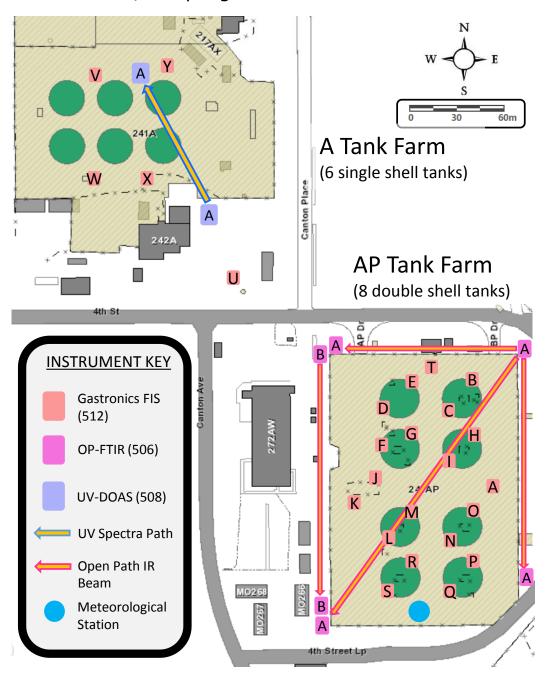
# <u>Vapor Monitoring Detection System Weekly Report - A and AP Tank Farm Field</u> <u>Instrument Report</u>

#### Revision 0 - Initial Release of Report

3/15/2017 6:00 - 3/22/2017 6:00

### Instrument/Sampling Locations -A & AP-Tank Farms



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#### **Abbreviations and Units**

 $CH_4$  = methane

COPC = chemicals of potential concern
DRI = direct reading instrument
FIS = fixed instrument skid

infrared IR = ND not detected =  $NH_3$ ammonia = NO nitric oxide =  $N_2O$ nitrous oxide =  $NO_2$ nitrogen dioxide =

 $O_3$  = ozone

OEL = occupational exposure limit

OP-FTIR = open path Fourier transform infrared spectrometer<sup>1</sup>
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<sup>2</sup>

VMDS = vapor monitoring and detection system

VOC = volatile organic compounds, which include both volatile and semi-volatile

compounds

#### **VMDS Instruments**

506A = OP-FTIR Multi-Path 506B = OP-FTIR Single-Path

508A = UV-DOAS

512 = FIS Gastronics Direct Reading Instrument

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

<sup>&</sup>lt;sup>2</sup> UV-DOAS Quick Sheet: <a href="http://hanfordvapors.com/wp-content/uploads/2016/10/UV-DOAS-Fact-Sheet.pdf">http://hanfordvapors.com/wp-content/uploads/2016/10/UV-DOAS-Fact-Sheet.pdf</a>

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#### Introduction

This summary contains Vapor Monitoring and Detection System (VMDS) pilot-scale data collected over one week (3/15/2017 at 6:00 a.m. through 3/22/2017 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 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 Gastronics (512) units with sensors for detecting  $NH_3$  and VOCs.

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#### Summary for 3/15/2017 through 3/22/2017

The following sections summarize data reporting for vapor monitoring and detection instruments at AP and A Tank Farms for the 3/15/2017 through 3/22/2017 period. Instruments at AP Tank Farm include open path FTIR instruments (multi-path and single-path) and the Gastronics direct reading instruments. Instruments at A Tank Farm include UV-DOAS 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 ( $N_2O$ ), methane ( $CH_4$ ), and 1-butanol (BuOH). Nitrous oxide and  $CH_4$  are typically found in the atmosphere at background levels of approximately 0.33 ppm for  $N_2O$  and 1.8 ppm for  $CH_4$ <sup>3</sup>. The recurring pattern of simultaneous  $N_2O$  and  $CH_4$  spikes on this instrument was noted again this week.

Instruments 506A and 506B went offline and stopped reporting data at 09:35 and 14:47, respectively, on 3/16/2017 due to a communication/power interruption. This interruption lasted until 08:40 on 3/20/2017, when power was restored and communication was re-established. Near the end of the week, starting at  $\sim 22:00$ , 3/21/2017, the methane and nitrous oxide readings were affected by high relative humidity conditions (Figures 1 and 2). The detection of 1-butanol during high humidity/precipitation conditions is considered suspect.

Most compounds detected by both 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. Specific instrument information is reported in Table 1 and Figures 1 and 2 below.

