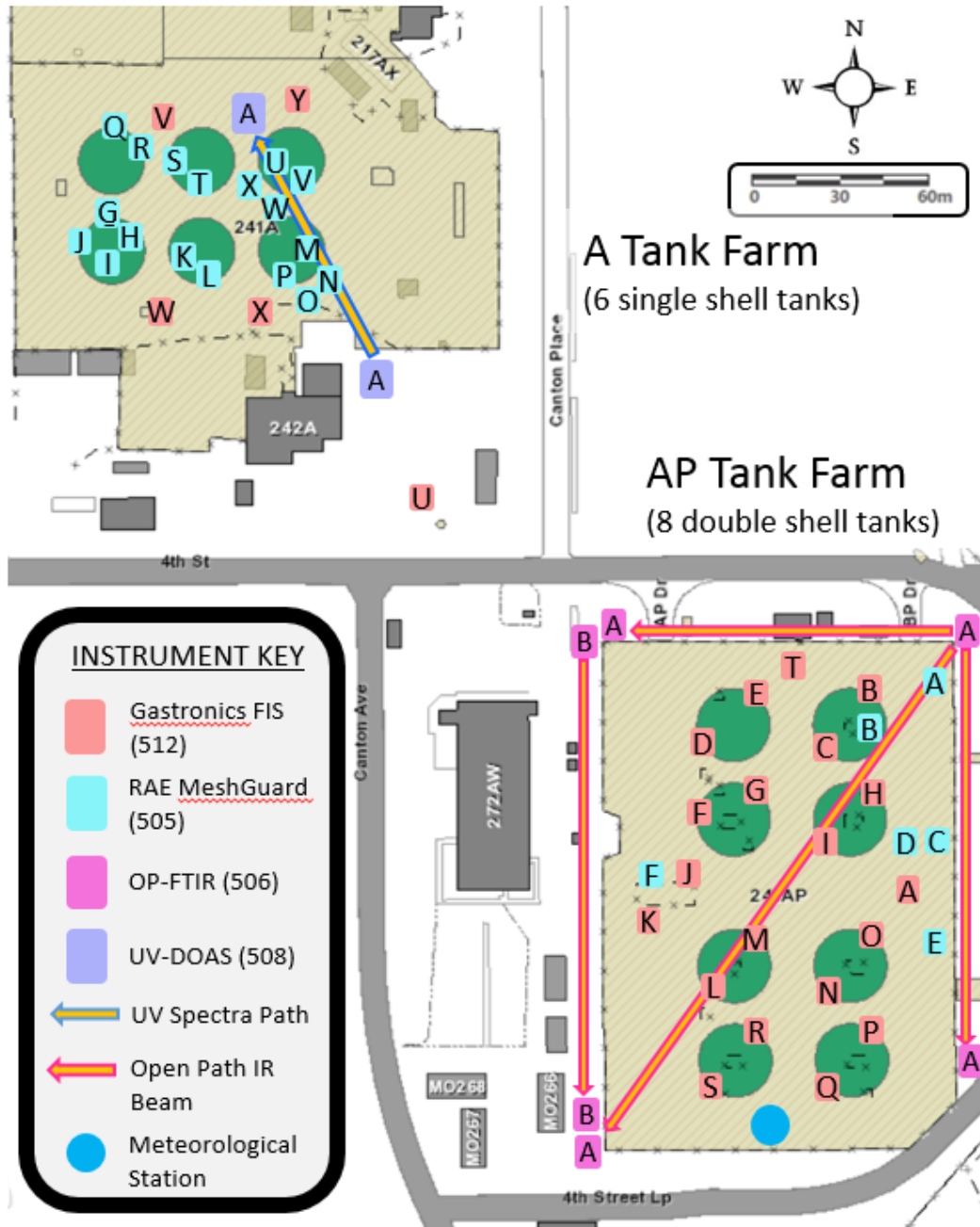


Vapor Monitoring and Detection System Weekly Report - A and AP Tank Farm Field Instrument Report

