene	TIC	0.143	N/A	0.049	N/A
10/18/2018	Site 4	Carbotrap-300	1,3-butadiene	0.122	0.236	ND	0.180	N/A
			acetonitrile	TIC	0.077	7.710	2.129	-72
			benzene	0.084	0.250	0.209	0.166	-20
			2-hexanone	0.066	0.100	ND	0.015	N/A
			acetone	0.114	0.251	3.542	3.389	-4
			toluene	0.072	0.111	0.152	0.092	-39
			m,p-xylene	0.062	0.178	ND	0.050	N/A
			o-xylene	0.062		ND		
			ethylbenzene	0.062		ND		
			styrene	0.063	0.306	ND	0.014	N/A
			furan	TIC	0.071	N/A	0.028	N/A
			isoprene	TIC	0.143	N/A	0.053	N/A

Table A-3. Comparison of TO-17 Results to Proton Transfer Reaction – Mass Spectrometer. (13 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	% diff
10/20/2018	Site 6	Carbotrap-300	1,3-butadiene	0.119	0.236	ND	0.433	264
			acetonitrile	TIC	0.077	0.753	0.467	-38
			benzene	0.082	0.250	0.528	0.482	-9
			2-hexanone	0.064	0.100	ND	0.030	N/A
			acetone	0.111	0.251	4.437	4.418	0
			toluene	0.070	0.111	1.203	0.683	-43
			m,p-xylene	0.061	0.178	0.583	0.446	-54
			o-xylene	0.061		0.238		
			ethylbenzene	0.061		0.158		
			styrene	0.062	0.306	ND	0.042	N/A
			furan	TIC	0.071	N/A	0.062	N/A
			isoprene	TIC	0.143	N/A	0.162	N/A
10/20/2018	Site 6 (Duplicate)	Carbotrap-300	1,3-butadiene	0.119	0.236	ND	0.433	N/A
			acetonitrile	TIC	0.077	0.245	0.467	91
			benzene	0.083	0.250	0.529	0.482	-9
			2-hexanone	0.064	0.100	ND	0.030	N/A
			acetone	0.111	0.251	4.446	4.418	-1
			toluene	0.070	0.111	1.205	0.683	-43
			m,p-xylene	0.061	0.178	0.657	0.446	-60
			o-xylene	0.061		0.268		
			ethylbenzene	0.061		0.178		
			styrene	0.062	0.306	ND	0.042	N/A
			furan	TIC	0.071	N/A	0.062	N/A
			isoprene	TIC	0.143	N/A	0.162	N/A

Table A-3. Comparison of TO-17 Results to Proton Transfer Reaction – Mass Spectrometer. (13 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	% diff
10/20/2018	Site 6 (Blank)	Carbotrap-300	1,3-butadiene	N/A	0.236	ND	N/A	N/A
			acetonitrile	TIC	0.077	N/A	N/A	N/A
			benzene	N/A	0.250	ND	N/A	N/A
			2-hexanone	N/A	0.100	ND	N/A	N/A
			acetone	N/A	0.251	N/A	N/A	N/A
			toluene	N/A	0.111	ND	N/A	N/A
			m,p-xylene	N/A	0.178	ND	N/A	N/A
			o-xylene	N/A		ND		
			ethylbenzene	N/A		ND		
			styrene	N/A	0.306	ND	N/A	N/A
			furan	TIC	0.071	N/A	N/A	N/A
			isoprene	TIC	0.143	N/A	N/A	N/A
10/21/2018	Site 1	Carbotrap-300	1,3-butadiene	0.121	0.236	ND	0.195	N/A
			acetonitrile	TIC	0.077	0.574	0.296	-48
			benzene	0.084	0.250	0.205	0.148	-28
			2-hexanone	0.065	0.100	ND	0.015	N/A
			acetone	0.113	0.251	2.886	3.436	19
			toluene	0.071	0.111	0.114	0.085	-26
			m,p-xylene	0.062	0.178	ND	0.047	N/A
			o-xylene	0.062		ND		
			ethylbenzene	0.062		ND		
			styrene	0.063	0.306	ND	0.013	N/A
			furan	TIC	0.071	N/A	0.034	N/A
			isoprene	TIC	0.143	N/A	0.064	N/A

Table A-3. Comparison of TO-17 Results to Proton Transfer Reaction – Mass Spectrometer. (13 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	% diff
10/22/2018	Site 2	Carbotrap-300	1,3-butadiene	0.122	0.236	ND	0.235	N/A
			acetonitrile	TIC	0.077	0.393	0.277	-29
			benzene	0.085	0.250	0.176	0.163	-7
			2-hexanone	0.066	0.100	ND	0.016	N/A
			acetone	0.114	0.251	2.779	3.366	21
			toluene	0.072	0.111	0.181	0.122	-32
			m,p-xylene	0.062	0.178	ND	0.060	N/A
			o-xylene	0.062		ND		
			ethylbenzene	0.062		ND		
			styrene	0.064	0.306	ND	0.016	N/A
			furan	TIC	0.071	N/A	0.038	N/A
			isoprene	TIC	0.143	N/A	0.068	N/A
10/23/2018	Site 3	Carbotrap-300	1,3-butadiene	0.122	0.236	ND	0.247	N/A
			acetonitrile	TIC	0.077	N/A	0.271	N/A
			benzene	0.084	0.250	0.206	0.181	-12
			2-hexanone	0.066	0.100	ND	0.020	N/A
			acetone	0.114	0.251	3.678	3.693	0
			toluene	0.072	0.111	0.258	0.161	-38
			m,p-xylene	0.062	0.178	0.075	0.087	N/A
			o-xylene	0.062		ND		
			ethylbenzene	0.062		ND		
			styrene	0.063	0.306	ND	0.019	N/A
			furan	TIC	0.071	N/A	0.038	N/A
			isoprene	TIC	0.143	N/A	0.077	N/A

Table A-3. Comparison of TO-17 Results to Proton Transfer Reaction – Mass Spectrometer. (13 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	% diff
10/24/2018	Site 4	Carbotrap-300	1,3-butadiene	0.121	0.236	ND	0.160	N/A
			acetonitrile	TIC	0.077	0.409	0.190	-54
			benzene	0.084	0.250	ND	0.130	N/A
			2-hexanone	0.066	0.100	ND	0.014	N/A
			acetone	0.113	0.251	0.949	2.291	141
			toluene	0.071	0.111	ND	0.179	N/A
			m,p-xylene	0.062	0.178	ND	0.062	N/A
			o-xylene	0.062		ND		
			ethylbenzene	0.062		ND		
			styrene	0.063	0.306	ND	0.009	N/A
			furan	TIC	0.071	N/A	0.029	N/A
			isoprene	TIC	0.143	N/A	0.062	N/A
10/25/2018	Site 5	Carbotrap-300	1,3-butadiene	0.120	0.031	ND	0.226	N/A
			acetonitrile	TIC	0.013	N/A	0.171	N/A
			benzene	0.083	0.053	0.149	0.169	13
			2-hexanone	0.065	0.011	ND	0.029	N/A
			acetone	0.111	0.038	2.227	2.692	21
			toluene	0.070	0.016	1.320	0.970	-27
			m,p-xylene	0.061	0.017	0.183	0.152	N/A
			o-xylene	0.061		0.068		
			ethylbenzene	0.061		ND		
			styrene	0.062	0.015	ND	0.013	N/A
			furan	TIC	0.012	N/A	0.036	N/A
			isoprene	TIC	0.018	N/A	0.091	N/A

Table A-3. Comparison of TO-17 Results to Proton Transfer Reaction – Mass Spectrometer. (13 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	% diff
10/26/2018	Site 6	Carbotrap-300	1,3-butadiene	0.122	0.031	ND	0.235	N/A
			acetonitrile	TIC	0.013	N/A	0.277	N/A
			benzene	0.085	0.053	0.200	0.163	-18
			2-hexanone	0.066	0.011	ND	0.016	N/A
			acetone	0.114	0.038	1.141	3.366	195
			toluene	0.072	0.016	0.345	0.122	-65
			m,p-xylene	0.062	0.017	0.180	0.060	N/A
			o-xylene	0.062		0.067		
			ethylbenzene	0.062		ND		
			styrene	0.064	0.015	ND	0.016	N/A
			furan	TIC	0.012	N/A	0.038	N/A
			isoprene	TIC	0.018	N/A	0.068	N/A
10/26/2018	Site 6 (Duplicate)	Carbotrap-300	1,3-butadiene	0.122	0.031	ND	0.159	N/A
			acetonitrile	TIC	0.013	N/A	0.181	N/A
			benzene	0.085	0.053	0.200	0.188	-6
			2-hexanone	0.066	0.011	ND	0.012	N/A
			acetone	0.114	0.038	1.229	1.467	19
			toluene	0.072	0.016	0.281	0.234	-17
			m,p-xylene	0.062	0.017	0.100	0.155	N/A
			o-xylene	0.062		ND		
			ethylbenzene	0.062		ND		
			styrene	0.063	0.015	ND	0.012	N/A
			furan	TIC	0.012	N/A	0.036	N/A
			isoprene	TIC	0.018	N/A	0.071	N/A

Table A-3. Comparison of TO-17 Results to Proton Transfer Reaction – Mass Spectrometer. (13 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	% diff
10/27/2018	Site 1 (Blank)	Carbotrap-300	1,3-butadiene	N/A	0.031	ND	N/A	N/A
			acetonitrile	TIC	0.013	N/A	N/A	N/A
			benzene	N/A	0.053	ND	N/A	N/A
			2-hexanone	N/A	0.011	ND	N/A	N/A
			acetone	N/A	0.038	ND	N/A	N/A
			toluene	N/A	0.016	ND	N/A	N/A
			m,p-xylene	N/A	0.017	ND	N/A	N/A
			o-xylene	N/A		ND		
			ethylbenzene	N/A		ND		
			styrene	N/A	0.015	ND	N/A	N/A
			furan	TIC	0.012	N/A	N/A	N/A
			isoprene	TIC	0.018	N/A	N/A	N/A
10/28/2018	Site 2	Carbotrap-300	1,3-butadiene	0.121	0.031	ND	0.080	N/A
			acetonitrile	TIC	0.013	N/A	0.122	N/A
			benzene	0.084	0.053	0.084	0.094	12
			2-hexanone	0.065	0.011	ND	0.009	N/A
			acetone	0.112	0.038	1.079	1.292	20
			toluene	0.071	0.016	ND	0.114	N/A
			m,p-xylene	0.061	0.017	ND	0.036	N/A
			o-xylene	0.061		ND		
			ethylbenzene	0.061		ND		
			styrene	0.063	0.015	ND	0.007	N/A
			furan	TIC	0.012	N/A	0.027	N/A
			isoprene	TIC	0.018	N/A	0.063	N/A

Table A-3. Comparison of TO-17 Results to Proton Transfer Reaction – Mass Spectrometer. (13 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	% diff
10/30/2018	Site 4	Carbotrap-300	1,3-butadiene	0.120	0.031	ND	0.078	N/A
			acetonitrile	TIC	0.013	N/A	0.106	N/A
			benzene	0.083	0.053	0.096	0.093	-3
			2-hexanone	0.065	0.011	ND	0.008	N/A
			acetone	0.111	0.038	0.846	0.855	1
			toluene	0.070	0.016	0.081	0.076	-6
			m,p-xylene	0.061	0.017	ND	0.036	N/A
			o-xylene	0.061		ND		
			ethylbenzene	0.061		ND		
			styrene	0.062	0.015	ND	0.005	N/A
			furan	TIC	0.012	N/A	0.025	N/A
			isoprene	TIC	0.018	N/A	0.038	N/A
10/31/2018	Site 5	Carbotrap-300	1,3-butadiene	0.120	0.031	ND	0.162	N/A
			acetonitrile	TIC	0.013	N/A	0.129	N/A
			benzene	0.083	0.053	0.229	0.163	-29
			2-hexanone	0.065	0.011	ND	0.015	N/A
			acetone	0.112	0.038	1.609	1.491	-7
			toluene	0.070	0.016	0.592	0.234	-60
			m,p-xylene	0.061	0.017	0.196	0.105	N/A
			o-xylene	0.061		0.076		
			ethylbenzene	0.061		ND		
			styrene	0.062	0.015	ND	0.010	N/A
			furan	TIC	0.012	N/A	0.045	N/A
			isoprene	TIC	0.018	N/A	0.069	N/A

Table A-3. Comparison of TO-17 Results to Proton Transfer Reaction – Mass Spectrometer. (13 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	% diff
11/1/2018	Site 6	Carbotrap-300	1,3-butadiene	0.122	0.031	ND	0.108	N/A
			acetonitrile	TIC	0.013	N/A	0.125	N/A
			benzene	0.084	0.053	0.331	0.224	-32
			2-hexanone	0.066	0.011	ND	0.008	N/A
			acetone	0.114	0.038	0.772	0.846	10
			toluene	0.072	0.016	0.658	0.253	-62
			m,p-xylene	0.062	0.017	0.323	0.181	-66
			o-xylene	0.062		0.122		
			ethylbenzene	0.062		0.092		
			styrene	0.063	0.015	ND	0.010	N/A
			furan	TIC	0.012	N/A	0.044	N/A
			isoprene	TIC	0.018	N/A	0.052	N/A
11/2/2018	Site 1	Carbotrap-300	1,3-butadiene	0.123	0.031	ND	0.052	N/A
			acetonitrile	TIC	0.013	0.520	0.110	-79
			benzene	0.085	0.053	0.096	0.066	-31
			2-hexanone	0.067	0.011	ND	0.006	N/A
			acetone	0.115	0.038	0.781	0.925	18
			toluene	0.072	0.016	ND	0.025	N/A
			m,p-xylene	0.063	0.017	ND	0.012	N/A
			o-xylene	0.063		ND		
			ethylbenzene	0.063		ND		
			styrene	0.064	0.015	ND	0.005	N/A
			furan	TIC	0.012	N/A	0.018	N/A
			isoprene	TIC	0.018	N/A	0.023	N/A

Table A-3. Comparison of TO-17 Results to Proton Transfer Reaction – Mass Spectrometer. (13 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	% diff
11/3/2018	Site 2	Carbotrap-300	1,3-butadiene	0.120	0.031	ND	0.056	N/A
			acetonitrile	TIC	0.013	N/A	0.101	N/A
			benzene	0.083	0.053	0.110	0.082	-25
			2-hexanone	0.065	0.011	ND	0.006	N/A
			acetone	0.112	0.038	0.493	0.790	60
			toluene	0.071	0.016	ND	0.032	N/A
			m,p-xylene	0.061	0.017	ND	0.014	N/A
			o-xylene	0.061		ND		
			ethylbenzene	0.061		ND		
			styrene	0.063	0.015	ND	0.003	N/A
			furan	TIC	0.012	N/A	0.023	N/A
			isoprene	TIC	0.018	N/A	0.025	N/A
11/4/2018	Site 3	Carbotrap-300	1,3-butadiene	0.124	0.031	ND	0.065	N/A
			acetonitrile	TIC	0.013	N/A	0.099	N/A
			benzene	0.086	0.053	0.113	0.078	-9
			2-hexanone	0.067	0.011	ND	0.006	N/A
			acetone	0.115	0.038	0.646	0.858	33
			toluene	0.073	0.016	ND	0.030	N/A
			m,p-xylene	0.063	0.017	ND	0.013	N/A
			o-xylene	0.063		ND		
			ethylbenzene	0.063		ND		
			styrene	0.064	0.015	ND	0.003	N/A
			furan	TIC	0.012	N/A	0.017	N/A
			isoprene	TIC	0.018	N/A	0.025	N/A

Table A-3. Comparison of TO-17 Results to Proton Transfer Reaction – Mass Spectrometer. (13 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	% diff
11/5/2018	Site 4	Carbotrap-300	1,3-butadiene	0.122	0.031	ND	0.062	N/A
			acetonitrile	TIC	0.013	N/A	0.091	N/A
			benzene	0.084	0.053	0.118	0.081	-31
			2-hexanone	0.066	0.011	ND	0.005	N/A
			acetone	0.113	0.038	0.498	0.691	39
			toluene	0.071	0.016	ND	0.031	N/A
			m,p-xylene	0.062	0.017	ND	0.022	N/A
			o-xylene	0.062		ND		
			ethylbenzene	0.062		ND		
			styrene	0.063	0.015	ND	0.003	N/A
			furan	TIC	0.012	N/A	0.014	N/A
			isoprene	TIC	0.018	N/A	0.022	N/A
11/6/2018	Site 5	Carbotrap-300	1,3-butadiene	0.121	0.031	ND	0.052	N/A
			acetonitrile	TIC	0.013	N/A	0.076	N/A
			benzene	0.083	0.053	0.127	0.081	-36
			2-hexanone	0.065	0.011	ND	0.005	N/A
			acetone	0.112	0.038	0.436	0.604	39
			toluene	0.071	0.016	ND	0.029	-59
			m,p-xylene	0.061	0.017	ND	0.012	N/A
			o-xylene	0.061		ND		
			ethylbenzene	0.061		ND		
			styrene	0.063	0.015	ND	0.002	N/A
			furan	TIC	0.012	N/A	0.014	N/A
			isoprene	TIC	0.018	N/A	0.020	N/A

Table A-3. Comparison of TO-17 Results to Proton Transfer Reaction – Mass Spectrometer. (13 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	% diff
11/7/2018	Site 6	Carbotrap-300	1,3-butadiene	0.118	0.031	ND	0.215	N/A
			acetonitrile	TIC	0.013	N/A	0.283	N/A
			benzene	0.082	0.053	0.489	0.351	-28
			2-hexanone	0.064	0.011	ND	0.013	N/A
			acetone	0.110	0.038	1.228	1.156	-6
			toluene	0.069	0.016	0.940	0.434	-54
			m,p-xylene	0.060	0.017	0.480	0.284	-65
			o-xylene	0.060		0.185		
			ethylbenzene	0.060		0.139		
			styrene	0.061	0.015	ND	0.019	N/A
			furan	TIC	0.012	N/A	0.037	N/A
			isoprene	TIC	0.018	N/A	0.089	N/A
11/7/2018	Site 6 (Duplicate)	Carbotrap-300	1,3-butadiene	0.118	0.031	ND	0.215	N/A
			acetonitrile	TIC	0.013	N/A	0.283	N/A
			benzene	0.082	0.053	0.457	0.351	-23
			2-hexanone	0.064	0.011	ND	0.013	N/A
			acetone	0.110	0.038	1.273	1.156	-9
			toluene	0.069	0.016	0.941	0.434	-54
			m,p-xylene	0.060	0.017	0.504	0.284	-66
			o-xylene	0.060		0.187		
			ethylbenzene	0.060		0.139		
			styrene	0.061	0.015	ND	0.019	N/A
			furan	TIC	0.012	N/A	0.037	N/A
			isoprene	TIC	0.018	N/A	0.089	N/A

The table below shows comparison between Thermosorb/N sorbent samples as analyzed by NIOSH 2522 and average PTR data taken over the corresponding time period as the sample was drawn. Reporting limits for NIOSH 2522 analysis were provided by ALS. Reporting limits for PTR were calculated using a Method Detection Limit Study, as described in Section 4.2. Note that the RLs calculated in this report apply to all data taken after October 25, 2018. Data prior to October 25, 2018, used the RLs calculated in 53005-81-RPT-019. Cells shaded in orange represent values that fall below their respective reporting limits.

Table A-4. Comparison of NIOSH 2522 Results to Proton Transfer Reaction – Mass Spectrometer. (4 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	Relative % diff
10/15/2018	Site 1	Thermosorb	NDEA	0.013	0.078	ND	ND	N/A
			NDMA	0.009	0.098	ND	ND	N/A
			NEMA	0.007	0.091	ND	ND	N/A
			NMOR	0.006	0.121	ND	ND	N/A
10/16/2018	Site 2	Thermosorb	NDEA	0.013	0.078	ND	ND	N/A
			NDMA	0.009	0.098	ND	ND	N/A
			NEMA	0.007	0.091	ND	ND	N/A
			NMOR	0.006	0.121	ND	ND	N/A
10/17/2018	Site 3	Thermosorb	NDEA	0.013	0.078	ND	ND	N/A
			NDMA	0.009	0.098	ND	ND	N/A
			NEMA	0.007	0.091	ND	ND	N/A
			NMOR	0.006	0.121	ND	ND	N/A
10/18/2018	Site 4	Thermosorb	NDEA	0.013	0.078	ND	ND	N/A
			NDMA	0.009	0.098	ND	0.048	N/A
			NEMA	0.008	0.091	ND	ND	N/A
			NMOR	0.006	0.121	ND	ND	N/A
10/20/2018	Site 6	Thermosorb	NDEA	0.013	0.078	ND	ND	N/A
			NDMA	0.009	0.098	ND	0.107	N/A
			NEMA	0.007	0.091	ND	0.033	N/A
			NMOR	0.006	0.121	ND	ND	N/A
10/20/2018	Site 6 (Duplicate)	Thermosorb	NDEA	0.013	0.078	ND	ND	N/A
			NDMA	0.009	0.098	ND	0.107	N/A
			NEMA	0.007	0.091	ND	0.033	N/A
			NMOR	0.006	0.121	ND	ND	N/A
10/20/2018	Site 6 (Blank)	Thermosorb	NDEA	N/A	0.078	ND	N/A	N/A
			NDMA	N/A	0.098	ND	N/A	N/A
			NEMA	N/A	0.091	ND	N/A	N/A
			NMOR	N/A	0.121	ND	N/A	N/A

Table A-4. Comparison of NIOSH 2522 Results to Proton Transfer Reaction – Mass Spectrometer. (4 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	Relative % diff
10/21/2018	Site 1	Thermosorb	NDEA	0.013	0.078	ND	ND	N/A
			NDMA	0.009	0.098	ND	0.044	N/A
			NEMA	0.007	0.091	ND	ND	N/A
			NMOR	0.006	0.121	ND	ND	N/A
10/22/2018	Site 2	Thermosorb	NDEA	0.013	0.078	ND	ND	N/A
			NDMA	0.009	0.098	ND	0.046	N/A
			NEMA	0.007	0.091	ND	ND	N/A
			NMOR	0.006	0.121	ND	ND	N/A
10/23/2018	Site 3	Thermosorb	NDEA	0.013	0.078	ND	ND	N/A
			NDMA	0.009	0.098	ND	0.077	N/A
			NEMA	0.007	0.091	ND	ND	N/A
			NMOR	0.006	0.121	ND	ND	N/A
10/24/2018	Site 4	Thermosorb	NDEA	0.013	0.078	ND	ND	N/A
			NDMA	0.009	0.098	ND	ND	N/A
			NEMA	0.007	0.091	ND	ND	N/A
			NMOR	0.006	0.121	ND	ND	N/A
10/25/2018	Site 5	Thermosorb	NDEA	0.013	0.007	ND	0.004	N/A
			NDMA	0.009	0.013	ND	0.025	N/A
			NEMA	0.007	0.008	ND	0.013	N/A
			NMOR	0.006	0.007	ND	0.005	N/A
10/26/2018	Site 6	Thermosorb	NDEA	0.013	0.007	ND	0.004	N/A
			NDMA	0.009	0.013	ND	0.027	N/A
			NEMA	0.008	0.008	ND	0.013	N/A
			NMOR	0.006	0.007	ND	0.005	N/A
10/26/2018	Site 6 (Duplicate)	Thermosorb	NDEA	0.013	0.007	ND	0.004	N/A
			NDMA	0.009	0.013	ND	0.027	N/A
			NEMA	0.008	0.008	ND	0.013	N/A
			NMOR	0.006	0.007	ND	0.005	N/A

