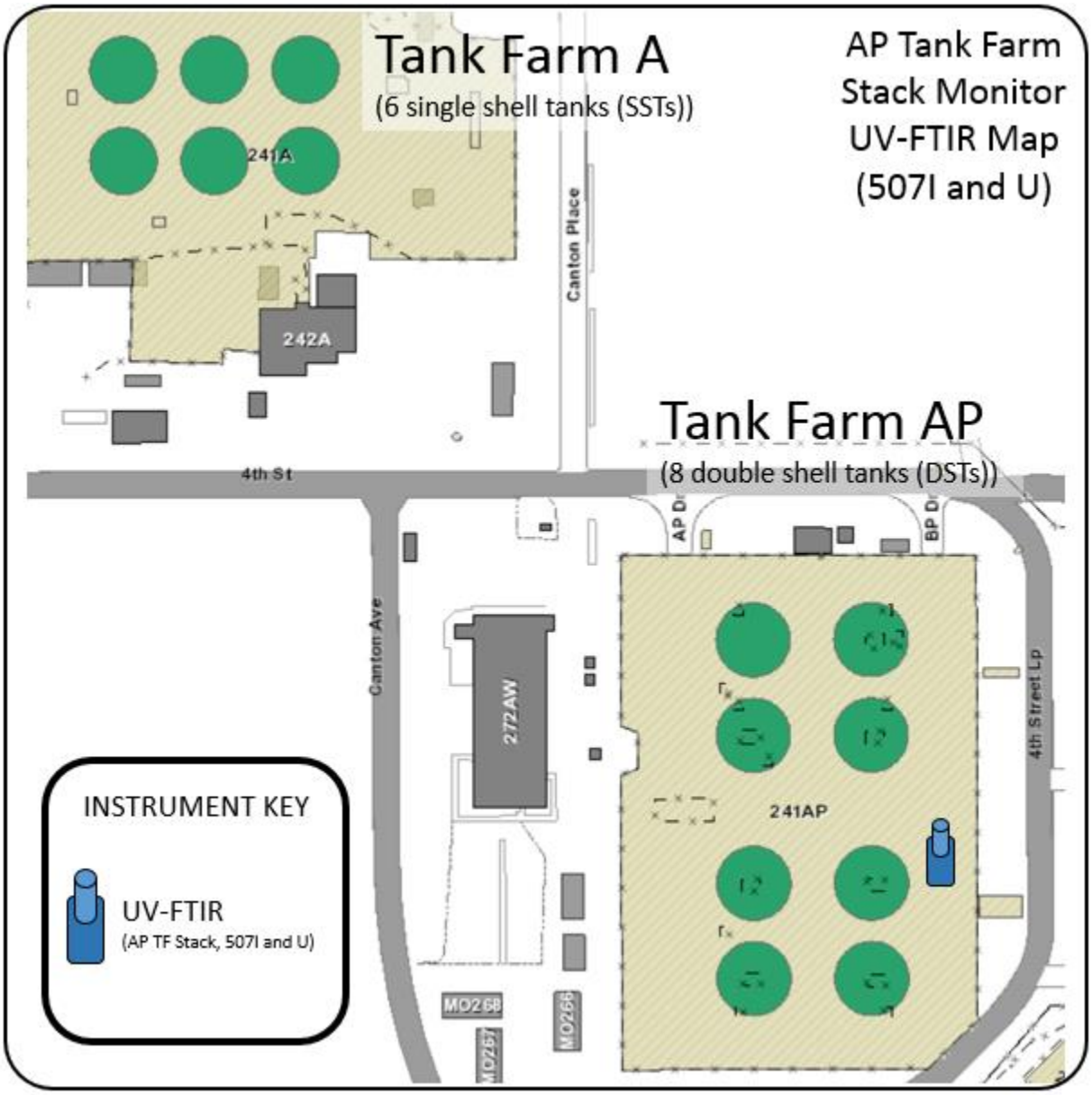
Vapor Monitoring Detection System Weekly Report – AP Tank Farm Stack Monitoring