Revision 0 – Initial Release of Report

2/8/2017 6:00 – 2/15/2017 6:00

Instrument/Sampling Locations – A and AP Tank Farms



Vapor Monitoring and Detection System Weekly Report

2/8/2017 6:00 – 2/15/2017 6:00

Abbreviations and Units

CH ₄	=	methane
COPC	=	chemicals of potential concern
DRI	=	direct reading instrument
FIS	=	fixed instrument skid
IR	=	infrared
ND	=	not detected
NH ₃	=	ammonia
NO	=	nitric oxide
N ₂ O	=	nitrous oxide
NO ₂	=	nitrogen dioxide
OEL	=	occupational exposure limit
OP-FTIR	=	open path Fourier transform infrared spectrometer ¹
OSHA	=	Occupational Safety and Health Administration
PEL	=	permissible exposure limit
ppb	=	parts per billion
ppm	=	parts per million
UV	=	ultraviolet
UV-DOAS	=	ultraviolet differential optical absorption spectrometer ²
VMDS	=	vapor monitoring and detection system
VOC	=	volatile organic compounds, which include both volatile and semi-volatile compounds

VMDS Instruments

505	=	RAE MeshGuard
506A	=	OP-FTIR Multi-Path
506B	=	OP-FTIR Single-Path
508A	=	UV-DOAS
512	=	FIS Gastronics Direct Reading Instrument

¹ OP-FTIR Fact Sheet: <http://hanfordvapors.com/wp-content/uploads/2016/10/OP-FTIR-fact-sheet.pdf>

² UV-DOAS Quick Sheet: <http://hanfordvapors.com/wp-content/uploads/2016/10/UV-DOAS-Fact-Sheet.pdf>

Vapor Monitoring and Detection System Weekly Report

2/8/2017 6:00 – 2/15/2017 6:00

Introduction

This summary contains Vapor Monitoring and Detection System (VMDS) pilot-scale data collected over one week (2/8/2017 at 6:00 a.m. through 2/15/2017 at 6:00 a.m.) using direct reading vapor detection instruments, the open path Fourier transform infrared spectrometer (OP-FTIR), and the ultraviolet differential optical absorption spectrometer (UV-DOAS).

Pilot-scale testing is focused on evaluating component integration and functionality. Data shown may include results for calibration and calibration check (bump test) tests performed to verify sensors are functioning; these tests are visible in the data as spikes. Raw spectra (data) may need to be reprocessed and reviewed as understanding of the particular instruments being used as part of the VMDS pilot test are deployed and the company's ability to align the instruments with the overall objectives of the pilot test improves.

The spectrometer instruments—OP-FTIR and UV-DOAS—provide real-time multi-gas measurement (qualitative and quantitative) of gases. Even though the instrument is very accurate regarding the quantification of chemical compounds, reported results cannot be directly calculated into a concentration for a specific location, this is due to its sample size – an open path between two points. The sample path is defined by the location of the emitter and the reflector which may be tens to hundreds of meters apart. Therefore data from these instrument types will not be directly compared to the Occupational Exposure Limits (OELs) and Action Levels, but used to determine concentrations of compounds along the path of the instrument's beam.

For the spectrographic instruments (OP-FTIR and UV-DOAS), each analyte has a specific reference spectrum, which represents the absorption characteristics for that chemical in the IR or UV spectral regions. Reference spectra for each analyte are stored in an instrument software library (library) that specifies which absorption features are analyzed, how analysis is performed, and reporting criteria. Revisions to the library are periodically performed to improve accuracy of analysis for analytes; the optimization of the library is iterative and periodic changes to the library are being performed. Revisions to the library may result in the identification of a compound not previously thought to be present, or conversely determine that a previously reported analyte was not actually present. Identification of an analyte depends on the analytical method (UV or IR), the library used, analyte concentration, other chemical compounds present, and other factors. The compounds present can interfere/overlap with the analyte spectral signature, especially for compounds having the same functional groups (e.g., methyl or ketone groups). Work is ongoing to optimize the library and minimize these interferences.

The direct read instruments located within AP and A Tank Farms include the RAE MeshGuard (505) sensors for detecting NH₃ and the Fixed Instrument Skid (FIS) Gastronics (512) units with sensors for detecting NH₃ and VOCs.