Table A-4. Comparison of NIOSH 2522 Results to Proton Transfer Reaction – Mass Spectrometer. (4 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	Relative % diff
10/27/2018	Site 1 (Blank)	Thermosorb	NDEA	N/A	0.007	ND	N/A	N/A
			NDMA	N/A	0.013	ND	N/A	N/A
			NEMA	N/A	0.008	ND	N/A	N/A
			NMOR	N/A	0.007	ND	N/A	N/A
10/28/2018	Site 2	Thermosorb	NDEA	0.013	0.007	ND	0.003	N/A
			NDMA	0.009	0.013	ND	0.017	N/A
			NEMA	0.007	0.008	ND	0.009	N/A
			NMOR	0.006	0.007	ND	0.003	N/A
10/30/2018	Site 4	Thermosorb	NDEA	0.013	0.007	ND	ND	N/A
			NDMA	0.009	0.013	ND	0.011	N/A
			NEMA	0.007	0.008	ND	0.006	N/A
			NMOR	0.006	0.007	ND	0.003	N/A
10/31/2018	Site 5	Thermosorb	NDEA	0.013	0.007	ND	0.003	N/A
			NDMA	0.009	0.013	ND	0.021	N/A
			NEMA	0.007	0.008	ND	0.010	N/A
			NMOR	0.006	0.007	ND	0.005	N/A
11/1/2018	Site 6	Thermosorb	NDEA	0.013	0.007	ND	ND	N/A
			NDMA	0.009	0.013	ND	0.016	N/A
			NEMA	0.007	0.008	ND	0.008	N/A
			NMOR	0.006	0.007	ND	0.004	N/A
11/2/2018	Site 1	Thermosorb	NDEA	0.013	0.007	ND	ND	N/A
			NDMA	0.009	0.013	ND	0.012	N/A
			NEMA	0.008	0.008	ND	0.007	N/A
			NMOR	0.006	0.007	ND	ND	N/A
11/3/2018	Site 2	Thermosorb	NDEA	0.013	0.007	ND	ND	N/A
			NDMA	0.009	0.013	ND	0.012	N/A
			NEMA	0.007	0.008	ND	0.007	N/A
			NMOR	0.006	0.007	ND	ND	N/A

Table A-4. Comparison of NIOSH 2522 Results to Proton Transfer Reaction – Mass Spectrometer. (4 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	Relative % diff
11/4/2018	Site 3	Thermosorb	NDEA	0.013	0.007	ND	ND	N/A
			NDMA	0.009	0.013	ND	0.011	N/A
			NEMA	0.008	0.008	ND	0.006	N/A
			NMOR	0.006	0.007	ND	ND	N/A
11/5/2018	Site 4	Thermosorb	NDEA	0.013	0.007	ND	ND	N/A
			NDMA	0.009	0.013	ND	0.012	N/A
			NEMA	0.007	0.008	ND	0.005	N/A
			NMOR	0.006	0.007	ND	ND	N/A
11/6/2018	Site 5	Thermosorb	NDEA	0.013	0.007	ND	ND	N/A
			NDMA	0.009	0.013	ND	0.009	N/A
			NEMA	0.007	0.008	ND	0.004	N/A
			NMOR	0.006	0.007	ND	ND	N/A
11/7/2018	Site 6	Thermosorb	NDEA	0.012	0.007	ND	0.003	N/A
			NDMA	0.009	0.013	ND	0.054	N/A
			NEMA	0.007	0.008	ND	0.015	N/A
			NMOR	0.005	0.007	ND	0.009	N/A
11/7/2018	Site 6 (Duplicate)	Thermosorb	NDEA	0.012	0.007	ND	0.003	N/A
			NDMA	0.009	0.013	ND	0.054	N/A
			NEMA	0.007	0.008	ND	0.015	N/A
			NMOR	0.005	0.007	ND	0.009	N/A

The table below shows comparison between DNPH sorbent samples as analyzed by TO-11a and average PTR data taken over the corresponding time period as the sample was drawn. Reporting limits for TO-11a analysis were provided by ALS. Reporting limits for PTR were calculated using a Method Detection Limit Study, as described in Section 4.2. Note that the RLs calculated in this report apply to all data taken after October 25, 2018. Data prior to October 25, 2018, used the RLs calculated in 53005-81-RPT-019. Cells shaded in orange represent values that fall below their respective reporting limits.

Table A-5. Comparison of TO-11A Results to Proton Transfer Reaction – Mass Spectrometer. (3 Sheets)

Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	% diff
10/15/2018	Site 1	DNPH	Formaldehyde	0.217	0.738	1.997	1.387	-31
			Acetaldehyde	0.148	0.868	1.361	3.604	165
			Acetone	0.112	0.251	1.706	1.898	11
			Acrolein	0.116	0.506	ND	0.160	38
			Butyraldehyde	0.090	0.101	ND	0.185	104
10/16/2018	Site 2	DNPH	Formaldehyde	0.218	0.738	0.379	1.680	344
			Acetaldehyde	0.148	0.868	0.386	3.302	756
			Acetone	0.113	0.251	0.315	2.049	550
			Acrolein	0.117	0.506	ND	0.190	63
			Butyraldehyde	0.091	0.101	ND	0.175	94
10/17/2018	Site 3	DNPH	Formaldehyde	0.217	0.738	0.956	1.513	58
			Acetaldehyde	0.148	0.868	0.830	4.384	428
			Acetone	0.112	0.251	0.607	2.744	352
			Acrolein	0.116	0.506	ND	0.188	61
			Butyraldehyde	0.091	0.101	ND	0.230	155
10/18/2018	Site 4	DNPH	Formaldehyde	0.222	0.738	0.667	1.613	142
			Acetaldehyde	0.152	0.868	0.758	5.107	574
			Acetone	0.115	0.251	1.149	3.596	213
			Acrolein	0.119	0.506	ND	0.233	96
			Butyraldehyde	0.093	0.101	ND	0.368	297
10/29/2018	Site 3	DNPH	Formaldehyde	0.217	0.105	0.382	0.394	3
			Acetaldehyde	0.148	0.106	0.272	1.038	281
			Acetone	0.112	0.038	0.719	0.894	24
			Acrolein	0.116	0.075	ND	0.069	-41
			Butyraldehyde	0.090	0.016	ND	0.054	-40
10/29/2018	Site 3 (Duplicate)	DNPH	Formaldehyde	0.218	0.105	0.436	0.394	-10
			Acetaldehyde	0.149	0.106	0.327	1.038	217
			Acetone	0.113	0.038	0.519	0.894	72
			Acrolein	0.117	0.075	2.009	0.069	-97
			Butyraldehyde	0.091	0.016	ND	0.054	-40

Table A-5. Comparison of TO-11A Results to Proton Transfer Reaction – Mass Spectrometer. (3 Sheets)

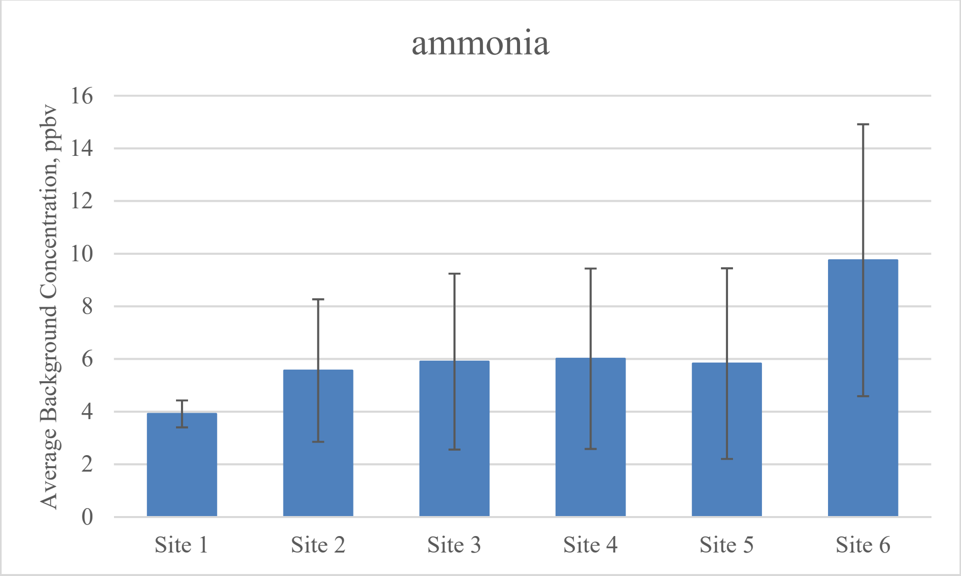
Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	% diff
10/30/2018	Site 4 (Sample Lost at ALS)	DNPH	Formaldehyde	N/A	0.105	N/A	0.471	N/A
			Acetaldehyde	N/A	0.106	N/A	1.203	N/A
			Acetone	N/A	0.038	N/A	0.859	N/A
			Acrolein	N/A	0.075	N/A	0.104	N/A
			Butyraldehyde	N/A	0.016	N/A	0.090	N/A
10/31/2018	Site 5	DNPH	Formaldehyde	0.216	0.105	0.864	0.523	-39
			Acetaldehyde	0.147	0.106	ND	1.840	N/A
			Acetone	0.112	0.038	ND	1.777	N/A
			Acrolein	0.116	0.075	1.759	0.188	-89
			Butyraldehyde	0.090	0.016	ND	0.458	N/A
11/1/2018	Site 6	DNPH	Formaldehyde	0.219	0.105	4.125	0.281	-93
			Acetaldehyde	0.150	0.106	0.449	1.711	281
			Acetone	0.113	0.038	ND	0.837	N/A
			Acrolein	0.118	0.075	2.233	0.122	-95
			Butyraldehyde	0.091	0.016	ND	0.076	-16
11/1/2018	Site 6 (Blank)	DNPH	Formaldehyde	0.219	0.105	ND	N/A	N/A
			Acetaldehyde	0.149	0.106	ND	N/A	N/A
			Acetone	0.113	0.038	ND	N/A	N/A
			Acrolein	0.117	0.075	ND	N/A	N/A
			Butyraldehyde	0.091	0.016	ND	N/A	N/A
11/2/2018	Site 1	DNPH	Formaldehyde	0.223	0.105	ND	0.309	39
			Acetaldehyde	0.152	0.106	ND	0.904	496
			Acetone	0.115	0.038	ND	0.981	752
			Acrolein	0.119	0.075	2.218	0.060	-97
			Butyraldehyde	0.093	0.016	ND	0.068	-27
11/3/2018	Site 2	DNPH	Formaldehyde	0.217	0.105	0.260	0.324	25
			Acetaldehyde	0.148	0.106	0.325	0.849	161
			Acetone	0.112	0.038	ND	0.788	603
			Acrolein	0.116	0.075	3.254	0.058	-98
			Butyraldehyde	0.090	0.016	ND	0.069	-24

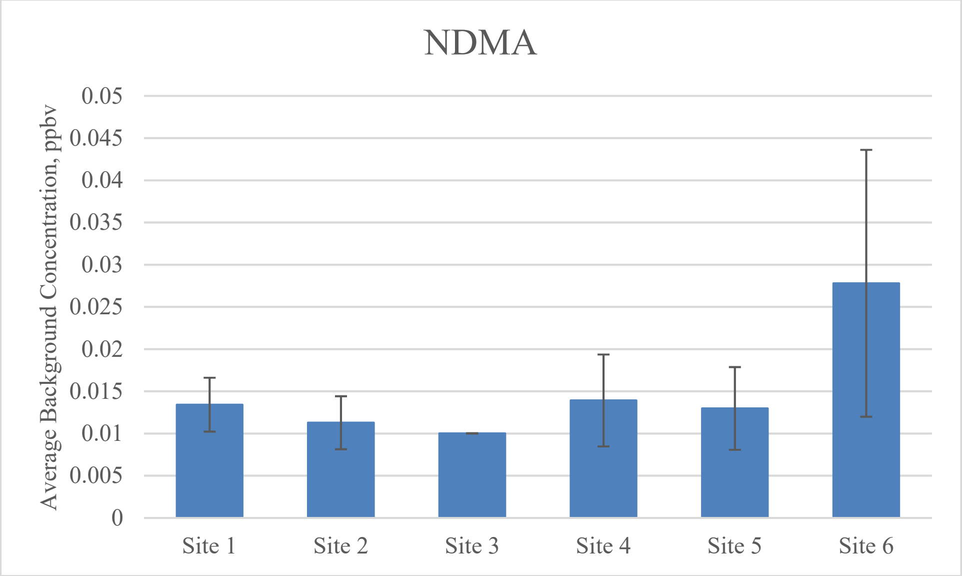
Table A-5. Comparison of TO-11A Results to Proton Transfer Reaction – Mass Spectrometer. (3 Sheets)

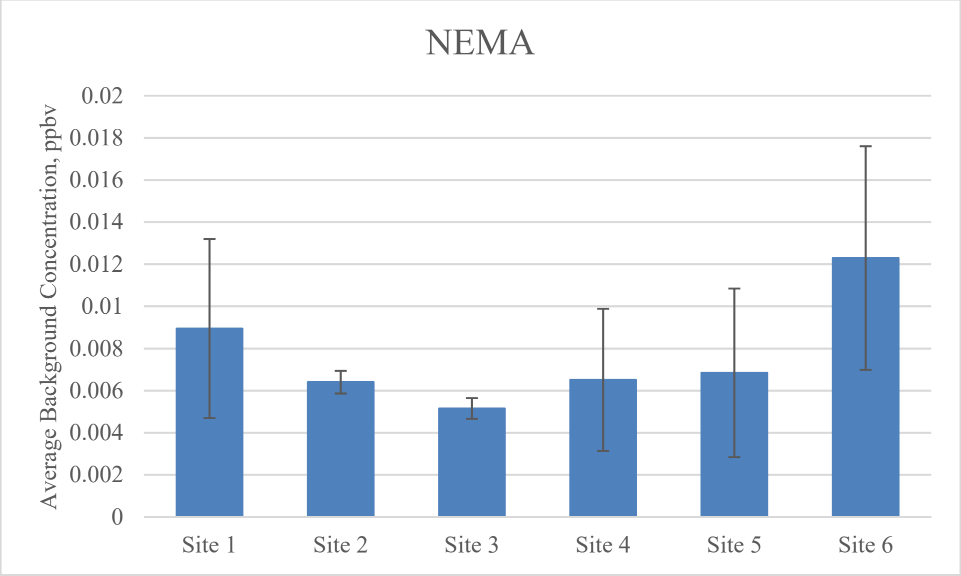
Date Taken	Study Site	Media Type	Analyte	ALS RL (ppbv)	PTR RL (ppbv)	ALS Result (ppbv)	PTR Avg. Result (ppbv)	% diff
11/4/2018	Site 3	DNPH	Formaldehyde	0.224	0.105	0.332	0.317	-4
			Acetaldehyde	0.153	0.106	ND	0.946	520
			Acetone	0.116	0.038	ND	0.860	643
			Acrolein	0.120	0.075	2.400	0.055	-98
			Butyraldehyde	0.093	0.016	ND	0.069	-26
11/5/2018	Site 4	DNPH	Formaldehyde	0.219	0.105	ND	0.335	53
			Acetaldehyde	0.149	0.106	ND	0.801	437
			Acetone	0.113	0.038	ND	0.670	492
			Acrolein	0.117	0.075	1.336	0.047	-96
			Butyraldehyde	0.091	0.016	ND	0.057	-37
11/6/2018	Site 5	DNPH	Formaldehyde	0.299	0.105	0.335	0.324	-3
			Acetaldehyde	0.204	0.106	ND	0.674	230
			Acetone	0.155	0.038	ND	0.593	283
			Acrolein	0.160	0.075	2.534	0.050	-98
			Butyraldehyde	0.125	0.016	ND	0.050	-60
11/7/2018	Site 6	DNPH	Formaldehyde	0.213	0.105	0.935	1.023	9
			Acetaldehyde	0.145	0.106	0.725	4.181	477
			Acetone	0.110	0.038	0.119	1.428	1103
			Acrolein	0.114	0.075	0.128	0.377	196
			Butyraldehyde	0.089	0.016	ND	0.183	106
11/7/2018	Site 6	DNPH	Formaldehyde	0.212	0.105	1.016	1.023	1
			Acetaldehyde	0.144	0.106	0.078	4.181	5263
			Acetone	0.109	0.038	0.171	1.428	736
			Acrolein	0.113	0.075	1.475	0.377	-74
			Butyraldehyde	0.088	0.016	ND	0.183	107

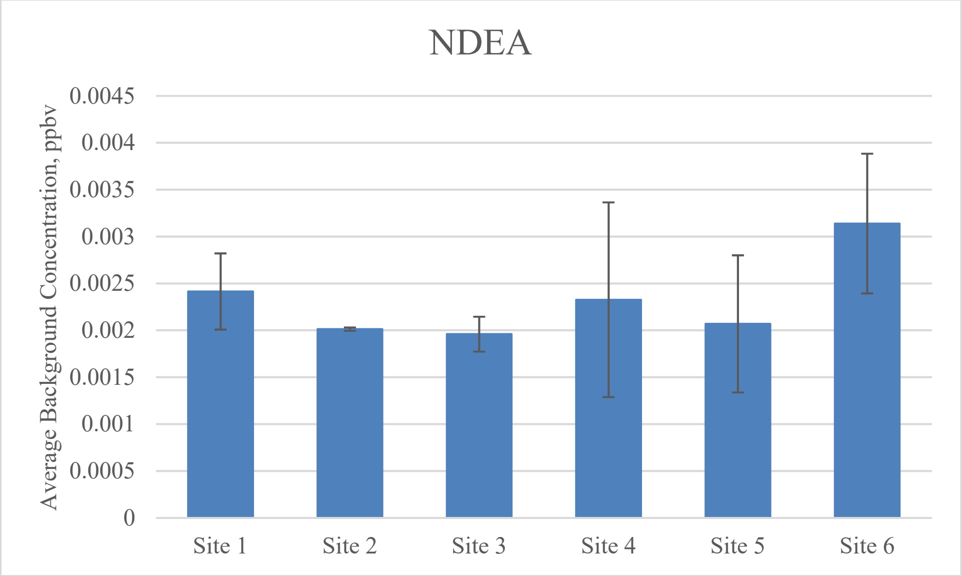
APPENDIX B

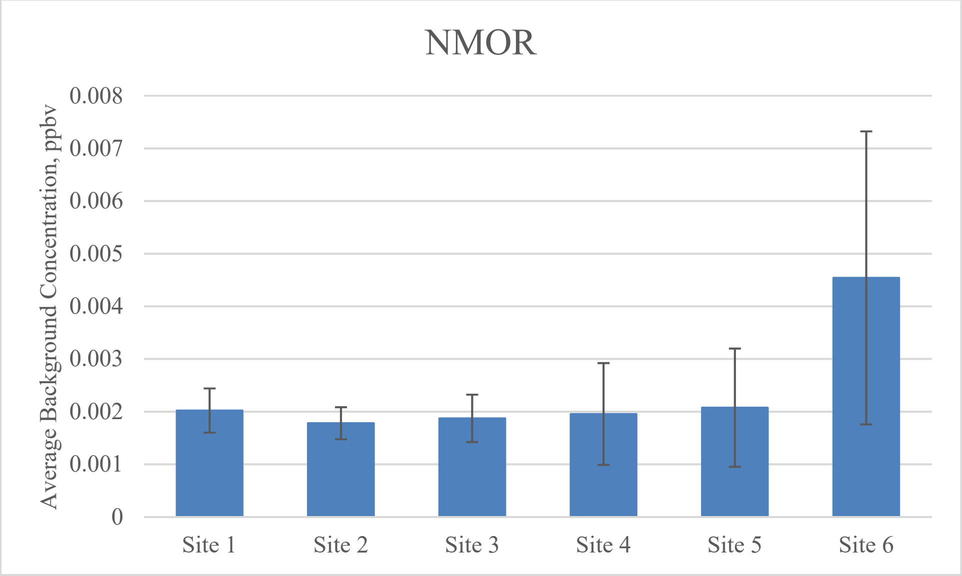
SITE COMPARISONS PLOTS

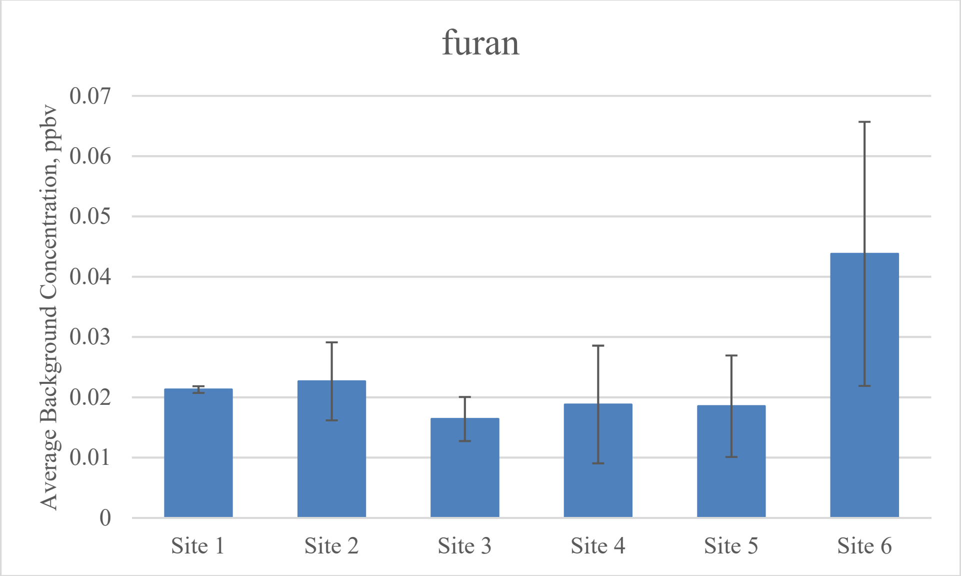

ammonia
Average Background Concentration, ppbv
16
14
12
10
8
6
4
2
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

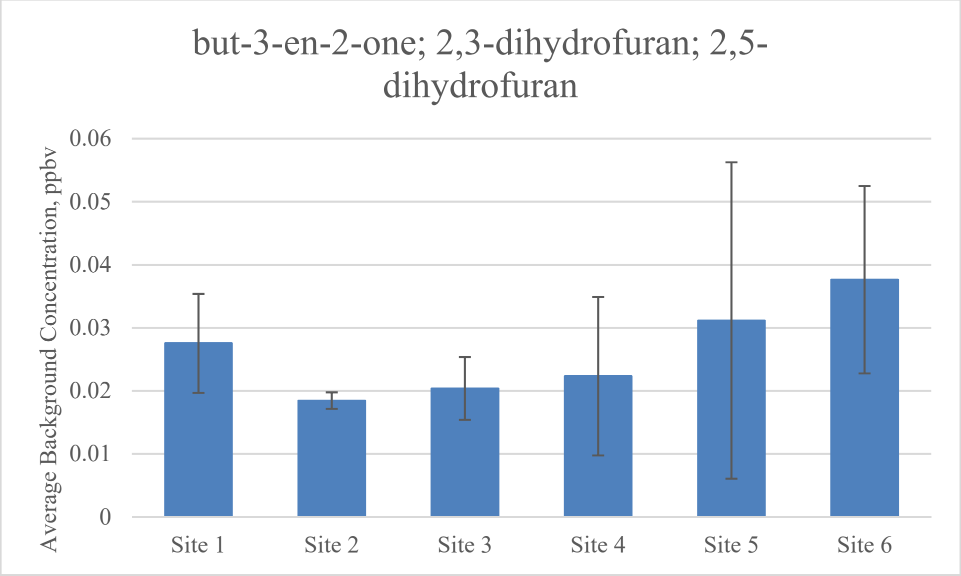

NDMA
Average Background Concentration, ppbv
0.05
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

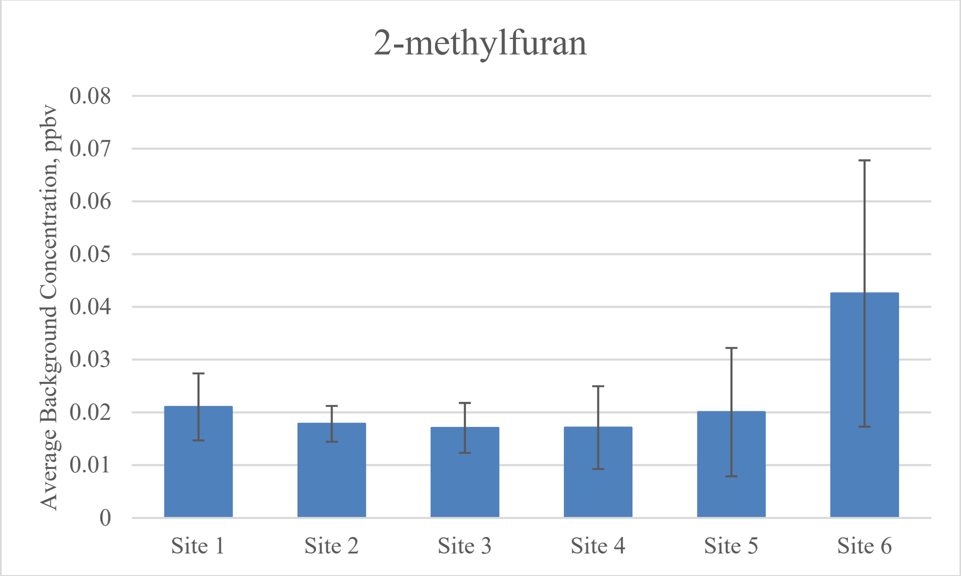

NEMA
Average Background Concentration, ppbv
0.02
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

