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006	Monthly Report 1							00

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Chemical Vapor Initiative
1.0 Monthly Report, Rev. 0

January 2017

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Submittal Number: 61485-006

Project Number: 61485

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EXECUTIVE SUMMARY

A mobile vapor monitoring laboratory developed by RJ Lee Group, Inc. was used for a field campaign study occurring over the course of several weeks between December 9, 2016 and January 17, 2017, in support of the Chemical Vapor Initiative by Washington River Protection Solutions, LLC (WRPS).

The work was based on Statement of Work #292684 “Proton Transfer Reaction-Mass Spectrometer Mobile Laboratory,” Rev. 0, and dated August 8, 2016. Subcontract #61485 was awarded on October 26, 2016. The contract consists of 52 weeks of continuous laboratory operations throughout the 200 East area of the Hanford site. These weeks of laboratory sampling take place primarily during the day shift; however, there are activities that require the time of sampling to take place during off-shift hours on occasion, as well as during any activities directed by WRPS, such as AOP-015 events. In particular, this report includes the results of analysis over 16 days of monitoring during the day-shift hours and 4 days during the off-shift hours.

The original objective of the mobile laboratory and Proton Transfer Reaction Mass Spectrometer (PTR-MS) system was to provide supportive data for the various direct reading instruments deployed by the Vapor Monitoring Group. The monitoring and results included in this report pertain to Waste Retrieval activities performed regarding AY-102 Recovery. Several of these monitoring shifts occurred both during day-shift hours as well as off-shift hours.

A mobile laboratory containing a PTR-MS has been utilized to support vapor monitoring activities at the tank farms. The PTR-MS measurement campaign has detected several local vapor incidences occurring on any given day. There were certain instances where occupational exposure limits were approached or exceeded for specific compounds. Numerous point sources of vapor emissions have been observed in the general area of the tank farms, particular those around the AP and AY Tank Farms that contribute to the overall vapor burden. The discovery of and observation of vapor plumes, previously undetected by the former technologies and approaches, has demonstrated the effectiveness of PTR-MS as an analytical tool for this application.

The improved mass resolution of the PTR-TOF 4000 allows for the independent detection of two COPCs that interfered with one another in 2016; 2-octylfuran (m/z=181.159) and 1,4-butanediol dinitrate (m/z=181.046) as well as furan (m/z = 69.034) and isoprene (m/s = 69.070). In all, there are 45 ion signals assigned to the COPCs, which represent a total of 52 compounds. Although there are 59 COPCs, seven are incompatible with the measurement process applied to this project. These compounds are: ammonia, nitrous oxide, mercury, tributylphosphate, dibutylbutylphosphonate, 2-fluoropropene, and diethyl phthalate.

Though the statement of work for this campaign called for the identification of local vapor sources (Statement of Work #292684), WRPS' Data Quality Objective (DQO) Group and the Fugitive Emissions/Source Apportionment Sub-team were still developing a strategy to accurately pursue a process to monitor and identify these vapor sources. This strategy had not yet been finalized by the time the retrieval activities took place nor by the completion of this monthly report.

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List of Terms

amu	atomic mass unit
AOP-015	abnormal operating procedure related to chemical odors and changing conditions in tanks
CAPA	Corrective Action-Preventative Action
CBAL	Columbia Basin Analytical Laboratory
COPC	chemical of potential concern
DQO	Data Quality Objective
DOE	U.S. Department of Energy
FY	Fiscal Year
GC-MS	Gas Chromatography - Mass Spectrometry or Spectrometer
GC-TEA	Gas Chromatography - Thermal Energy Analysis
HPLC-UV	High Performance Liquid Chromatography - Ultraviolet
LCU	liquid calibration unit
ML	Mobile Laboratory
NDEA	N-nitrosodiethylamine
NDMA	N-nitrosodimethylamine
NEMA	N-nitrosoethylmethylamine
NIOSH	National Institute for Occupational Safety and Health
NMOR	N-nitrosomorpholine
OEL	occupational exposure limit
PCB	polychlorinated biphenyl
PFA	perfluoroalkoxy alkanes
ppbV	parts per billion by volume
pptV	parts per trillion by volume
PTR-MS	proton transfer reaction spectrometry or spectrometer
PTR-TOF	proton transfer reaction - time of flight
QA	Quality Assurance
sccm	standard cubic centimeters per minute
TOF-MS	time of flight - mass spectrometer
VOC	volatile organic compound
WRPS	Washington River Protection Solutions, LLC

1.0 INTRODUCTION

As part of an ongoing campaign in support of the Chemical Vapor Initiative by the U.S. Department of Energy (DOE) contractor, Washington River Protection Solutions, LLC (WRPS), RJ Lee Group's Mobile Organic Monitoring Laboratory (hereafter referred to as the Mobile Laboratory) was used over the course of a five-week period spanning from December 9, 2016, to January 17, 2017. This Mobile Laboratory was used to measure levels of airborne concentrations of potential waste vapors within the Hanford site atmosphere.

The work was based on Statement of Work #292684, "Proton Transfer Reaction-Mass Spectrometer Mobile Laboratory," Rev. 0, and dated August 8, 2016. Subcontract #61485 was awarded on October 26, 2016. The contract consists of 52 weeks of continuous laboratory operations throughout the 200 East area of the Hanford site. These weeks of laboratory sampling primarily took place during the day shift, however there are activities that required sampling to take place during off-shift hours on occasion, as well as during any activities directed by WRPS, such as AOP-015 events. In particular, this report includes the results of analysis over 16 days of monitoring during the day-shift hours and four days during the off-shift hours.

Description of tests that were conducted are as follows:

- Week 1.1
    - Monitoring was focused on AY-102 retrieval and the AP farm and was performed only during day shifts. Weather data are not available for December 9, 2016. Details for this incident are explained in Section 5.2.
- Week 1.2
    - Monitoring of AY, AP, and greater east tank farm areas, and was performed only during night-shift hours. On December 22, 2016, and December 26, 2016, proton transfer reaction - time of flight (PTR-TOF) data are unavailable for one hour due to an unknown instrument communication error. On December 28, 2016, no CO_2 data were collected. Details for this incident are explained in Section 5.1.
- Week 1.3
    - Monitoring was focused on the AP Farm and was performed only during day shifts.
- Week 1.4
    - Monitoring was focused on the AP Farm located in 200 East area and was performed during day shifts only.
- Week 1.5
    - Monitoring was focused on the AP Farm located in 200 East area and was performed during day shifts only. On January 15, 2017, one hour of PTR-MS data are unavailable.

The main task during this monthly period was to define the protocol for deploying the Mobile Laboratory during AY-102 retrieval operations. To perform this task, the Mobile Laboratory was deployed during AY-102 retrieval operations to monitor the status of chemical vapors in the retrieval area as well as other areas of interest. The task was successfully completed, and experience from this monthly period resulted in the generation of two Corrective Actions-Preventive Actions (CAPAs), 1665 and 1667. These CAPAs were generated to ensure greater completeness of data acquired in future monitoring periods. Further details concerning these CAPAs can be found in Section 5.

Appendices for this document contain graphs, statistic tables, and weekly reports during this month, as well as Certificates of Analysis for the PTR-MS and Gas Chromatography - Mass Spectrometer (GC/MS). They are as follows:

- Appendix A
    - Certificates of Analysis
- Appendix B
    - Month 1.0 Daily Graphs with OEL Scale
- Appendix C
    - Month 1.0 Daily Graphs with Auto Scale
- Appendix D
    - Month 1.0 Histograms
- Appendix E
    - Month 1.0 COPC Statistical Analysis
- Appendix F
    - Month 1.0 Local Sources

This report structure is based on reporting requirements, as defined in the original statement of work.

2.0 MEASUREMENT SYSTEM DESIGN

This section describes the details of the sampling methods used during this monitoring campaign, as well as the instrumentation and confirmatory measurements.

2.1 SAMPLING METHODS

The Mobile Laboratory (ML) is housed in a Mercedes Sprinter Van that has been retrofitted with the necessary power lines, gas plumbing, and communications wiring to support a variety of instruments used in the real-time measurement of volatile constituents in air. The van is capable of maintaining internal temperatures for instrument operation and worker comfort, and has the option of utilizing either shore power or on-board diesel generator power for operation of the instruments. The vehicle is diesel powered which is advantageous as diesel exhaust is generally lower in volatile organic compound (VOC) emissions as compared to gasoline exhaust. The issue of van emissions is further mitigated by positioning of the van to avoid sampling ML-generated emissions.

The ML sample collection lines are designed to sample air from either of two locations. Measurements for this monthly report utilize only the collection line located above the wind shear zone of the van for on-the-road, real-time collection and analysis of emission excursion. Both mobile and stationary monitoring were performed in the measurements for this monthly period. The other sampling interface is located on the side of the van and is used for stationary measurements only. Air samples are pulled into the sampling system by an oil-free diaphragm pump. The pumping of the air sample is controlled by a needle valve located after a digital flow meter that is in series with the flow stream which are co-located after the analytical sampling stations. The 3/8” perfluoroalkoxy alkanes (PFA) tubing is generally pumped at a volumetric flow rate of approximately 20-25 liters per minute which corresponds to a linear velocity of approximately 12 meters per second.

Both lines interface to the PFA Teflon internal gas manifold which connects to the PTR-MS or auxiliary sampling stations. At this point, the sample enters the PTR-MS. Section 2.2.1 describes how the sample is processed through the PTR-MS.

For further details on the Mobile Laboratory’s structure, please refer to the Project Test Plan, Requisition #283842.

2.2 INSTRUMENTATION AND METHODS USED

2.2.1 Instrumentation

The PTR-MS TOF-4000 is used to quantify chemicals of potential concern (COPCs) from the sampled air. The sampled air enters the PTR drift tube. In the drift tube, VOCs with proton affinities greater than water undergo chemical ionization via a fast proton transfer reaction using the reagent ion, hydronium. The hydronium is produced from water vapor via a series of reactions in the hollow cathode PTR ion source. This is a soft ionization method and VOC fragmentation is minimized. These ionized compounds and hydronium then travel through the drift tube to the transfer lens system, subsequently entering the time of flight - mass spectrometer (TOF-MS) where they are separated by mass and monitored. The signal from the TOF-MS is used to identify the VOCs based on their mass, as well as to calculate individual compound concentration based on the ratio of compound signal to hydronium signal.

2.2.2 Methods Used

Two methods of COPC quantification are available with the PTR-MS TOF-4000. The method utilized in this project is based on kinetic properties and quantifies COPC concentration based on the use of relative ion signals of target compound versus that of the reagent ion with an applied reaction rate constant. This method is advantageous because it does not require calibration curves of compounds with authentic standards. This project monitors a variety of COPCs of which the stability of gas phase standards is frequently unknown. The only requirement is the analysis of a VOC free air blank and a standard which provides the data necessary of verification of sensitivity.

Rate constants used for this method are based on reference document; Cappellin, L.; Karl,T.; Probst, M.; Ismailova, O.; Winkler, P. M.; Soukoulis, C.; Aprea, E.; Märk, T.D.; Gasperi, F.; Biasioli, F. On Quantitative Determination of Volatile Organic Compound Concentrations Using Proton Transfer Reaction Time-of-Flight Mass Spectrometry. Environ. Sci. Technol. 2012, 46 (4), 2283–2290. These values are shown below in Table 2-1.

Table 2-1. PTR-MS Kinetic Rate Constants.

