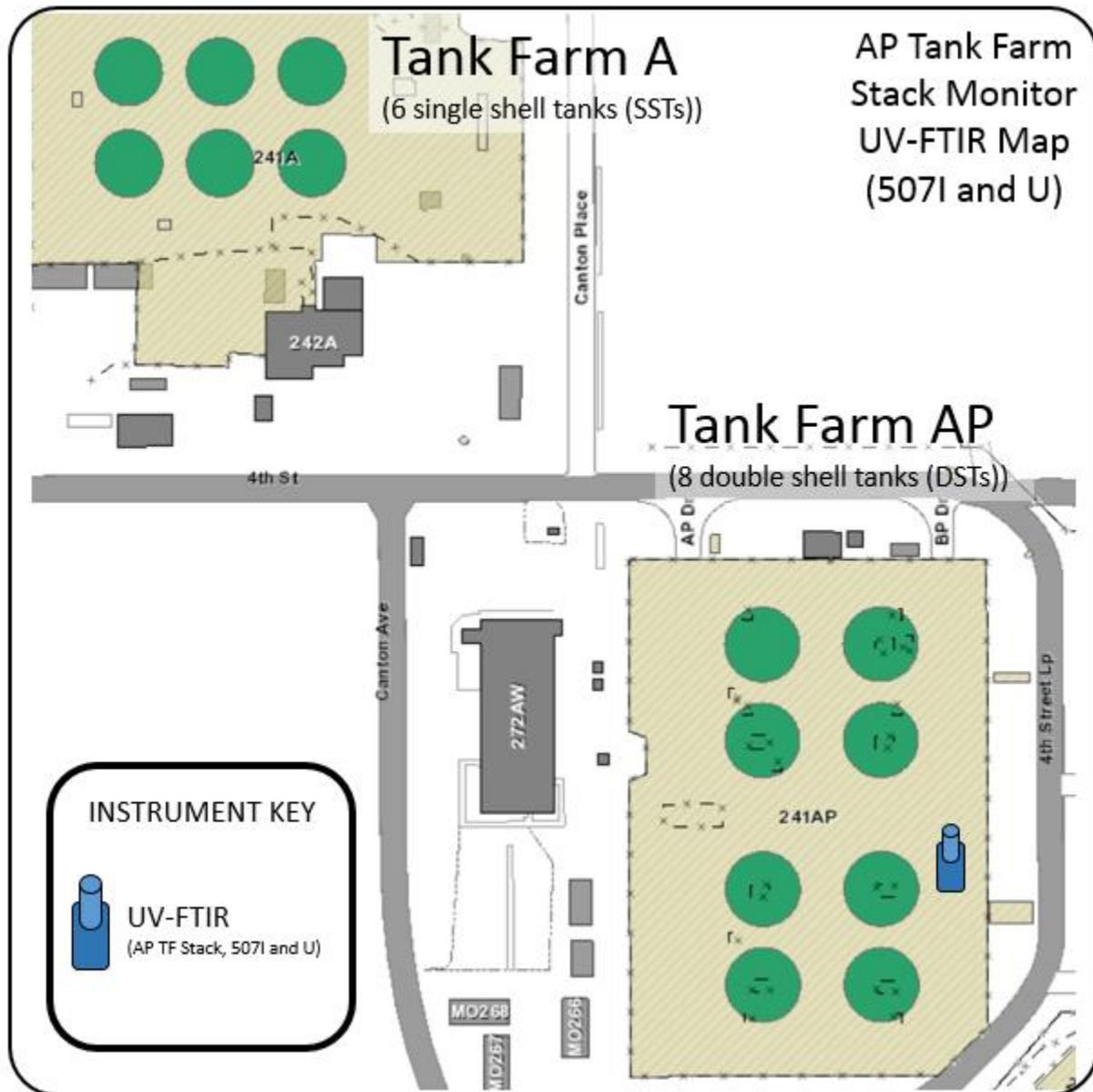


Vapor Monitoring Detection System Weekly Report – AP Tank Farm Stack Monitoring

Revision 0: Initial Release of Report

1/25/2017

AP-Tank Farm Stack Monitor (north is up)



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Abbreviations and Units

CH ₄	=	methane
COPC	=	chemicals of potential concern
FTIR	=	Fourier transform infrared spectrometer
IDMS	=	Integrated Document Management System
IR	=	infrared
ND	=	not detected
NH ₃	=	ammonia
NO	=	nitric oxide
N ₂ O	=	nitrous oxide
OEL	=	occupational exposure limit
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
UV-FTIR	=	ultraviolet - Fourier transform infrared (representing both analytical elements of the instrument, the UV and IR modules)
VMDS	=	vapor monitoring detection system