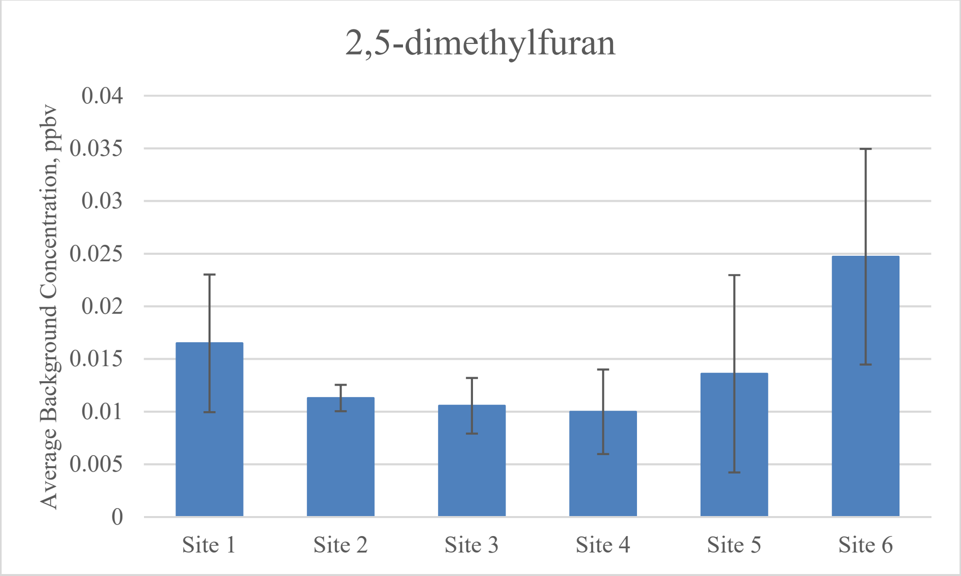

NDEA
Average Background Concentration, ppbv
0.0045
0.004
0.0035
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

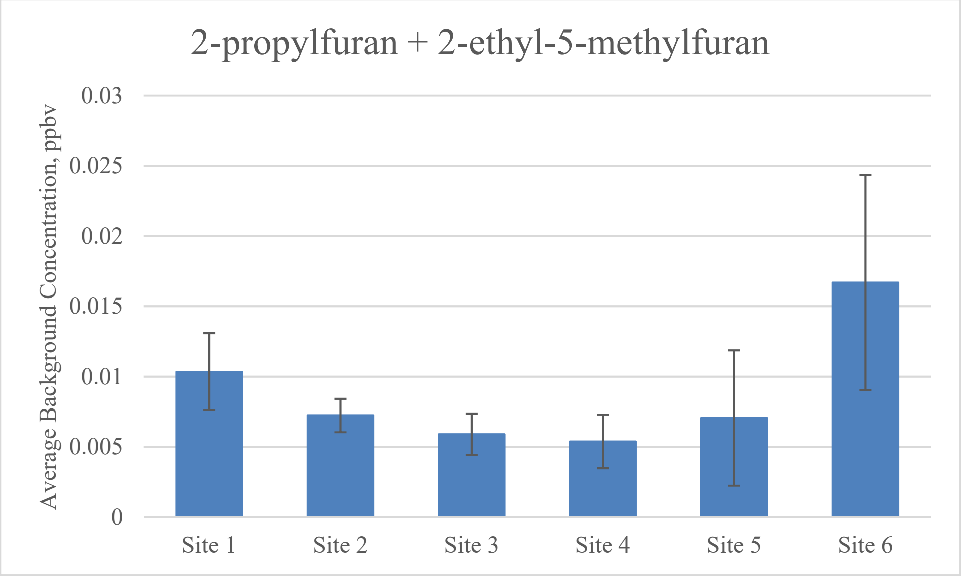

NMOR
Average Background Concentration, ppbv
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

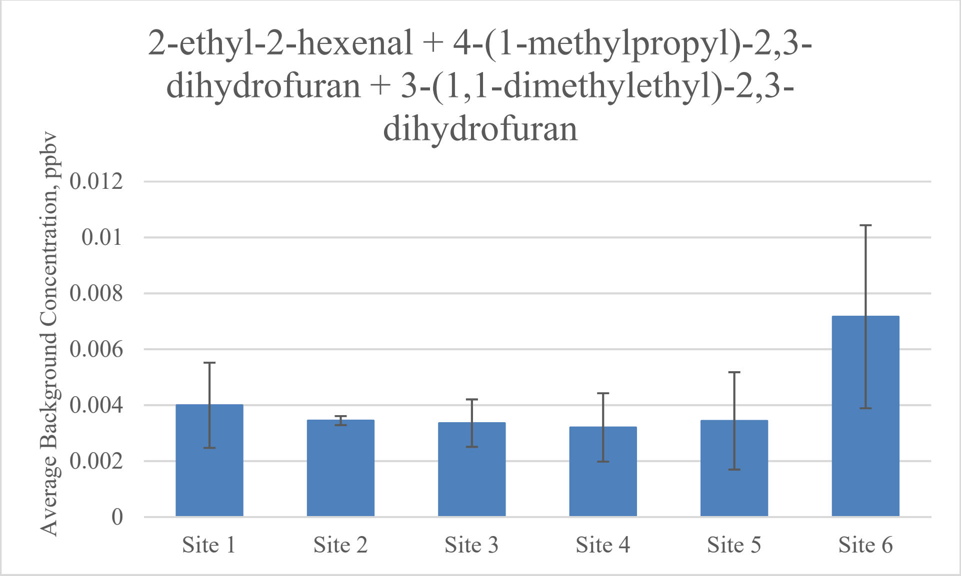

furan
Average Background Concentration, ppbv
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

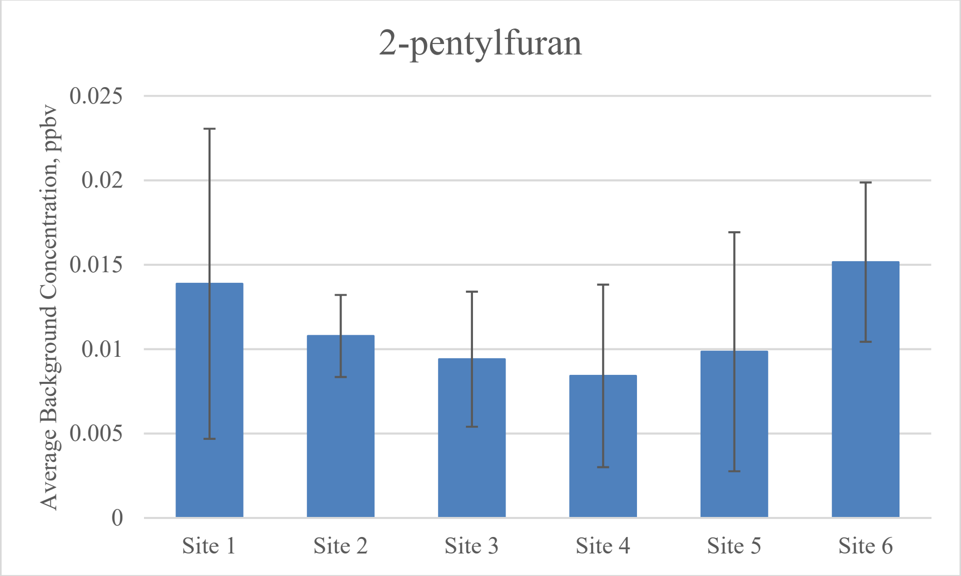

but-3-en-2-one; 2,3-dihydrofuran; 2,5-dihydrofuran
Average Background Concentration, ppbv
0.06
0.05
0.04
0.03
0.02
0.01
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

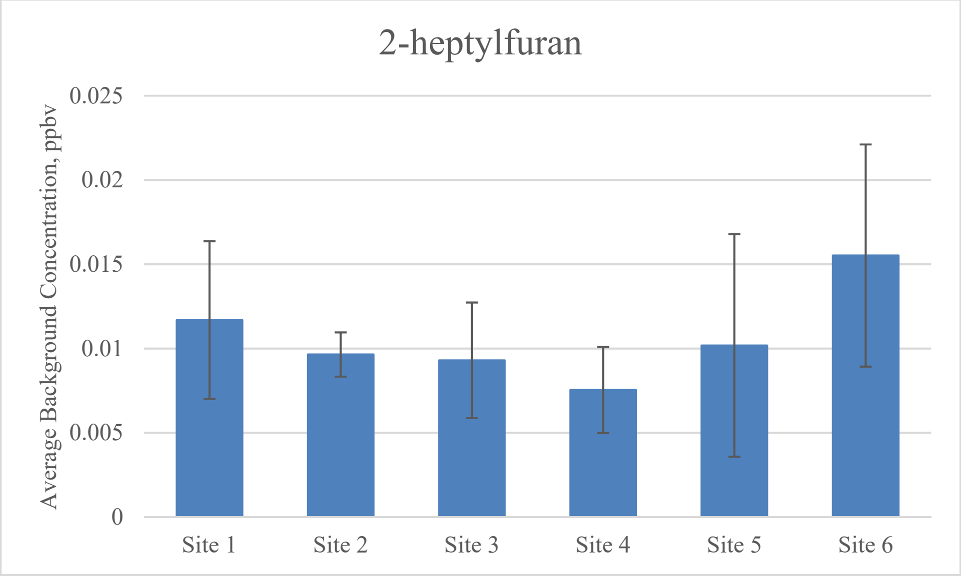

2-methylfuran
Average Background Concentration, ppbv
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

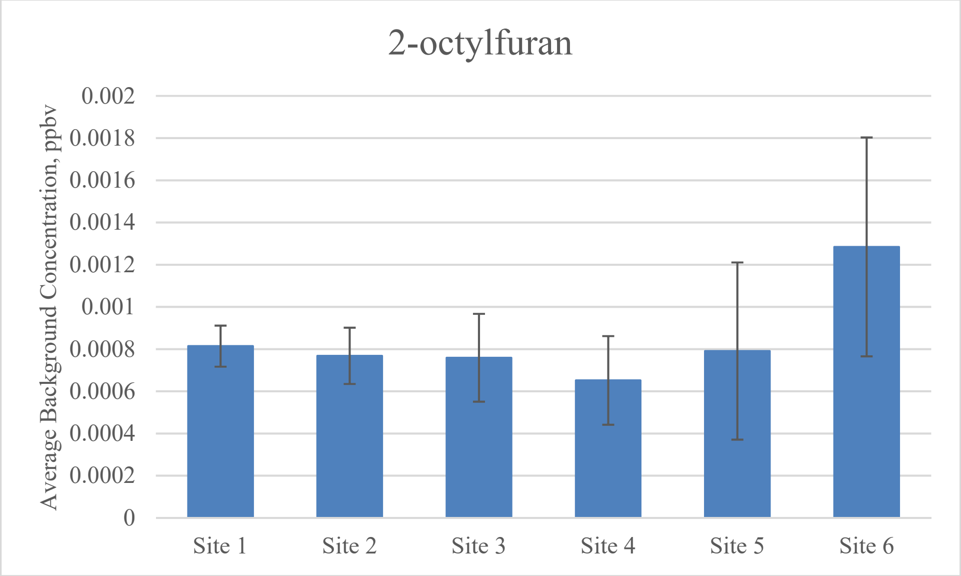

2,5-dimethylfuran
Average Background Concentration, ppbv
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

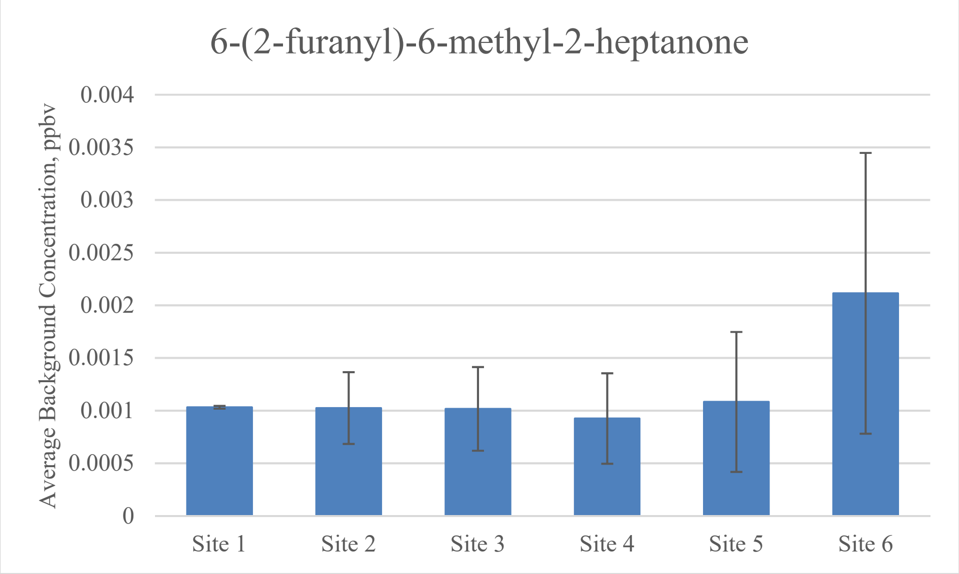

2-propylfuran + 2-ethyl-5-methylfuran
Average Background Concentration, ppbv
0.03
0.025
0.02
0.015
0.01
0.005
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

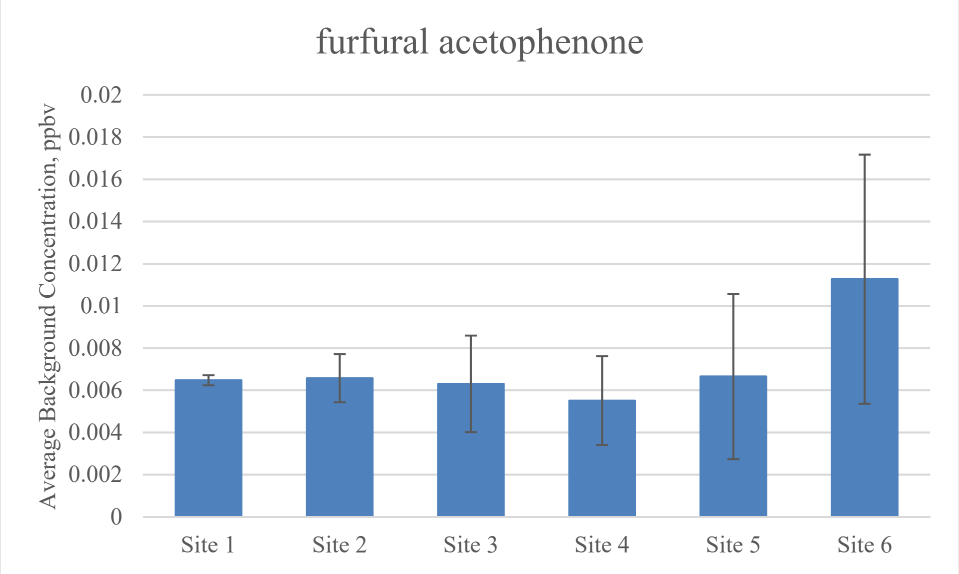

2-ethyl-2-hexenal + 4-(1-methylpropyl)-2,3-dihydrofuran + 3-(1,1-dimethylethyl)-2,3-dihydrofuran
Average Background Concentration, ppbv
0.012
0.01
0.008
0.006
0.004
0.002
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

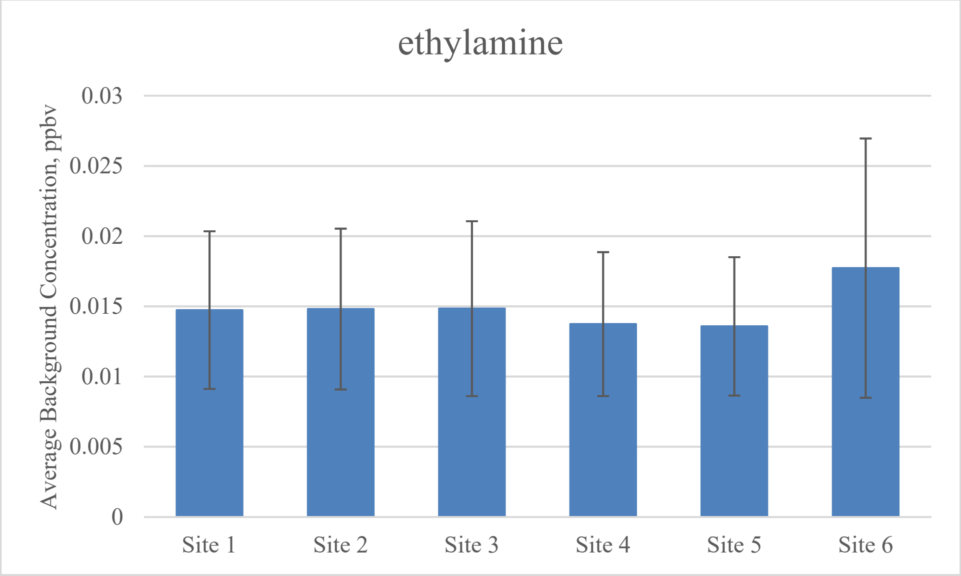

2-pentylfuran
Average Background Concentration, ppbv
0.025
0.02
0.015
0.01
0.005
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

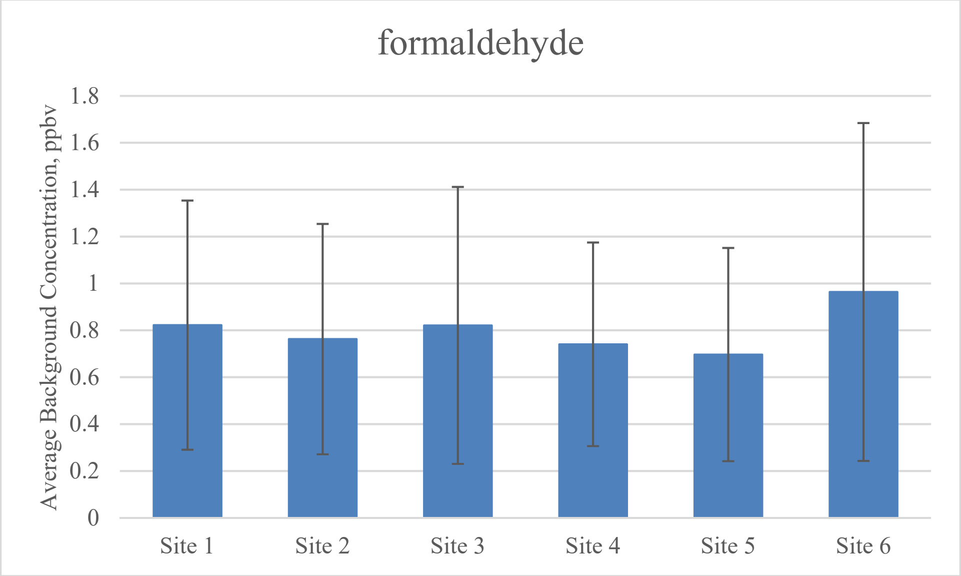

2-heptylfuran
Average Background Concentration, ppbv
0.025
0.02
0.015
0.01
0.005
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

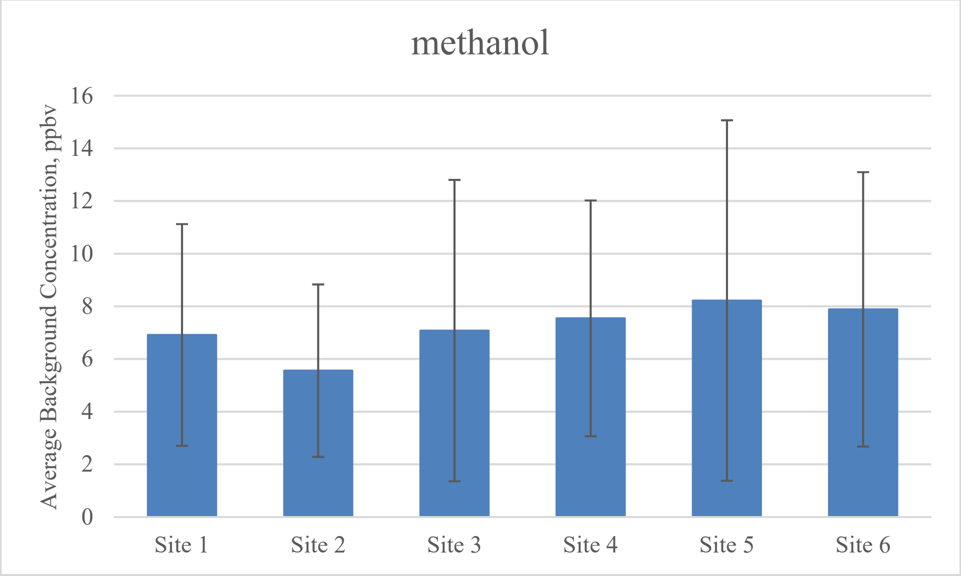

2-octylfuran
Average Background Concentration, ppbv
0.002
0.0018
0.0016
0.0014
0.0012
0.001
0.0008
0.0006
0.0004
0.0002
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

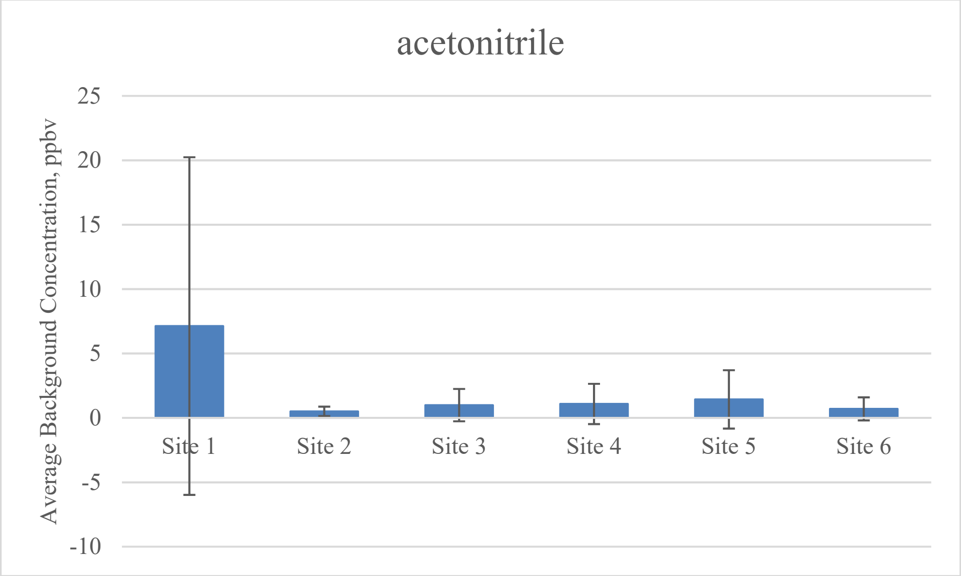

6-(2-furanyl)-6-methyl-2-heptanone
Average Background Concentration, ppbv
0.004
0.0035
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