Compound	**k_c**
ammonia	2.28
formaldehyde; NO+	2.00
methanol	2.69
acetonitrile	4.74
acetaldehyde	3.36

Compound	**k_c**
ethylamine	1.97
hydronium hydrate; 1,3-butadiene	2.00
propanenitrile	2.00
1-butanol; butenes	2.16
methyl isocyanate	2.00
methyl nitrite	2.00
Furan; isoprene	1.7
butanenitrile	2.00
3-buten-2-one (MVK); 2,3-dihydrofuran; 2,5-dihydrofuran	4.1
butanal	3.11
N-nitrosodimethylamine (NDMA)	2.00
benzene	1.93
2,4-pentadienenitrile; pyridine	2.00
2-methylene butanenitrile	2.00
2-methylfuran	2.00
pentanenitrile	2.00
3-methyl-3-buten-2-one; 2-methyl-2-butenal	2.00
N-nitrosomethylethylamine (NEMA)	2.00
2,5-dimethylfuran	2.00
hexanenitrile	2.00
2-hexanone (MBK)	2.00
N-nitrosodiethylamine (NDEA)	2.00
butyl nitrite; 2-nitro-2-methylpropane	2.00
2,4-dimethylpyridine	2.00
2-ethyl-5-methylfuran; 2-propylfuran	2.00
heptanenitrile	2.00
4-methyl-2-hexanone	2.00
N-nitrosomorpholine (NMOR)	2.00
butyl nitrate	2.00
2-ethyl-2-hexenal; 4-(1-methylpropyl)-2,3-dihydrofuran; 3-(1,1-dimethylethyl)-2,3-dihydrofuran	2.00
6-methyl-2-heptanone	2.00
2-pentylfuran	2.00

Compound	**k_c**
biphenyl	2.00
2-heptylfuran	2.00
1,4-butanediol, dinitrate	2.00
2-octylfuran	2.00
1,2,3-propanetriol, 1,3-dinitrate	2.00
PCB ($C_{12}H_9Cl$)	2.00
6-(2-furanyl)-6-methyl-2-heptanone	2.00
furfural acetophenone (3-(2-furanyl)-1-phenyl-2-propen-1-one)	2.00
PCB ($C_{12}H_8Cl_2$)	2.00

2.3 CONFIRMATORY MEASUREMENTSMEASUREMENTS

While PTR-MS technology can provide near real-time measurements of COPCs and is sensitive to mass, it is not sensitive enough to distinguish between compounds of similar mass. It also is limited to compounds with a proton affinity greater than that of water. More traditional techniques, such as GC/MS, High Performance Liquid Chromatography - Ultraviolet (HPLC-UV), and Gas Chromatology - Thermal Energy Analysis (GC-TEA) technology cannot provide real-time measurements, but are capable of distinguishing complex mixtures of compounds with similar molecular formulae. The GC/MS uses a harder form of ionization for sampled compounds, thus creating unique fracturing patterns that can be identified definitively. Method TO-11a is an HPLC-UV method that is very selective for certain aldehydes and ketones. Method National Institute for Occupational Safety and Health (NIOSH) 2522 is a GC-TEA method that is very selective and sensitive to nitrosamines.

No air samples were obtained on alternate media for analysis by GC/MS or other methods. It was of the professional discretion of the analyst operating the Mobile Laboratory at the time of the PTR-MS measurements that there were no measureable signals (peak intensity and/or time duration) that would provide responses above a reporting limit by either TO-15 (air canisters) or TO-17 (thermal desorption tubes). This is based on the reporting limits established by the 222-S Laboratory for the respective methods; 5 ppbv for air canisters and 5 ng/component for thermal desorption tubes. No samples were analyzed using GC/MS, HPLC, or GC-TEA during this monthly period. During periods when samples are analyzed, they would simultaneously be collected manually on the appropriate solid air sampling media and in air canisters. These samples would then be analyzed using methods TO-11a, TO-15, TO-17, and NIOSH 2522 as appropriate for the VOCs of interest.

3.0 SENSITIVITY MEASUREMENTS

This section describes the sensitivity measurements for the PTR-MS, the GC/MS, and discusses the COPCs that are assigned to ion signals in the PTR-MS.

3.1 PROTON TRANSFER REACTION-MASS SPECTROMETER (PTR-MS)

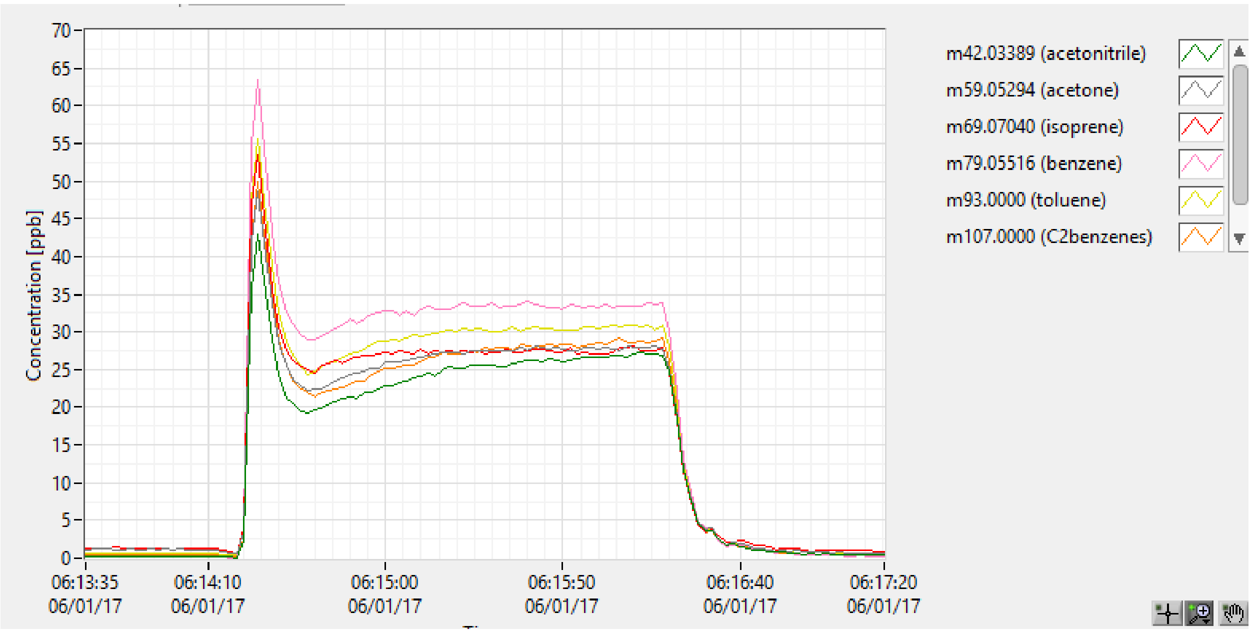
The PTR-TOF 4000 instrument used in Fiscal Year (FY) 2017 field activities provides more mass resolution than the PTR-TOF 1000 model used in 2016. This allows many COPCs to be resolved from potential interfering compounds at the same nominal mass, although some COPCs are still susceptible to interfering compounds. This can manifest in a few different ways. Either an interfering compound can appear sporadically and create false positives for COPCs or a continuous presence of an interfering compound can cause elevated perceived ambient air concentrations for a COPC. The first month of deployment of the PTR-TOF 4000 has provided enough information to better predict the accuracy of the estimated COPC concentrations. Specific comparison to the performance of the PTR-TOF 1000 used in 2016 will be made when applicable. Potential interfering compounds will be discussed in Section 3.3 when they are recognized but it is important to remember that any isomeric compounds will cause interference resulting in elevated estimated concentrations. It is impossible to predict all possible interferences theoretically.

The improved mass resolution of the PTR-TOF 4000 also allows for the independent detection of two COPCs that interfered with one another in 2016; 2-octylfuran and 1,4-butanediol dinitrate, as well as furan and isoprene. In all, there are 45 ion signals assigned to the COPCs, which represent a total of 52 compounds. Many more non-COPCs are also estimated in this work to aid in source identification but will not be discussed in detail in this section. The Certificate of Analysis of the PTR-MS is located in Appendix A of this report.

3.1.1 Sensitivity Checks

Sensitivity checks are performed on the PTR-MS at the beginning and end of a day of data collection, or every 12 hours, whichever is more frequent. The Liquid Calibration Unit (LCU) is generally used for performing zero air and sensitivity verifications on the PTR-MS using an automated sequence of standard dilution and gas introduction. A system of mass flow controllers (MFCs) is substituted for the LCU on those occasions when the LCU is out of service. Two gases are connected to the LCU. Output from the zero air generator (ZAG) is connected to Gas Inlet 1 and is referred to as the "Gas Flow Nebulizer" in the LCU software. The sensitivity verification standard is connected to Gas Inlet 2 on the LCU. The verification standard, generally at a nominal concentration of 2000 ppbv in an air canister, is referred to as the "Gas Flow Standard" in the LCU software. The LCU is used to create a dilution of the verification standard using zero air to a desired concentration using two calibrated mass flow controllers. The automated sequence for zero air and system sensitivity verification includes three steps: zero air, sensitivity verification, and zero air. The sensitivity verification is generally run at 50 ppbv and is produced by mixing a flow of 25 sccm sensitivity check standard at 2000 ppbv with 975 sccm of zero air. A flow of 975 sccm of zero air is used for the zero air checks. Each step in the sequence is performed for two minutes to ensure all compounds achieve equilibrium with tubing surfaces. Field measurements conducted over a long period of time are generally performed under constantly changing ambient conditions. To account for potential influence of variations in ambient humidity on long duration data sets, the accepted practice is to perform a zero air analysis approximately once each hour. The process is not performed during unattended operation of the Mobile Laboratory due to limited remote automation of all steps in the process. Generally the analyst qualifies the sensitivity checks in the field and interprets the real-time data to be acceptable based upon the observed signals for benzene. Figure 3-1 shows a sensitivity check performed on January 6th, 2017. The data are fully reviewed by the analyst or other qualified reviewer and introduced into a control chart for system quality control.

Figure 3-1. Sensitivity Check Performed on January 6, 2017.



3.2 GAS CHROMATOGRAPHY-MASS SPECTROMETER (GC-MS)

The GC-MS Certificate of Analysis for the TO-15/TO-17 standard is located in Appendix A of this report. It was of the professional discretion of the analyst operating the Mobile Laboratory at the time of the PTR-MS measurements that there were no measureable signals (peak intensity and/or time duration) that would provide responses above a reporting limit by either TO-15 (air canisters) or TO-17 (thermal desorption tubes).

3.3 MEASUREMENT UNCERTAINTY AND KNOWN SOURCES OF ERROR

This section discusses each Hanford COPC assigned to an ion signal in the PTR-TOF 4000 and discusses factors that affect its estimated concentration. Detection limits vary throughout the day and more significantly vary from day to day. Average daily detection limits will be used to define reporting limits once a few months of data have been collected. For the time being, no reporting limits are used and most detection limits during the first month of deployment ranged from 0.04 and 0.15 ppbV.

3.3.1 Formaldehyde, Protonated Nominal Mass 31 amu

The ion signal at nominal mass 31 is typically made up of two peaks: formaldehyde and the O-17 isotope of NO+ created in the ion source. The PTR-TOF 4000 can resolve these two ion signals which reduces the detection limit for formaldehyde compared to PTR-MS instruments previously deployed for tank farm work. Due to having a proton affinity very close to water, the ion signal for formaldehyde suffers a relatively severe humidity dependence. Correcting for this effect is labor and time intensive and is not done in this work, resulting in an absolute concentration error higher than most other compounds, especially at high relative humidity conditions where the perceived concentration is expected to be less than the true concentration.

