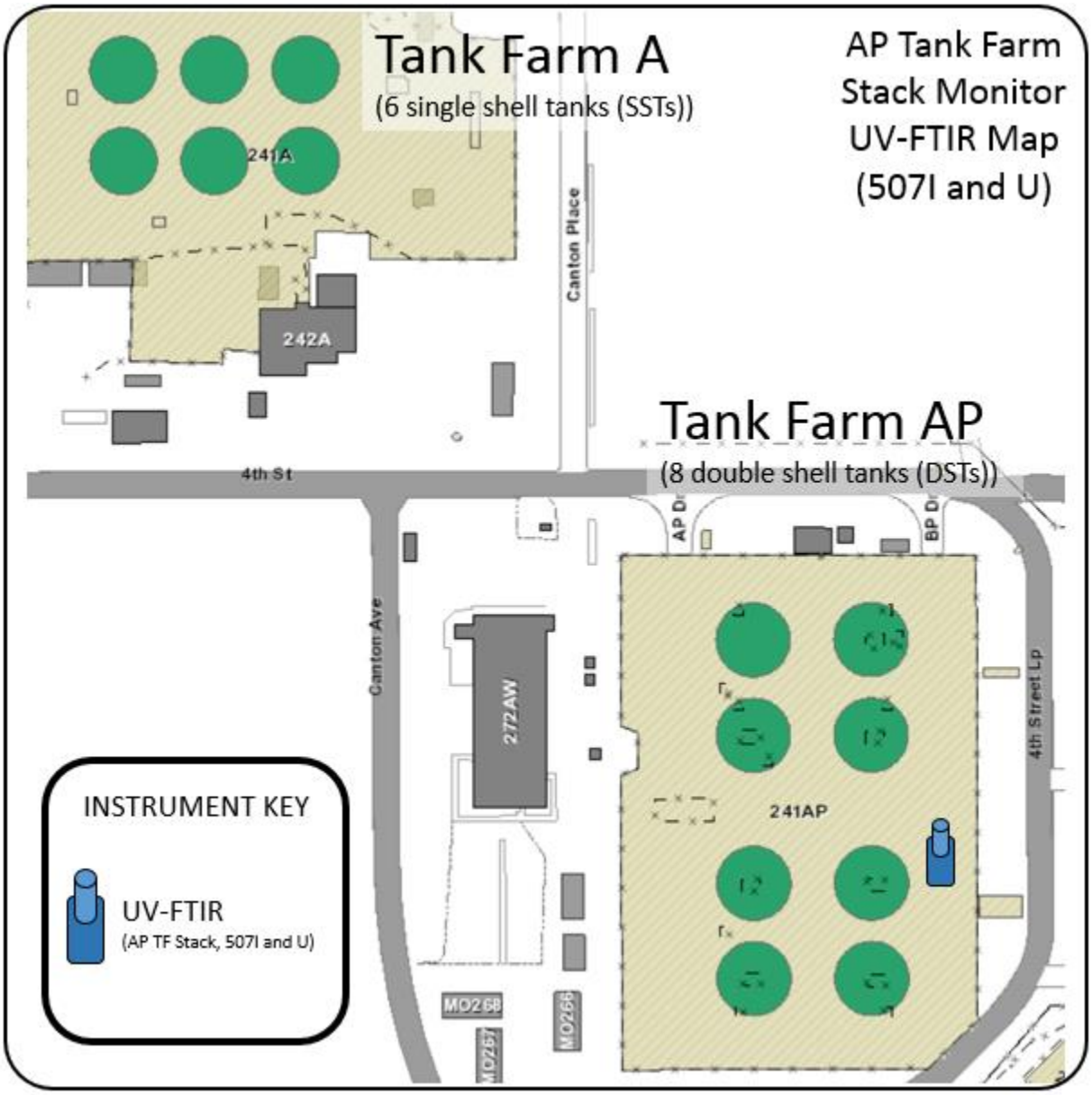
**Vapor Monitoring Detection System Weekly Report – AP Tank Farm Stack Monitoring**

**Revision 0: Initial Release of Report**

1/11/2017 6:00 – 1/18/2017 6:00

AP-Tank Farm Stack Monitor (north is up)



# Vapor Monitoring Detection System Weekly Report

1/11/2017 6:00 – 1/18/2017 6:00

## Abbreviations and Units

| | | |
|---|---|---|
| $CH_4$ | = | methane |
| 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 |
| 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 |

# Vapor Monitoring Detection System Weekly Report

1/11/2017 6:00 – 1/18/2017 6:00

## Introduction

This summary contains Vapor Monitoring and Detection System (VMDS) pilot-scale data collected over one week (1/11/2017 at 6:00 a.m. through 1/18/2017 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