Vapor Monitoring and Detection System Weekly Report

2/8/2017 6:00 – 2/15/2017 6:00

Summary for 2/8/2017 through 2/15/2017

The following sections summarize data reporting for vapor monitoring and detection instruments at AP and A Tank Farms for the 2/8/2017 through 2/15/2017 period. Instruments at AP Tank Farm include open path FTIR instruments (multi-path and single path) and the RAE MeshGuard and Gastronics direct reading instruments. Instruments at A Tank Farm includes the UV-DOAS spectrographic instrument and the RAE MeshGuard and Gastronics direct reading instruments. No waste retrieval activities occurred during this reporting period.

AP TANK FARM

AP Tank Farm OP-FTIR Instruments

During the week in review, instrument 506A detected nitrous oxide (N₂O), methane (CH₄), and ammonia (NH₃)(Table 1). Nitrous oxide and CH₄ are typically found in the atmosphere at background levels of approximately 0.33 ppm for N₂O and 1.8 ppm for CH₄³. The recurring pattern of simultaneous N₂O and CH₄ spikes on this instrument was noted again this week (Figure 1). Data disruptions reported for N₂O and CH₄ occurred on three occasions and were due to foggy and/or freezing rain conditions. These disruptions occurred between approximately 08:00 and 14:00, 2/8/2017, between approximately 23:00, 2/13/2017 and 11:00, 2/14/2017, and between approximately 21:00, 2/14/2017 and 05:00, 2/15/2017. A power interruption occurred between 14:07, 2/10/2017 and 07:05, 2/13/2017, resulting in no data reported to the OSI Pi system during this period. Ammonia was detected at a maximum of 0.024 ppm at 08:25, 2/13/2017. This concentration is well below the OEL of 25 ppm for ammonia⁴.

Instrument 506B reported detections of N₂O, CH₄, NH₃, 1-butanol (BuOH), and methyl nitrite (MeNO₂) to the OSI Pi System. Data disruptions reported for the N₂O and CH₄ 506B sensors occurred at nearly the same times as the data disruptions reported by the 506A instrument (Figure 2). Reported values for BuOH occurred during times of the data disruptions, therefore these reported BuOH values are considered suspect.

Most compounds detected by both OP-FTIR instruments are typically present in air at detectable levels. Consistency in measured values for these compounds indicates that the OP-FTIR units are effectively measuring composition of the gas components within its path. Compounds identified are reported in Table 1 and Figures 1 and 2 below.

³ Climate Change Indicators: Atmospheric Concentration of Greenhouse Gases: <https://www.epa.gov/climate-indicators/climate-change-indicators-atmospheric-concentrations-greenhouse-gases>

⁴RPP-22491, R1, Industrial Hygiene Chemical Vapor Technical Basis: <http://hanfordvapors.com/wp-content/uploads/2016/10/Industrial-Hygiene-Chemical-Vapor-Technical-Basis-RPP-22491 - Rev 1.pdf>

Vapor Monitoring and Detection System Weekly Report

2/8/2017 6:00 – 2/15/2017 6:00

Table 1. Chemical Species Detected^a on Open Path FTIRs at AP Tank Farm.

Chemical Compound	506A: OP-FTIR Multi-Path (ppm)	506B: OP-FTIR Single-Path (ppm)
Nitrous Oxide*	0.23 – 0.50 ^b	0.15 – 0.43 ^b
Ammonia*	ND – 0.024	ND – 0.021
Methane	1.1 – 2.3 ^b	0.67 – 1.8 ^b
1,3-Butadiene*	ND	ND
1-Butanol*	ND	ND – 1.9 ^c
2-Hexanone*	ND	ND
3-Buten-2-one*	ND	ND
Acetaldehyde*	ND	ND
Acetonitrile*	ND	ND
Benzene*	ND	ND
Butanal*	ND	ND
Butyl Nitrite*	ND	ND
Ethylamine*	ND	ND
Formaldehyde*	ND	ND
Furan*	ND	ND
Methanol*	ND	ND
Methyl Isocyanate*	ND	ND
Methyl Nitrite*	ND	ND – 0.16
N-Nitrosodiethylamine*	ND	ND
N-Nitrosodimethylamine*	ND	ND
N-Nitrosomorpholine*	ND	ND
Propanenitrile*	ND	ND
Pyridine*	ND	ND
Tributyl Phosphate*	ND	ND