3.3.2 Methanol, Protonated Nominal Mass 33 amu

The ion signal at nominal mass 33 is primarily from methanol, which is relatively abundant in ambient air. There is a minor ion signal from the O-17 isotope of O_2+ created in the ion source, which is resolved by the PTR-TOF 4000 and removed to improve methanol estimation. The PTR-MS instruments previously deployed for tank farm work did not eliminate this interference although this correction is not very significant in magnitude. Interfering compounds are unlikely at this mass although methanol is one of the more difficult VOCs to sample cleanly due to its high polarity. Occasional large sources of methanol are encountered around the tank farms and elevated methanol can persist in the sample line for several minutes.

3.3.3 Acetonitrile, Protonated Nominal Mass 42 amu

Acetonitrile is the major ion signal at nominal mass 42. There is an unknown ion at mass 42.008 atomic mass unit (amu) that is resolved and removed from the acetonitrile estimated concentration. This correction is new in FY2017, improving the accuracy of acetonitrile concentration estimation by approximately 5% in typical ambient tank farm air.

3.3.4 Acetaldehyde, Protonated Nominal Mass 45 amu

The major ion at nominal mass 45 is typically an unknown compound at mass 44.997. This ion is well resolved from the acetaldehyde ion, providing a much more accurate estimated acetaldehyde concentration in FY2017. This correction was not possible with previously deployed PTR-MS instruments at tank farms, which means ambient concentrations of acetaldehyde in previous work likely overestimated the acetaldehyde concentration.

3.3.5 Ethylamine, Protonated Nominal Mass 46 amu

The ion signal of ethylamine is very small or often not observable with the PTR-TOF 4000 during the first month of 2017 tank farm work. The most significant ion signal at nominal mass 46 has an unknown origin and can be fully resolved from ethylamine. A second minor ion signal is assigned to formamide (not a COPC) and can also be fully resolved from the ethylamine ion signal. In the end, the PTR-TOF 4000 appears capable of very sensitive ethylamine detection with no observed interference issues. Previously deployed PTR-MS instruments to tank farms could not resolve the prominent ion signals at nominal mass 46, meaning the historical estimated concentrations of ethylamine are likely all overestimated.

3.3.6 1,3-Butadiene, Protonated Nominal Mass 55 amu

Sensitivity for 1,3-butadiene is a problem in PTR-MS based measurements due to the prominence of the second hydrate of the hydronium ion from the ion source. The second hydrate of hydronium has a very large ion count rate in the instrument and fluctuates greatly with humidity. The ion signal for 1,3-butadiene appears as a shoulder on this larger instrumentally derived ion signal. Concentration of 1,3-butadiene is estimated using Gaussian functions to isolate the ion signal from the hydrate although the performance of this algorithm has not yet been determined experimentally. Previously deployed PTR-MS instruments to tank farms could not resolve these peaks so the average background for the mass 55 ion signal was assumed to be that of the hydrate and subtracted from all spectra that day. The problem with this approach is that humidity changes too often for this assumption and any quick increases in humidity (such as sampling a combustion exhaust) would be interpreted as elevated 1,3-butadiene. The PTR-TOF 4000 should not suffer false positives of 1,3-butadiene caused by humidity changes but will have poor overall sensitivity compared to other compounds.

3.3.7 Propanenitrile, Protonated Nominal Mass 56 amu

There is a single ion signal at nominal mass 56 amu, which is tentatively assigned to propanenitrile. Field work the past month has shown that the mass scale of the PTR-TOF 4000 is much more stable and reliable than previous models. The observed ion signal differs from the expected exact mass of propanenitrile by approximately 0.007 amu. This difference is large enough and consistent from day to day suggesting that this ion signal may not be due to the presence of propanenitrile, but an unidentified interfering compound with a similar mass. Until lab testing can show otherwise, this ion signal will be interpreted as propanenitrile, which is similar in performance to PTR-MS instruments previously deployed to tank farms. It is worth noting that the O-17 isotope of the second hydrate of hydronium ion is not the identity of the ion signal observed at this mass.

3.3.8 1-butanol, Protonated Nominal Mass 57 amu

The ion signal at nominal mass 57 is relatively complex. There are two large ion signals nearly always present in an ambient air sample. The first is the superposition of butanol and the butenes. 1-butanol is a COPC but cannot be isolated from butenes. The second major ion signal is the superposition of propenal (acrolein) and the O-18 isotope of the second hydrate of hydronium. PTR-MS instrumentation previously deployed to tank farm estimated the concentration of 1-butanol from the total nominal mass 57 ion signal, which included a falsely elevated baseline concentration caused by the isotope of the second hydrate of hydronium. The PTR-TOF 4000 will provide more sensitive 1-butanol estimates but will still suffer from interference by butenes. Interference from propenal has also been eliminated.

3.3.9 Methyl Isocyanate, Protonated Nominal Mass 58 amu

There are three prominent ion signals at nominal mass 58. The most significant peak is an unidentified compound that is easily resolved from other ion signals. One of the minor peaks has been assigned to methyl isocyanate, while the other ion signal is assigned to C_3H_7N isomers. All peaks are resolved from one another. The observed ion signal for methyl isocyanate differs from the expected exact mass by approximately 0.003 amu. The increasing confidence in the stability and accuracy of the mass scale puts the assignment of this ion to methyl isocyanate into question. Lab testing is needed to confirm the observed ion signal is truly methyl isocyanate. Previously deployed PTR-MS instruments interpreted the entire signal at nominal mass 58 as methyl isocyanate, which would have been an overestimation of approximately 60% compared to that of the PTR-TOF 4000.

3.3.10 Methyl nitrite, Protonated Nominal Mass 62 amu

There is only one ion signal at nominal mass 62 and it aligns well with the exact mass of methyl nitrite. The estimated concentrations for methyl nitrite would have been similar with previously deployed instrumentation. The improved mass resolution of the PTR-TOF 4000 does reduce the possibility of unforeseen interferences to cause a false positive signal of methyl nitrite.

3.3.11 Furan, Protonated Nominal Mass 69 amu

One of the primary recommendations from the FY2016 work was to use a PTR-MS instrument with sufficient mass resolution to isolate the furan ion signal from that of isoprene, which as many biogenic sources in the area and in general is much higher concentration in ambient air. The PTR-TOF 4000 resolves these two ion signals successfully. As expected, the bulk of the ion signal observed over the first month in the field has been due to isoprene rather than furan, although a reliable, very low concentration furan signal is often observed, even in ambient air. There are no other interfering ion signals observed at nominal mass 69. The ability to differentiate furan from isoprene is a significant improvement for COPC detection in FY2017. Lab-based experiments should be conducted to demonstrate the successful detection of furan in the presence of isoprene by a PTR-TOF 4000.

3.3.12 Butanenitrile, Protonated Nominal Mass 70 amu

The largest ion signal at nominal mass 70 amu is tentatively assigned to butanenitrile; however, the observed ion signal differs from the expected exact mass of butanenitrile by approximately 0.008 amu. This difference is consistent from day to day and large enough to suggest this ion signal may not be due to the presence of butanenitrile, but an unidentified interfering compound with a similar mass. Until lab testing can show otherwise, this ion signal will be interpreted as butanenitrile. There is a second small ion signal at nominal mass 70 from an unknown compound. This peak is resolved sufficiently to be removed from the butanenitrile concentration estimation. The PTR-MS instruments previously deployed to tank farms would have suffered a small over-estimation caused by the unknown ion signal. This error is approximately 15% in typical ambient air sampling.

3.3.13 Sum of 3-buten-2-one, 2,3-dihydrofuran, and 2,5-dihydrofuran, Protonated Nominal Mass 71 amu

There are three COPCs that have the same chemical formula of C_4H_6O; 3-buten-2-one, 2,3-dihydrofuran and 2,5-dihydrofuran. To complicate matters, 2-methylprop-2-enal (methacrolein) is another C_4H_6O compound that is typically present in ambient air, although it is not a COPC. 3-buten-2-one and 2-methylprop-2-enal are the two most common oxidative products of isoprene and are often observed in the upper pptV or very low ppbV concentration range. Complicating this further, 2-methylprop-2-enal is created by local sagebrush in the Pacific Northwest which may create a higher background at the Hanford site compared to most studies in the scientific literature. The sum of all four C_4H_6O isomers are detected as a single ion signal by PTR-MS. This creates a problematic situation since the occupational exposure limit (OEL) of the two dihydrofuran species is 1 ppbV, which should be occasionally breached by biogenic sources of 3-buten-2-one and 2-methylprop-2-enal.

There are two prominent ion signals at nominal mass 71 in ambient air. The largest peak is due to the C_4H_6O species mentioned above, while the smaller ion signal is assigned to the C_5H_{10} isomers. The PTR-TOF 4000 has sufficient mass resolution to isolate the C_5H_{10} ion signal and subtract it from the estimated concentration of the three COPCs. Concentration of the C_4H_6O isomers is determined using the reaction rate constant of 3-buten-2-one, which is expected to be the most abundant of the three COPCs in most ambient air situations. PTR-MS instruments deployed at tank farms in the past were not able to isolate the ion signal contribution from the C_5H_{10} species, which likely resulted in an overestimation of the three COPCs of approximately 10%. With the PTR-TOF 4000, we still expect to have an overestimation due to the biogenic presence of 2-methylprop-2-enal, which cannot be quantified and removed.

3.3.14 Butanal, Protonated Nominal Mass 73 amu

There are two significant ion signals at nominal mass 73 amu. The prominent peak is assigned to butanal. The smaller ion signal aligns with $C_3H_4O_2$ isomers, such as methyl glyoxal. These ion peaks can be resolved to improve the confidence in butanal concentration estimation. Potential interfering compounds of butanal include the isomers of C_4H_8O such as butanone and tetrahydrofuran. PTR-MS instruments previously deployed to tank farms were not able to resolve the $C_3H_4O_2$ contributions to the nominal mass 73 amu ion signal, resulting in an overestimate of butanal of approximately 15%. The PTR-TOF 4000 provides improved accuracy for butanal in FY2017.

3.3.15 N-nitrosodimethylamine (NDMA), Protonated Nominal Mass 75 amu

The major ion signal observed at nominal mass 75 amu is assigned to methyl acetate. NDMA would appear as a shoulder on this larger ion signal when it is present. Concentration of NDMA is estimated using Gaussian function to isolate the ion signal from the large methyl acetate ion signal. It is expected that NDMA will be successfully estimated any time its concentration is similar in order of magnitude to methyl acetate. Methyl acetate is typically observed in the low to mid pptV range, suggesting a typical detection limit of low pptV for NDMA. This is relatively poor compared to other compounds but likely falls below the 50% OEL limit for NDMA (150 pptV) at nearly all times. The performance of the algorithm to estimate concentration of NDMA in the presence of methyl acetate should be investigated with mixed standards of the two substances to better understand confidence in the NDMA concentrations reported. Previously deployed PTR-MS instruments at tank farms could not isolate methyl acetate from NDMA and reported the ion signal as the sum of the two compounds, which was likely often dominated by methyl acetate in ambient samples. Eliminating this interference is a significant improvement in 2017.