Revision 0: Initial Release of Report

1/4/2017 6:00 – 1/11/2017 6:00

AP-Tank Farm Stack Monitor (north is up)



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Abbreviations and Units

CH_4	=	methane
CO	=	carbon monoxide
CO_2	=	carbon dioxide
COPC	=	chemicals of potential concern
IDMS	=	Integrated Document Management System
FTIR	=	Fourier transform infrared spectrometer
IR	=	infrared
ND	=	not detected
NH_3	=	ammonia
NO	=	nitric oxide
N_2O	=	nitrous oxide
NO_2	=	nitrogen dioxide
O_3	=	ozone
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 (1/4/2017 at 6:00 a.m. through 1/11/2017 at 6:00 a.m.) using the AP-Farm stack monitor[1]. 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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1/4/2017 through 1/11/2017 Summary

Waste retrieval activities, consisting of activation of the supernate and slurry pumps required to retrieve waste from AY-102 to AP-102, were performed at 21:30 on 1/6/2017 and concluded at approximately 23:30 on 1/6/2017. There was also a time period after the exhaust had returned to typical non-waste disturbing activity levels, where both the 507I (FTIR) and the 507U (UV-DOAS) reported either non-detect or significantly lower than normal values for ammonia, nitrous oxide, and mercury from approximately 14:30 on 1/7/2017 until approximately 11:30 on 1/9/2017. These low values are likely due to changing the instrumentation valve line up to sample the stack that wasn't actively ventilating.

Review of the data collected while sampling the actively ventilating stack shows that ammonia concentrations ranged from 34 to 59 ppm (507I and 507U), nitrous oxide concentrations ranged from 2.9 to 4.2 ppm (507I), mercury concentration ranged from non-detect to 0.00012 ppm (507U) and m-xylene concentrations ranged from non-detect to 0.093 ppm (507U) (Table 1). The ammonia concentrations observed during the waste disturbing activity were similar to those observed during normal operations with no waste disturbing activities (i.e., no major concentrations peaks observed during the AY-102 to AP-102 transfer). Figures 1 and 2 show the concentrations of ammonia and nitrous oxide respectively reported by the 507I in the AP Farm stack during the period in review, as well as the time intervals of retrieval activities. Figure 3 shows ammonia for 507U, with AY-102 to AP Tank Farm retrieval activities identified. The increases in nitrous oxide and mercury during and shortly following the waste disturbing activity were anticipated and consistent with previous observations (Figures 2 and 4). Figure 5 shows a few individual observances of m-xylene from 507U during the reporting period; concentrations are in line with what can be seen in urban areas[2]. The 507I monitored for 100% and the 507U 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. The reprocessed data with the optimized library eliminates false-positive readings of compounds that showed as detections and reported in OSI PI[3]. 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[c] FTIR (ppm)	Chemical	507U[b] UV-DOAS (ppm)
Ammonia*	37 - 57	Ammonia*	34 - 59
Nitrous Oxide*	2.9 – 4.2	Nitric Oxide	ND
Methane	ND	1,3-Butadiene*	ND
1,3-Butadiene*	ND	2-Methyl-2-butenal*	ND
1-Butanol*	ND	2-Methylfuran*	ND
2-Hexanone*	ND	Acetaldehyde*	ND
3-Buten-2-one*	ND	Benzene*	ND
Acetaldehyde*	ND	Butanal*	ND
Acetonitrile*	ND	Ethylamine*	ND
Benzene*	ND	Formaldehyde*	ND
Butanal*	ND	Furan*	ND
Butyl Nitrite*	ND	Mercury*	ND – 0.00012
Ethylamine*	ND	Methyl Nitrite*	ND
Formaldehyde*	ND	Pyridine*	ND
Furan*	ND	1,2,4 Trimethylbenzene	ND
Methanol*	ND	1,3,5 Trimethylbenzene	ND
Methyl Isocyanate*	ND	Ethylbenzene	ND
Methyl Nitrite*	ND	m-Xylene	ND – 0.093
N-Nitrosodiethylamine*	ND	Nitrogen Dioxide	ND
N-Nitrosodimethylamine*	ND	o-Xylene	ND
N-Nitrosomorpholine*	ND	p-Xylene	ND
Propanenitrile*	ND	Styrene	ND
Pyridine*	ND	Sulfur dioxide	ND
Tributyl Phosphate*	ND	Toluene	ND