# Vapor Monitoring Detection System Weekly Report

1/11/2017 6:00 – 1/18/2017 6:00

## 1/11/2017 through 1/18/2017 Summary

Table 1 shows that ammonia concentrations ranged from 2.9 to 79 ppm (507I and 507U), nitrous oxide concentrations ranged from non-detect to 8.5 ppm (507I) and mercury concentrations ranged from non-detect to 0.00023 ppm (507U) (mercury shows a spike to ~0.00027 ppm that trails off to non-detect post exhauster swap). Waste retrieval activities, consisting of several starts and stops of the supernate and slurry pumps, were performed starting at 02:08 on 1/12/2017 and concluded at approximately 03:20 on 1/16/2017. The exhauster was moved to the B Train at about 06:00 on 1/12/2017. The 507I (FTIR) and 507U (UV-DOAS) spectrometers were not aligned to the B Train until 09:30 on 1/13/2017.

The concentrations of ammonia detected by the 507I and 507U in the AP Farm stack during the reporting period, as well as the time intervals of B Train misalignment and retrieval activities are shown in Figure 1. The ammonia concentration detected was lower than usual (<30 ppm) the morning of 1/14/2017 and the afternoon of 1/16/2017. The ammonia concentration peaked at 22:20 on 1/16/2017. Nitrous oxide concentrations increased after the start of the supernate pump at approximately 02:00 on 1/12/2017 (Figure 2). There was a period when there were no data because the instrumentation was sampling the wrong stack, as stated above. Mercury concentrations fluctuated with the supernate pump starts and stops, which is typical, during the period from 1/12/2017 through 1/16/2017 (Figure 3). The highest concentration of mercury detected was at approximately 04:20 on 1/12/2017 shortly after the first supernate pump start. The non-detect concentrations of mercury were from the afternoon of 1/13/2017 through the morning of 1/14/2017. The concentrations in all the compounds ($NH_3$, $N_2O$, and Hg) reported non-typical behavior on 1/16/2017 from about 9:00 to 22:00 and are indicated by lines "A" (B stack offline) and "B" (B stack back online) on Figures 1, 2, and 3. The non-typical compound concentrations are assumed to be due to AP Farm stack switches that occurred during that time, see Figure 5. The ammonia peak concentration, mentioned earlier, corresponds to B stack being brought back online.

Table 2 shows the reporting time of the stack monitors. The FTIR 507I monitored for 100% and the UV-DOAS 507U monitored for 100% of the reporting period.

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[2]. The data were reprocessed and the output data can be obtained from Integrated Document Management System (IDMS).

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

# Vapor Monitoring Detection System Weekly Report

1/11/2017 6:00 – 1/18/2017 6:00

**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* | 6.3 - 71 | Ammonia* | 2.9 - 79 |
| Nitrous Oxide* | ND – 8.5 | 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 – 0.00027 |
| 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 |
| 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