- Notes:
- (a) Based on data retrieved from OSI PI; OSI PI System is a data visualization software package from OSIsoft.
 - (b) Disrupted data for nitrous oxide and ammonia due to weather-related events are not included in the table for these compounds
 - (c) Suspect data
- *Chemical is on COPC list
 ND – Not detected by instrument

Vapor Monitoring and Detection System Weekly Report

2/8/2017 6:00 – 2/15/2017 6:00

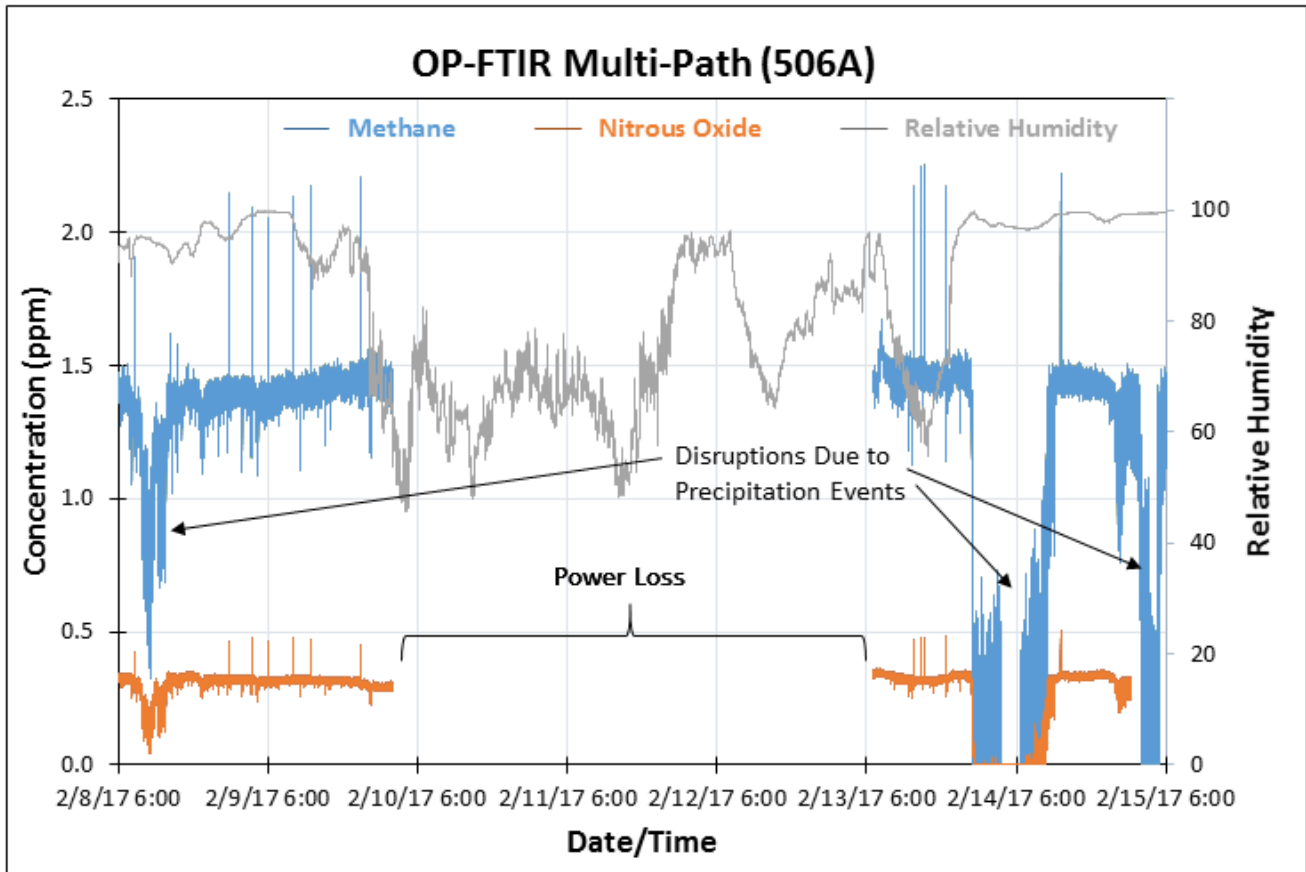


Figure 1. OP-FTIR Multi-Path (506A) Plot for CH₄ and N₂O. Relative Humidity Reported by the Coastal Meteorological Station (did not lose power).