3.3.16 Benzene, Protonated Nominal Mass 79 amu

The ion signal at nominal mass 79 amu is nearly all attributed to benzene. There is a very small ion signal from an unknown compound that is resolved and removed, although this correction is typically less than a 2% correction compared to PTR-MS instruments deployed at tank farms in previous work. Benzene is one of the most reliable compounds to quantify with the primary interferences resulting from larger aromatic compounds fragmenting to the same ion. Benzene is selected as the primary instrument performance check in the field because of its ideal behavior and limited concern for interfering ion signals.

3.3.17 Sum of 2,4-Pentadienenitrile and Pyridine, Protonated Nominal Mass 80 amu

There is a single ion signal at nominal mass 80 amu that is assigned to the sum of two COPCs with the same chemical formula (C_5H_5N); 2,4-pentadienenitrile and pyridine. The observed ion signal differs from the expected exact mass of C_5H_5N by approximately 0.006 amu. This difference is large enough and consistent from day to day suggesting that this ion signal may not be due to the presence of 2,4-pentadienenitrile and pyridine, but an unidentified interfering compound with a similar mass. Until lab testing can show otherwise, this ion signal will be interpreted as the sum of these two COPCs, which is similar in performance to PTR-MS instruments previously deployed to tank farms.

3.3.18 2-methylene Butanenitrile, Protonated Nominal Mass 82 amu

The ion signal at nominal mass 82 aligns with the exact mass of 2-methylene butanenitrile. The improved mass resolution of the PTR-TOF 4000 reduces the possibility of unforeseen interferences to cause false positive results for 2-methylene butanenitrile but no interferences have been observed in the first month on-site. The estimated concentration predicted for 2-methylene butanenitrile by previously deployed PTR-MS instrumentation likely provided reasonable results due to the lack of observed interferences by the PTR-TOF 4000.

3.3.19 2-methylfuran, Protonated Nominal Mass 83 amu

The primary ion signal at nominal mass 83 consists of the C_6H_{12} isomers. 2-methylfuran is a COPC that appears as a minor shoulder on the larger C_6H_{12} ion signal, when present. Concentration of 2-methylfuran is estimated using a Gaussian function to isolate the ion signal of 2-methylfuran from the larger C_6H_{12} ion signal. It is expected that 2-methylfuran will be successfully estimated any time its concentration is similar in order of magnitude to C_6H_{12}. The performance of the algorithm to estimate concentration of 2-methylfuran in the presence of C_6H_{12} isomers should be investigated using mixed standards of the two substances to better understand confidence in the 2-methylfuran concentrations reported. Previously deployed PTR-MS instruments at tank farms could not isolate C_6H_{12} isomers from 2-methylfuran and reported an overestimation of 2-methylfuran any time C_6H_{12} compounds were present.

3.3.20 Pentanenitrile, Protonated Nominal Mass 84 amu

There are two prominent ion signals at nominal mass 84. The larger ion signal is assigned to COPC pentanenitrile while the second ion signal is an unknown compound. The two ion signals are fully resolved and the unknown compound does not interfere with the pentanenitrile concentration estimation. The observed ion signal for pentanenitrile differs from the expected exact mass by approximately 0.009 amu. The increasing confidence in the stability and accuracy of the mass scale puts the assignment of this ion to pentanenitrile into question. Lab testing is needed to confirm the observed ion signal is truly pentanenitrile. Until lab confirmation shows that this ion is in fact not pentanenitrile it will be used to estimate pentanenitrile concentration. Previously deployed PTR-MS instruments interpreted the entire signal at nominal mass 84 as pentanenitrile, which would have been a consistent overestimation due to the presence of the second unknown ion signal. The 2017 estimated concentrations for pentanenitrile are improved with the PTR-TOF 4000 although the lab work is required to confirm the presence of a second interfering compound resulting in overestimation.

3.3.21 Sum of 3-methyl-3-buten-2-one and 2-methyl-2-butenal, Protonated Nominal Mass 85 amu

There are three ion signals observed at nominal mass 85 amu in ambient air. One is assigned to the sum of two COPCs; 3-methyl-3-buten-2-one and 2-methyl-2-butenal. The other two ion signals are assigned to isomers of C_6H_{12} and $C_4H_4O_2$. The PTR-TOF 4000 has sufficient mass resolution to isolate the COPC ion signal from the other compounds and provide concentration estimates without these interfering compounds. PTR-MS instrumentation previously deployed to the tank farms likely overestimated the concentration of the sum of 3-methyl-3-buten-2-one and 2-methyl-2-butenal due to C_6H_{12} and $C_4H_4O_2$.

3.3.22 N-nitrosomethylethylamine (NEMA), Protonated Nominal Mass 89 amu

The major ion signal observed at nominal mass 89 amu is assigned to ethyl acetate. NEMA would appear as a shoulder on this larger ion signal when it is present. Concentration of NEMA is estimated using a Gaussian function to isolate the ion signal from the large ethyl acetate ion signal. It is expected that NEMA will be successfully estimated any time its concentration is similar in order of magnitude to ethyl acetate. The performance of the algorithm to estimate concentration of NEMA in the presence of ethyl acetate should be investigated with mixed standards of the two substances to better understand confidence in the NEMA concentrations reported. Previously deployed PTR-MS instruments at tank farms could not isolate ethyl acetate from NEMA and reported the ion signal as the sum of the two compounds, which was likely often dominated by ethyl acetate in ambient samples. The potential elimination of the ethyl acetate interference on the NEMA ion signal would be a major improvement in 2017. Field data from the first month of deployment in 2017 appear promising.

3.3.23 2,5-dimethylfuran, Protonated Nominal Mass 97 amu

2,5-dimethylfuran is a COPC that is detected at nominal mass 97 amu by PTR-MS. There are three ion signals observed in ambient air at this nominal mass, although none of them align with 2-5-dimethylfuran. The largest ion signal observed is assigned to the isomers of C_7H_{12}, while there is a smaller ion signal assigned to $C_5H_4O_2$ and an unknown compound. All four ion signals (including the 2,5-dimethylfuran when it is present) can be resolved from one another by the PTR-TOF 4000. The results presented in 2017 reflect estimated concentrations for 2,5-dimethylfuran after applying the Gaussian algorithm to isolate it from the other ion signals nearby. Lab experiments are needed to verify this algorithm is effective and that the 2,5-dimethylfuran estimations are reliable. Previously deployed PTR-MS instruments at tank farms could not resolve the interfering ion signals and likely overestimated 2,5-dimethylfuran concentrations in ambient and low concentration situations. The 2,5-dimethylfuran estimates are greatly improved in 2017.

3.3.24 Hexanenitrile, Protonated Nominal Mass 98 amu

The largest ion signal at nominal mass 98 is assigned to COPC hexanenitrile. There are two small ion signals from unknown compounds that are resolved and removed from the hexanenitrile estimated concentration using the PTR-TOF 4000. The observed ion signal for hexanenitrile differs from the expected exact mass by approximately 0.006 amu. The increasing confidence in the stability and accuracy of the mass scale puts the assignment of this ion to hexanenitrile into question. Lab testing is needed to confirm the observed ion signal is truly hexanenitrile. Until lab confirmation shows that this ion is in fact not hexanenitrile it will be used to estimate hexanenitrile concentration. Previously deployed PTR-MS instruments interpreted the entire signal at nominal mass 84 as pentanenitrile, which would have been a consistent overestimation due to the presence of the two minor interfering ion signals. The 2017 estimated concentrations for hexanenitrile are slightly improved with the PTR-TOF 4000 although the lab work is required to confirm that the bulk of this ion signal is a third interfering compound.

3.3.25 2-hexanone (MBK), Protonated Nominal Mass 101 amu

The major ion signal observed at nominal mass 101 amu is assigned to the isomers of $C_5H_8O_2$. 2-hexanone (or methyl butyl ketone, MBK) is a COPC that appears as a minor peak very close to the $C_5H_8O_2$ ion signal. Concentration of 2-hexanone is estimated using a Gaussian function to isolate the ion signal from the larger $C_5H_8O_2$ ion signal. It is expected that 2-hexanone is successfully estimated any time its concentration is similar in order of magnitude or larger than the sum of all $C_5H_8O_2$ isomers. The performance of the algorithm to estimate concentration of 2-hexanone in the presence of high $C_5H_8O_2$ concentrations should be investigated with mixed standards of the two substances to better understand confidence in the 2-hexanone concentrations reported. Previously deployed PTR-MS instruments at tank farms could not isolate 2-hexanone from $C_5H_8O_2$ and reported the ion signal as the sum of the two compounds, which was likely often dominated by the $C_5H_8O_2$ isomers in ambient air. Field data from the first month of deployment in 2017 appear to be providing reliable 2-hexanone estimations.

3.3.26 N-nitrosodiethylamine (NDEA), Protonated Nominal Mass 103 amu

The major ion signal observed at nominal mass 103 amu is assigned to ethyl propionate and other $C_5H_{10}O_2$ isomers. NDEA is a COPC that would appear as a shoulder on this larger ion signal when it is present. Concentration of NDEA is estimated using a Gaussian function to isolate the ion signal from the large $C_5H_{10}O_2$ ion signal. It is expected that NDEA will be successfully estimated any time its concentration is similar in order of magnitude to the sum of all $C_5H_{10}O_2$ isomers. The performance of the algorithm to estimate concentration of NDEA in the presence of $C_5H_{10}O_2$ compounds should be investigated with mixed standards of the two substances to better understand confidence in the NDEA concentrations reported. Previously deployed PTR-MS instruments at tank farms could not isolate $C_5H_{10}O_2$ from NDEA and reported the ion signal as the sum of the two compounds, which was likely often dominated by ethyl propionate or other $C_5H_{10}O_2$ compounds in ambient air. The potential elimination of the $C_5H_{10}O_2$ compounds from interfering with the estimation of NDEA concentration is a major improvement in 2017. Field data from the first month of deployment in 2017 appear promising.

3.3.27 Sum of butyl nitrite and 2-nitro-2-methylpropane, Protonated Nominal Mass 104 amu

There is a single prominent ion signal at nominal mass 104 which is assigned to the sum of two COPCs with the same chemical formula; butyl nitrite and 2-nitro-2-methylpropane. The observed ion signal differs from the expected exact mass for these two compounds by approximately 0.010 amu. The increasing confidence in the stability and accuracy of the mass scale puts the assignment of this ion to the sum of butyl nitrite and 2-nitro-2-methylpropane into question. Lab testing is needed to confirm the observed ion signal is truly due to these two COPCs. Until lab confirmation shows that this ion is in fact due to an unknown interfering compound it will be used to estimate the sum of butyl nitrite and 2-nitro-2-methylpropane concentration. If this ion signal is shown to be an interfering compound, the two COPCs will be estimated using a Gaussian function to isolate the correct ion signal from the unknown compound. Previously deployed PTR-MS instruments interpreted the entire signal at nominal mass 104 as the sum of butyl nitrite and 2-nitro-2-methylpropane which is similar to what is reported in the first month of 2017 using the PTR-TOF 4000.

3.3.28 2,4-dimethylpyridine, Protonated Nominal Mass 108 amu

The ion signal at nominal mass 108 aligns with the exact mass of 2,4-dimethylpyridine. The improved mass resolution of the PTR-TOF 4000 reduces the possibility of unforeseen interferences to cause false positive results for 2,4-dimethylpyridine but no interferences have been observed in the first month on-site. The estimated concentration predicted for 2,4-dimethylpyridine by previously deployed PTR-MS instrumentation likely provided reasonable results due to the lack of observed interferences by the PTR-TOF 4000.