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<sup>&</sup>lt;sup>3</sup> Climate Change Indicators: Atmospheric Concentration of Greenhouse Gases: <a href="https://www.epa.gov/climate-indicators/climate-change-indicators-atmospheric-concentrations-greenhouse-gases">https://www.epa.gov/climate-indicators-atmospheric-concentrations-greenhouse-gases</a>

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

Chemical	506A: OP-FTIR Multi- Path (ppm)	506B: OP-FTIR Single-Path (ppm)
Nitrous Oxide*	0.19 - 0.46 <sup>b</sup>	0.30 - 0.39 <sup>b</sup>
Ammonia*	ND	ND
Methane	0.86 - 2.4 <sup>b</sup>	1.3 - 1.7 <sup>b</sup>
1-3-Butadiene*	ND	ND
1-Butanol*	ND - 1.9 <sup>b</sup>	ND
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
N-Nitrosodiethylamine*	ND	ND
N-Nitrosodimethylamine*	ND	ND
N-Nitrosomorpholine*	ND	ND
Propanenitrile*	ND	ND
Pyridine*	ND	ND
Tributyl Phosphate*	ND	ND

Notes:

<sup>(</sup>a) Based on data retrieved from OSI PI; OSI PI System is a data visualization software package from OSIsoft.

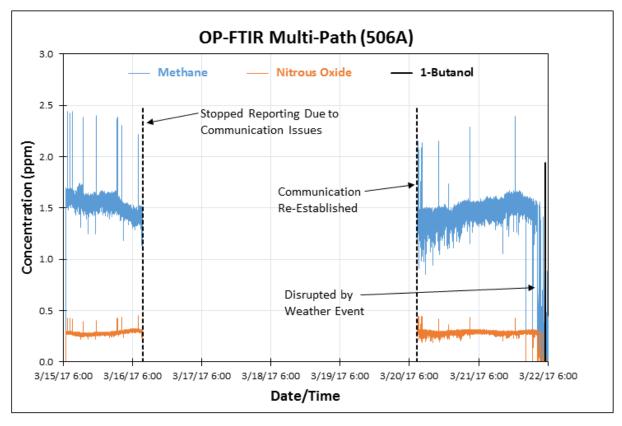
<sup>(</sup>b) Data affected by atmospheric conditions not included in the table for these compounds

<sup>\*</sup>Chemical is on COPC list

ND - Not detected

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Figure 1. Chemical Compounds Detected by the OP-FTIR (506A) Instrument.



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OP-FTIR Single-Path (506B)

Methane
Nitrous Oxide

Stopped Reporting Due to Communication Issues

Communication
Re-Established

Disrupted by Weather Event

Figure 2. Chemical Compounds Detected by the OP-FTIR (506B) Instrument.

#### **AP Tank Farm Direct Reading Instruments**

Instruments located between AP and A tank farms, just southeast of the 242-A evaporator and northwest of AP Tank Farm, are included.

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Date/Time

<u>Gastronics (512 - NH<sub>3</sub>, VOCs, N<sub>2</sub>O):</u> 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. Calibration checks were performed on all these Gastronics instruments during this week (3/20/2017) and only instruments 512L, N, S, and T passed calibration for VOC. Instruments 512A, B, C, D, E, F, G, H, I, J, K, L, M, O, P, Q, T, and U passed calibration for NH<sub>3</sub>. 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. Two units reported VOC at <2 ppm and no units reported VOCs ≥2 ppm (Table 2). A total VOC action limit of 2 ppm currently is prescribed by Fact Sheet EH-09-001.<sup>4</sup> N<sub>2</sub>O sensors are suspect and

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<sup>&</sup>lt;sup>4</sup> Fact Sheet for Action Limit for Volatile Organic Compounds, Washington River Protection Solutions, Richland, Washington: \\ap014\EnvironmentalHealth\Fact Sheets\EH-09-001 Turnback value for VOCs.pdf

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no data are reported. Only instruments that are reporting to OSI PI and in calibration are reported on here.

Table 2. AP Tank Farm Gastronics (512) Comments.

	Compound (units)	Comment	OEL	Action Level	Detection Range
	NH₃ (ppm)	No ammonia reported on any instrument  Out of Calibration*: 512N, R, S	25	12	1 - 100
`	/OC (ppm)	<ul> <li>Out of Calibration*: 512A, B, C, D, E, F, G, H, I, J, K, M, O, P, Q, R and U</li> <li>Instruments that reported no VOCs detected: 512N and S</li> <li>Instruments that reported a maximum value of &lt;2 ppm: 512L and T</li> <li>Instruments that reported maximum values ≥2 ppm: None</li> </ul>	N/A	2	0.005 - 50.0 <sup>5</sup>

<sup>\*</sup> Only instruments reading within 10% of the calibration gas concentration during their most recent bump/calibration test are reported here.