Vapor Monitoring and Detection System Weekly Report

2/8/2017 6:00 – 2/15/2017 6:00

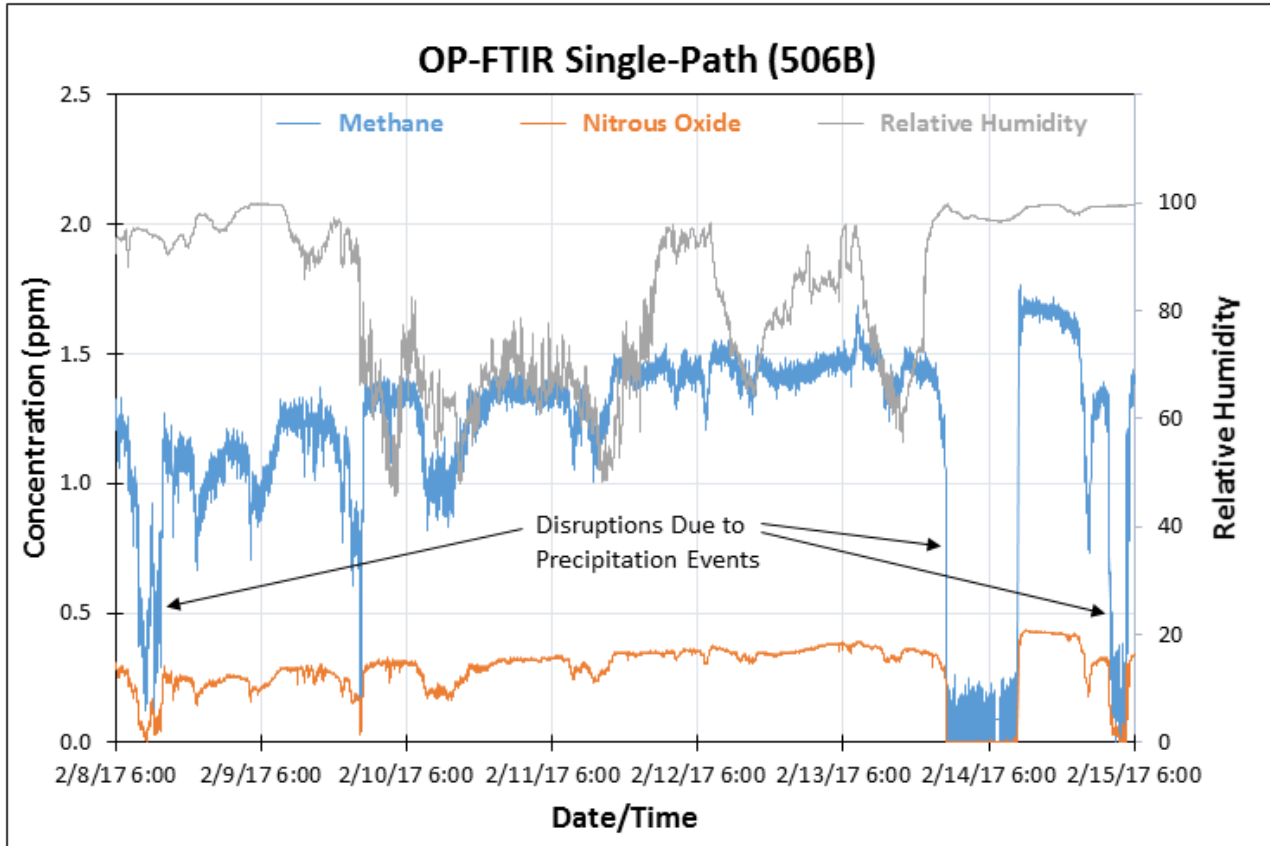


Figure 2. OP-FTIR Single-Path (506B) Plot for CH₄ and N₂O. Relative Humidity Reported by the Coastal Meteorological Station.

AP Tank Farm Direct Reading Instruments

Instruments located between A and AP Tank Farm, are included.