Notes: a) Based on data retrieved from OSI PI; OSI PI System is a data visualization software package from OSIsoft.
b) Chemical concentration data was reprocessed to eliminate false-positive data
c) The low concentration readings from the 507I did not include the low readings taken during the time when the instrumentation was in line with the wrong stack.
* Chemical is on COPC list
ND – Not detected

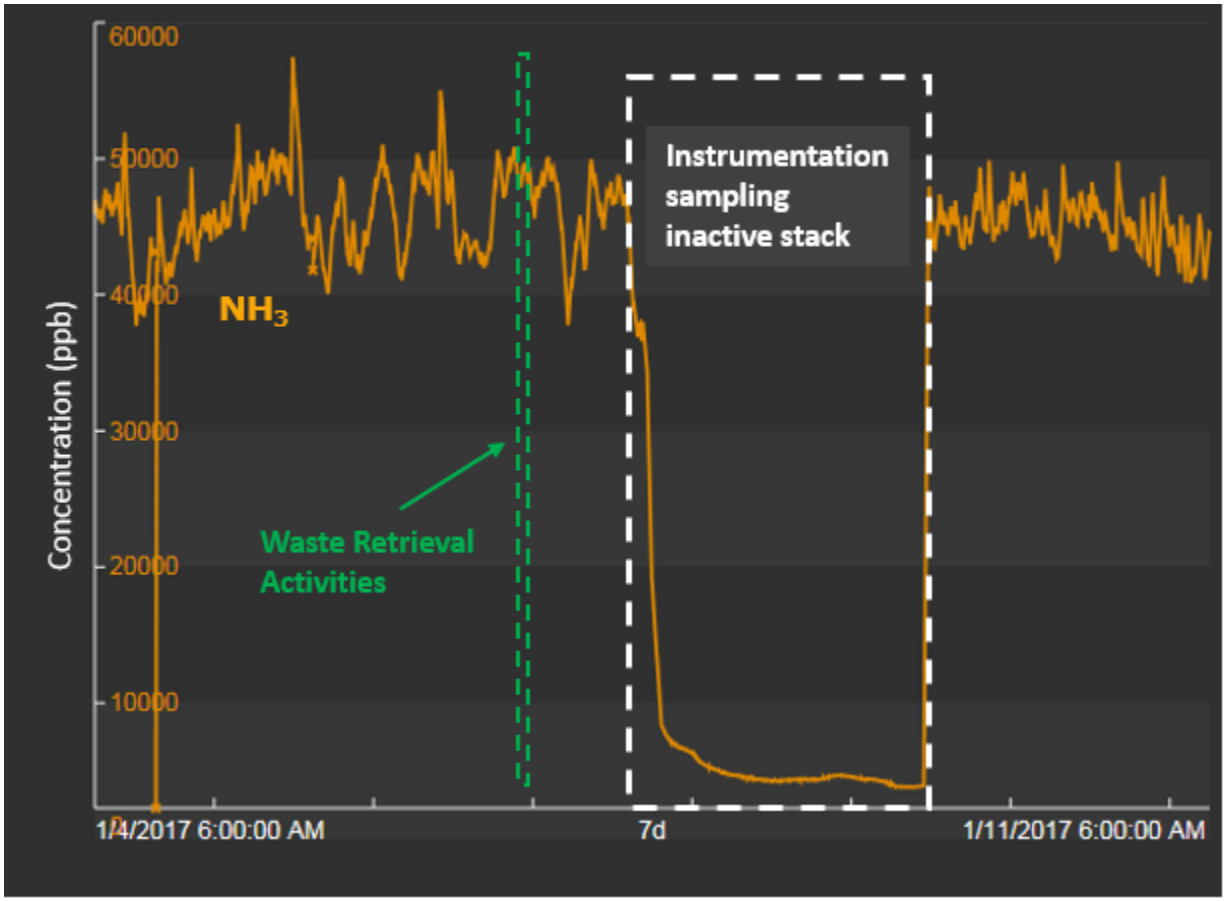

Figure 1. FTIR (507I) NH_3 Data recorded from AP Farm Exhauster (Note that concentration units are ppb)