3.3.29 Sum of 2-ethyl-5-methylfuran and 2-propylfuran, Protonated Nominal Mass 111 amu

There are three ion signals at ambient mass 111 amu observed in ambient air, but none align with the mass expected with two COPCs with the chemical formula $C_7H_{10}O$; 2-ethyl-5-methylfuran and 2-propylfuran. The largest ion signal observed is assigned to C_8H_{14} isomers while the other two ion signals represent unknown compounds. There is sufficient mass separation between the three observed ion signals and the expected ion signal for the sum of 2-ethyl-5-methylfuran and 2-propylfuran that positive detection and accurate estimation of the two COPCs is expected, when present. This is an improvement over PTR-MS instruments deployed to the tank farms in the past where all ion signals were combined into a single concentration for the entire nominal mass. Estimated concentrations in previous tank farm work likely resulted in overestimates of the sum of 2-ethyl-5-methylfuran and 2-propylfuran.

3.3.30 Heptanenitrile, Protonated Nominal Mass 112 amu

The prominent ion signal at nominal mass 112 amu aligns with the mass of COPC heptanenitrile, to which it is assigned. Two potentially interfering ion signals can be isolated and removed by the PTR-TOF 4000. The larger of these two is assigned to C_6H_9NO isomers and the smaller ion signal has an unknown source. The concentration estimates for heptanenitrile are improved in 2017 due to the ability of the PTR-TOF 4000 to isolate the potentially interfering compounds. PTR-MS instruments previously deployed to tank farms likely overestimated the heptanenitrile concentration when an isomer of C_6H_9NO was present.

3.3.31 4-methyl-2-hexanone, Protonated Nominal Mass 115 amu

4-methyl-2-hexanone is a COPC that is detected at nominal mass 115 amu by PTR-MS. The ion signal at this mass is mostly composed of an unknown compound that cannot be resolved from 4-methyl-2-hexanone, even when using the PTR-TOF 4000. The estimated concentration includes the ion signal of the unknown compound making reported concentrations overestimates at low concentrations. When 4-methyl-2-hexanone is observed at higher concentrations, this interference may be insignificant. The estimated concentrations in 2017 have a similar confidence to results from prior PTR-MS work at tank farms. Use of the top-of-the-line PTR-TOF instrument may provide sufficient mass resolution to improve this measurement.

3.3.32 N-nitrosomorpholine (NMOR), Protonated Nominal Mass 117 amu

There are two ion signals observed at nominal mass 117 amu, which are resolved by PTR-TOF 4000. One ion signal is assigned to COPC NMOR while the other is assigned to the isomers of $C_6H_{12}O_2$. Previously deployed PTR-MS instruments to tank farms could not resolve these two ion signals and reported concentrations for NMOR that represented the sum of all nominal mass 117 amu compounds. This likely resulted in overestimates for NMOR considering the $C_6H_{12}O_2$ isomers were observed at much larger concentrations than NMOR during the first month of FY2017 field work. The specificity of the PTR-TOF 4000 to detect NMOR without the interference of $C_6H_{12}O_2$ isomers is a significant improvement in FY2017. Due to the low OEL of NMOR it is suggested that lab experiments validate the performance of isolating NMOR from large concentrations of $C_6H_{12}O_2$.

3.3.33 Butyl nitrate, Protonated Nominal Mass 120 amu

The major ion signal observed at nominal mass 120 amu is an unidentified compound. Butyl nitrate is a COPC that would appear as a minor shoulder peak of this ion signal, when present. Concentration of butyl nitrate is estimated using a Gaussian function to isolate the ion signal from the larger unidentified ion signal. It is expected that butyl nitrate will be successfully estimated any time its concentration is similar or larger than the unknown substance. Previously deployed PTR-MS instruments at tank farms could not isolate this unknown compound and reported higher estimated butyl nitrate concentrations as a result. The elimination of this interference in 2017 using the PTR-TOF 4000 is a significant improvement on butyl nitrate detection.

3.3.34 Sum of 2-ethyl-2-hexenal, 4-(1-methylpropyl)-2,3-dihydrofuran, and 3-(1,1-dimethylethyl)-2,3-dihydrofuran, Protonated Nominal Mass 127 amu

The primary ion signal observed at nominal mass 127 amu in ambient air is assigned to a group of three COPCs with the chemical formula $C_8H_{14}O$; 2-ethyl-2-hexenal, 4-(1-methylpropyl)-2,3-

dihydrofuran, and 3-(1,1-dimethylethyl)-2,3-dihydrofuran. There are additional ion signals of unknown origin that are resolved and removed. These potential interfering compounds were not resolved by PTR-MS instruments previously deployed to tank farms although the magnitude of these unknown compounds are quite small on most days during the first month of 2017 field work. Field data from December 2016 suggest previously deployed instruments may have overestimated concentration of the sum of 2-ethyl-2-hexenal, 4-(1-methylpropyl)-2,3-dihydrofuran, and 3-(1,1-dimethylethyl)-2,3-dihydrofuran by up to 10%.

3.3.35 6-methyl-2-heptanone, Protonated Nominal Mass 129 amu

The major ion signal observed at nominal mass 129 amu is assigned to naphthalene. 6-methyl-2-heptanone is a COPC that would appear as a shoulder on the naphthalene ion signal when it is present. Concentration of 6-methyl-2-heptanone is estimated using a Gaussian function to isolate the ion signal from the large naphthalene ion signal. It is expected that 6-methyl-2-heptanone will be successfully estimated any time its concentration is similar or larger in order of magnitude to naphthalene. The performance of the algorithm to estimate concentration of 6-methyl-2-heptanone in the presence of naphthalene should be investigated with mixed standards of the two substances to better understand confidence in the 6-methyl-2-heptanone concentrations reported. Previously deployed PTR-MS instruments at tank farms could not isolate 6-methyl-2-heptanone from naphthalene and reported the ion signal as the sum of the two compounds, which was likely often dominated by naphthalene in ambient air. The elimination of naphthalene from interfering with the estimation of 6-methyl-2-heptanone concentration is a major improvement in 2017. Field data from the first month of deployment in 2017 appear promising.

3.3.36 2-pentylfuran, Protonated Nominal Mass 139 amu

The ion signal at nominal mass 139 amu is assigned to COPC 2-pentylfuran. Most days there are no other ion signals but there is a transient small ion signal from an unknown compound that appears occasionally. This unknown ion signal cannot be resolved from the 2-pentylfuran response and poses a potential interference, although it was not observed to be significant during the first month of 2017 work. Previously deployed PTR-MS instruments at tank farms have provided similar results.

3.3.37 Biphenyl, Protonated Nominal Mass 155 amu

There are multiple ion signals clustered closely together at nominal mass 155 amu. One of the ion signals can be assigned to COPC biphenyl although it cannot be resolved from other ion signals. The reported concentration estimates include the ion signal from all compounds detected at nominal mass 155 amu, resulting in a known overestimated value of biphenyl. These results are similar to what would have been observed by previously deployed PTR-MS instruments at tank farms. It is possible that some of the interferences may be resolved using the top performing PTR-TOF model instrument.

3.3.38 2-heptylfuran, Protonated Nominal Mass 167 amu

There are two ion signals of unknown origin at nominal mass 167 amu that appear in close proximity to the expected ion signal for COPC 2-heptylfuran. These unknown compounds are present in ambient air and may prevent 2-heptylfuran from being fully resolved unless the concentration of 2-heptylfuran is very high. Lab experiments are required to determine what the minimum concentration of 2-heptylfuran is to reliably estimate its concentration. Currently, the reported estimated concentration of 2-heptylfuran includes both of the two unknown ion signals and is likely an overestimation at low concentrations. The PTR-MS instruments previously deployed to tank farms had similar interferences included in the reported estimated concentrations. Lab experiments may improve the accuracy of 2-heptylfuran estimation at low concentrations later in 2017. Even overestimated, 2-heptylfuran typically does not approach concentrations of concern at tank farms.

3.3.39 1,4-butanediol, Dinitrate, Protonated Nominal Mass 181 amu

There are five distinct ion signals at nominal mass 181 amu. Two COPCs appear at this nominal mass but have different chemical formulas so they can also be resolved from one another. 1,4-butanediol, dinitrate and 2-octylfuran are assigned to two different ion signals while the other three ion signals of unknown origin are isolated and removed. Previously deployed PTR-MS instruments at tank farms reported a single estimated concentration for the sum of the two COPCs, which also included contributions from the three unknown interfering compounds. Removing the interfering compounds and separating the two COPCs is a significant improvement for FY2017 work.

3.3.40 1,2,3-propanetriol, 1,3-dinitrate, Protonated Nominal Mass 183 amu

There are two ion signals of unknown origin at nominal mass 183 amu that appear in close proximity to the expected ion signal for COPC 1,2,3-propanetriol, 1,3-dinitrate. These unknown compounds are present in ambient air and may prevent 1,2,3-propanetriol, 1,3-dinitrate from being fully resolved unless the concentration of 1,2,3-propanetriol, 1,3-dinitrate is very high. Lab experiments are required to determine what the minimum concentration of 1,2,3-propanetriol, 1,3-dinitrate is to reliably estimate its concentration. Currently, the reported estimated concentration of 1,2,3-propanetriol, 1,3-dinitrate includes both of the two unknown ion signals and is likely an overestimation at low concentrations. The PTR-MS instruments previously deployed to tank farms had similar interferences included in the reported estimated concentrations. Lab experiments may improve the accuracy of 1,2,3-propanetriol, 1,3-dinitrate estimation at low concentrations later in 2017. Even overestimated, 1,2,3-propanetriol, 1,3-dinitrate typically does not approach concentrations of concern at tank farms.

3.3.41 PCBs, Protonated Nominal Mass 189 and 223 amu

There are many varieties of polychlorinated biphenyls (PCBs) possible. Two of the more volatile PCBs are monitored in this work; PCB1 ($C_{12}H_9Cl$) is protonated to nominal mass 189 amu and PCB2 ($C_{12}H_8Cl_2$) is protonated to mass 223 amu. The ion signal for PCB1 is isolated from a large unknown ion signal at nominal mass 189 amu. Estimations of PCB1 concentration in 2017 are therefore improved over previous instruments deployed. PCB2 is isolated from two large unknown peaks at nominal mass 223 amu, which is also an improvement over previous instruments deployed. More lab work is needed to improve the confidence in estimating the concentration of these two PCB species but is not suggested at this time due to the fact that these compounds are not observed in field work to date. The reported estimated concentrations can be considered an overestimation until further scrutiny is required.

3.3.42 6-(2-furanyl)-6-methyl-2-heptanone, Protonated Nominal Mass 195 amu

There are two significant ion signals at nominal mass 195 amu, neither of which are assigned to COPC 6-(2-furanyl)-6-methyl-2-heptanone. The estimated concentration of 6-(2-furanyl)-6-methyl-2-heptanone is determined by a Gaussian function that can resolve it from the two unknown ion signals. Previously deployed PTR-MS instrumentation reported a single estimated concentration for all ions at nominal mass 195 amu, likely resulting in an overestimation of 6-(2-furanyl)-6-methyl-2-heptanone in most situations. The mass resolution of the PTR-TOF 4000 has greatly improved this estimation in FY2017 although this compound has not yet been observed in significant concentrations in field work.