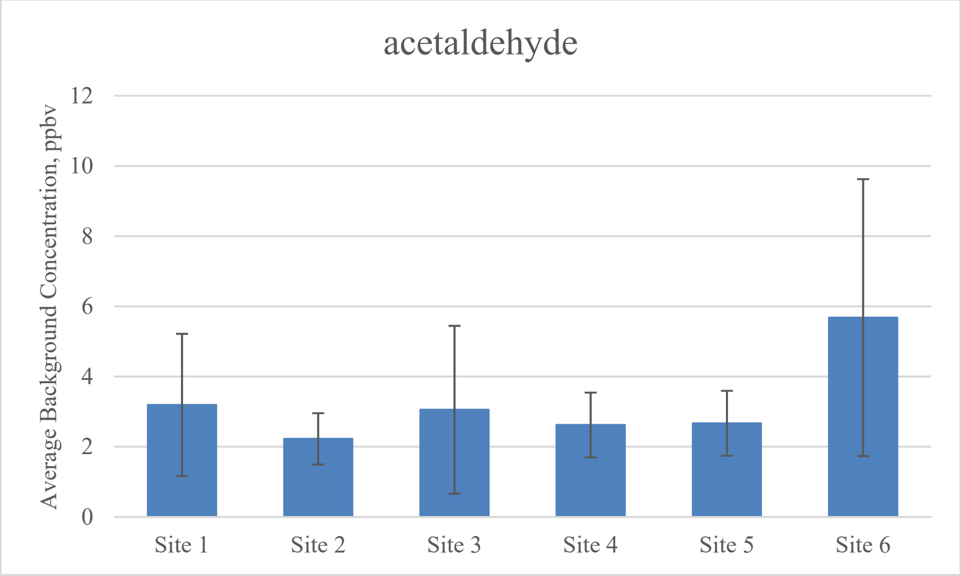

furfural acetophenone
Average Background Concentration, ppbv
0.02
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

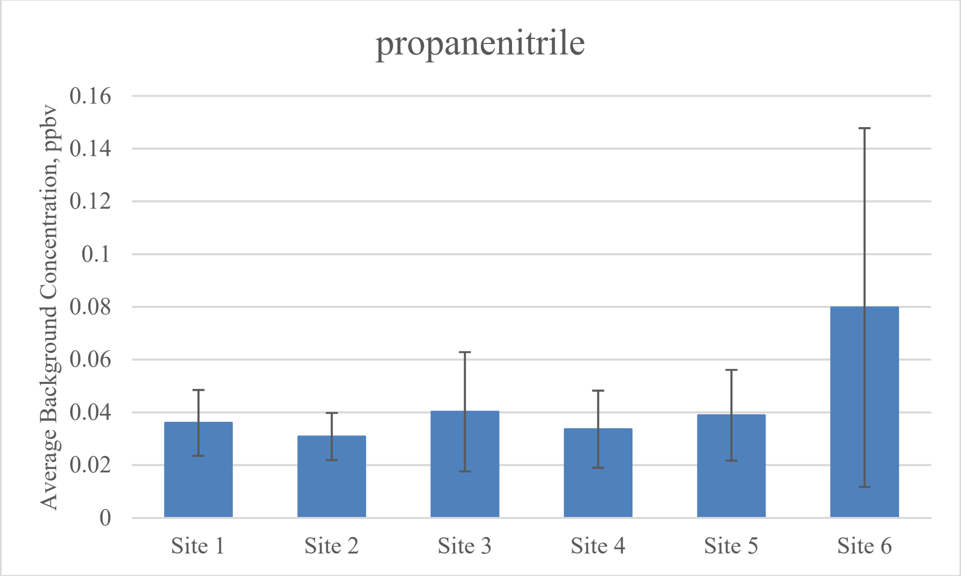

ethylamine
Average Background Concentration, ppbv
0.03
0.025
0.02
0.015
0.01
0.005
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6


formaldehyde
Average Background Concentration, ppbv
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6


methanol
Average Background Concentration, ppbv
16
14
12
10
8
6
4
2
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6


acetonitrile
Average Background Concentration, ppbv
25
20
15
10
5
0
-5
-10
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6


acetaldehyde
Average Background Concentration, ppbv
12
10
8
6
4
2
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6


propanenitrile
Average Background Concentration, ppbv
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
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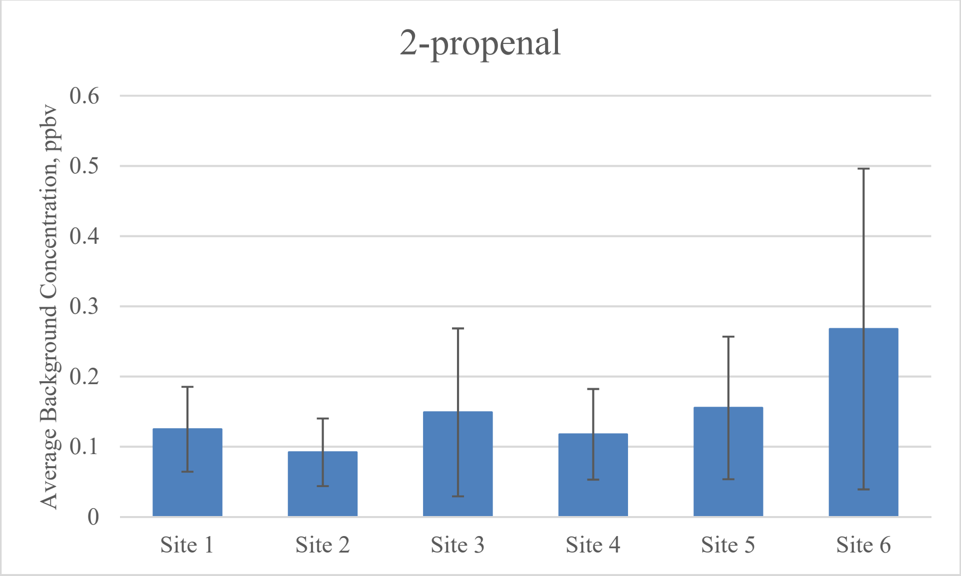
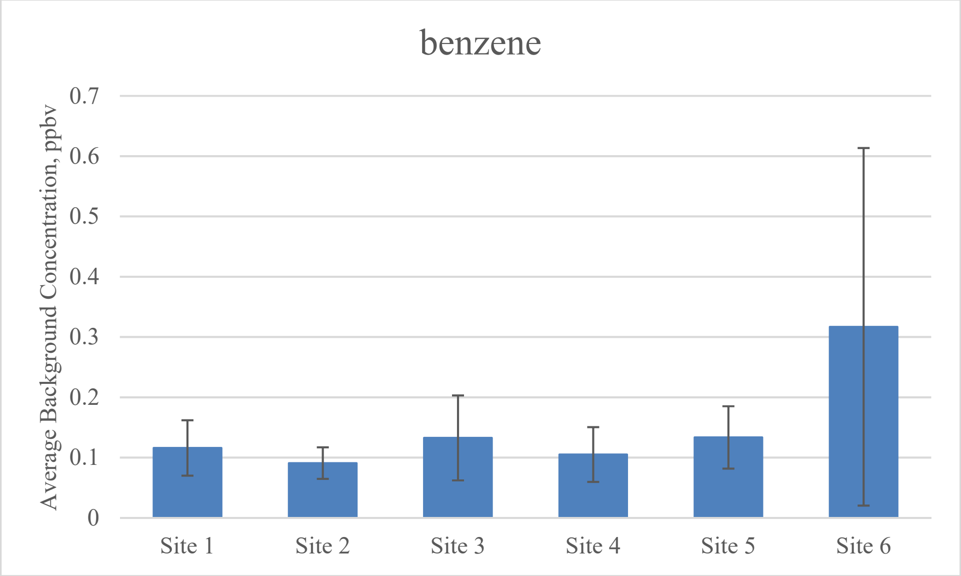
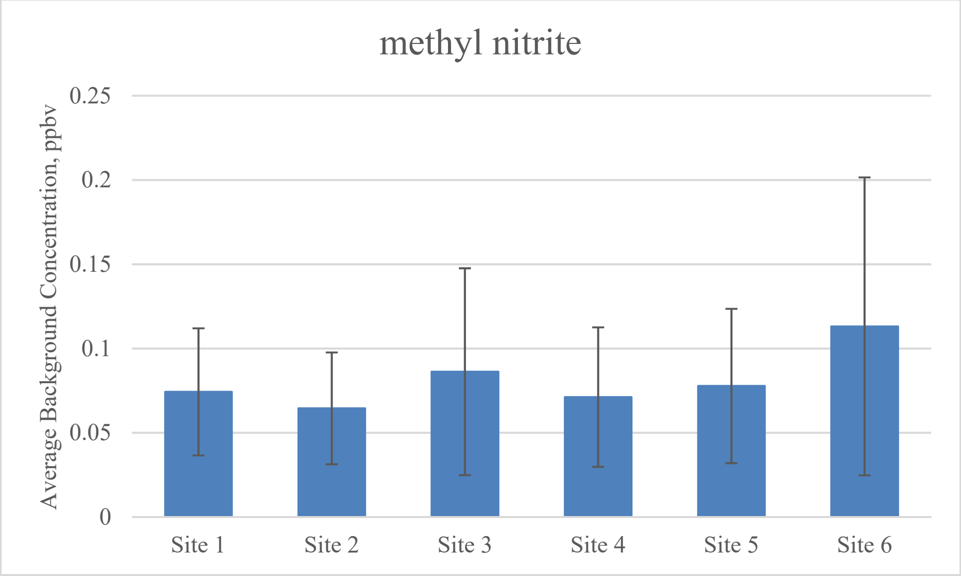
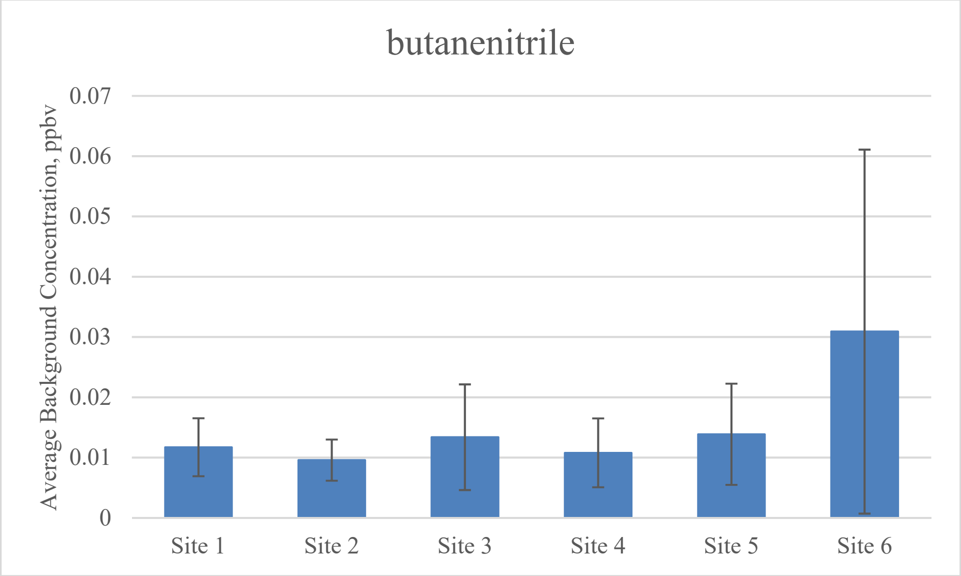
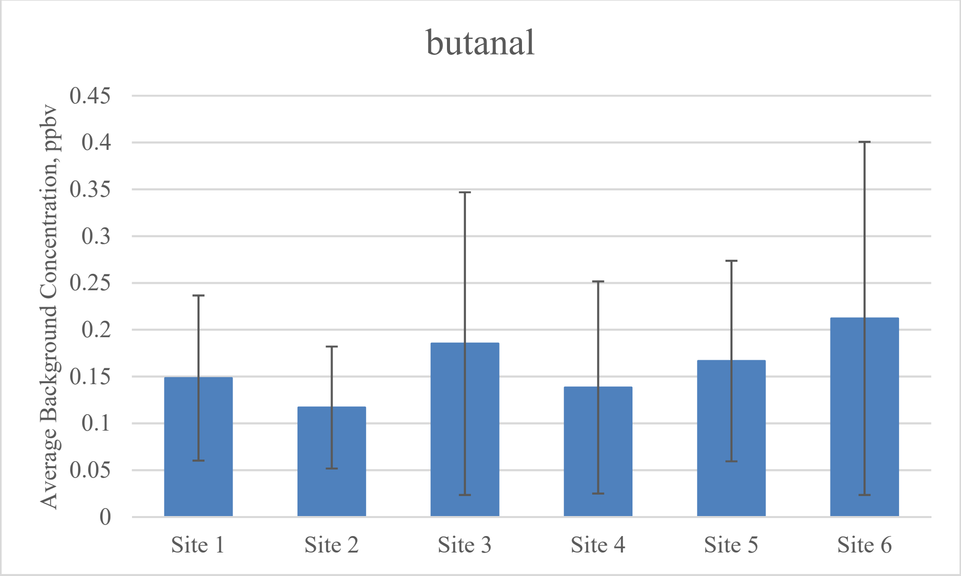
Site 2
Site 3
Site 4
Site 5
Site 6

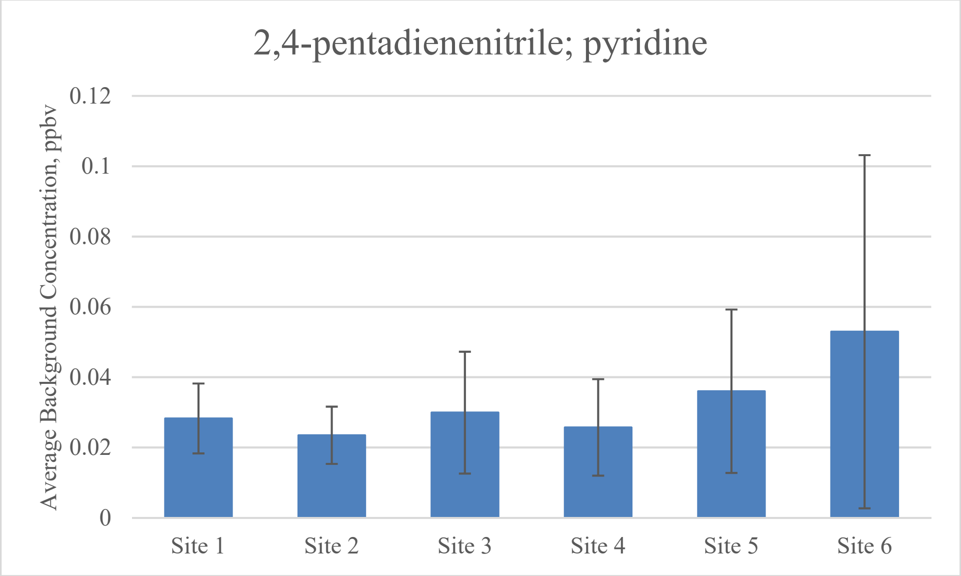

2-propenal
Average Background Concentration, ppbv
0.6
0.5
0.4
0.3
0.2
0.1
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

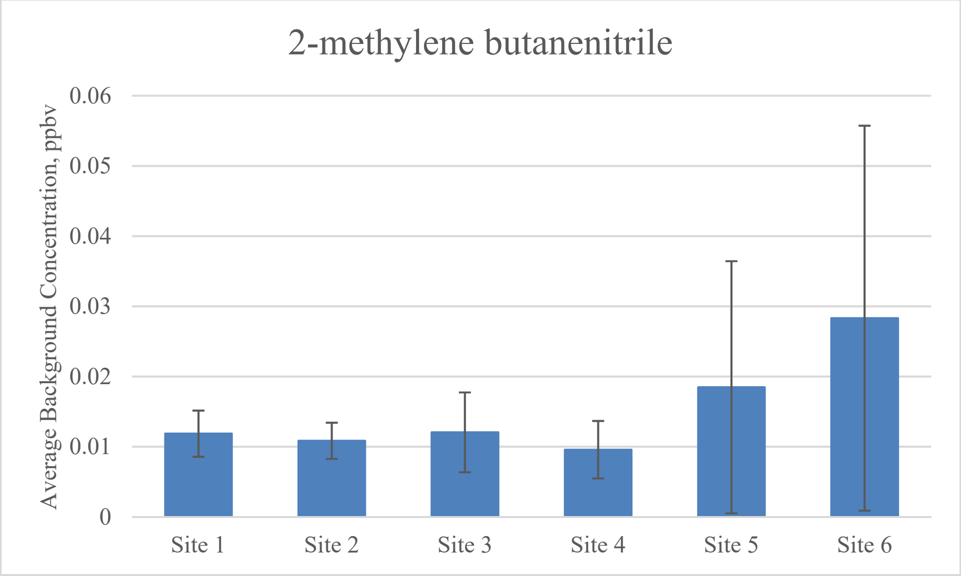

benzene
Average Background Concentration, ppbv
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

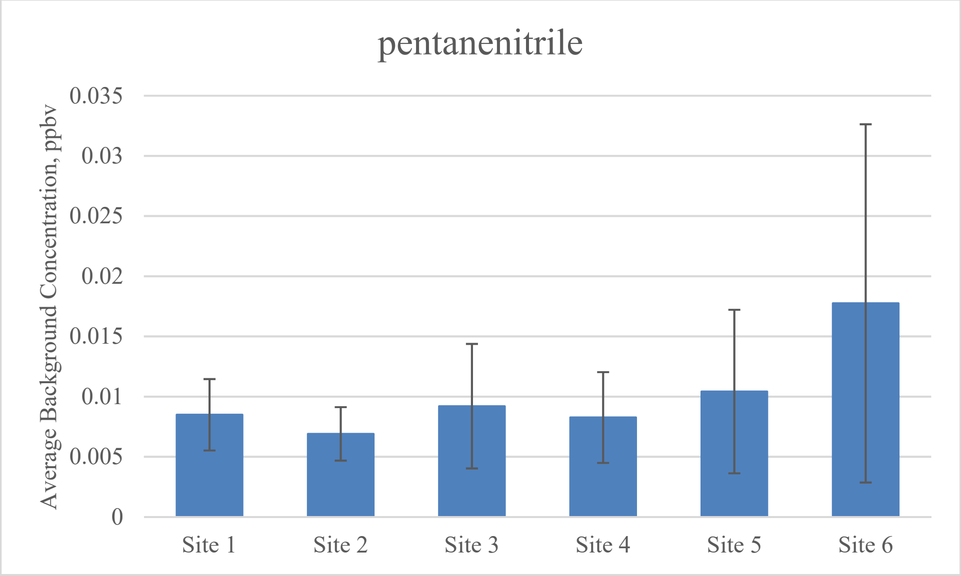

methyl nitrite
Average Background Concentration, ppbv
0.25
0.2
0.15
0.1
0.05
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

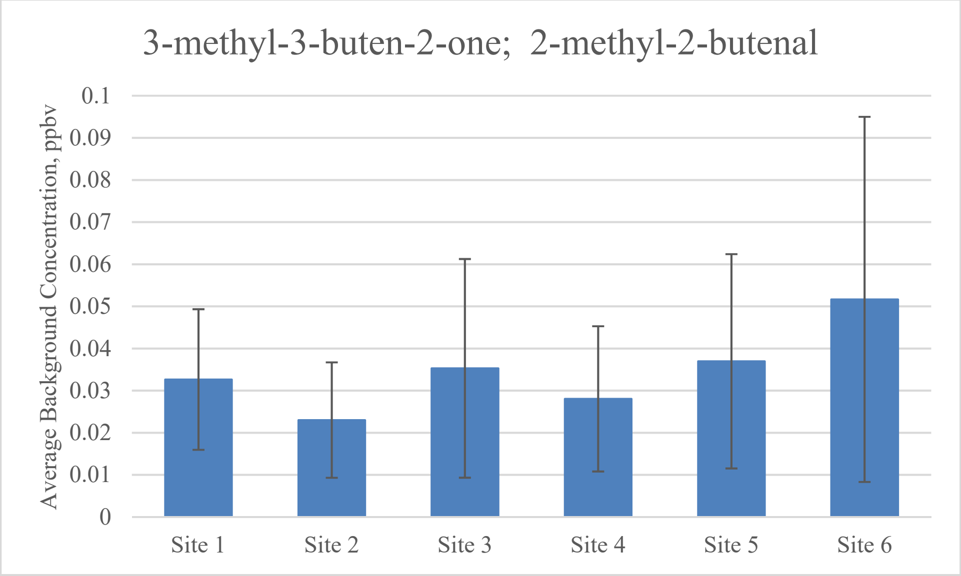

butanenitrile
Average Background Concentration, ppbv
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

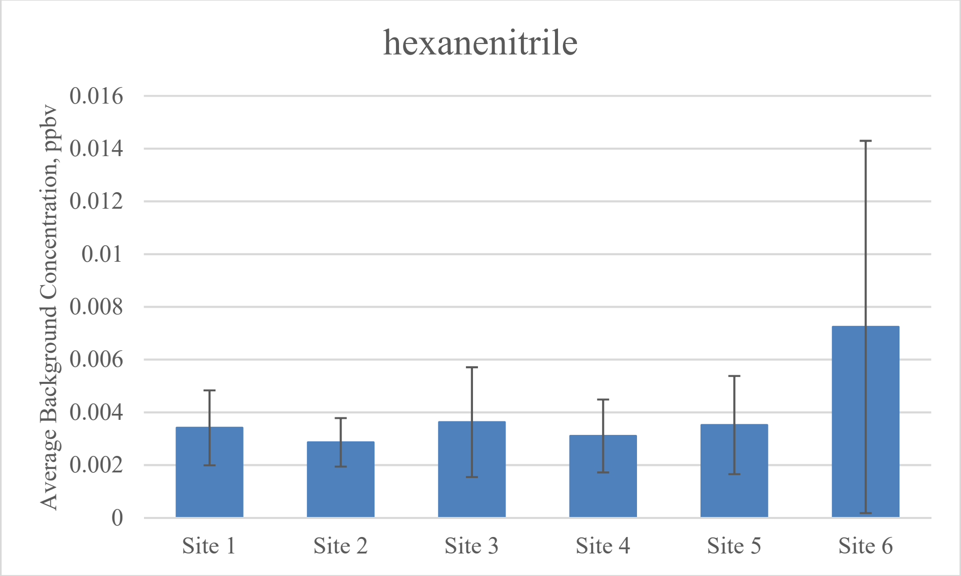

butanal
Average Background Concentration, ppbv
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

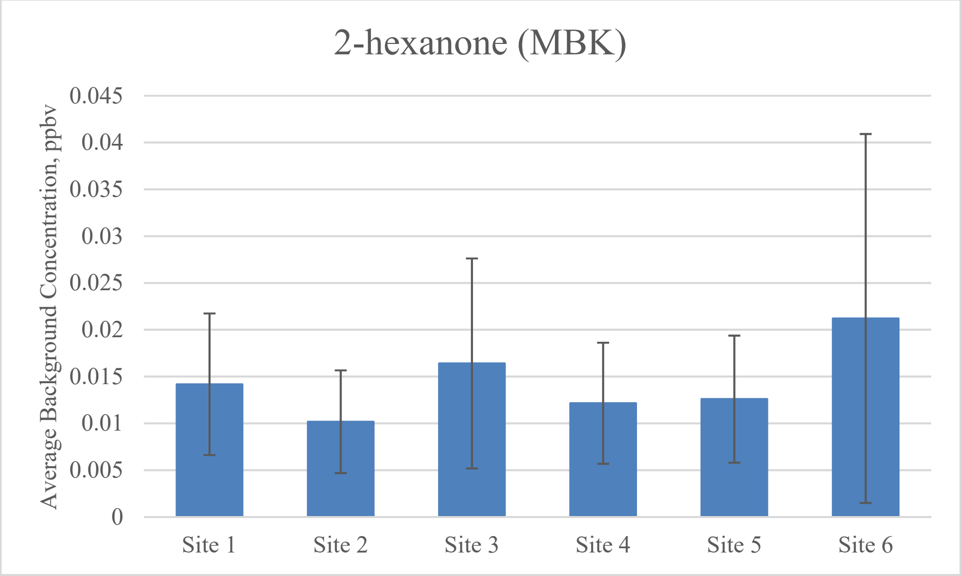

2,4-pentadienenitrile; pyridine
Average Background Concentration, ppbv
0.12
0.1
0.08
0.06
0.04
0.02
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