RAE MeshGuards (505 - NH₃): The 505 sensors located in AP Tank Farm are 505A, B, C, D, E, and F. RAE MeshGuard sensors went offline on 2/5/2017 due to communication software errors and initial attempts to restart the system on 2/5/2017 were unsuccessful. No NH₃ data were reported by the RAE MeshGuards during this week (Table 2).

Table 2. AP Tank Farm RAE MeshGuard (505) Comments.

Compound (units)	Comment	OEL	Action Level	Detection Range
NH ₃ (ppm)	• Instruments reporting: None	25	12.5	1 – 50

FIS Gastronics (512 - NH₃, VOCs, N₂O): Units located in AP Tank Farm include: 512A, B, C, D, E, F, G, H, I, J, K, L, M, N, O, P, Q, R, S, and T. Unit 512U is located between AP Tank Farm and the A Tank farm. During this week, instruments 512C, E, H, I, T were calibrated on

Vapor Monitoring and Detection System Weekly Report

2/8/2017 6:00 – 2/15/2017 6:00

2/8/2017. Later in the week, instruments 512D, F, and G were calibrated on 2/13/2017 and instruments 512A, C, D, E, F, G, H, I, J, K, L, M, N, O, P, Q, R, and T were bump tested (checked) the next day. Only sensor 512S could not be checked because power to the instrument was too low. Many of the 512 units that were in calibration for VOC much of the week were out of calibration by 2/14/2017 (Table 3).

No ammonia was detected by Gastronics instruments that were in calibration and reporting this week. Two of the 512 units reported non-detectable levels of VOC. One unit reported VOC at <2 ppm and no units reported VOCs ≥ 2 ppm (Table 3). A total VOC action limit of 2 ppm currently is prescribed by Fact Sheet EH-09-001.⁵ The N₂O sensors on the 512 instruments have been difficult to keep in calibration and the N₂O data will remain suspect until the stability of the sensor and calibration can be confirmed.

Table 3. AP Tank Farm Gastronics (512) Comments.

Compound (units)	Comment	OEL	Action Level	Detection Range
NH ₃ (ppm)	<ul style="list-style-type: none"> Out of calibration (as of 2/14/2017)*: 512A, N, P, and Q No ammonia detected 	25	12	1 – 100
VOC (ppm)	<ul style="list-style-type: none"> Out of Calibration (as of 2/14/2017)*: 512A, C, D, E, F, G, H, J, L, M, O, P, Q, R, and T Instruments that reported no VOCs detected: 512I and N Instruments that reported a maximum value of <2 ppm: 512K Instruments that reported maximum values ≥ 2 ppm: None 	N/A	2	0.001 – 50

* NH₃/VOC: Only instruments reading within 10% of the calibration gas concentration during their most recent bump/calibration test are reported here⁶.

⁵ Fact Sheet for Action Limit for Volatile Organic Compounds, Washington River Protection Solutions, Richland, Washington.

⁶ Calibrating and Testing Direct-Reading Portable Gas Monitors: <https://www.osha.gov/dts/shib/shib093013.html>

Vapor Monitoring and Detection System Weekly Report

2/8/2017 6:00 – 2/15/2017 6:00

A TANK FARM

UV-DOAS

Ammonia, nitric oxide (NO), ozone (O₃), and p-xylene (pXy) were detected by the instrument during the period under review (Table 4). Many of these are typically found in detectable quantities in background air⁷. The PEL for p-xylene⁸ is 100 ppm. Analyte concentrations are reported in Table 4 and Figure 3 below. The noisy ozone data reported between 23:20, 2/13/2017 and 10:30, 2/14/2017 corresponds with zero ammonia and nitric oxide readings reported during the same period, as indicated by the vertical dashed lines in Figure 3. These anomalous readings during this period are due to interference by foggy and/or freezing rain conditions.