3.3.43 Furfural acetophenone (3-(2-furanyl)-1-pheynyl-2-propen-1-one), Protonated Nominal Mass 199 amu

Most of the ion signal at nominal mass 199 amu appears to be a single unknown origin. The COPC furfural acetophenone (3-(2-furanyl)-1-phenyl-2-propen-1-one) cannot be resolved from the major unknown peak. As a result, the entire ion signal is used to estimate the concentration of furfural acetophenone (3-(2-furanyl)-1-phenyl-2-propen-1-one), resulting in a known overestimation of this COPC. Previously deployed PTR-MS instruments at tank farms reported similar results. It is possible that the interfering ion signal may be resolved using the top performing PTR-TOF model instrument.

4.0 TEST RESULTS

This sections describes the test findings during this month's monitoring campaign.

4.1 TEST ACTIVITIES AND OBSERVATIONS

Each monitoring period started in the 200 East Area with a stop at the shift office to pick up a radio for the purpose of relaying pertinent information regarding tank farm operations and potential vapor events. The period of monitoring was chosen based on waste disturbing activities. The location monitored was primarily around the AY and AP Tank Farms in the 200 East Area. The routes were determined by personnel in the mobile laboratory as well as the daily stationary monitoring sites. Monitoring was directed around the Waste Retrieval activities.

Personnel in the mobile laboratory determined optimum monitoring locations based on ambient conditions and activities. A prime goal was to identify the compounds that are not monitored by the current vapor monitoring and detection system; this system is designed to monitor leading indicator compounds, but not all of the COPCs.

Table 4-1 summarizes the dates, monitoring activity, and start/stop times of the daily measurements.

Table 4-1. Dates and Times of Monitoring Activities.

Week	Date	Description	Start Time	End Time
1.1	12/09/16	Mobile + stationary	05:34	15:18
	12/10/16	Mobile + stationary	07:10	16:53
	12/12/16	Mobile + stationary	05:34	17:15
	12/13/16	Mobile + stationary	06:00	16:59
1.2	12/22/16	Mobile + stationary	16:37	05:02 (12/23/16)
	12/26/16	Mobile + stationary	18:33	05:10 (12/27/16)
	12/27/16	Mobile + stationary	17:04	05:01 (12/28/16)
	12/28/16	Mobile + stationary	17:29	05:06 (12/29/16)
1.3	12/30/16	Mobile + stationary	05:06	17:00
	12/31/16	Mobile + stationary	05:32	17:09
1.4	01/06/17	Mobile + stationary	05:47	17:12
	01/08/17	Mobile + stationary	05:26	11:44

Table 4-1. Dates and Times of Monitoring Activities.

Week	Date	Description	Start Time	End Time
	01/10/17	Mobile + stationary	5:40	9:36
1.5	01/13/17	Mobile + stationary	6:21	15:23
	01/15/17	Mobile + stationary	5:27	15:46
	01/16/17	Mobile + stationary	5:40	15:09
	01/17/17	Mobile + stationary	5:24	13:14

The data collected during this monitoring campaign have been displayed in a variety of forms that are displayed in the Appendices following this document. This data are arranged as follows:

- Appendix B
    - Daily Graphs on OEL Scale: Shown is the concentration per COPC throughout the day with the COPC's OEL being the range of the graph.
- Appendix C
    - Daily Graphs on Auto Scale: Shown is the concentration per COPC throughout each day with Auto Scaling for the COPCs where graphs are too low to observe in Appendix B with the OEL scaling.
- Appendix D
    - Histograms: Shown are Histograms per COPC for each day of monitoring.
- Appendix E
    - Statistical Analysis: Shown are tables of statistical data for each COPC per day of monitoring.
- Appendix F
    - Weekly Report Local Sources: Shown are the local sources observed in the weekly reports.

4.2 WEEKLY REPORT LOCAL SOURCES

The weekly reports that were submitted during the 1.0 Month monitoring campaign can be found in Appendix F of this report. Per local source that was observed, there is a graph, a map, and a table description.

4.3 VAPOR SOURCES IDENTIFICATION, COMPOSITION AND ANALYSIS

At the completion of this report, WRPS' DQO Group and a Fugitive Emissions/Source Apportionment Sub-team had not yet developed a process for the Mobile Laboratory to sample and monitor certain sources for analysis or vapor composition. Due to this, vapor source identification and quantitative analysis of vapor composition could not be completed for this report. Source identification processes are being developed by WRPS' DQO Team and the Fugitive Emissions/Source Apportionment Sub-team with input from RJ Lee Group and will be documented in the FY2017 Test Plan.

5.0 QUALITY ASSESSMENT

The RJ Lee Group Quality Assurance (QA) Team monitored and assisted in a three tier data review for all mobile lab monitoring data for this report. The QA Team engaged the scientific staff in weekly internal Vapor Initiative meetings to discuss ongoing operations and assist in maintaining the highest possible level of quality assurance. As stated in Section 1.0 of this monthly report, there were two anomalies that include unrecorded weather data on December 9, 2016, during Week 1.1, as well as unrecorded carbon dioxide data on December 28, 2016, during Week 1.2. These anomalies were addressed and documented as needed by RJ Lee group's Quality Assurance Team. These anomalies launched the implementation of CAPA protocol. Details for each CAPA are described below. These CAPAs were generated to ensure greater completeness of data acquired in future monitoring periods.

5.1 CAPA 1665

CAPA 1665 describes the anomaly of unrecorded CO_2 during the monitoring period on December 28, 2016. Upon investigation it was determined that the analyst failed to turn on the analyzer for this day. Preventative actions for this CAPA are to perform a surveillance of the Mobile Laboratory as well as interview the analyst(s) and review operational logbooks. Though the current data review and surveillance procedures are adequate, the CAPA showed that the procedure was not followed.

5.2 CAPA 1667

CAPA 1667 describes the anomaly of unrecorded weather data during the monitoring period on December 9, 2016. Upon investigation it was determined that the analyst failed to turn on the analyzer for this day. Preventative actions for this CAPA are to perform a surveillance of the Mobile Laboratory as well as interview the analyst(s) and review operational logbooks. Though the current data review and surveillance procedures are adequate, the CAPA showed that the procedure was not followed.

6.0 CONCLUSIONS AND RECOMMENDATIONS

The highlight of the first month of FY2017 tank farm air monitoring has been the first deployment of a high mass resolution time of flight instrument focused on the Hanford COPCs. The instrument is an IONICON Analytik PTR-TOF 4000, the second manufactured instrument of its generation and the first in the United States. The improved mass resolution was a recommendation from 2016 field work to resolve compounds of similar nominal mass but different elemental composition. The impact of the improved mass resolution to eliminate some interferences is obvious when looking at the decrease of local sources exceeding 50% OEL for COPCs and more generally, the average concentration of furan or the four nitrosamines encountered around tank farms.

Table 6-1 provides a summary of what the PTR-MS had measured over the course of this monitoring period. The Peak Value that is recorded for both On-Site and Off-Site monitoring is accompanied by the date at which it is recorded in the next column.

Table 6-2 displays the time-weighted averages per day of monitoring during each week of this month. Note that units are in parts per billion. For comparison purposes, the OEL is listed next to each COPC. Further data are located in the appendices following this document.

Table 6-1. Site PTR-Measurements during Reporting Period for COPCs.

		On-Site PTR-MS Measurements During Reporting Period						Off-Site PTR-MS Measurements During Reporting Period				
COPD2+A1:A36	OEL	Total No. Measurements	No. Measurements Between AL and OEL	Maximum Continuous Time Above OEL (seconds)	Peak Value	Date Recorded	Total No. Measurements	No. Measurements Between AL and OEL	Continuous Time Above OEL (seconds)	Peak Value	Date Recorded
formaldehyde	300	204,843	0	0	114.181	12/26/2016	53,173	1	0	154.722	12/26/2016
methanol	200000	204,843	0	0	655.285	12/30/2016	53,173	0	0	975.663	12/26/2016
acetonitrile	20000	204,843	0	0	8.606	12/26/2016	53,173	0	0	1.218	1/10/2017
acetaldehyde	25000	204,843	0	0	88.526	12/26/2016	53,173	0	0	12.313	12/30/2016
ethylamine	5000	204,843	0	0	0.602	12/26/2016	53,173	0	0	0.114	12/30/2016
1,3-butadiene	1000	204,843	0	0	8.928	12/12/2016	53,173	0	0	9.365	12/30/2016
propanenitrile	6000	204,843	0	0	1.545	1/16/2017	53,173	0	0	1.398	1/6/2017
1-butanol + butenes	20000	204,843	0	0	16.049	1/6/2017	53,173	0	0	48.526	12/26/2016
methyl isocyanate	20	204,843	0	0	0.616	12/31/2016	53,173	0	0	0.384	12/30/2016
methyl nitrite	100	204,843	0	0	23.752	12/26/2016	53,173	0	0	2.938	1/17/2017
furan	1	204,843	0	0	0.467	12/31/2016	53,173	0	0	0.396	1/17/2017
butanenitrile	8000	204,843	0	0	0.508	1/6/2017	53,173	0	0	1.213	12/26/2017
but-3-en-2-one (MVK), 2,3-dihydrofuran,	1	204,843	874	14	3.762	12/31/2016	53,173	128	8	1.731	1/17/2017
butanal	25000	204,843	0	0	2.016	12/31/2016	53,173	0	0	8.855	12/26/2016
NDMA	0.3	204,843	466	6	0.385	1/15/2016	53,173	96	2	0.33	12/26/2016
benzene	500	204,843	0	0	21.413	12/26/2016	53,173	0	0	19.773	1/6/2017
pyridine, 2,4-pentadienenitrile	300	204,843	0	0	1.488	12/26/2016	53,173	0	0	1.313	1/6/2017
2-methylene butanenitrile	30	204,843	0	0	0.3	12/22/2016	53,173	0	0	0.13	12/30/2016
2-methylfuran	1	204,843	136	8	1.157	12/22/2016	53,173	10	0	0.633	12/30/2016
pentanenitrile	6000	204,843	0	0	0.359	12/31/2016	53,173	0	0	0.564	12/26/2016
3-methyl-3-buten-2-one, 2-methyl-2-but	20	204,843	0	0	2.572	12/31/2016	53,173	0	0	1.081	12/13/2016
NEMA	0.3	204,843	0	0	0.139	1/15/2017	53,173	0	0	0.118	12/12/2016
2,5-dimethylfuran	1	204,843	29	8	1.19	12/31/2016	53,173	1	0	0.604	12/13/2016
hexanenitrile	6000	204,843	0	0	0.961	12/12/2016	53,173	0	0	0.979	12/12/2016
2-hexanone (MBK)	5000	204,843	0	0	0.642	12/31/2016	53,173	0	0	3.595	1/13/2017
NDEA	0.1	204,843	105	0	0.09	12/12/2016	53,173	22	0	0.075	12/12/2016
butyl nitrite, 2-nitro-2-methylpropane	30	204,843	0	0	0.15	12/13/2016	53,173	0	0	0.144	12/12/2016
2,4-dimethylpyridine	500	204,843	0	0	2.309	1/6/2017	53,173	0	0	2.857	12/13/2016
2-propylfuran, 2-ethyl-5-methylfuran	1	204,843	6	0	0.792	12/31/2016	53,173	0	0	0.352	12/13/2016
heptanenitrile	6000	204,843	0	0	0.247	12/31/2016	53,173	0	0	0.385	12/26/2016
4-methyl-2-hexanone	500	204,843	0	0	1.075	12/31/2016	53,173	0	0	0.435	12/13/2016
NMOR	0.6	204,843	5	0	0.37	12/12/2016	53,173	1	0	0.44	12/30/2016
butyl nitrate	2500	204,843	0	0	0.057	1/6/2017	53,173	0	0	0.04	12/13/2016
2-ethyl-2-hexenal, 4-(1-methylpropyl)-2,3	1	204,843	8	2	1.004	12/31/2016	53,173	2	0	0.551	1/8/2017
6-methyl-2-heptanone	8000	204,843	0	0	0.472	12/31/2016	53,173	0	0	0.205	12/13/2016
2-pentylfuran	1	204,843	17	0	0.832	12/12/2016	53,173	1	0	0.608	12/26/2016
biphenyl	200	204,843	0	0	0.54	12/31/2016	53,173	0	0	0.268	12/13/2016
2-heptylfuran	1	204,843	0	0	0.44	12/31/2016	53,173	0	0	0.158	12/13/2016
1,4-butanediol dinitrate	50	204,843	0	0	0.373	12/12/2016	53,173	0	0	0.03	1/10/2017
2-octylfuran	1	204,843	0	0	0.114	12/31/2016	53,173	0	0	0.111	12/13/2016
1,2,3-propanetriol, 1,3-dinitrate	50	204,843	0	0	0.389	12/31/2016	53,173	0	0	0.161	12/22/2016
PCB	1000	204,843	0	0	0.882	12/12/2016	53,173	0	0	0.017	12/12/2016
6-(2-furanyl)-6-methyl-2-heptanone	1	204,843	0	0	0.072	1/15/2017	53,173	0	0	0.047	12/26/2016
furfural acetophenone	1	204,843	0	0	0.223	12/22/2016	53,173	0	0	0.16	12/22/2016
PCB2	1000	204,843	0	0	0.429	12/12/2016	53,173	0	0	0.019	12/12/2016