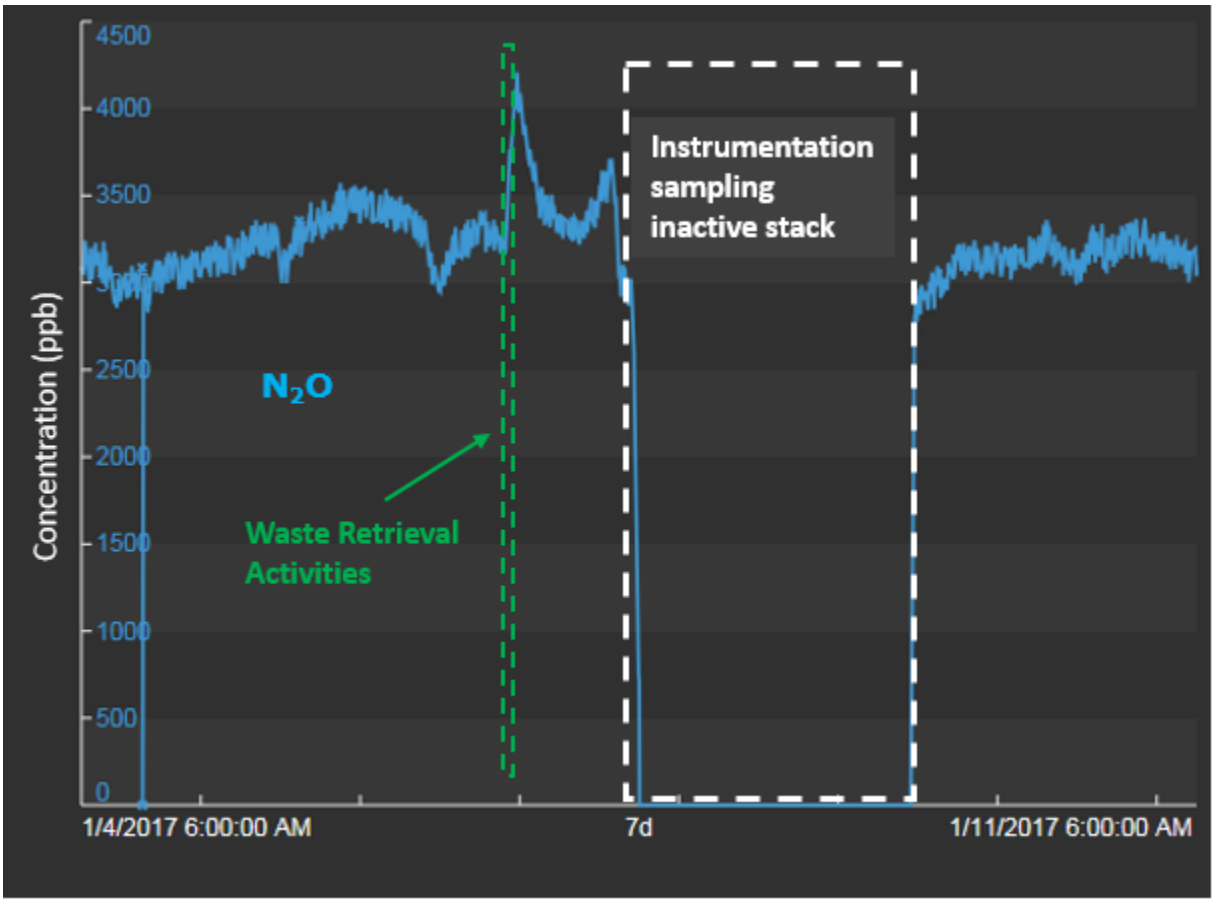

Figure 2. FTIR (507I) N_2O Data recorded from AP Farm Exhauster (Note that concentration units are ppb)