VMDS Instruments

507	=	ultraviolet - Fourier transform infrared (UV-FTIR) AP Farm Stack
507I	=	FTIR AP Farm Stack
507U	=	UV-DOAS AP Farm Stack

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Introduction

This summary contains Vapor Monitoring and Detection System (VMDS) pilot-scale data collected over one week (1/25/2017 at 6:00 a.m. through **Error! Reference source not found.** at 6:00 a.m.) using the AP-Farm stack monitor¹. This instrument is a dual channel FTIR/UV-DOAS spectrometer that provides real-time multi-gas measurement (qualitative and quantitative) of gases. The concentrations detected for the 507I (FTIR) and 507U (UV-DOAS) shall be reported separately. The implementation method for this instrument allows for very accurate identification and quantification of compounds found in the AP-Farm exhauster stack.

Chemical compounds found in the stack are not representative of what is found in the work environment, so their concentrations are not reviewed against Occupational Exposure Limits (OELs) or other limits implemented in work environments. This review focuses on chemicals present, patterns, and observations during waste disturbing activities.

Pilot-scale testing is focused on evaluating component integration and functionality. Data shown may include results for calibration and calibration check (bump test) 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.

For the stack monitor, 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.

¹ AP-Farm Stack Monitor Fact Sheet: <https://hanfordvapors.com/wp-content/uploads/2016/11/UV-FTIR-Fact-Sheet.pdf>

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1/25/2017 through Error! Reference source not found. Summary

During the current reporting week, waste retrieval activities for tank AY-102 (to AP Farm tank AP-102) were ongoing during off-shifts (between 16:30 and 5:00) each weekday and on the weekend from 1/25/2017 through 1/28/2017. High-pressure water operations and supernatant sluicing occurred on 1/29/2017 and continued through 1/30/2017. Retrieval operations resumed on 1/30/2017 followed by high-pressure water operations and supernatant sluicing on 1/31/2017. Retrieval activities associated with supernate pump starts and stops are shown in each figure.

The power was off and data were not reported during much of the reporting period (Table 1). During this power outage, the 507I instrument (FTIR) module was replaced. Following replacement of the IR module on 1/30/2017, the software was re-installed, but the library loaded to the software was not updated with the appropriate reporting thresholds and spectral ranges. As a result, the 507I data for many of the chemical compounds were reported as large positive and negative values that are considered erroneous. Ammonia and nitrous oxide have typically been detected by the 507I instrument in the past, but ammonia and nitrous oxide data reported this week are considered erroneous because the reporting thresholds were not correctly applied. Therefore, 507I data and graphs are not included for these compounds.

Chemical species detected by the 507U (UV-DOAS) instrument include ammonia, mercury, and m-xylene and are presented in Table 1 and Figures 1, 2, and 3. Ammonia concentrations detected during the waste disturbing activities by the 507U were within the observed range typical for the AP Tank Farm Stack when there is no waste disturbing activities. During waste disturbing activities, mercury concentration reported by 507U increased after the supernate pump was started and recovered after the pump was stopped (Figure 2). The observed increase and decrease in mercury concentration during supernate pump operation was typical of what we have previously observed. Figure 3 shows individual observations of m-xylene from 507U during the reporting period; concentrations are in line with what can be seen in urban areas² and do not correlate to the waste disturbing activities. The 507I instrument monitored for 29% and the 507U instrument monitored for 100% of the reporting period (Table 2).

The collection of 507U data for this reporting week preceded library changes performed on 3/8/2017, so data were reprocessed to determine if compounds were correctly detected by the instrument (i.e., the data was not obtained through OSI PI). The reprocessed data with the optimized library eliminates false-positive and false-negative readings of compounds reported in OSI PI³. The data were reprocessed and the output data can be obtained from Integrated Document Management System (IDMS).

² EPA Xylenes: <https://www.epa.gov/sites/production/files/2016-09/documents/xylenes.pdf>

³ OSI PI System is a data visualization software package from [OSIsoft](#).