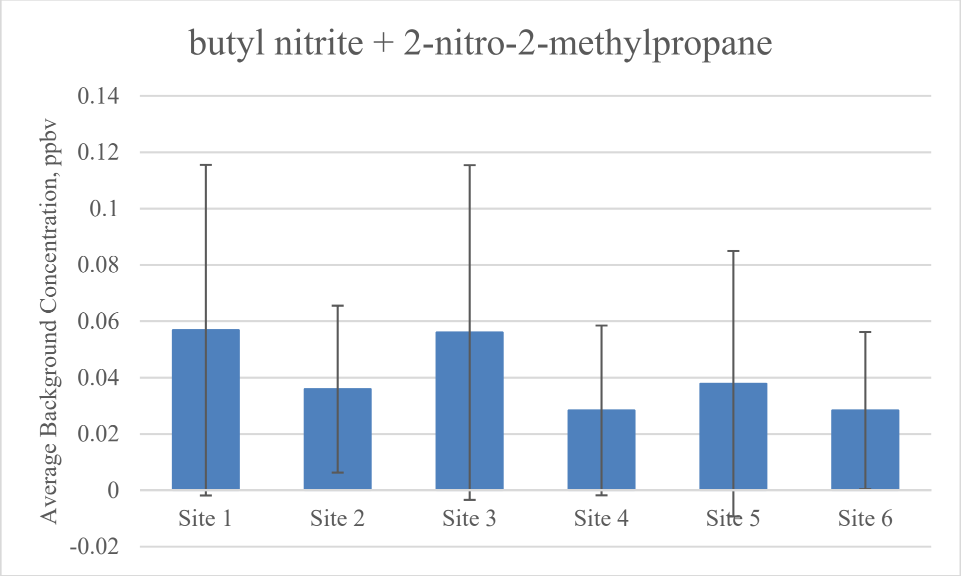

2-methylene butanenitrile
Average Background Concentration, ppbv
0.06
0.05
0.04
0.03
0.02
0.01
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

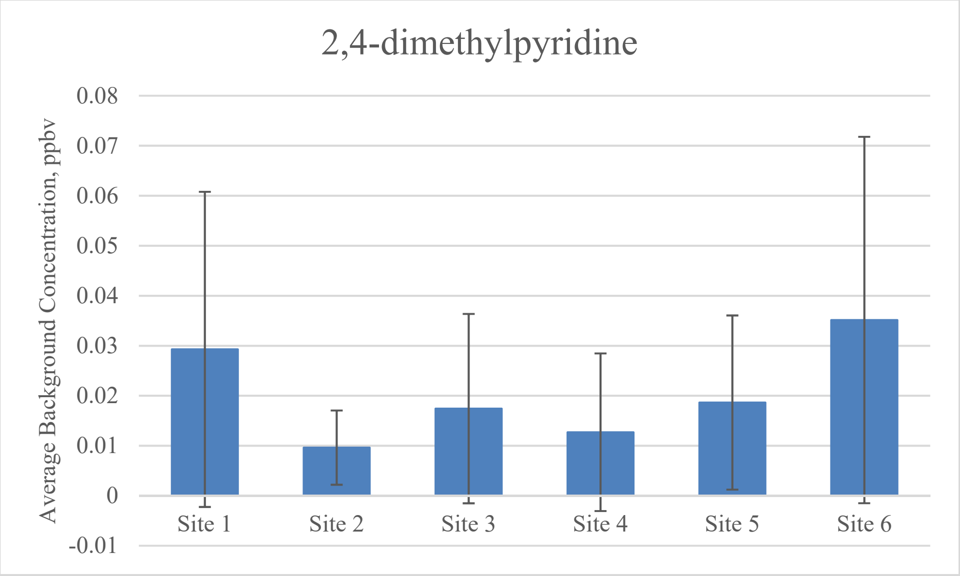

pentanenitrile
Average Background Concentration, ppbv
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

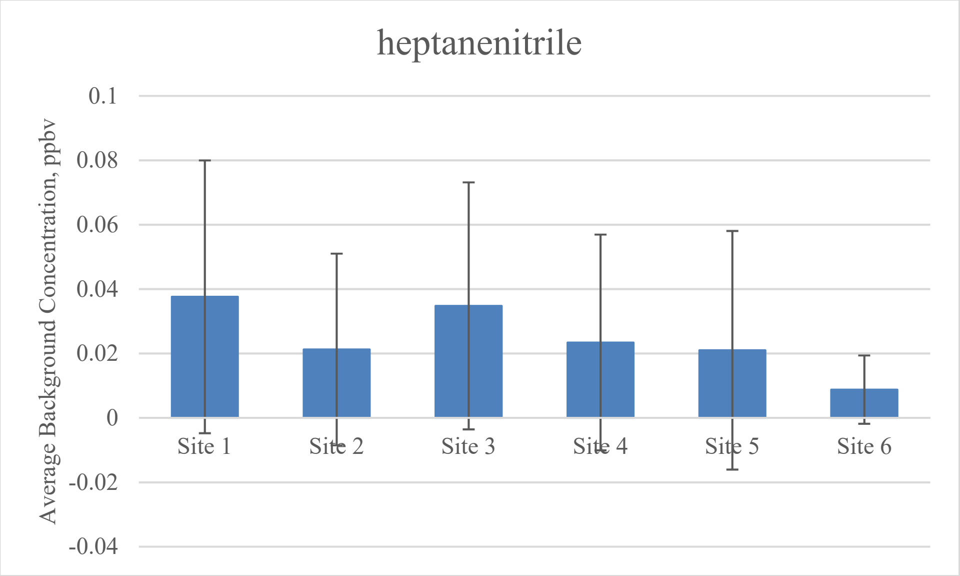

3-methyl-3-buten-2-one; 2-methyl-2-butenal
Average Background Concentration, ppbv
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

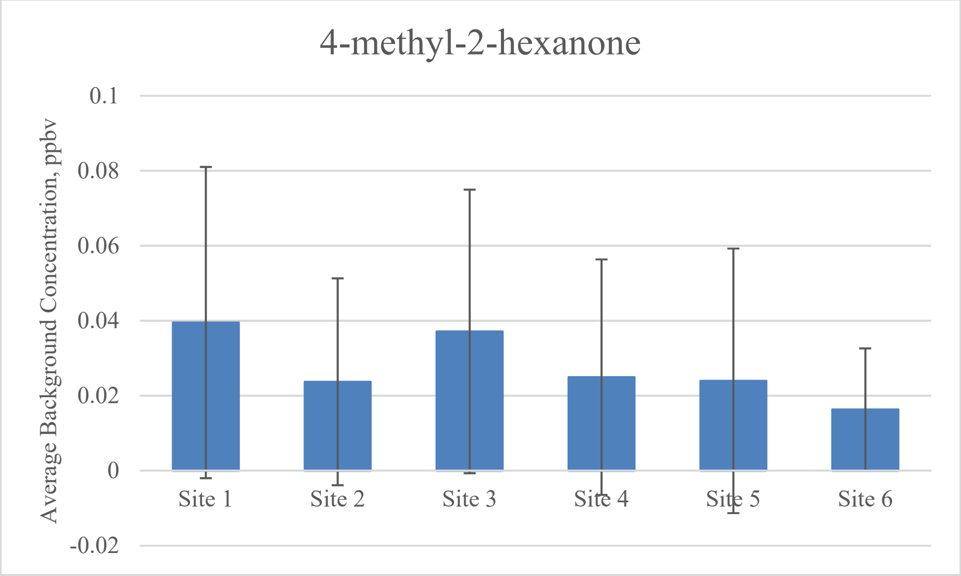

hexanenitrile
Average Background Concentration, ppbv
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

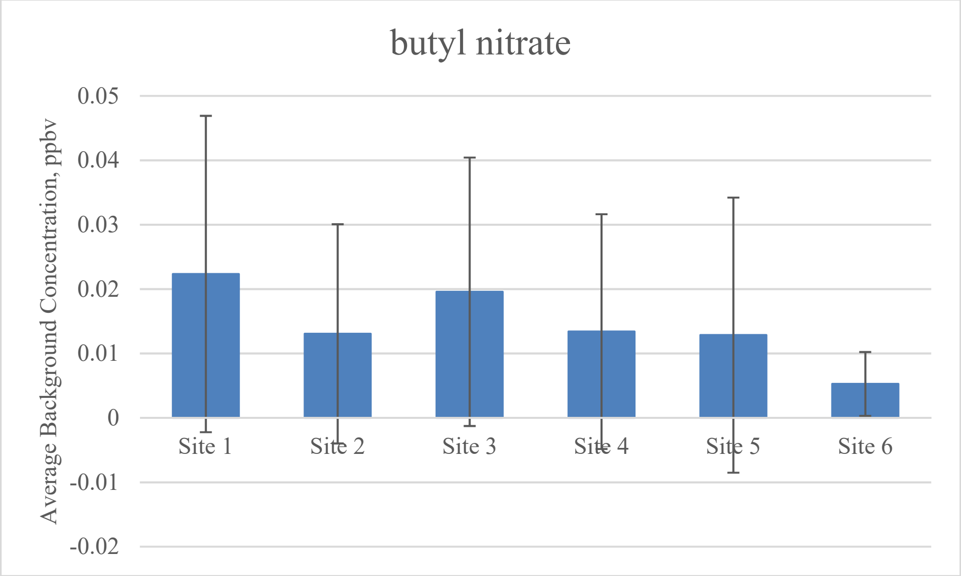

2-hexanone (MBK)
Average Background Concentration, ppbv
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

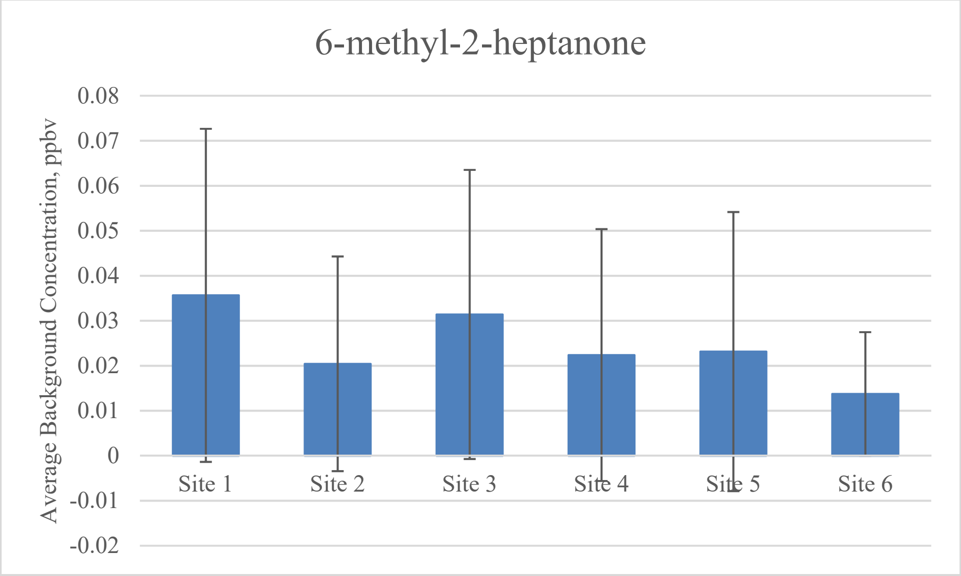

butyl nitrite + 2-nitro-2-methylpropane
Average Background Concentration, ppbv
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
-0.02
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

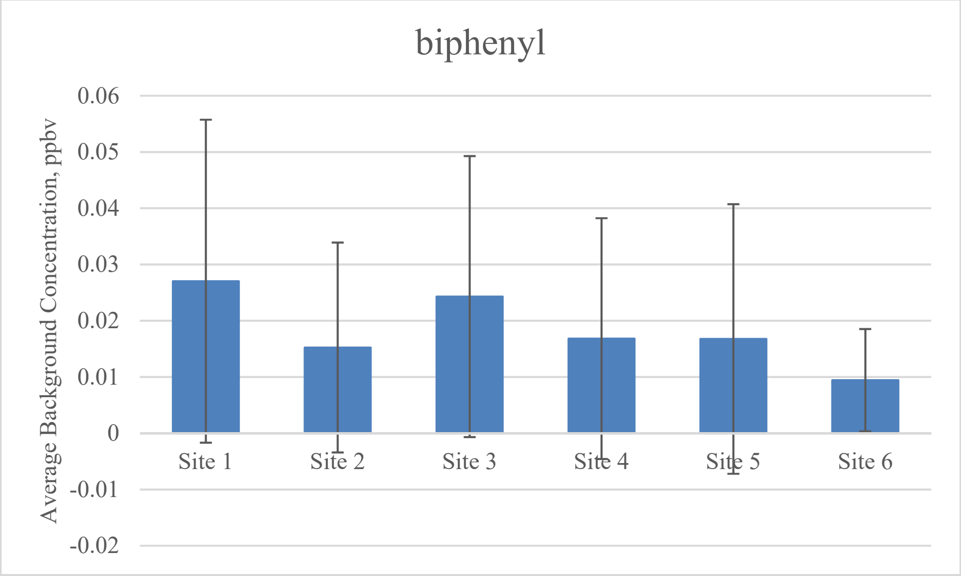

2,4-dimethylpyridine
Average Background Concentration, ppbv
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
-0.01
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

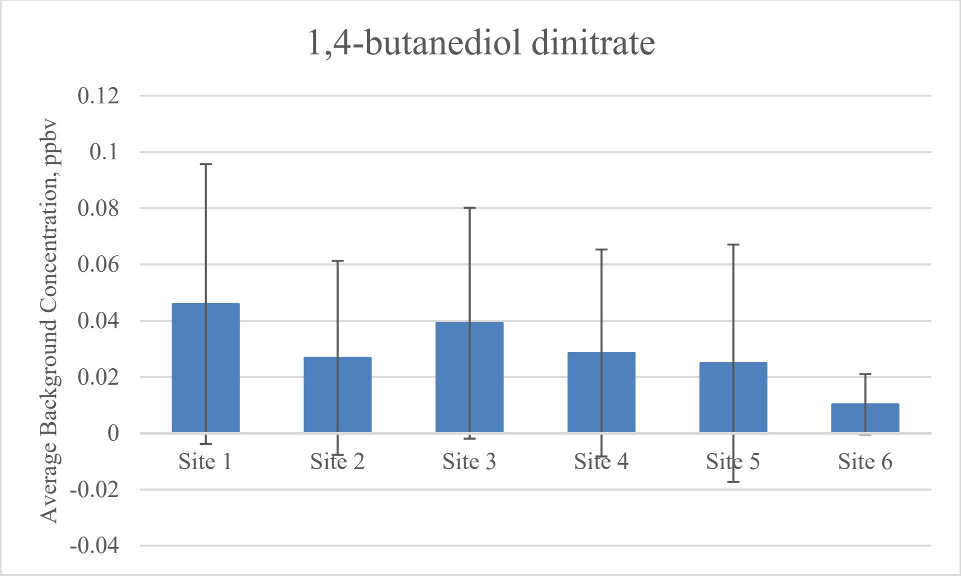

heptanenitrile
Average Background Concentration, ppbv
0.1
0.08
0.06
0.04
0.02
0
-0.02
-0.04
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

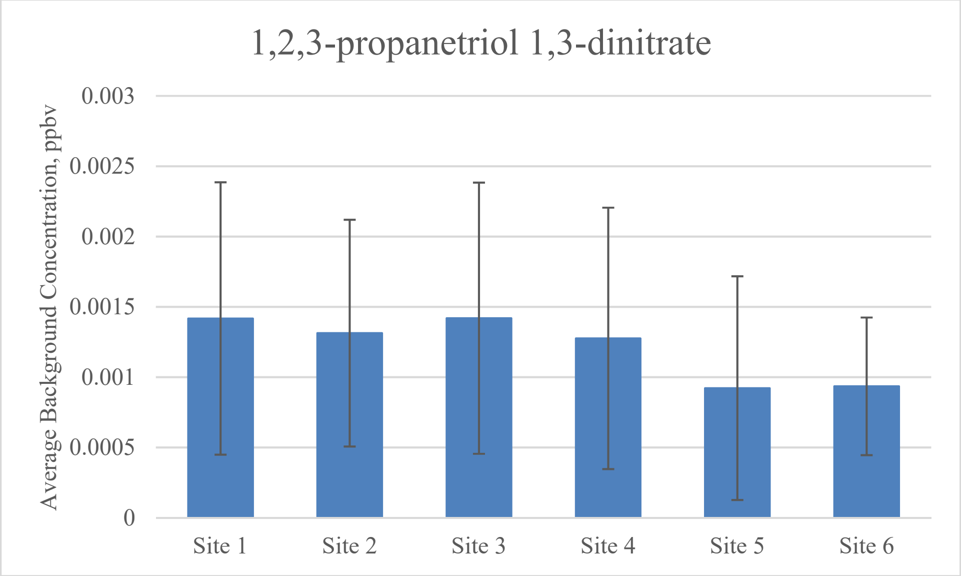

4-methyl-2-hexanone
Average Background Concentration, ppbv
0.1
0.08
0.06
0.04
0.02
0
-0.02
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

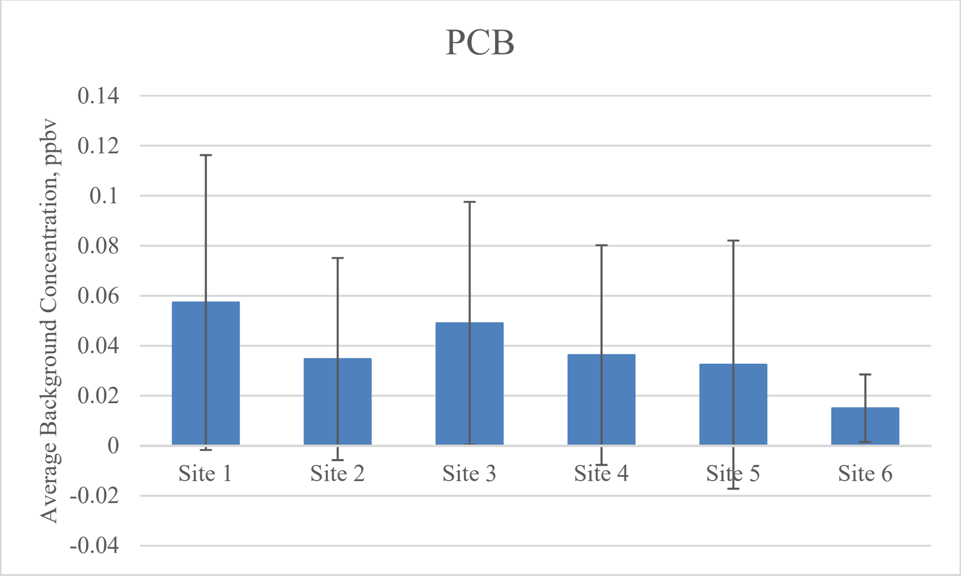

butyl nitrate
Average Background Concentration, ppbv
0.05
0.04
0.03
0.02
0.01
0
-0.01
-0.02
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6


6-methyl-2-heptanone
Average Background Concentration, ppbv
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
-0.01
-0.02
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6


biphenyl
Average Background Concentration, ppbv
0.06
0.05
0.04
0.03
0.02
0.01
0
-0.01
-0.02
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

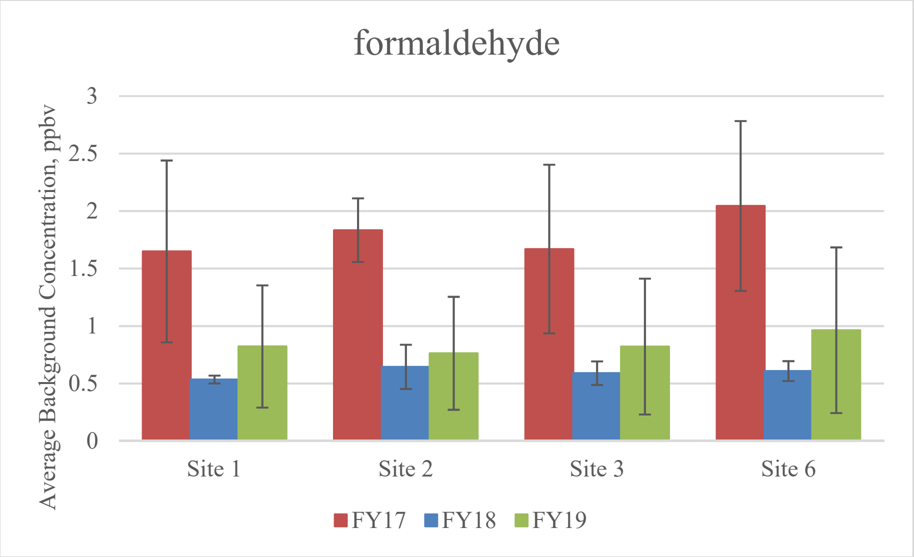

1,4-butanediol dinitrate
Average Background Concentration, ppbv
0.12
0.1
0.08
0.06
0.04
0.02
0
-0.02
-0.04
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

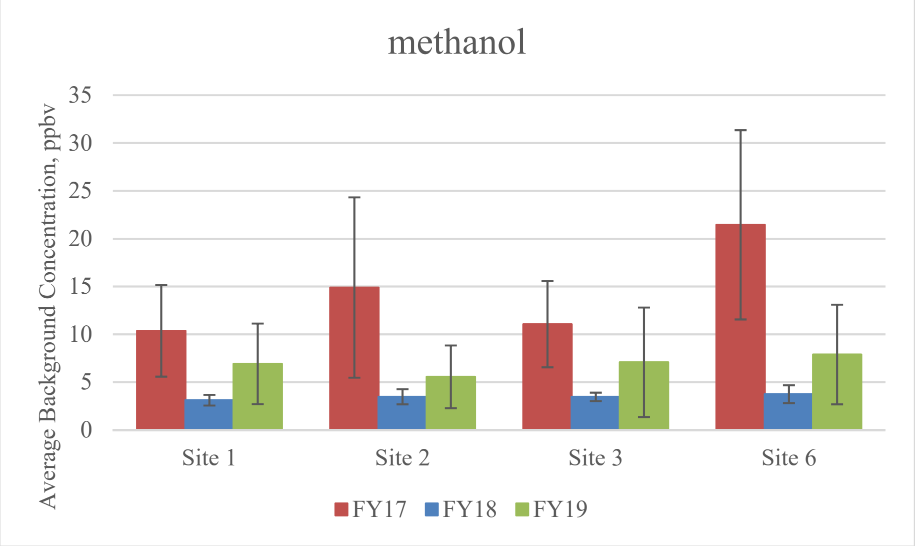

1,2,3-propanetriol 1,3-dinitrate
Average Background Concentration, ppbv
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

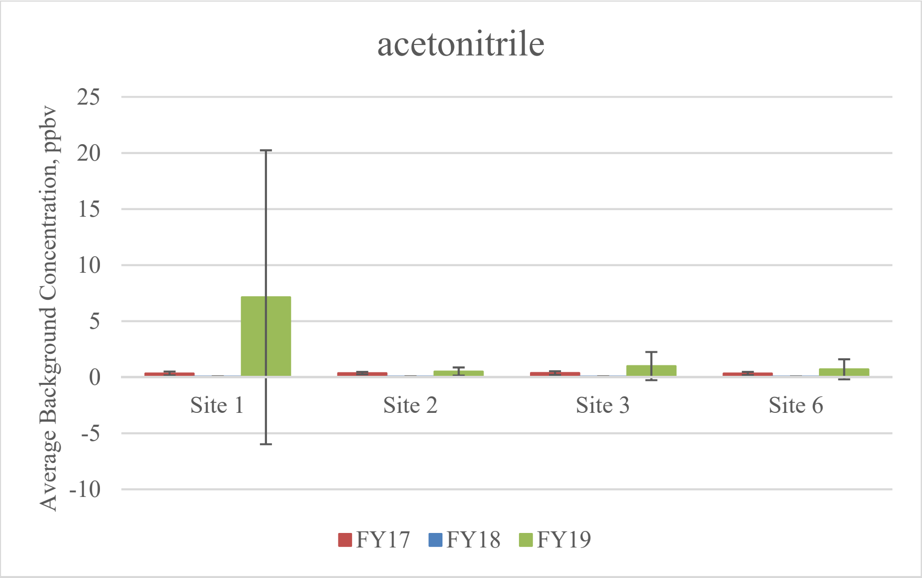

PCB
Average Background Concentration, ppbv
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
-0.02
-0.04
Site 1
Site 2
Site 3
Site 4
Site 5
Site 6