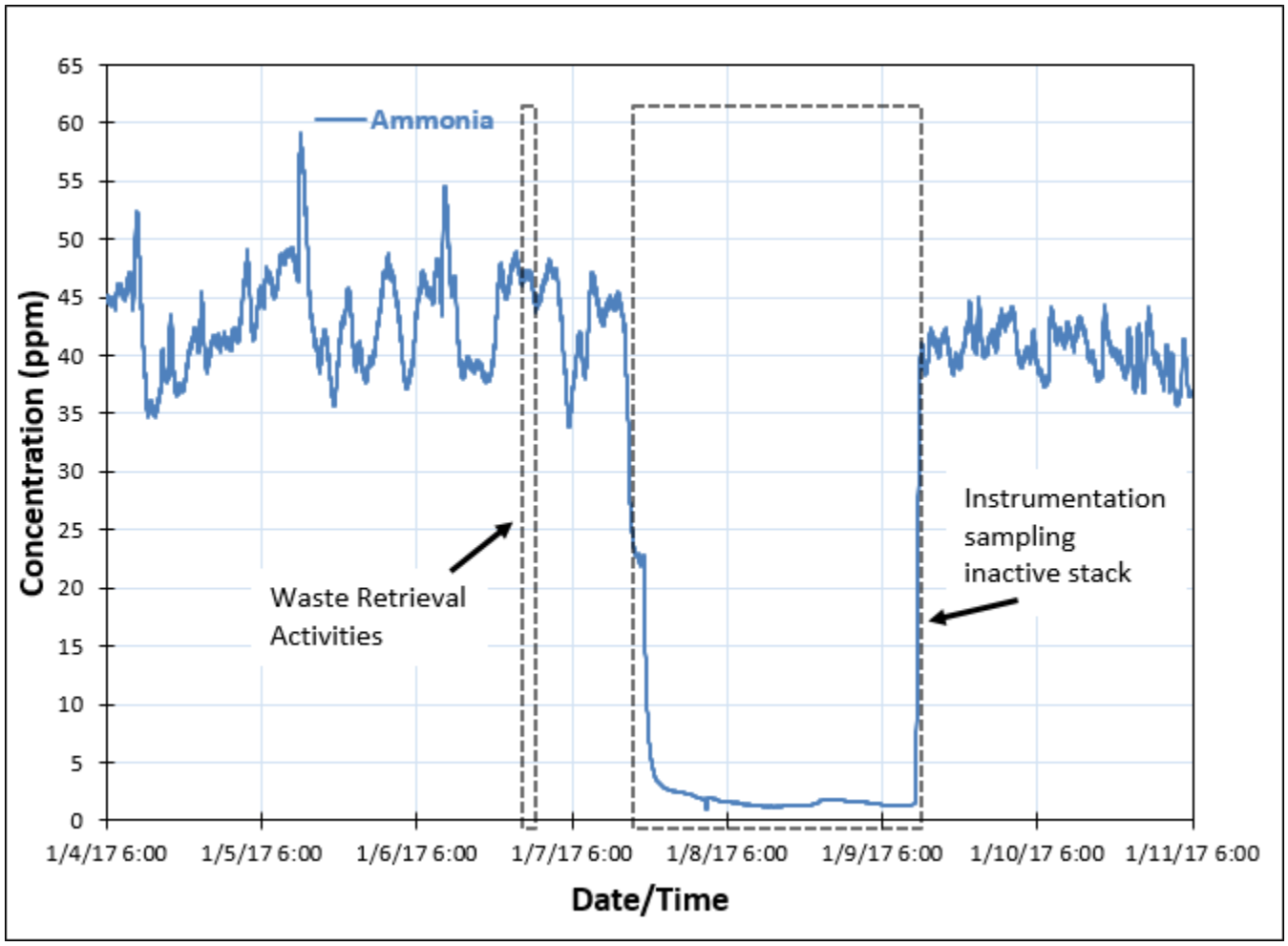

Figure 3. UV-DOAS (507U) Ammonia Data Review.
(Note that concentration units are ppm)