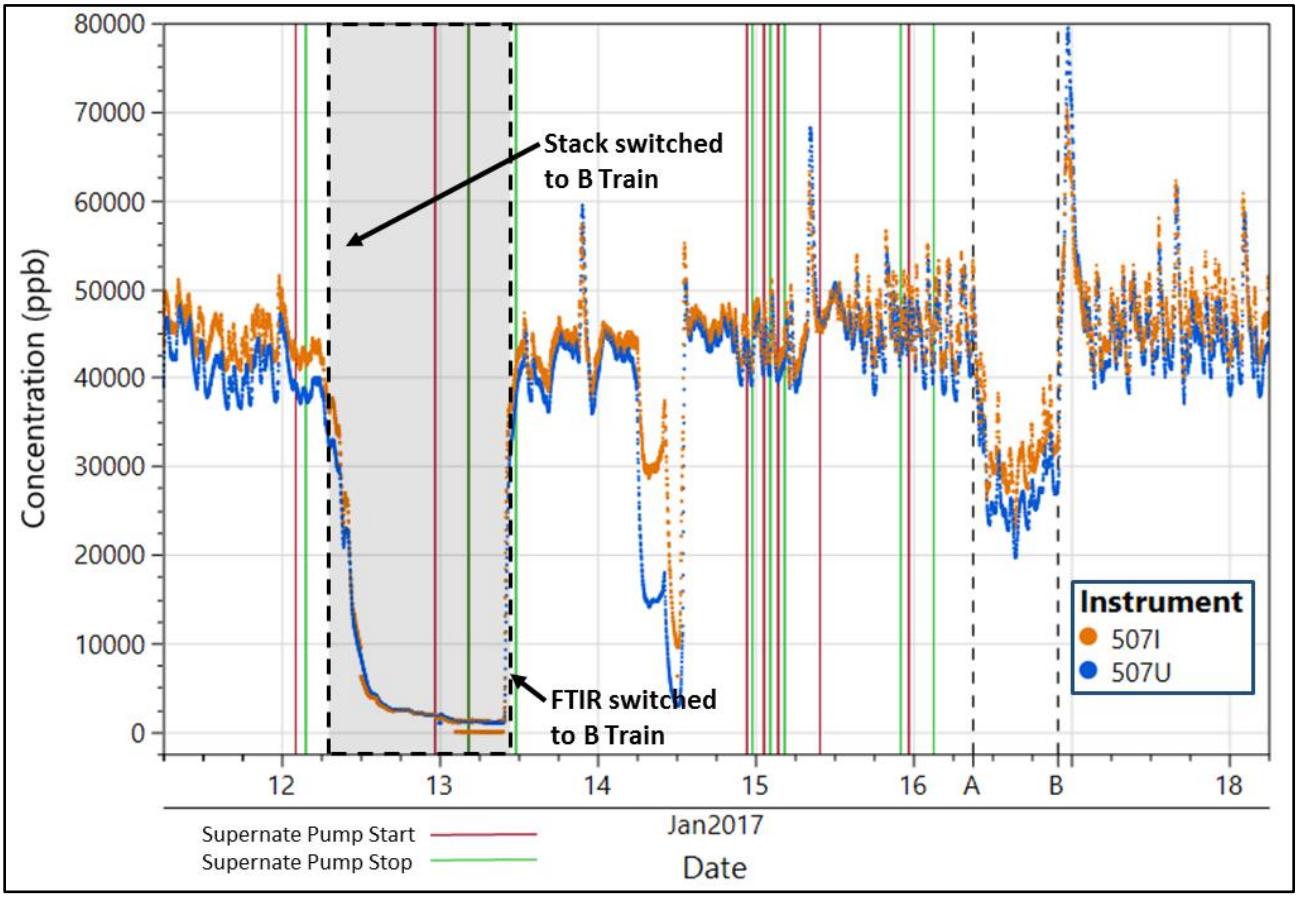



**Figure 1. 507I (FTIR) and 507U (UV) Ammonia Data Recorded from AP Farm Exhauster**

**(Note that Concentration Units are ppb)**

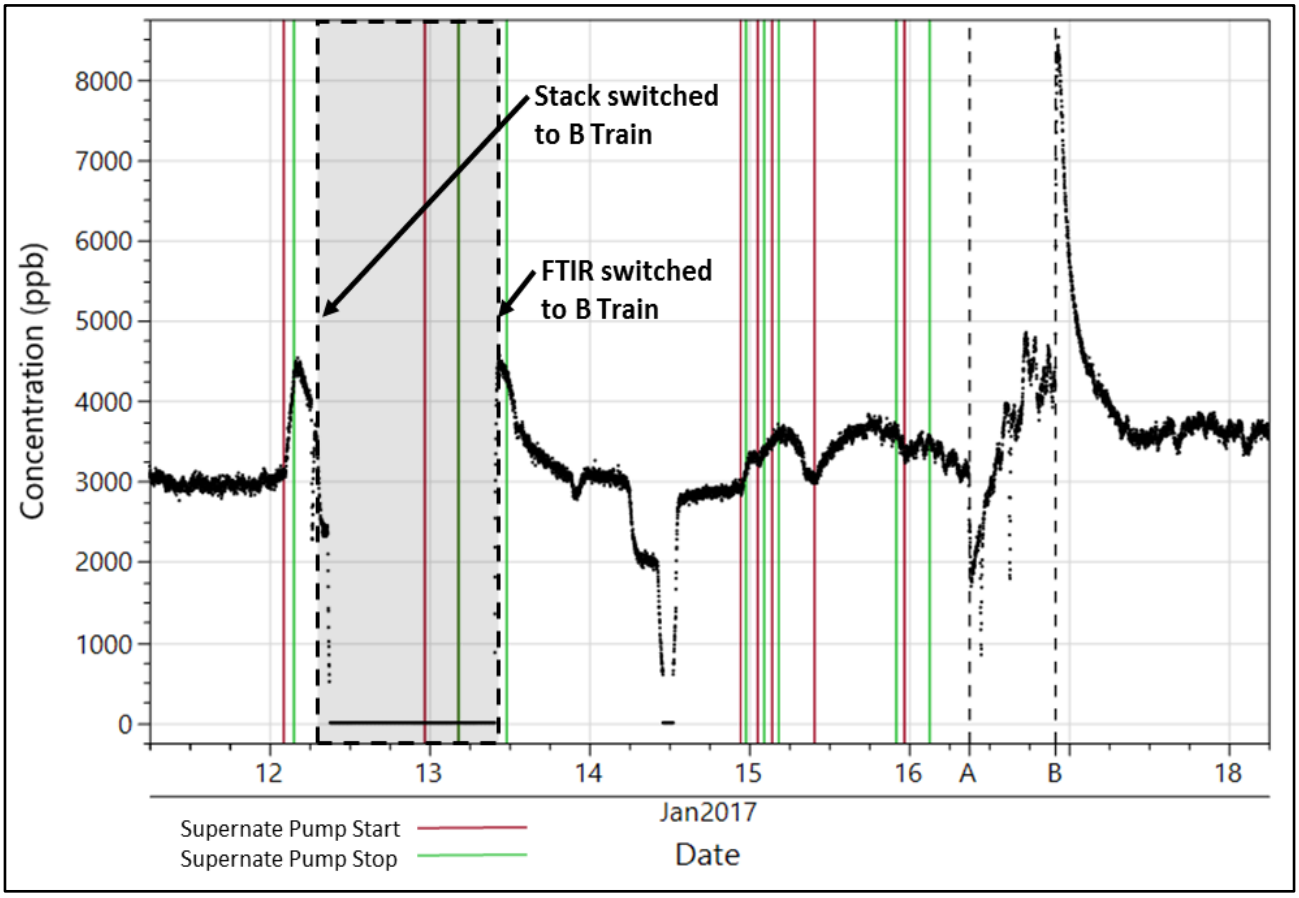