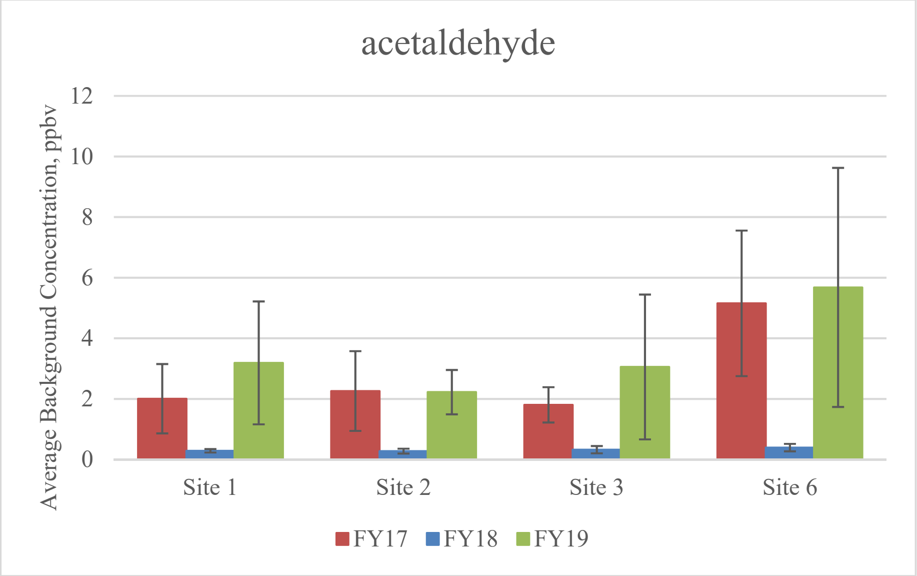
APPENDIX C

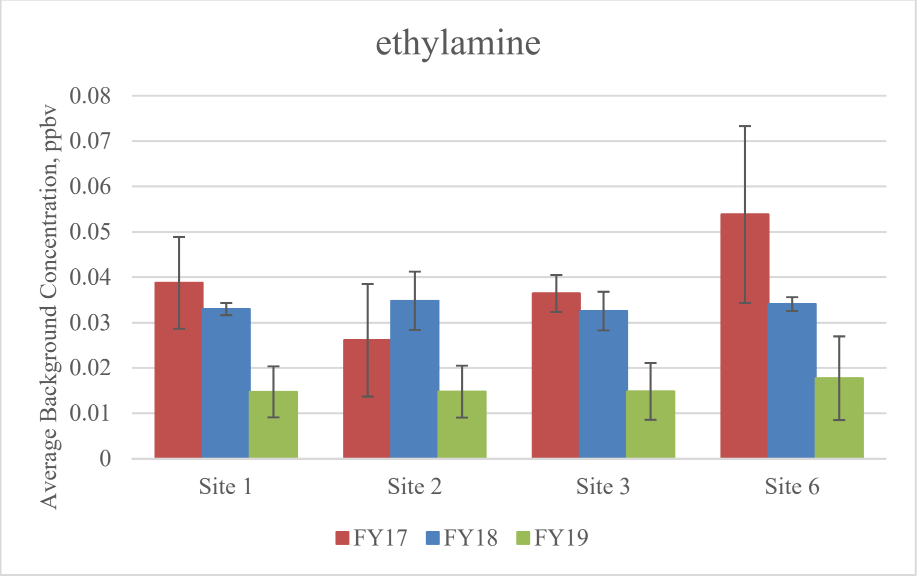
COMPARISONS TO FY17 AND SPRING FY18 STUDY ADDITIONAL PLOTS

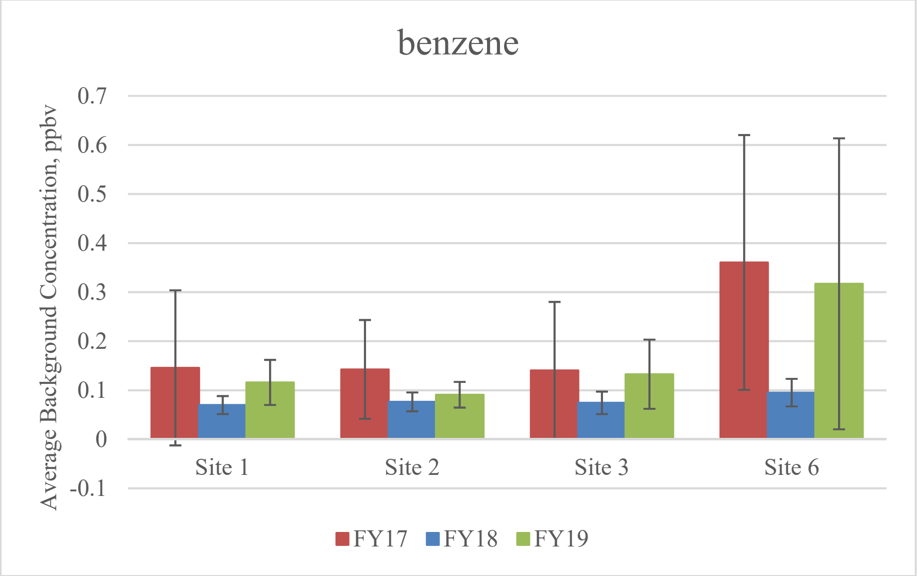

formaldehyde
Average Background Concentration, ppbv
3
2.5
2
1.5
1
0.5
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

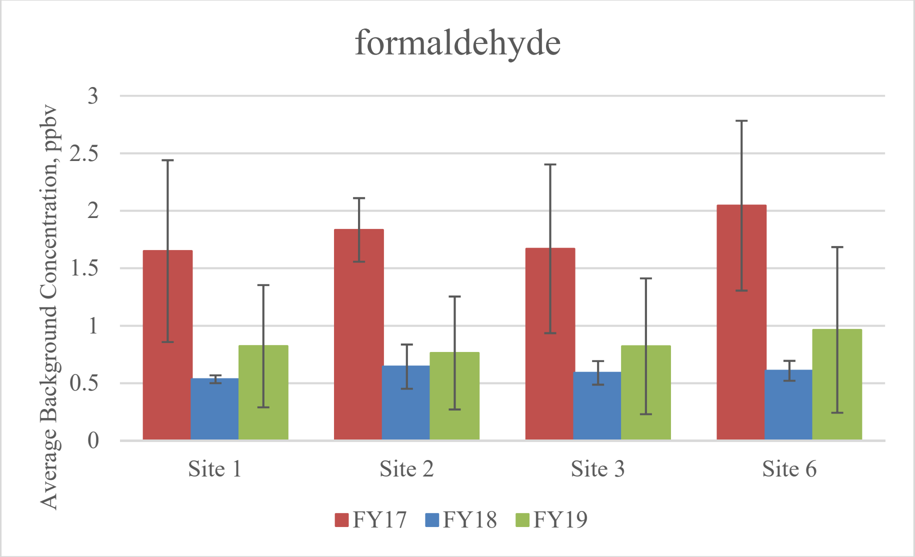

methanol
Average Background Concentration, ppbv
35
30
25
20
15
10
5
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

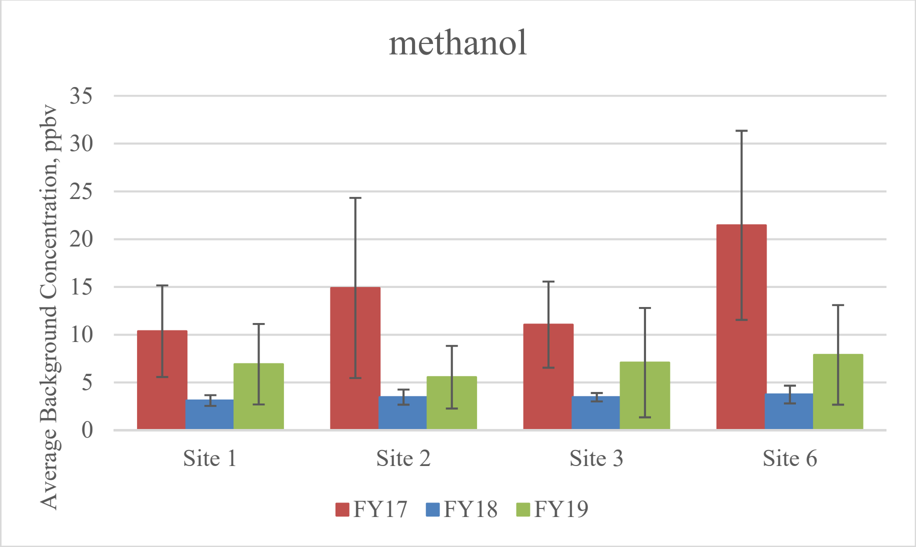

acetonitrile
Average Background Concentration, ppbv
25
20
15
10
5
0
-5
-10
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

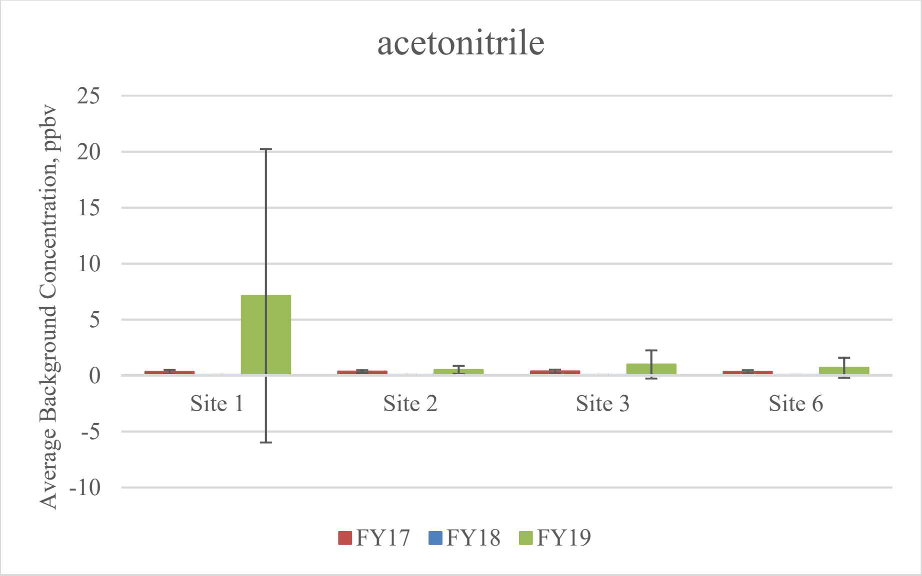

acetaldehyde
Average Background Concentration, ppbv
12
10
8
6
4
2
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

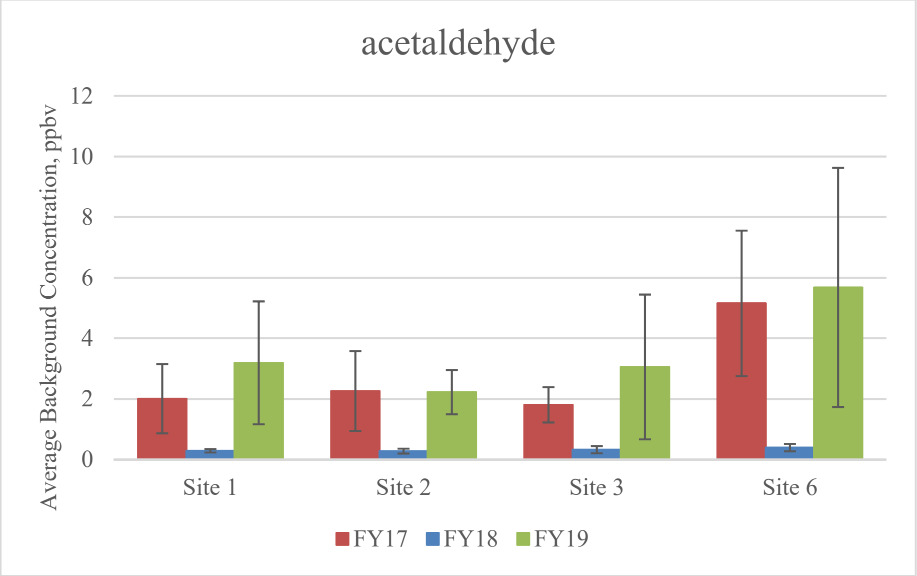

ethylamine
Average Background Concentration, ppbv
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

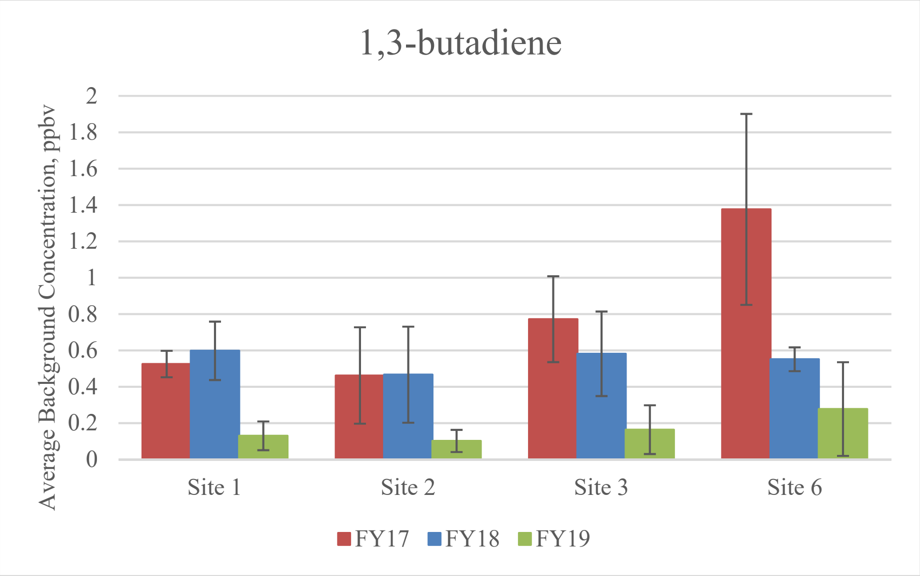

benzene
Average Background Concentration, ppbv
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

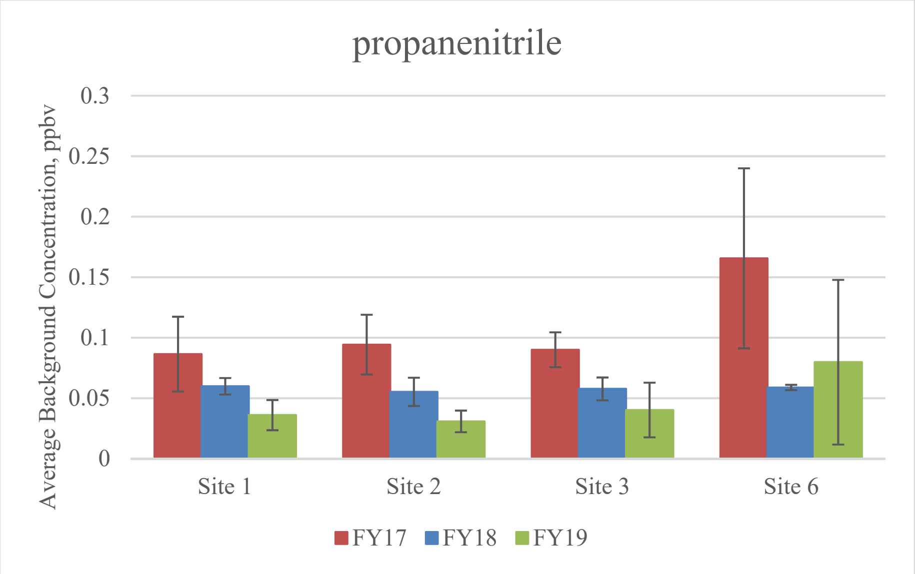

formaldehyde
Average Background Concentration, ppbv
3
2.5
2
1.5
1
0.5
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

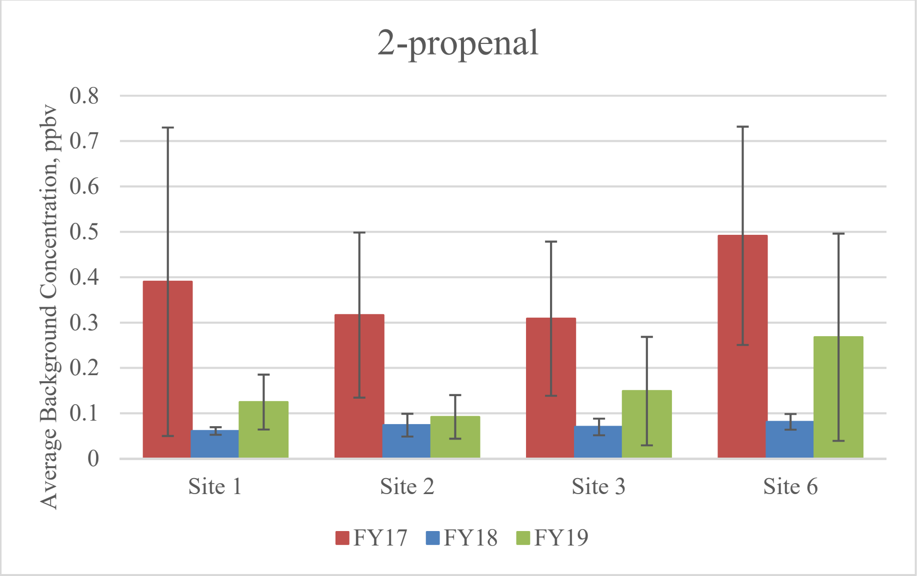

methanol
Average Background Concentration, ppbv
35
30
25
20
15
10
5
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

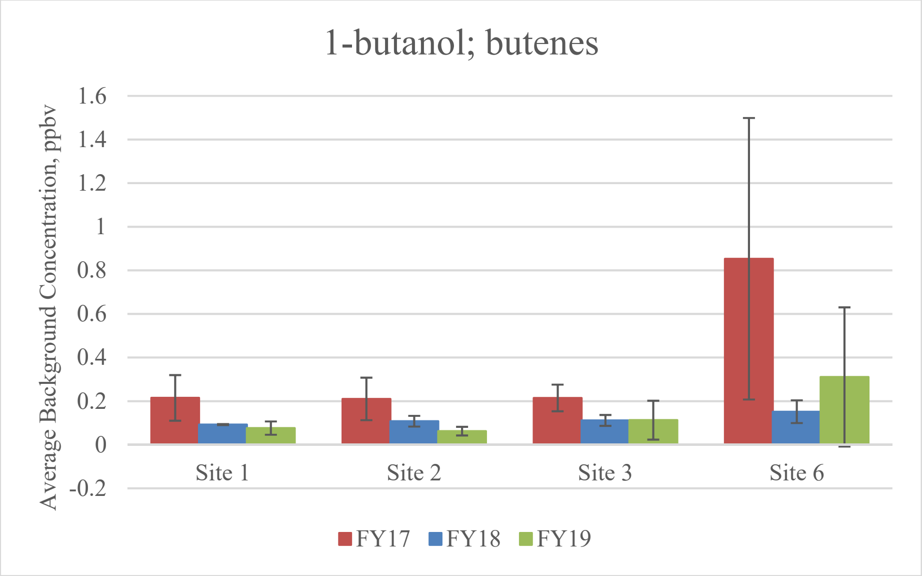

acetonitrile
Average Background Concentration, ppbv
25
20
15
10
5
0
-5
-10
Site 1
Site 2
Site 3
Site 6
🟥 FY17
🟦 FY18
🟩 FY19

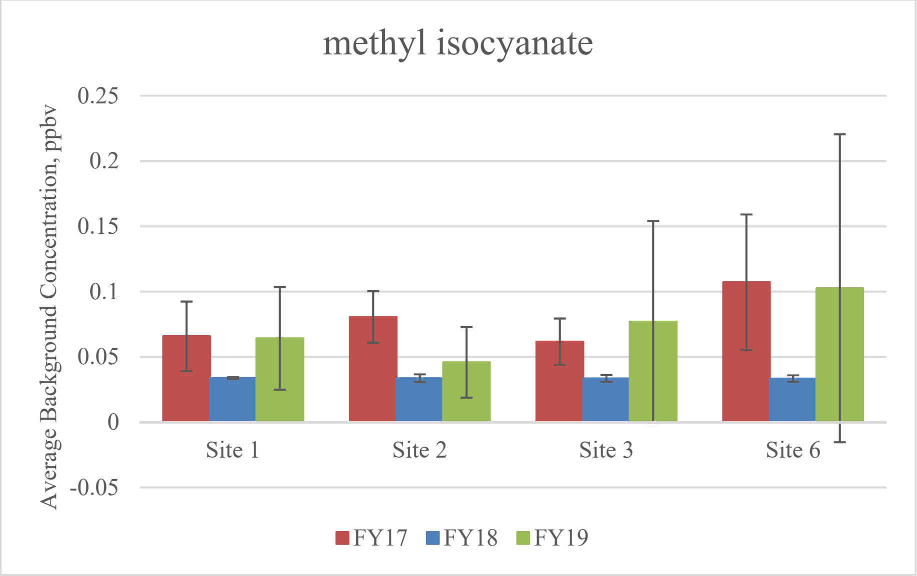

acetaldehyde
Average Background Concentration, ppbv
12
10
8
6
4
2
0
Site 1
Site 2
Site 3
Site 6
🟥 FY17
🟦 FY18
🟩 FY19

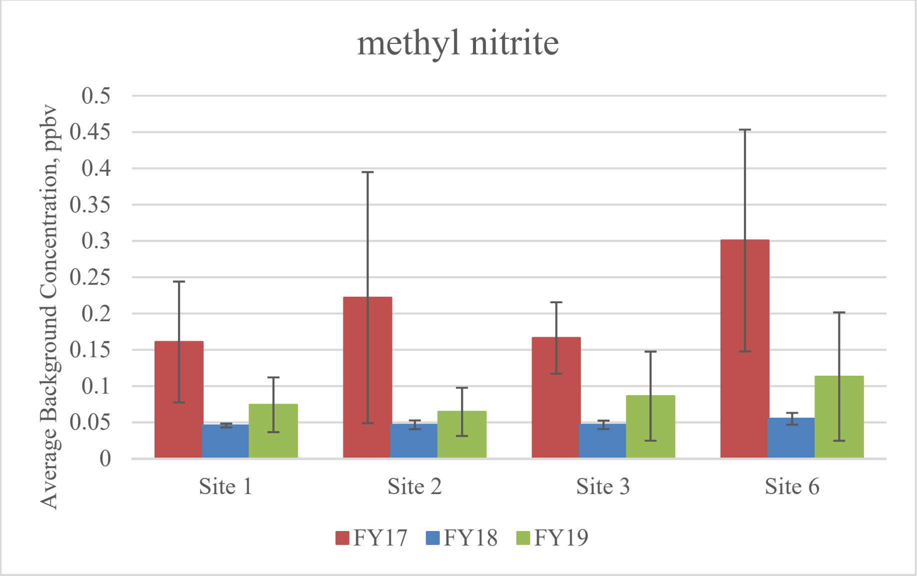

1,3-butadiene
Average Background Concentration, ppbv
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