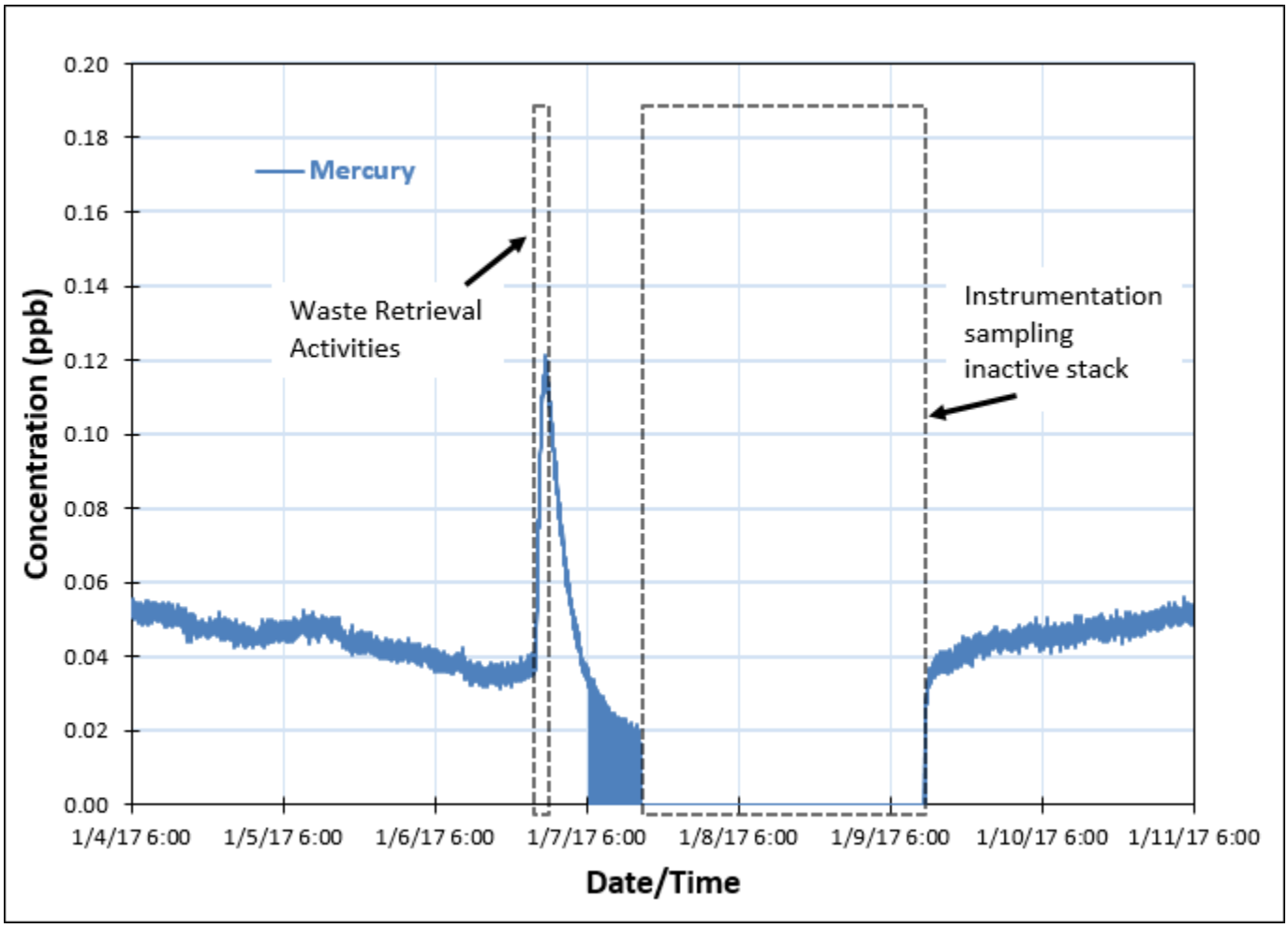

Figure 4. UV-DOAS (507U) Mercury Data Review.
(Note that concentration units are ppb)