Table 4. Chemical Species Detected^a on UV-DOAS at A Tank Farm

Chemical Compound	508A: UV-DOAS (ppm)	Chemical Compound	508A: UV-DOAS (ppm)
Ammonia*	ND – 0.035	Methyl Nitrite*	ND
Nitric Oxide	ND – 0.038	Pyridine*	ND
Ozone	0.053 – 0.16 ^b	1,2,4-Trimethylbenzene	ND
1,3-Butadiene*	ND	1,3,5-Trimethylbenzene	ND
2-Methyl-2-butenal*	ND	Ethylbenzene	ND
2-Methylfuran*	ND	m-Xylene	ND
Acetaldehyde*	ND	Nitrogen Dioxide	ND
Benzene*	ND	o-Xylene	ND
Butanal*	ND	p-Xylene	ND – 0.037
Ethylamine*	ND	Styrene	ND
Formaldehyde*	ND	Sulfur Dioxide	ND
Furan*	ND	Toluene	ND
Mercury*	ND		

Notes: (a) Based on data retrieved from OSI PI; OSI PI System is a data visualization software package from OSIsoft.

(b) Isolated spikes equal to zero do not follow the general trend for ozone, and therefore were not included in the table

*Chemical is on COPC list

ND – Not detected by instrument

⁷ Air Composition from "The Engineering ToolBox": http://www.engineeringtoolbox.com/air-composition-d_212.html