<sup>&</sup>lt;sup>5</sup> One-Page Fact Sheet for Gastronics Fixed Instrument Skid, Tank Farm Vapors Control Team, Version 1.0 2016/7/21 RBC.

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#### **A TANK FARM**

#### **A Tank Farm UV-DOAS Instrument**

Ammonia, nitric oxide (NO), and ozone ( $O_3$ ) were reported by the instrument during the period under review (Table 3). These chemicals are typically found in detectable quantities in air<sup>6</sup>. The 508A UV-DOAS instrument stopped running at 14:47 on 3/16/2017, due to software communication/power issues, but began reporting again at 08:40 on 3/20/2017. Analyte concentrations are reported in Table 3 and Figure 3 below.

Table 3. Chemical Species Detected on UV-DOAS at A Tank Farm

Chemical	508A: UV-DOAS (ppm)	Chemical	508A: UV-DOAS (ppm)
Ammonia*	ND - 0.020	Methyl Nitrite*	ND
Nitric Oxide	ND - 0.075	Pyridine*	ND
Ozone	0.026 - 0.11 <sup>b</sup>	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
Ethylamine*	ND	Styrene	ND
Formaldehyde*	ND	Sulfur Dioxide	ND
Furan*	ND	Toluene	ND
Mercury*	ND		

Notes:

<sup>(</sup>a) Based on data retrieved from OSI PI; OSI PI System is a data visualization software package from OSIsoft.

<sup>(</sup>b) Isolated spikes to zero do not follow the general trend for ozone, therefore these spikes are not included in the table

<sup>\*</sup>Chemical is on COPC list

ND - Not detected

<sup>&</sup>lt;sup>6</sup> Air Composition from "The Engineering ToolBox": <a href="http://www.engineeringtoolbox.com/aircomposition-d">http://www.engineeringtoolbox.com/aircomposition-d</a> 212.html

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**UV-DOAS 508A** 0.16 Nitric Oxide Ammonia Ozone 0.14 0.12 Concentration (ppm) Stopped Reporting Due to 0.10 Communication Issues 0.08 Communication 0.06 Re-Established 0.04 0.02 0.00 3/15/17 6:00 3/16/17 6:00 3/17/17 6:00 3/18/17 6:00 3/19/17 6:00 3/20/17 6:00 3/21/17 6:00 3/22/17 6:00 Date/Time

Figure 3. Concentrations of Chemicals Detected by UV-DOAS (508A).

#### **A Tank Farm Direct Reading Instruments**

<u>Gastronics</u> ( $512 - NH_{3}$ , <u>VOCs</u>,  $N_2O$ ): Units located in A Tank Farm include: 512V, W, X, and Y (Table 4). None of these instruments reported data during the week. Calibration checks were performed on 512V, W, X, and Y during this week (3/20/2017) and none of them were within 10% of the test gas concentration for VOC.

Compound (units)	Comment	OEL	Action Level	Detection Range
NH₃ (ppm)	No data reported on any instrument	25	12	1 - 100
VOC (ppm)	<ul> <li>Out of Calibration*: 512V, W, X, and Y</li> <li>No data reported on any instrument</li> </ul>	N/A	2	0.005 - 50.0 <sup>7</sup>

Table 4. A Tank Farm Gastronics (512) Comments.

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

<sup>&</sup>lt;sup>7</sup> One-Page Fact Sheet for Gastronics Fixed Instrument Skid, Tank Farm Vapors Control Team, Version 1.0 2016/7/21 RBC.

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### **3/15/2017 – 3/22/2017 Instrument Operational Status:**

Time reporting is calculated using the time sensors are reporting to OSI PI System<sup>8</sup> for each instrument (Tables 5 and 6).

Table 5. Gastronics Direct Reading Instruments (512) % Time Reporting<sup>a</sup>.

Instrument	% Time Reporting	Instrument	% Time Reporting
512A	44	512N	22
512B	0	5120	22
512C	0	512P	0
512D	22	512Q	43
512E	0	512R	13
512F	18	512S	0
512G	20	512T	43
512H	9	512U	21
512I	0	512V	0
512J	0	512W	0
512K	45	512X	0
512L	46	512Y	0
512M	44		

a) % time reporting based on NH<sub>3</sub>.

**Table 6. Spectrometer Instruments Time Reporting.** 

Instrument	% Time Reporting
506A	43
506B	46
508A	46

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<sup>&</sup>lt;sup>8</sup> OSI PI System is a data visualization software package from OSIsoft.