Table 6-2. Time-Weighted Average Concentrations (Units in ppb)

		On-Site																	Off-Site																	
		Week 1.1				Week 1.2				Week 1.3		Week 1.4			Week 1.5				Week 1.1				Week 1.2				Week 1.3		Week 1.4			Week 1.5			
COPC[1]	OEL (ppb)	12/9	12/10	12/12	12/13	12/22	12/26	12/27	12/28	12/30	12/31	1/6	1/8	1/10	1/13	1/15	1/16	1/17	12/9	12/10	12/12	12/13	12/22	12/26	12/27	12/28	12/30	12/31	1/6	1/8	1/10	1/13	1/15	1/16	1/17
Ammonia	2,500	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
formaldehyde	300	0.950	1.091	1.000	0.598	0.707	1.038	0.785	0.694	0.665	1.003	1.448	0.670	0.620	1.572	1.499	1.358	1.357	N/A	1.066	0.963	0.805	1.301	0.940	0.701	0.427	0.677	0.472	0.958	0.747	0.658	0.883	0.946	1.143	1.250
methanol	200,000	25.944	7.712	5.194	14.433	6.340	3.632	2.367	9.567	8.825	8.189	3.497	2.312	4.047	3.912	2.120	3.151	5.533	N/A	20.951	12.035	7.064	6.528	21.104	13.592	2.423	5.371	2.866	4.055	3.006	5.761	4.129	3.707	3.298	16.352
acetonitrile	20,000	0.056	0.088	0.067	0.064	0.039	0.049	0.042	0.036	0.039	0.040	0.045	0.042	0.048	0.065	0.050	0.050	0.045	N/A	0.104	0.074	0.071	0.051	0.055	0.040	0.043	0.050	0.042	0.050	0.043	0.055	0.060	0.048	0.046	0.047
acetaldehyde	25,000	0.855	0.866	1.020	0.787	0.887	0.940	0.549	0.483	0.528	0.576	0.657	0.637	0.674	1.169	0.720	0.811	0.919	N/A	0.984	1.095	1.282	1.249	0.721	0.547	0.538	0.730	0.484	0.752	0.753	0.825	0.976	0.732	0.857	1.047
ethylamine	5,000	0.021	0.021	0.018	0.017	0.021	0.025	0.022	0.017	0.016	0.018	0.034	0.023	0.021	0.026	0.023	0.028	0.025	N/A	0.018	0.021	0.018	0.023	0.021	0.022	0.018	0.018	0.018	0.038	0.031	0.021	0.018	0.027	0.034	0.030
1,3-butadiene	1,000	0.268	0.297	0.334	0.403	0.214	0.270	0.197	0.201	0.198	0.217	0.170	0.181	0.194	0.304	0.267	0.174	0.171	N/A	0.356	0.361	0.544	0.242	0.308	0.211	0.217	0.282	0.190	0.207	0.168	0.237	0.330	0.196	0.150	0.174
propanenitrile	6,000	0.037	0.045	0.045	0.051	0.031	0.033	0.029	0.030	0.029	0.029	0.029	0.028	0.030	0.043	0.031	0.026	0.026	N/A	0.051	0.053	0.062	0.037	0.038	0.034	0.030	0.036	0.027	0.041	0.027	0.030	0.042	0.033	0.026	0.027
1-butanol; butenes	20,000	0.292	0.359	0.369	0.318	0.334	0.267	0.257	0.296	0.235	0.320	0.329	0.233	0.189	0.377	0.361	0.302	0.273	N/A	0.398	0.615	0.652	0.426	0.371	0.453	0.275	0.422	0.212	0.587	0.223	0.260	0.478	0.303	0.280	0.284
methyl isocyanate	20	0.028	0.031	0.036	0.030	0.021	0.021	0.021	0.019	0.020	0.020	0.024	0.020	0.020	0.033	0.027	0.022	0.024	N/A	0.034	0.033	0.034	0.022	0.023	0.017	0.017	0.021	0.018	0.023	0.021	0.021	0.028	0.023	0.020	0.024
methyl nitrite	100	0.073	0.115	0.089	0.073	0.069	0.081	0.092	0.075	0.060	0.080	0.107	0.047	0.051	0.184	0.114	0.110	0.102	N/A	0.090	0.084	0.084	0.154	0.055	0.042	0.043	0.062	0.042	0.053	0.051	0.052	0.074	0.056	0.051	0.080
furan	1	0.030	0.036	0.028	0.023	0.023	0.028	0.020	0.015	0.017	0.018	0.022	0.024	0.020	0.035	0.027	0.019	0.028	N/A	0.036	0.030	0.028	0.025	0.028	0.016	0.016	0.021	0.018	0.021	0.026	0.023	0.030	0.024	0.018	0.027
butanenitrile	8,000	0.023	0.026	0.024	0.020	0.020	0.023	0.017	0.015	0.015	0.017	0.017	0.015	0.015	0.024	0.023	0.016	0.015	N/A	0.028	0.026	0.027	0.020	0.028	0.020	0.014	0.019	0.012	0.021	0.015	0.017	0.021	0.019	0.014	0.015
3-buten-2-one;2,3-dihydrofuran; 2,5-dihydrofuran	1	0.063	0.065	0.081	0.061	0.050	0.044	0.049	0.053	0.046	0.051	0.047	0.039	0.040	0.067	0.074	0.044	0.051	N/A	0.069	0.072	0.089	0.051	0.055	0.030	0.032	0.048	0.033	0.037	0.038	0.045	0.055	0.037	0.034	0.051
butanal	25,000	0.093	0.127	0.121	0.099	0.086	0.074	0.057	0.073	0.081	0.089	0.097	0.094	0.078	0.127	0.138	0.122	0.142	N/A	0.127	0.133	0.123	0.100	0.081	0.058	0.067	0.091	0.081	0.096	0.105	0.086	0.128	0.128	0.126	0.145
N-nitrosodiemethylamine (NDMA)	0.3	0.021	0.024	0.026	0.023	0.015	0.015	0.014	0.014	0.016	0.014	0.019	0.022	0.017	0.030	0.024	0.021	0.027	N/A	0.029	0.026	0.024	0.015	0.021	0.014	0.015	0.018	0.015	0.024	0.021	0.019	0.036	0.030	0.024	0.028
benzene	500	0.109	0.157	0.150	0.143	0.119	0.113	0.104	0.113	0.102	0.123	0.151	0.121	0.100	0.169	0.142	0.162	0.175	N/A	0.203	0.236	0.300	0.232	0.126	0.166	0.135	0.207	0.117	0.368	0.140	0.148	0.235	0.173	0.155	0.200
2,4-pentadienenitrile; pyridine	300	0.018	0.023	0.023	0.021	0.042	0.018	0.015	0.016	0.015	0.017	0.019	0.017	0.016	0.024	0.018	0.018	0.020	N/A	0.027	0.029	0.032	0.026	0.017	0.018	0.018	0.023	0.016	0.033	0.019	0.019	0.026	0.023	0.018	0.023
2-methylene butanenitrile	300	0.013	0.016	0.015	0.013	0.014	0.012	0.010	0.010	0.011	0.011	0.011	0.010	0.010	0.015	0.013	0.010	0.010	N/A	0.016	0.015	0.015	0.014	0.014	0.010	0.010	0.012	0.009	0.011	0.011	0.011	0.013	0.012	0.009	0.011
2-methylfuran	1	0.031	0.034	0.036	0.029	0.028	0.027	0.023	0.022	0.019	0.022	0.023	0.023	0.021	0.035	0.035	0.022	0.027	N/A	0.038	0.035	0.038	0.027	0.024	0.014	0.016	0.023	0.017	0.020	0.024	0.025	0.026	0.024	0.018	0.027
pentanenitrile	6,000	0.018	0.022	0.018	0.015	0.014	0.016	0.013	0.013	0.012	0.013	0.013	0.011	0.011	0.018	0.018	0.012	0.011	N/A	0.023	0.017	0.019	0.013	0.022	0.014	0.010	0.013	0.010	0.014	0.011	0.012	0.016	0.014	0.010	0.010
3-methyl-3-buten-2-one; 2-methyl-2-butenal	20	0.057	0.065	0.075	0.050	0.042	0.036	0.038	0.037	0.037	0.043	0.042	0.039	0.036	0.058	0.066	0.044	0.049	N/A	0.076	0.067	0.069	0.044	0.047	0.027	0.028	0.039	0.031	0.035	0.040	0.039	0.049	0.044	0.040	0.050
N-nitrosomethylethylamine (NEMA)	0.3	0.002	0.006	0.005	0.005	0.006	0.006	0.003	0.006	0.007	0.007	0.006	0.007	0.005	0.007	0.005	0.005	0.008	N/A	0.006	0.006	0.006	0.008	0.004	0.004	0.007	0.010	0.007	0.007	0.009	0.006	0.008	0.008	0.008	0.008
2,5-dimethylfuran	1	0.024	0.024	0.031	0.024	0.021	0.018	0.019	0.019	0.016	0.021	0.020	0.019	0.017	0.029	0.028	0.019	0.024	N/A	0.025	0.028	0.034	0.022	0.017	0.012	0.014	0.018	0.014	0.016	0.020	0.020	0.022	0.017	0.015	0.023
hexanenitrile	6,000	0.015	0.017	0.019	0.014	0.013	0.013	0.013	0.013	0.011	0.013	0.012	0.009	0.009	0.017	0.017	0.012	0.011	N/A	0.018	0.018	0.019	0.013	0.016	0.012	0.009	0.012	0.008	0.013	0.010	0.010	0.013	0.012	0.009	0.010
2-hexanone	5,000	0.030	0.040	0.032	0.025	0.023	0.020	0.018	0.022	0.021	0.023	0.022	0.021	0.019	0.029	0.024	0.020	0.023	N/A	0.046	0.038	0.033	0.027	0.025	0.020	0.022	0.024	0.021	0.021	0.024	0.021	0.031	0.022	0.021	0.024
N-nitrosodiethylamine (NDEA)	0.1	0.002	0.003	0.003	0.003	0.002	0.003	0.002	0.003	0.003	0.002	0.002	0.003	0.003	0.003	0.002	0.002	0.002	N/A	0.005	0.003	0.003	0.001	0.002	0.002	0.003	0.002	0.003	0.003	0.002	0.002	0.003	0.003	0.002	0.002
butyl nitrite; 2-nitro-2-methylpropane	100	0.010	0.012	0.012	0.010	0.009	0.009	0.007	0.007	0.007	0.007	0.008	0.008	0.009	0.011	0.009	0.008	0.008	N/A	0.012	0.013	0.013	0.012	0.010	0.007	0.008	0.009	0.008	0.010	0.009	0.009	0.011	0.010	0.009	0.010
2,4-dimethylpyridine	500	0.019	0.020	0.020	0.018	0.015	0.012	0.011	0.013	0.012	0.017	0.016	0.013	0.012	0.017	0.018	0.015	0.016	N/A	0.026	0.035	0.044	0.031	0.023	0.036	0.019	0.028	0.015	0.039	0.015	0.019	0.032	0.035	0.017	0.018
2-ethyl-5-methylfuran; 2-propylfuran	1	0.012	0.012	0.016	0.012	0.012	0.014	0.010	0.010	0.010	0.013	0.011	0.013	0.011	0.020	0.014	0.010	0.014	N/A	0.011	0.016	0.023	0.012	0.016	0.008	0.009	0.012	0.009	0.010	0.013	0.012	0.020	0.012	0.008	0.016
heptanenitrile	6,000	0.007	0.009	0.009	0.007	0.007	0.006	0.007	0.007	0.006	0.007	0.006	0.004	0.004	0.008	0.009	0.006	0.005	N/A	0.009	0.007	0.009	0.007	0.008	0.007	0.005	0.006	0.004	0.005	0.005	0.004	0.007	0.005	0.004	0.005
4-methyl-2-hexanone	500	0.113	0.106	0.116	0.082	0.057	0.048	0.053	0.049	0.051	0.056	0.066	0.061	0.061	0.094	0.081	0.064	0.072	N/A	0.122	0.128	0.087	0.081	0.062	0.049	0.046	0.054	0.048	0.058	0.062	0.064	0.080	0.071	0.064	0.072
N-nitrosomorpholine (NMOR)	0.6	0.009	0.007	0.011	0.008	0.007	0.006	0.007	0.006	0.006	0.007	0.007	0.006	0.006	0.009	0.010	0.008	0.011	N/A	0.010	0.012	0.014	0.009	0.008	0.007	0.006	0.011	0.006	0.008	0.006	0.009	0.010	0.008	0.009	0.010
butyl nitrate	2,500	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	N/A	0.002	0.003	0.003	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
2-ethyl-2-hexenal; 4-1(1-methylpropyl)-2,3-dihydrofuran; 3-(1,1-dimethylethyl)-2,3-dihydrofuran	1	0.050	0.062	0.046	0.033	0.062	0.060	0.036	0.031	0.034	0.037	0.032	0.033	0.027	0.041	0.059	0.033	0.029	N/A	0.074	0.037	0.038	0.045	0.104	0.031	0.027	0.030	0.024	0.023	0.043	0.027	0.031	0.030	0.029	0.030
6-methyl-2-heptanone	8,000	0.018	0.023	0.019	0.013	0.015	0.011	0.014	0.014	0.015	0.015	0.013	0.011	0.011	0.016	0.016	0.012	0.012	N/A	0.027	0.019	0.016	0.015	0.016	0.012	0.013	0.014	0.012	0.010	0.011	0.011	0.013	0.013	0.012	0.012
2-pentylfuran	1	0.051	0.049	0.053	0.042	0.045	0.041	0.037	0.038	0.034	0.040	0.038	0.034	0.033	0.049	0.056	0.039	0.038	N/A	0.051	0.044	0.046	0.043	0.049	0.030	0.028	0.034	0.028	0.028	0.040	0.034	0.037	0.034	0.033	0.036
biphenyl	200	0.035	0.030	0.033	0.028	0.053	0.033	0.030	0.027	0.028	0.033	0.029	0.026	0.025	0.034	0.045	0.032	0.029	N/A	0.032	0.029	0.032	0.039	0.040	0.024	0.022	0.028	0.023	0.022	0.029	0.026	0.028	0.027	0.031	0.028
2-heptylfuran	1	0.019	0.017	0.021	0.019	0.022	0.018	0.018	0.018	0.016	0.021	0.019	0.015	0.014	0.020	0.027	0.018	0.016	N/A	0.017	0.016	0.019	0.019	0.022	0.013	0.012	0.014	0.012	0.012	0.017	0.015	0.015	0.014	0.015	0.015
1,4-butanediol, dinitrate	50	0.003	0.003	0.003	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.003	0.002	0.002	N/A	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
2-octylfuran	1	0.002	0.002	0.003	0.003	0.003	0.002	0.002	0.002	0.002	0.004	0.002	0.002	0.002	0.003	0.003	0.002	0.002	N/A	0.002	0.002	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
1,2,3-propanetriol; 1,3-dinitrate	50	0.022	0.021	0.027	0.026	0.059	0.031	0.030	0.025	0.032	0.038	0.033	0.034	0.025	0.037	0.042	0.033	0.029	N/A	0.019	0.019	0.022	0.068	0.029	0.023	0.016	0.028	0.023	0.020	0.053	0.027	0.023	0.020	0.036	0.030
PCB, C12H9Cl	1,000	0.002	0.003	0.003	0.002	0.002	0.002	0.001	0.001	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	N/A	0.003	0.003	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.003	0.002	0.002
6-(2-furanyl)-6-6methyl-2-heptanone	1	0.003	0.003	0.004	0.004	0.005	0.005	0.003	0.003	0.004	0.005	0.003	0.004	0.003	0.004	0.005	0.004	0.003	N/A	0.003	0.003	0.003	0.004	0.004	0.003	0.003	0.003	0.003	0.003	0.004	0.003	0.003	0.003	0.004	0.003
furfural acetophenone (3-(2-furanyl)-1-pheynyl-2-propen-1-one	1	0.028	0.021	0.024	0.024	0.035	0.028	0.023	0.021	0.023	0.024	0.022	0.020	0.018	0.026	0.031	0.022	0.020	N/A	0.023	0.019	0.019	0.038	0.023	0.019	0.017	0.022	0.016	0.015	0.028	0.018	0.018	0.021	0.021	0.019
PCB, C12H8Cl2	1,000	0.001	0.003	0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.001	0.001	N/A	0.002	0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.001	0.001