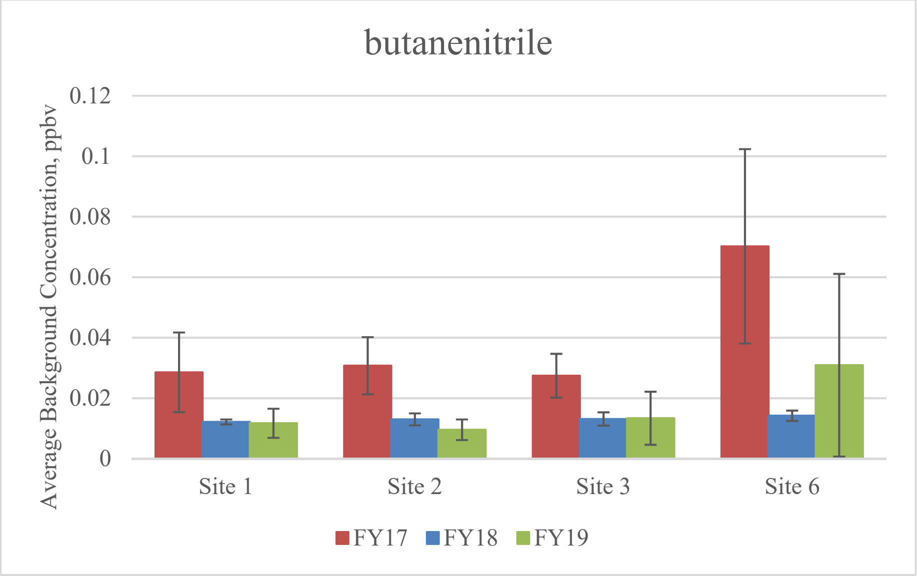

propanenitrile
Average Background Concentration, ppbv
0.3
0.25
0.2
0.15
0.1
0.05
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

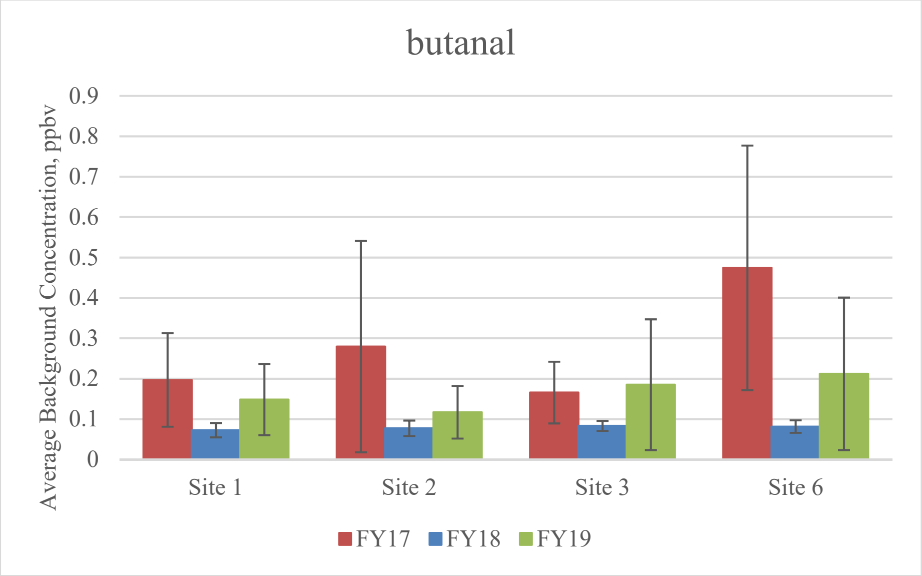

2-propenal
Average Background Concentration, ppbv
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

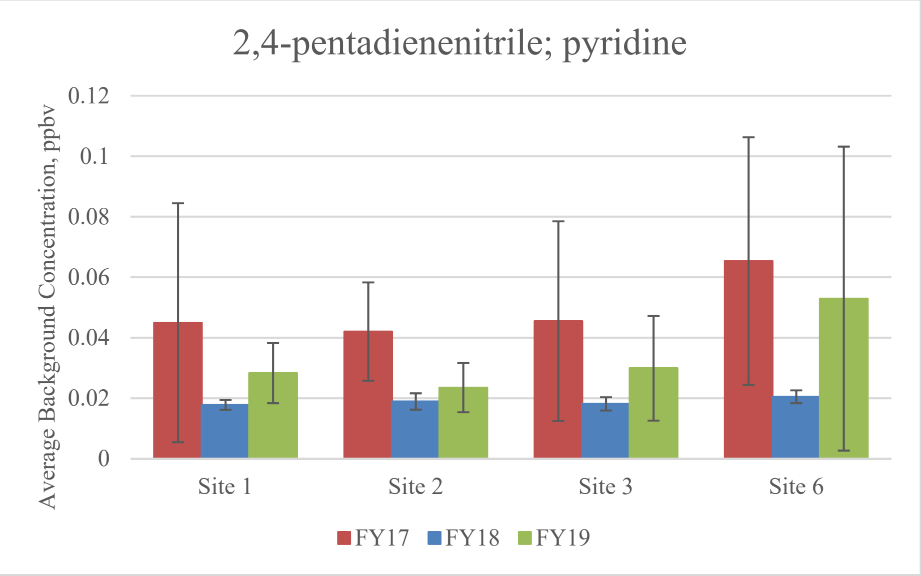

1-butanol; butenes
Average Background Concentration, ppbv
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

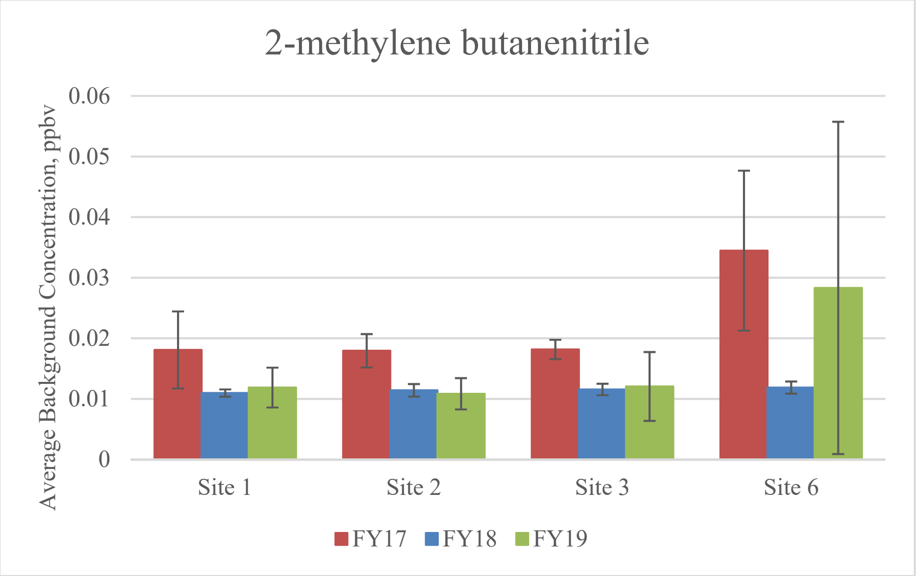

methyl isocyanate
Average Background Concentration, ppbv
0.25
0.2
0.15
0.1
0.05
0
-0.05
Site 1
Site 2
Site 3
Site 6
🟥 FY17 🟦 FY18 🟩 FY19

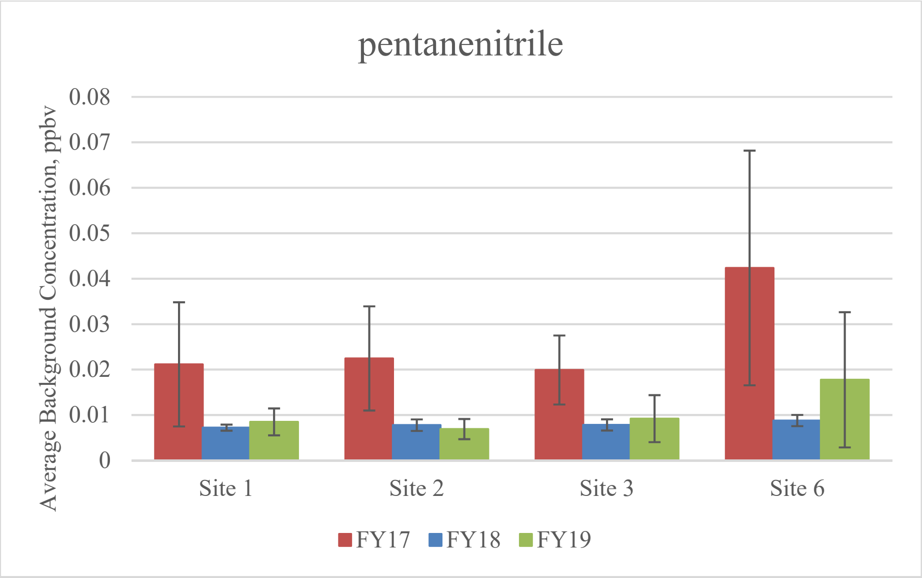

methyl nitrite
Average Background Concentration, ppbv
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Site 1
Site 2
Site 3
Site 6
🟥 FY17 🟦 FY18 🟩 FY19

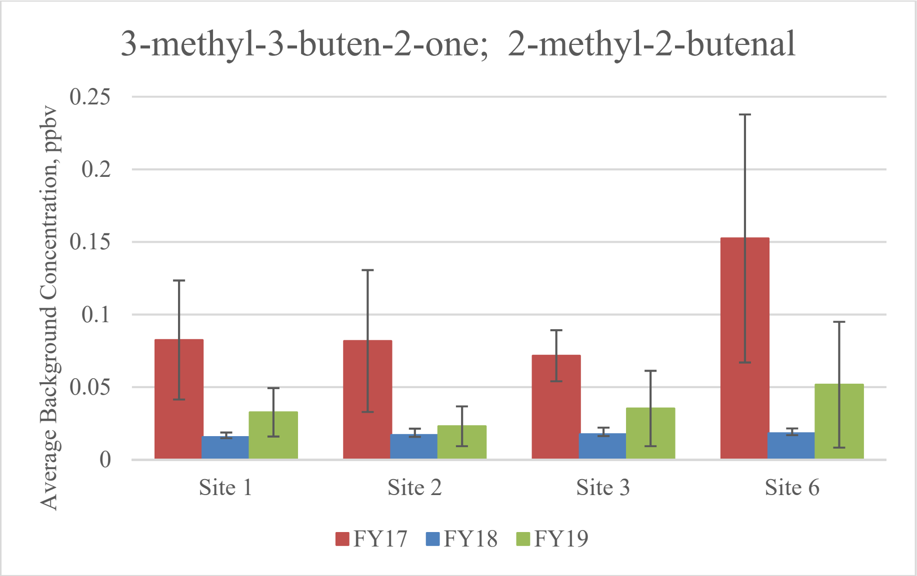

butanenitrile
Average Background Concentration, ppbv
0.12
0.1
0.08
0.06
0.04
0.02
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

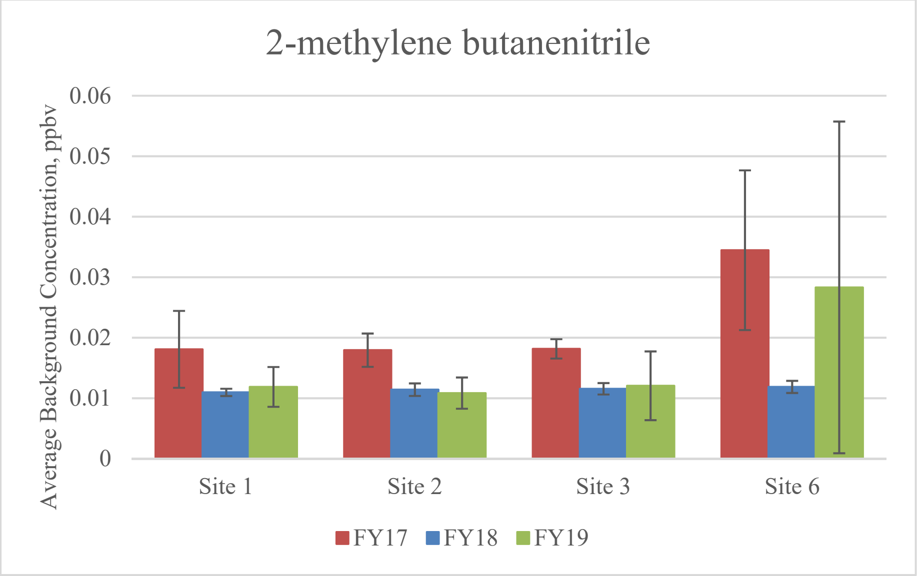

butanal
Average Background Concentration, ppbv
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

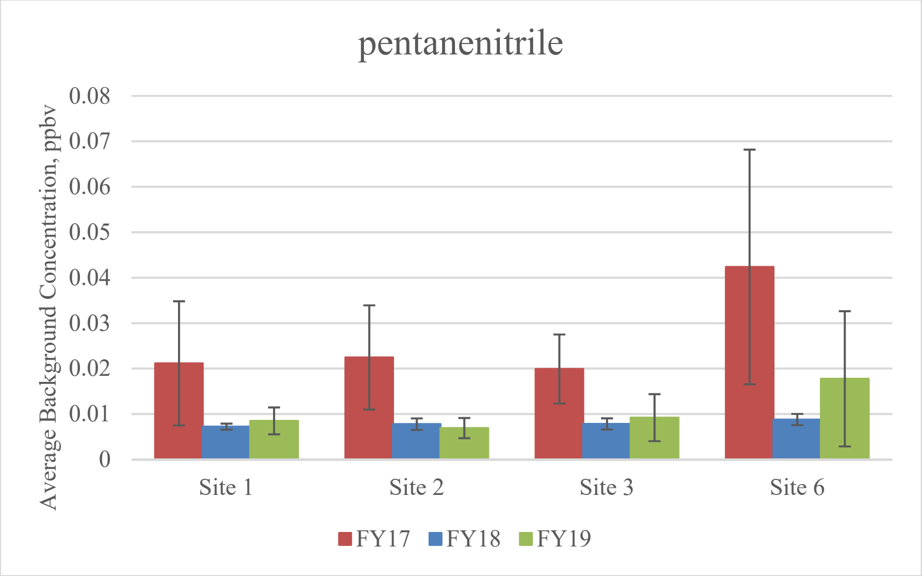

2,4-pentadienenitrile; pyridine
Average Background Concentration, ppbv
0.12
0.1
0.08
0.06
0.04
0.02
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

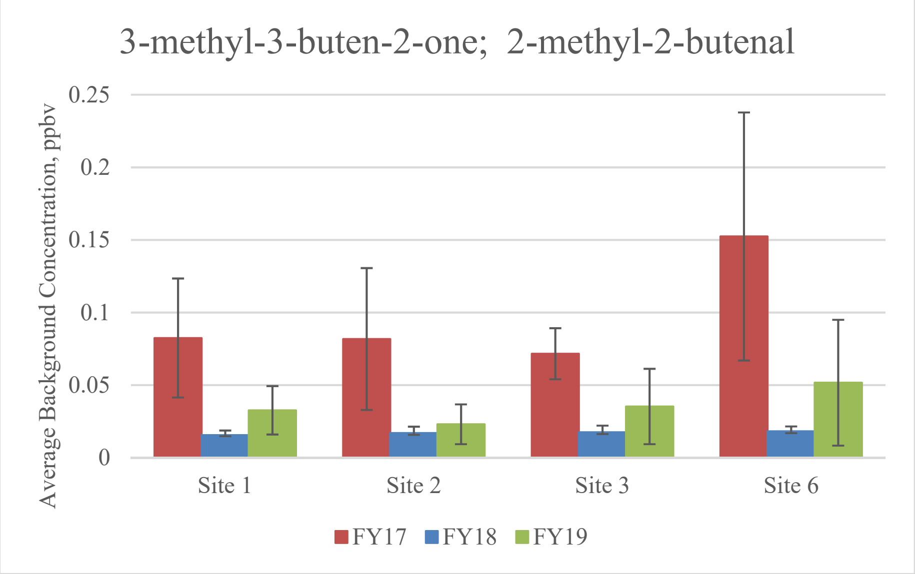

2-methylene butanenitrile
Average Background Concentration, ppbv
0.06
0.05
0.04
0.03
0.02
0.01
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

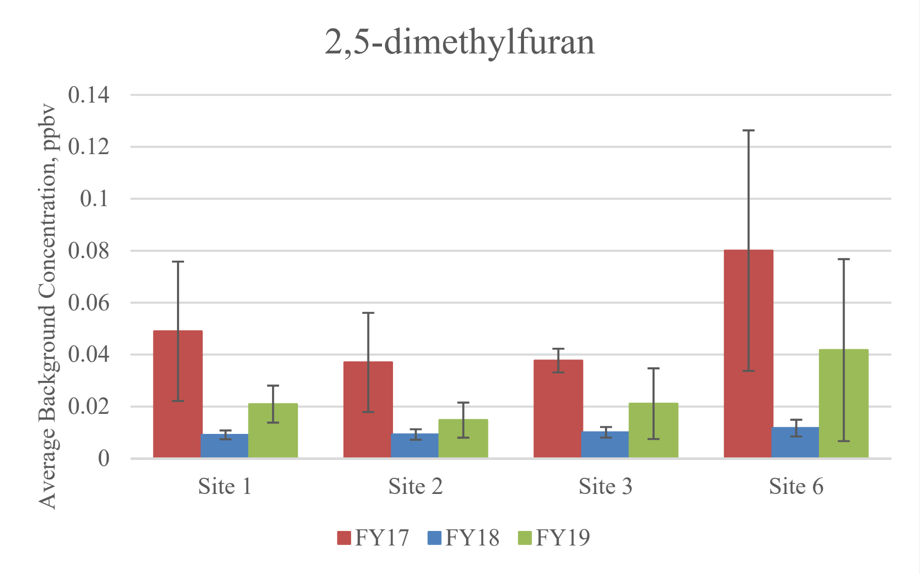

pentanenitrile
Average Background Concentration, ppbv
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

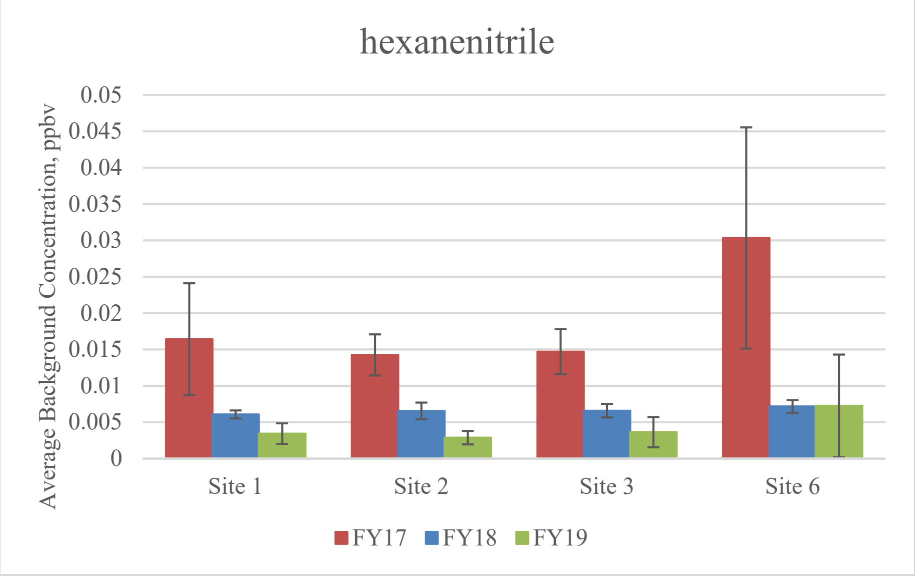

3-methyl-3-buten-2-one; 2-methyl-2-butenal
Average Background Concentration, ppbv
0.25
0.2
0.15
0.1
0.05
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

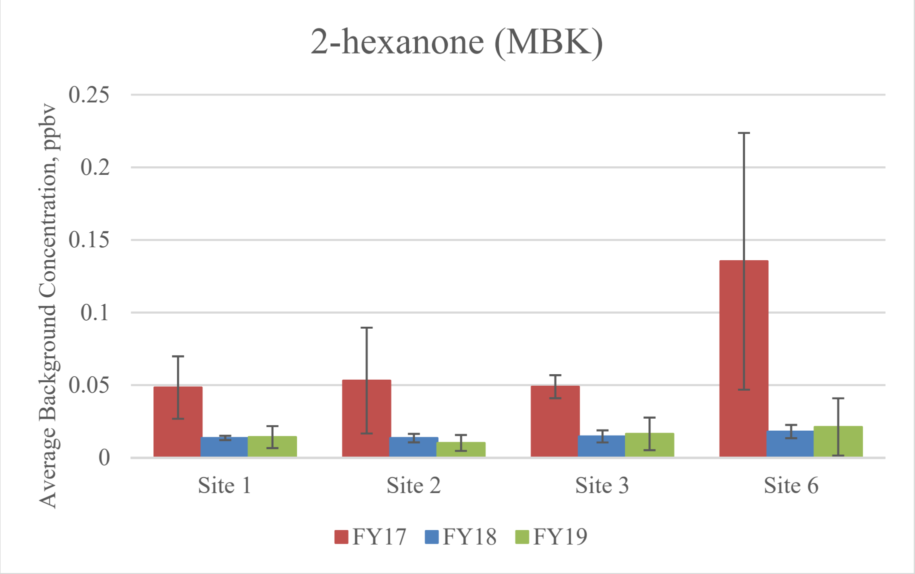

2-methylene butanenitrile
Average Background Concentration, ppbv
0.06
0.05
0.04
0.03
0.02
0.01
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

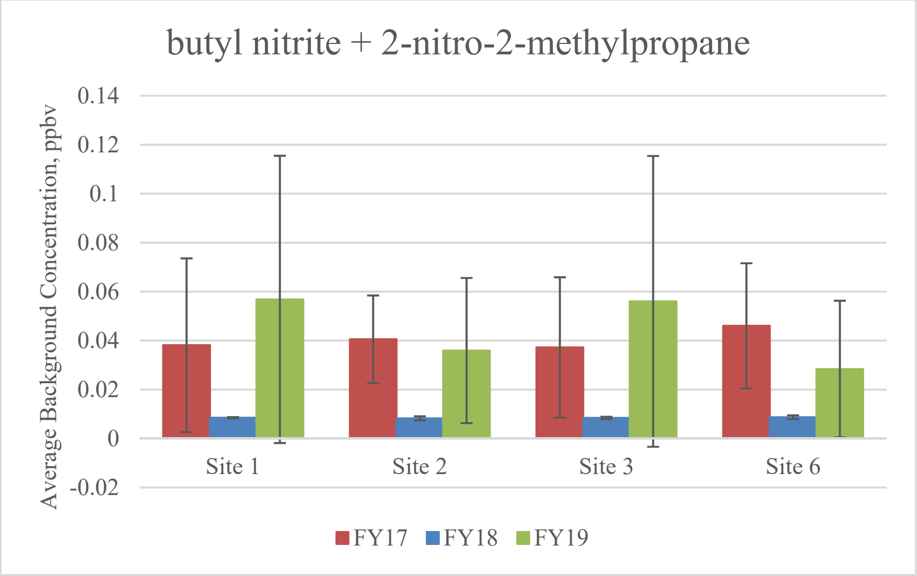

pentanenitrile
Average Background Concentration, ppbv
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

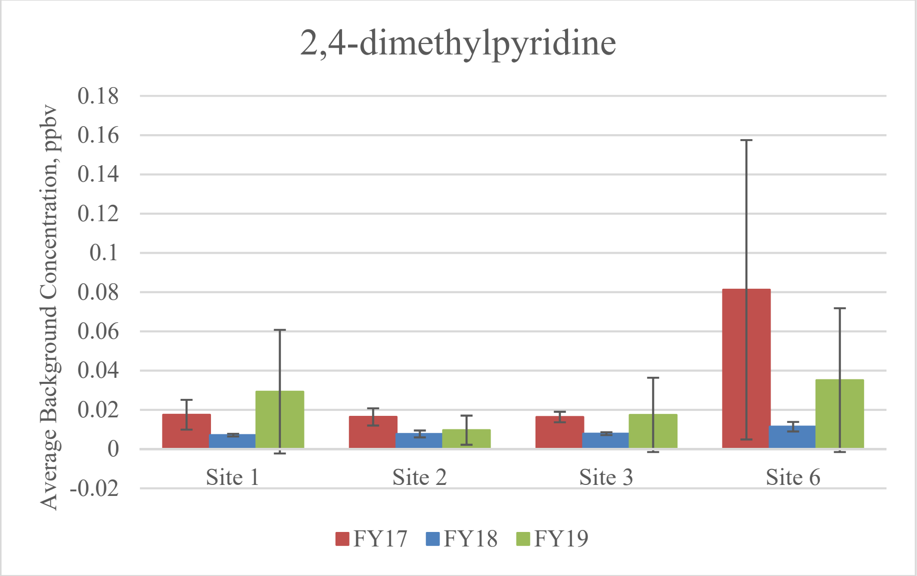

3-methyl-3-buten-2-one; 2-methyl-2-butenal
Average Background Concentration, ppbv
0.25
0.2
0.15
0.1
0.05
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