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Table 1. Chemical Species Detected^a in the AP Tank Farm Stack by Method

Chemical	507I ^b FTIR (ppm)	Chemical	507U ^c UV-DOAS (ppm)
Ammonia*	N/A	Ammonia*	33 - 57
Nitrous Oxide*	N/A	Nitric Oxide	ND
Methane	N/A	1,3-Butadiene*	ND
1,3-Butadiene*	N/A	2-Methyl-2-butenal*	ND
1-Butanol*	N/A	2-Methylfuran*	ND
2-Hexanone*	N/A	Acetaldehyde*	ND
3-Buten-2-one*	N/A	Benzene*	ND
Acetaldehyde*	N/A	Butanal*	ND
Acetonitrile*	N/A	Ethylamine*	ND
Benzene*	N/A	Formaldehyde*	ND
Butanal*	N/A	Furan*	ND
Butyl Nitrite*	N/A	Mercury*	ND - 0.00029
Ethylamine*	N/A	Methyl Nitrite*	ND
Formaldehyde*	N/A	Pyridine*	ND
Furan*	N/A	1,2,4 Trimethylbenzene	ND
Methanol*	N/A	1,3,5 Trimethylbenzene	ND
Methyl Isocyanate*	N/A	Ethylbenzene	ND
Methyl Nitrite*	N/A	m-Xylene	ND - 0.078
N-Nitrosodiethylamine*	N/A	Nitrogen Dioxide	ND
N-Nitrosodimethylamine*	N/A	o-Xylene	ND
N-Nitrosomorpholine*	N/A	p-Xylene	ND
Propanenitrile*	N/A	Styrene	ND
Pyridine*	N/A	Sulfur dioxide	ND
Tributyl Phosphate*	N/A	Toluene	ND

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

b) No data is reported from 507I due to incorrect software versions installed, see text.

c) Chemical concentration data was reprocessed to eliminate false-positive data

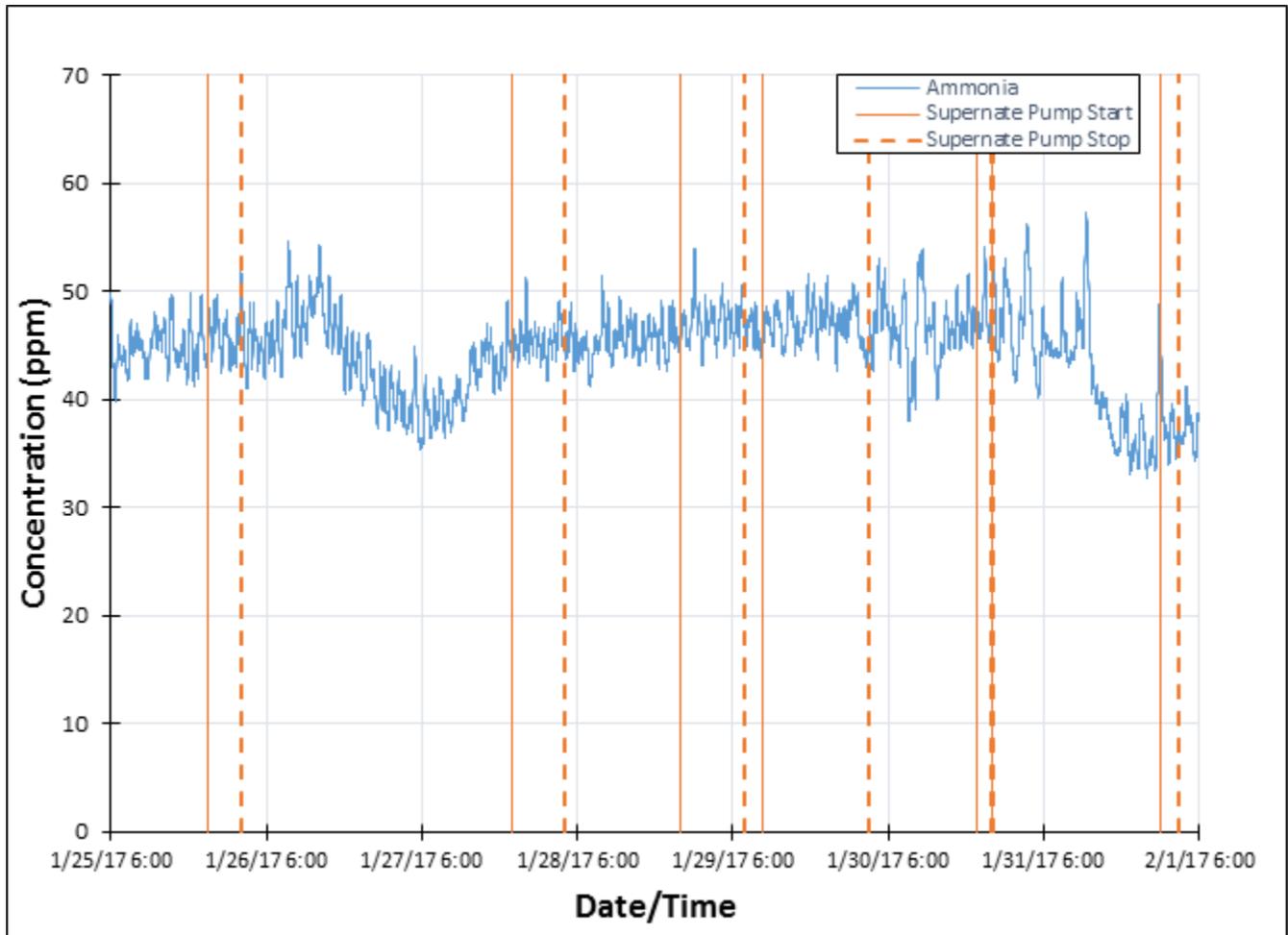
N/A) Not Applicable; the data reported into OSI PI by the instrument are considered erroneous because the reporting thresholds were not correctly applied, see text above.