[1] COPCs not measured by the PTR-MS include Ammonia, nitrous oxide, mercury, tributylphosphate, dibutyl butanephosphonate, 2-fluoropropene, and diethyl phthalate.

[2] Time weighted average utilizes detection limit values for time intervals when COPC of interest was not detected.

6.1 RECOMMENDATIONS

There are four primary recommendations from the RJ Lee Group team that can all be addressed over the next month.

1. Install and validate the Picarro Cavity Ring-Down spectrometer for ammonia detection. This should also include some dry runs including full data processing prior to field deployment.
2. Perform lab-based experiments to verify many of the mass assignments to the COPCs and their interfering compounds. Details of this recommendation are expanded below.
3. Perform direct sampling of tank vapors, whether at the AP stack or A farm passive breather filters, to provide an opportunity to apply mass assignment improvements made in recommendation 2 above and ensure the data processing algorithms for estimating COPCs perform well.
4. While sensitivity checks on a benzene standard have consistently passed, benzene concentration is consistently estimated lower than expected. This consistent bias suggests either an error in the dilution system of the standard or a drift in the transmission efficiency curve of the PTR-TOF. Neither is scheduled for calibration or maintenance but this bias should be investigated earlier than scheduled if the van is held from field work to perform the recommendations above.

Recommendation 2 is the result of the improvement in mass resolution of the PTR-TOF instrument deployed in 2017. For many of the compounds, the improved mass resolution has raised new questions that require a series of short lab-based experiments to finalize the algorithms used for the interpretation of the Hanford COPCs. The following lab-based experiments are recommended although the availability of some of these standards may be difficult to acquire:

A. Verify that 1,3-butadiene concentration is accurately estimated when humidity is varied. Also recommended is to determine detection limits of 1,3-butadiene at normal atmospheric humidity expected in our region.
B. Verify that furan and isoprene are clearly resolved from one another at all concentration ranges. This will require analysis of a few standard mixtures of the two compounds to ensure estimated concentrations are accurate. Multiple verifications are recommended due to the importance of furan in this work.
C. Verify that N-nitrosodimethylamine (NDMA) can be resolved from the methyl acetate ion signal. Detection limit of NDMA in the presence of a large concentration of methyl acetate (>10 ppbV) should also be determined. Field work suggests these ion signals are successfully resolved from one another.
D. Investigate the ability to resolve N-nitrosomethylethylamine (NEMA) from ethyl acetate in a similar manner to Recommendation 3 above.
E. Investigate the ability to resolve 2-methylfuran from an isomer of C_6H_{10} in a similar fashion to Recommendation 3 above.

F. Investigate the ability to resolve either 3-methyl-3-buten-2-one or 2-methyl-2-butenal from isomers of both $C_4H_4O_2$ and C_6H_{12} in a similar manner to Recommendation 3 above.
G. Verify that one of 3-buten-2-one, 2,3-dihydrofuran or 2,5-dihydrofuran can be clearly resolved from any one of the C_5H_{10} isomers in a similar fashion to Recommendation 3 above.
H. Verify that 2-hexanone can be resolved from an isomer of $C_5H_8O_2$ in a similar fashion to Recommendation 3 above.
I. Investigate the ability to resolve 6-methyl-2-heptanone from naphthalene in a similar fashion to Recommendation 3 above.
J. Investigate the ability to resolve NDEA from an isomer of $C_5H_{10}O_2$ in a similar fashion to Recommendation 3 above.
K. Investigate the ability to resolve NMOR from an isomer of $C_6H_{12}O_2$ in a similar fashion to Recommendation 3 above.
L. Verify that the two COPCs at nominal mass 181 are resolved from one another. Running a standard that contains both 1,4-butanediol dinitrate and 2-octylfuran will accomplish this.
M. Verifty that 2,5-dimethylfuran can be resolved from both isomers of C_7H_{12} and $C_5H_4O_2$ in a similar fashion to Recommendation 3 above.
N. Determine if the following compounds can be resolved from unidentified ion signals observed in ambient air; butyl nitrate, 2-heptylfuran, 1,2,3-propanetriol 1,3-dinitrate, PCB1($C_{12}H_9Cl$) and PCB2 ($C_{12}H_8Cl_2$).
O. Verify that the ion signal assigned to propanenitrile, methyl isocyanate, butanenitrile, 2,4-pentadienenitrile, pyridine, pentanenitrile, hexanenitrile, butyl nitrite, and 2-nitro-2-methylpropane are correct. The verification samples do not need to be standardized since the goal is to look at exact mass alignment with observed ion signals encountered at tank farms.

7.0 REFERENCES

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