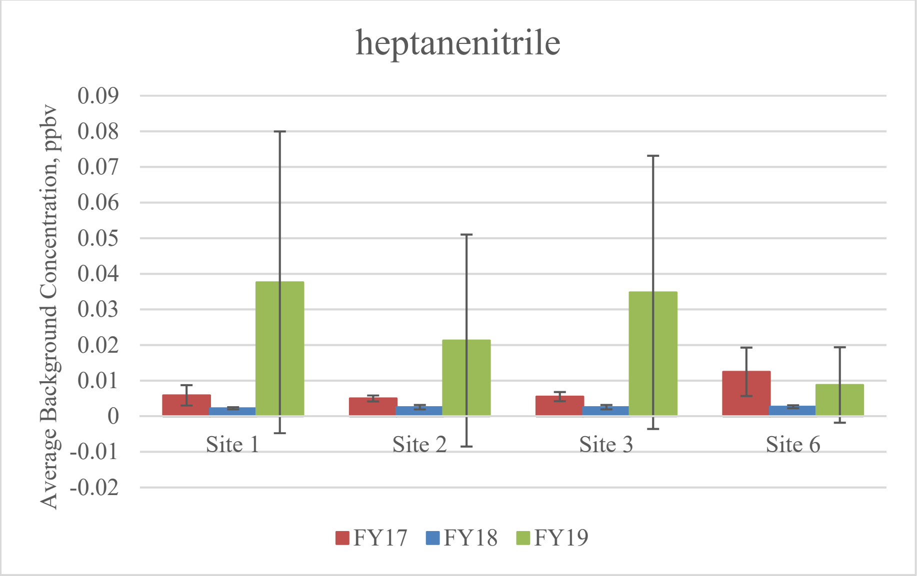

2,5-dimethylfuran
Average Background Concentration, ppbv
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

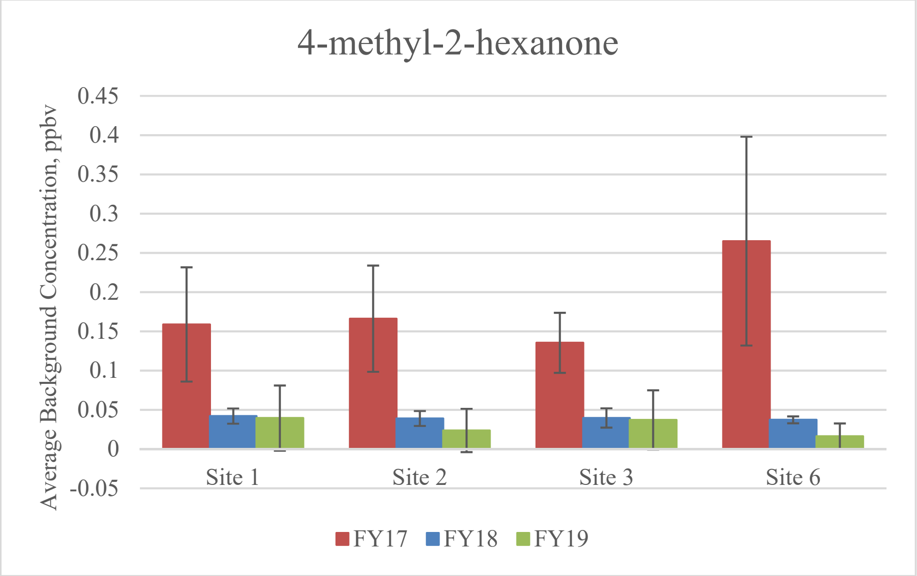

hexanenitrile
Average Background Concentration, ppbv
0.05
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

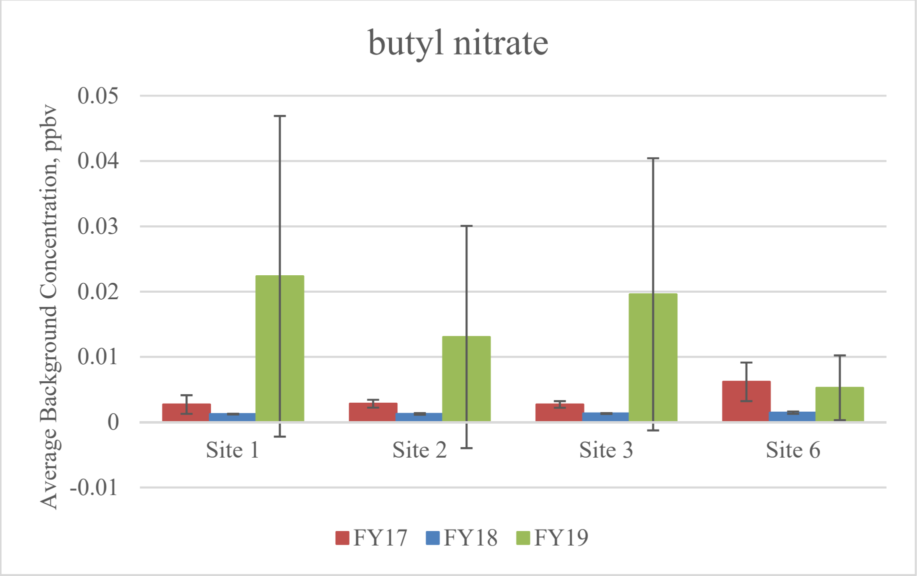

2-hexanone (MBK)
Average Background Concentration, ppbv
0.25
0.2
0.15
0.1
0.05
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

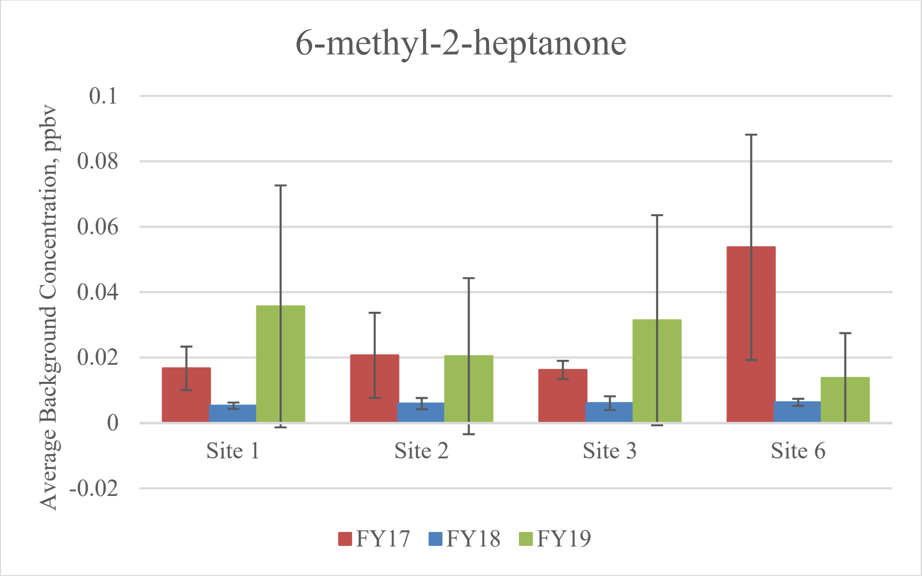

butyl nitrite + 2-nitro-2-methylpropane
Average Background Concentration, ppbv
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
-0.02
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

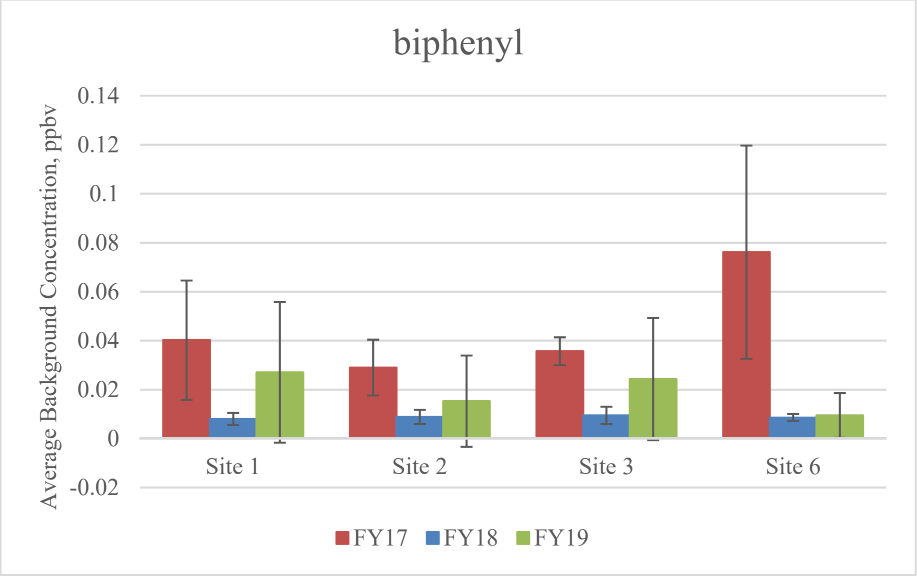

2,4-dimethylpyridine
Average Background Concentration, ppbv
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
-0.02
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

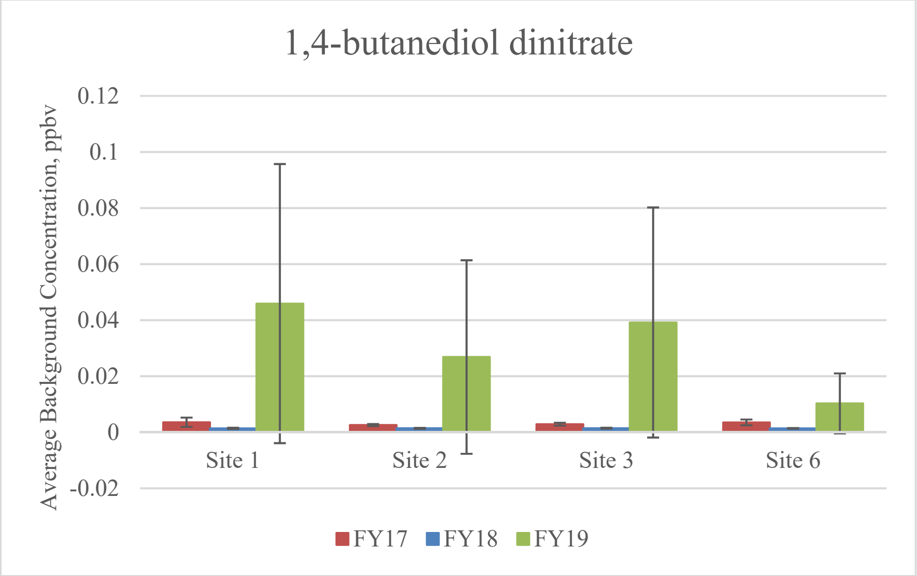

heptanenitrile
Average Background Concentration, ppbv
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
-0.01
-0.02
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

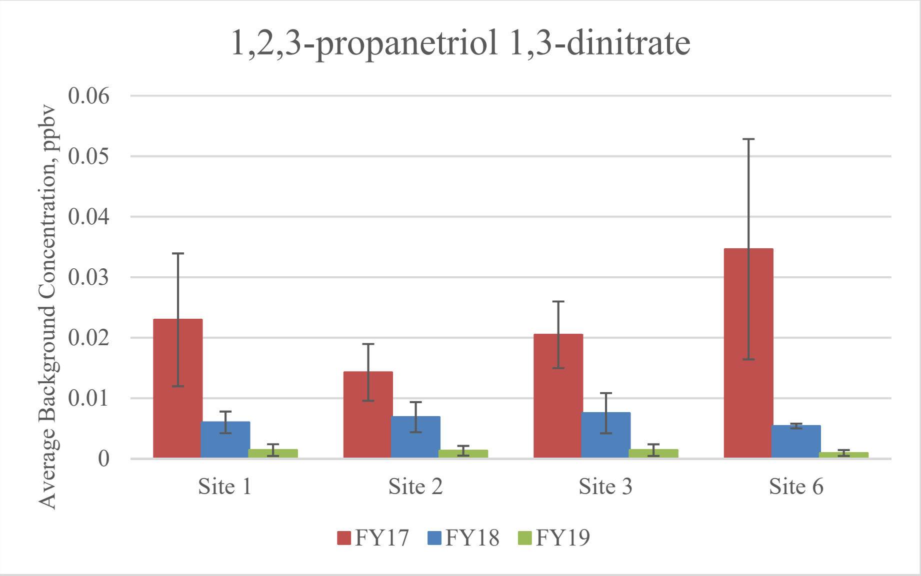

4-methyl-2-hexanone
Average Background Concentration, ppbv
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
-0.05
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

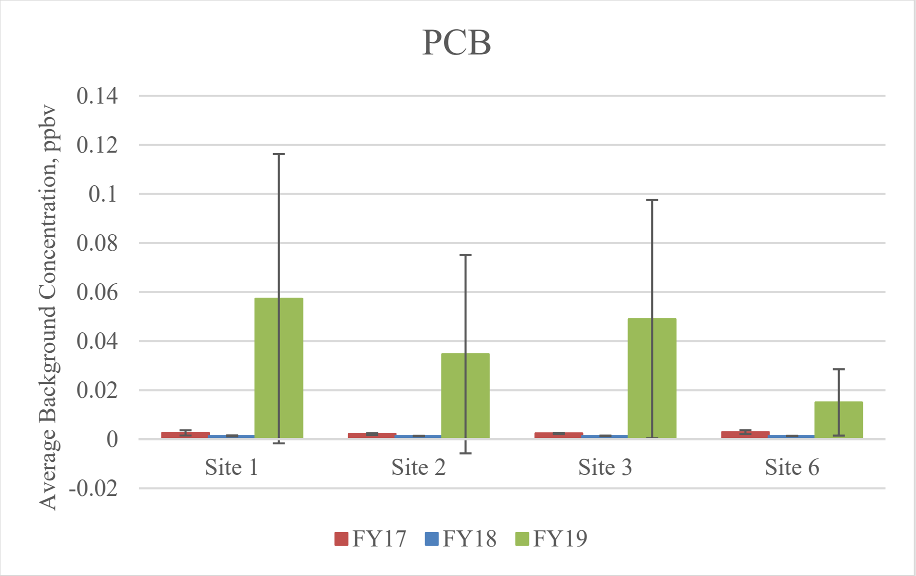

butyl nitrate
Average Background Concentration, ppbv
0.05
0.04
0.03
0.02
0.01
0
-0.01
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

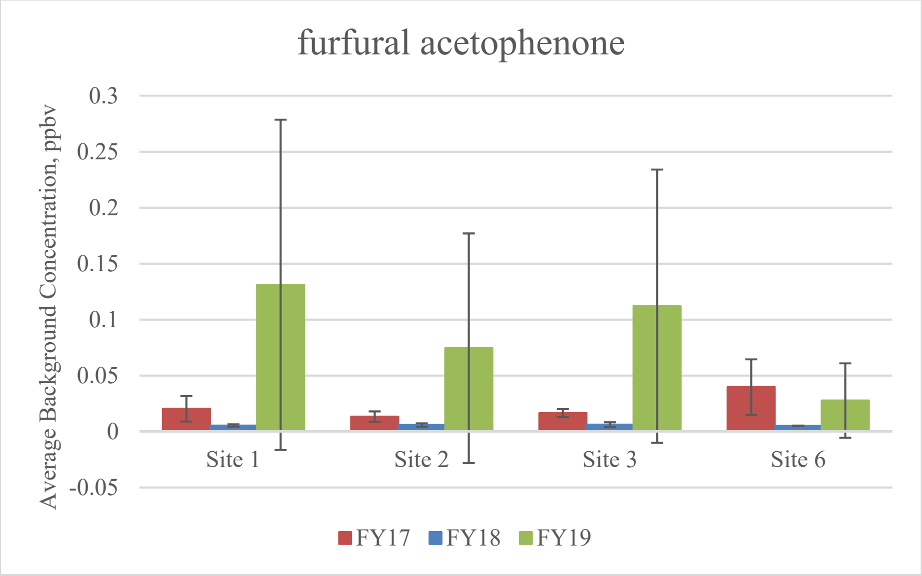

6-methyl-2-heptanone
Average Background Concentration, ppbv
0.1
0.08
0.06
0.04
0.02
0
-0.02
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19


biphenyl
Average Background Concentration, ppbv
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
-0.02
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19


1,4-butanediol dinitrate
Average Background Concentration, ppbv
0.12
0.1
0.08
0.06
0.04
0.02
0
-0.02
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19


1,2,3-propanetriol 1,3-dinitrate
Average Background Concentration, ppbv
0.06
0.05
0.04
0.03
0.02
0.01
0
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19


PCB
Average Background Concentration, ppbv
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
-0.02
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19


furfural acetophenone
Average Background Concentration, ppbv
0.3
0.25
0.2
0.15
0.1
0.05
0
-0.05
Site 1
Site 2
Site 3
Site 6
FY17
FY18
FY19

TerraGraphics

REVIEW COMMENT RECORD (RCR)

Project Number/Title.: 53005-81, Data Analysis for the Proton Transfer Reaction – Mass Spectrometer Mobile Laboratory		Page: 1 of 3
Document Number(s)/Title(s): 53005-81-RPT-032, PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report - Month 3	Reviewer(s): Eugene Morrey	Date: 2/5/2019

DISPOSITION CONCURRENCE/COMPLETION			
Reviewer Concurrence (Print & Sign): Eugene Morrey	Date:	Author/Originator Completion (Print & Sign): Todd Rogers/Anna Woehle Todd Rogers Anna Woehle	Date: 09/25/2019

Item No.:	Page/Section No.:	Reviewer Comments: (Provide Basis and Recommended Action)	Reviewer Initials:	Disposition: (Provide Justification if NOT Accepted)	Status:
1	Section 1.2, Site 1 in bolded list	Farm should be plural – “Farms”		Corrected. -AW	Complete
2	Section 1.2, Site 5 in bolded list	Official name is “Waste Treatment Plant.”		Corrected. -AW	Complete
3	Table 4-2	Table does not indicate units.		Added units (ppbv). -AW	Complete
4	Figure 5-2	I think we agreed that the m/z 35 was H2S and should be indicated in the figure.		Corrected in future reports. -AW	Complete
5	Section 5.2.1.3, First Paragraph	The main purpose of the off-line media samples is to help speciate the PTR-MS results and confirm the existence or lack of interfering compounds. This should be the primary discussion and the comparison of precision of easy to compare compounds should be secondary.		The problem with the off-line results shown in this section is that the TO-17, TO-11A and NIOSH 2522 methods are pushed beyond their reliable limits and it is believed their results are poor in quality compared to the more sensitive PTR-TOF. The focus on precision in this section is to highlight this fact, and to show they are not appropriate for identifying potential interferences in the PTR-TOF mass spectra. In general, the reviewer's comment is correct, but the off-line results were shown to be too poor in quality for use for their primary function. -TR	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 3
Document Number(s)/Title(s): 53005-81-RPT-032, PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report - Month 3	Reviewer(s): Eugene Morrey	Date: 2/5/2019

6	Section 5.2.1.5, Second Paragraph	Why is it assumed to be a positive bias and not the presence of interfering compounds?		This seems most likely since the peak deconvolution from the neighboring acetate peaks is near the limit of this instrument's ability to reliably quantify some of the nitrosamines. The detection limit seems more volatile as the peak deconvolution is, at times, more reliable than other times. The reviewer points out that it could also simply be an interfering compound at the same exact mass and this language as added as a second possible explanation. This would become clear with a comparative sample that the NIOSH method could confidently quantify. -TR	Complete
7	Table 5-7	For all sites, please check to see that the ammonia maximum is actually a peak or plume and not just an artifact of ammonia decay following calibration check.		Ammonia ax in Tables 5-7 through 5-12 are the total averages max values for all Site 1 through 6 visits. -AW	Complete
8	Section 5.2.4	George has requested a separate report to discuss the comparison between all four background studies. Please confirm with him as to whether he wants this section in this report or reserve it until the new report.		Confirmed with George Weeks. -AW	Complete
9	Section 5.2.5	I will provide this as soon as I get the analysis from Scott Cooley.		Received and updated. -AW	Complete

REVIEW COMMENT RECORD (RCR)

Project Number/Title.: 53005-81, Data Analysis for the Proton Transfer Reaction – Mass Spectrometer Mobile Laboratory		Page: 3 of 3
Document Number(s)/Title(s): 53005-81-RPT-032, PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report - Month 3	Reviewer(s): Eugene Morrey	Date: 2/5/2019

10	Section 6.1, First Paragraph	Identify this as acetonitrile. Acetonitrile is used as the solvent in the coating of the silica with DNPH. Residual acetonitrile comes off during sampling or storage. I have references if you want.		Corrected. -AW	Complete
11	Section 7.0, First Paragraph, Second Sentence	Add H2S.		Corrected. -AW	Complete
12	Section 7.0, Second Paragraph, First Sentence	Start confirmatory sample discussion with conclusions regarding resolution of interference issues - even if inconclusive.		The fact that the bulk of the off-line analysis was non-detect essentially becomes the story here rather than the identification of any previously unknown interferences. See Sections 5.2.1.2, 5.2.1.3, 5.2.1.4, 5.2.1.5. -TR	Complete
13	Section 7.0, Fourth Paragraph	Consult with George to see if this paragraph stays.		Paragraph not removed. -AW	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-032, PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report -Month 3	Reviewer(s): George Weeks	Date: 2/4/2019

DISPOSITION CONCURRENCE/COMPLETION

Reviewer Concurrence (Print & Sign): George Weeks	Date:	Author/Originator Completion (Print & Sign): Anna Woehle Anna Woehle	Date: 09/26/2019

Item No.:	Page/Section No.:	Reviewer Comments: (Provide Basis and Recommended Action)	Reviewer Initials:	Disposition: (Provide Justification if NOT Accepted)	Status:
1	Section 2.0	Much of Sections 2 and 4 have been copied directly from all of the previous monthly reports. If you have discussed this in previous months, please reference the appropriate monthly report and then describe any pertinent changes. It is not necessary to repeat this information in every report. This makes it hard to focus on the changes rather than things that have remained the same from the beginning of the contract.		Determined in previous meetings: monthly reports are standalone reports and keeping Sections 2.0 through 4.0 allows for greater comprehension. -AW	Complete
2	Section 5.2.1.5, First Paragraph, First Sentence	Shouldn't DNPH be Thermosorb/N?		Corrected. -AW	Complete
3	Section 5.2.1.5, First Paragraph, Pg. 30	Thought we were talking about NIOSH-2522.		Corrected. -AW	Complete
4	Section 5.2.4, Second Paragraph	This is a direct copy of a previous paragraph. Rather than repeat it, just reference the previous paragraph and just restate the bottom line.		Removed repetitive statements. -AW	Complete

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-032, PTR-MS Mobile Laboratory Vapor Monitoring Monthly Report -Month 3	Reviewer(s): George Weeks	Date: 2/4/2019

5	Section 5.2.4, Fifth Paragraph, Fourth Sentence	Suggest: “In addition, higher average concentrations were observed at Site 6.”		Corrected. -AW	Complete
6	Section 5.2.4, Fifth Paragraph, Fifth Sentence	Delete, “as much before detection.”		Corrected. -AW	Complete
7	Section 7.0, Third Paragraph, First Sentence	Am I misreading this or are Site 4 and Site 6 reversed?		Corrected. -AW	Complete
8	Section 7.1, First Bullet	We need to discuss this before we put it in a report as a recommendation. At first pass, I disagree with the recommendation. Further, recommendations are tracked through the PER system, which increases everyone’s workload.		Removed. -AW	Complete
9	Section 7.1, Second Bullet	I agree for several reasons; not the least of which is the acetonitrile contamination problem. However, please don’t make this a recommendation in the report.		Removed. -AW	Complete
10	Section 7.1, Third Bullet	Where did this come from? I don’t see anything in the report that leads to this recommendation. Please remove.		Removed. -AW	Complete