ND - Not detected

* Chemical is on COPC list

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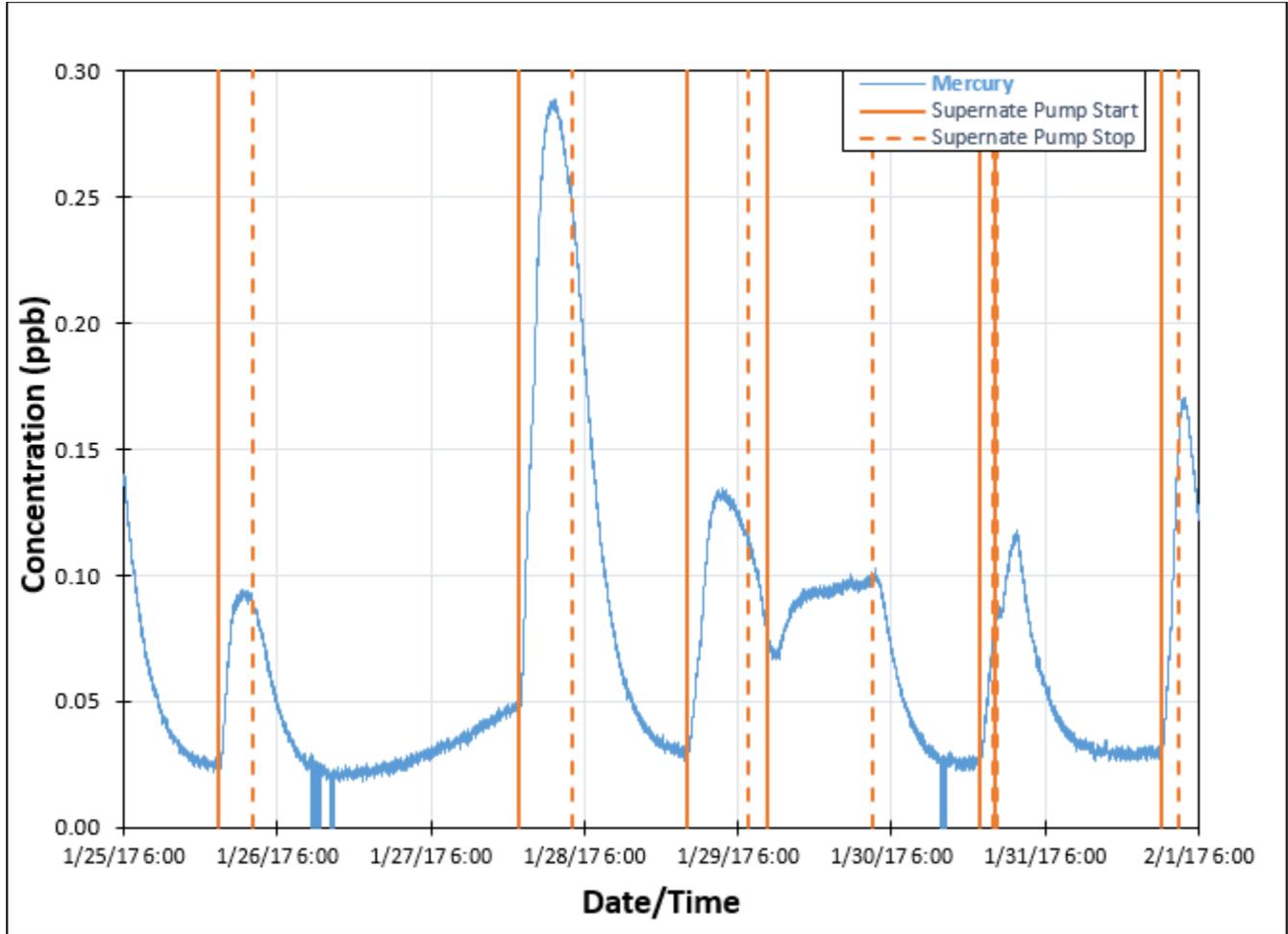
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**Figure 1. Ammonia Data Reported by the 507U (UV-DOAS) Instrument.
(Note that concentration units are ppm)**