**Figure 2. 507I (FTIR) $N_2O$ Data Recorded from AP Farm Exhauster (Note that Concentration Units are ppb)**

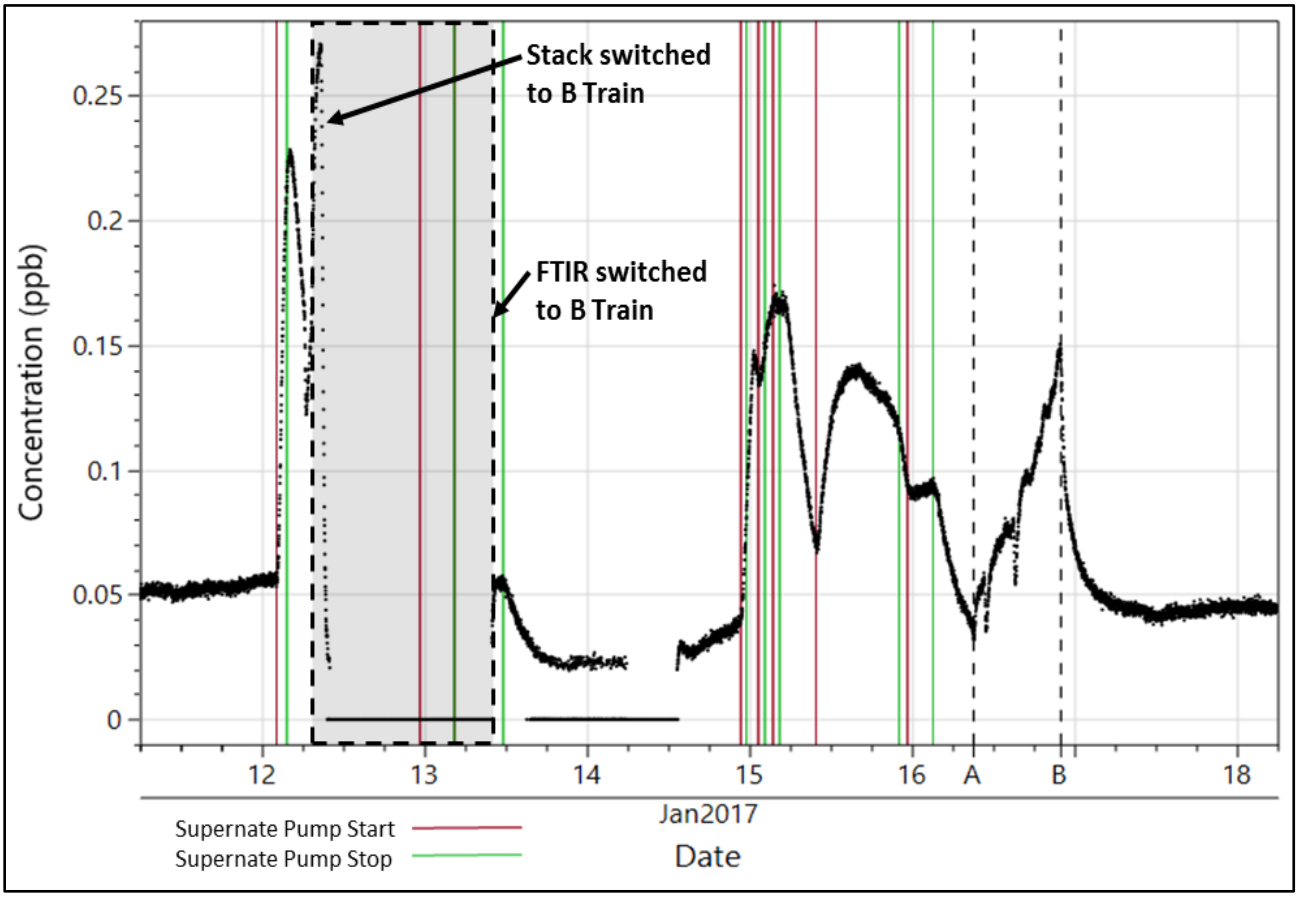



**Figure 3. 507U (UV-DOAS) Mercury Data Review.**
**(Note that Concentration Units are ppb)**

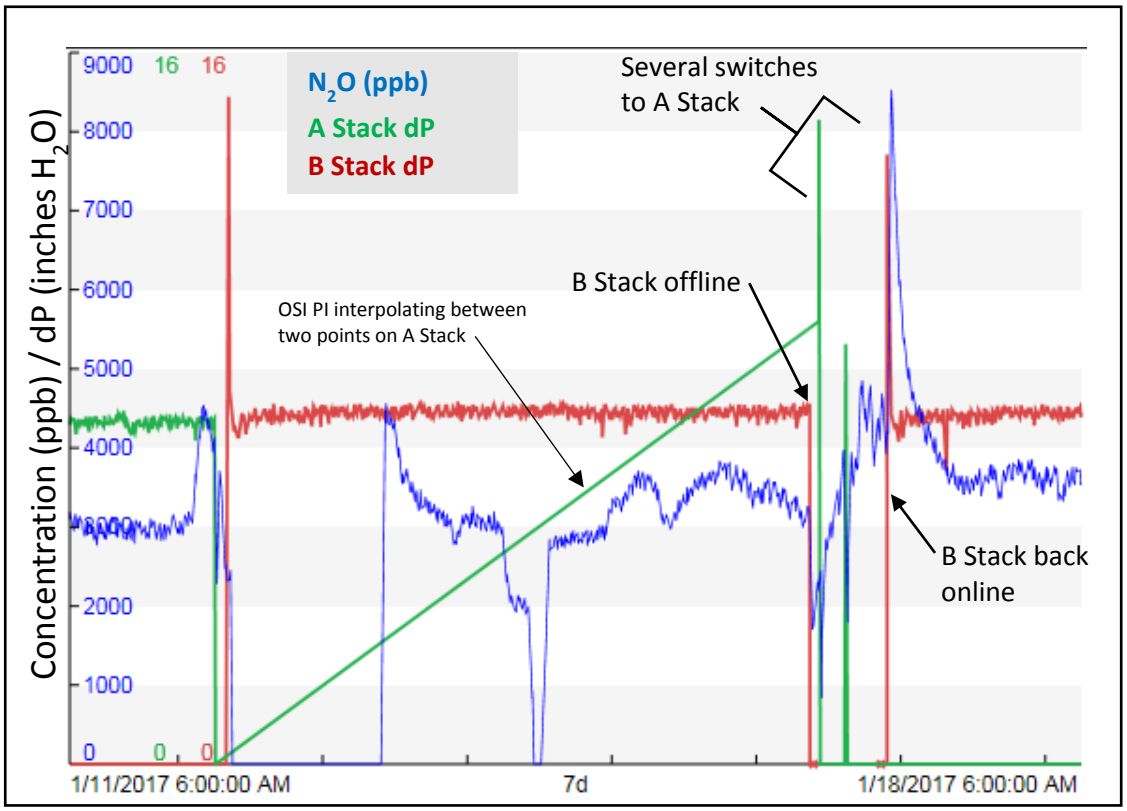



**Figure 4. 507I (FTIR) Nitrous Oxide and AP Stack Filter Differential Pressure Data Review. (Note that Concentration Units are ppb)**

**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[3]

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