⁸ OSHA: https://www.osha.gov/dts/chemicalsampling/data/CH_276400.html

Vapor Monitoring and Detection System Weekly Report

2/8/2017 6:00 – 2/15/2017 6:00

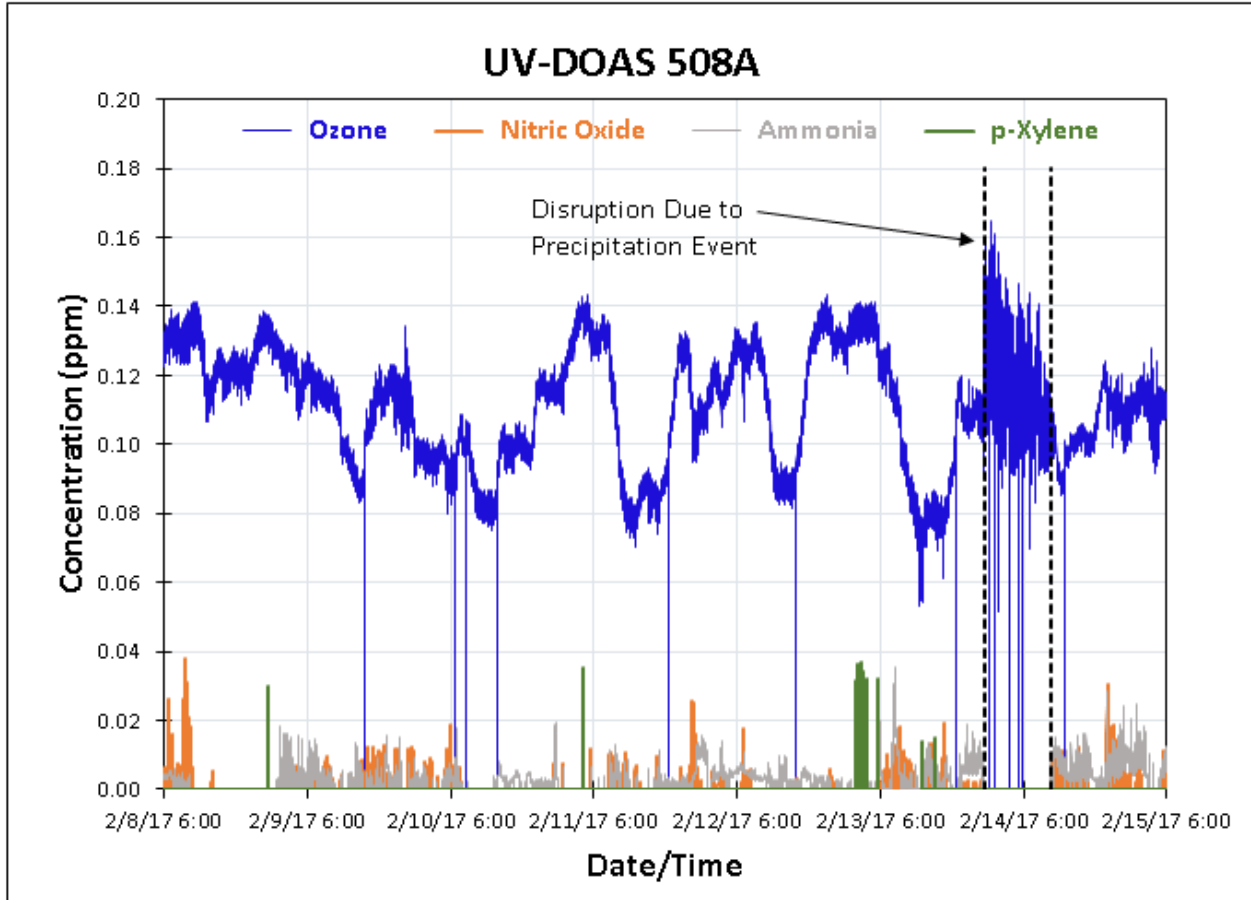


Figure 2. Chemical Species Detected by the UV-DOAS (508A) Instrument.

A Tank Farm Direct Reading Instruments

RAE MeshGuards (505 - NH₃): Sensors located in A Tank Farms include: 505G, H, I, J, K, L, M, N, O, P, Q, R, S, T U, V, W, and X. RAE MeshGuard sensors went offline on 2/5/2017 due to communication software errors and initial attempts to restart the system on 2/5/2017 were unsuccessful. No NH₃ data were reported by the RAE MeshGuards during this week (Table 5).

Table 5. A Tank Farm RAE MeshGuard (505) Comments.

Compound (units)	Comment	OEL	Action Level	Detection Range
NH ₃ (ppm)	• Instruments reporting: None	25	12.5	1 – 50

Gastronics (512 - NH₃, VOCs, N₂O): Units located in A Tank Farm include: 512V, W, X, and Y (Table 6). None of these instruments reported data during this week. All four instruments

Vapor Monitoring and Detection System Weekly Report

2/8/2017 6:00 – 2/15/2017 6:00

were calibrated on 2/13/2017 and were in calibration for NH₃ (100 ppm) and VOC (50 ppm). A total VOC action limit of 2 ppm currently is prescribed by Fact Sheet EH-09-001.⁹

Table 6. A Tank Farm Gastronics (512) Comments.

Compound (units)	Comment	OEL	Action Level	Detection Range
NH ₃ (ppm)	<ul style="list-style-type: none">• Out of calibration*: None• Instruments not reporting	25	12	1 – 100
VOC (ppm)	<ul style="list-style-type: none">• Out of Calibration*: None• Instruments not reporting	N/A	2	0.001 – 50

* NH₃/VOC: Only instruments reading within 10% of the calibration gas concentration during their most recent bump/calibration test are reported here.

⁹ Fact Sheet for Action Limit for Volatile Organic Compounds, Washington River Protection Solutions, Richland, Washington.

Vapor Monitoring and Detection System Weekly Report

2/8/2017 6:00 – 2/15/2017 6:00

2/8/2017 – 2/15/2017 Instrument Operational Status:

Time reporting is calculated using the time sensors that report to OSI PI System¹⁰ for each instrument (Tables 7 and 8).

Table 7. RAE MeshGuard (505) and Gastronics (512) % Time Reporting^a.

Instrument	% Time Reporting	Instrument	% Time Reporting	Instrument	% Time Reporting	Instrument	% Time Reporting
505A	0	505M	0	512A	50	512N	58
505B	0	505N	0	512B	94	512O	83
505C	0	505O	0	512C	0	512P	0
505D	0	505P	0	512D	86	512Q	73
505E	0	505Q	0	512E	8	512R	55
505F	0	505R	0	512F	96	512S	0
505G	0	505S	0	512G	0	512T	95
505H	0	505T	0	512H	97	512U	>99
505I	0	505U	0	512I	96	512V	0
505J	0	505V	0	512J	0	512W	0
505K	0	505W	0	512K	83	512X	0
505L	0	505X	0	512L	70	512Y	0
				512M	85		

(a) % time reporting based on NH₃.

Table 8. Spectrometer Instruments Time Reporting.

Instrument	% Time Reporting
506A	52
506B	100
508A	80 ^a

(a) % time reporting for 19 of the 26 chemical compounds. Seven compounds reported >99% of the time

¹⁰ OSI PI System is a data visualization software package from [OSIsoft](#).