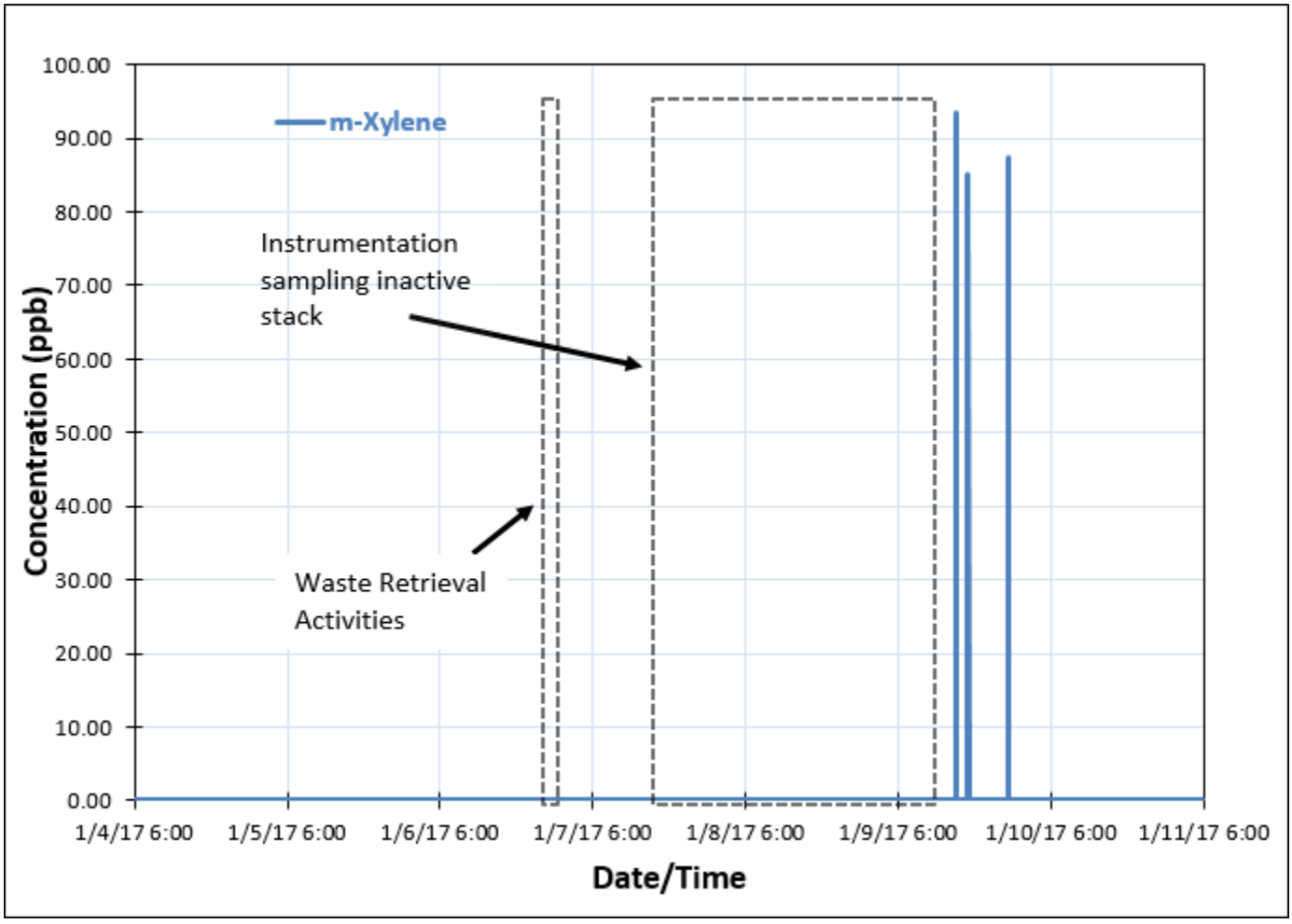

Figure 5. UV-DOAS (507U) m-Xylene Data Review.
(Note that concentration units are ppb)

Table 2. Stack Monitor Time Reporting.

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

Notes: % time reporting is based on data reported to OSI PI System[4]

[4] OSI PI System is a data visualization software package from OSIsoft.