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**Figure 2. Mercury Data Reported by the 507U (UV-DOAS) Instrument.
(Note that concentration units are ppb)**

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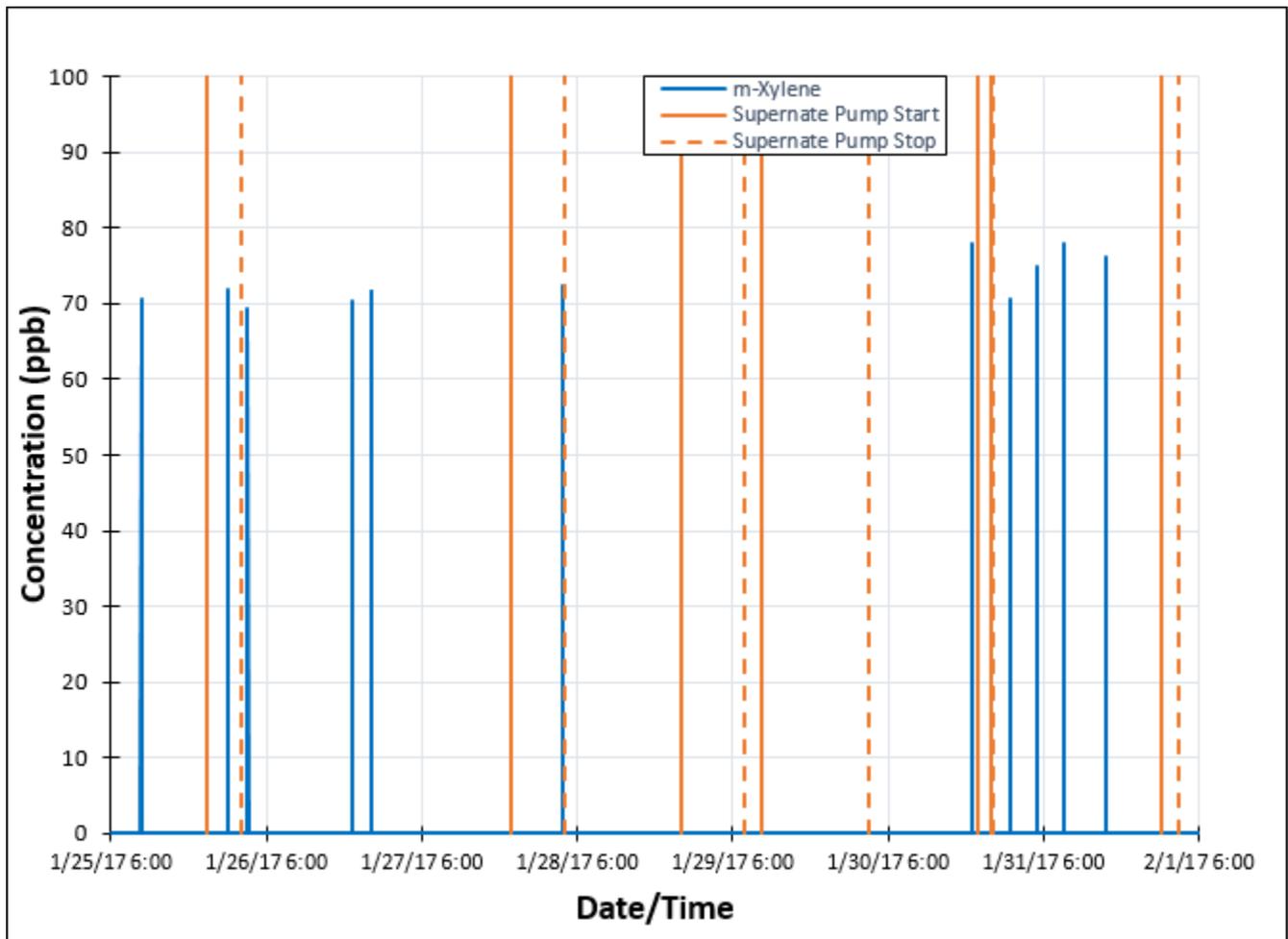


Figure 3. m-Xylene Data Reported by the 507U (UV-DOAS) Instrument. (Note that concentration units are ppb)

Table 2. Stack Monitor Time Reporting.

Instrument	% Time Reporting
507I	29%
507U	100%

Notes: % time reporting is based on data reported to OSI PI System³