

## **APPENDIX A. PIGS AND SUPER PIGS QA/QC**

The following are detailed descriptions of the quality control and quality assurance methods followed for the sampling, analysis, and reporting of the JU03 time-integrated sampler tracer data. Protocols established in the Environmental Protection Agency's (EPA) Guidance for Data Quality Assessment (U.S. EPA, 2000a), the general requirements for the competence of calibration and testing laboratories of International Standards Organization/IEC Guide 25 (ISO, 1990), the quality systems established by the National Environmental Laboratory Accreditation Conference (U.S. EPA, 2000b), and the Department of Defense Quality Systems Manual for Environmental Laboratories (U.S. Department of Defense, 2002) provided a basis for quality assurance and quality control procedures followed during analysis. Instrument and method limits of detection (ILOD/MLOD) were calculated based upon 40 CFR Part 136, Appendix B and the American Chemical Society Committee on Environmental Improvement's paper titled, "Principles of Environmental Analysis" (Keith, et al., 1983). ACS principles relative to detection limit calculations in 40 CFR Part 136, Appendix B are documented in "Revised assessment of Detection and Quantitation Approaches" (U.S. EPA, 2004). Although our research-based automated analysis of tracer gases has no specified method performance or regulatory criteria, compliance to the established quality control procedures stated above were followed, where applicable, to provide high quality data that is both accurate and reliable.

### **1. Pre-project maintenance of PIGS.**

Prior to deployment to the field, each PIGS was extensively tested for proper operation in the field and to ensure the collection of an adequate sample volume.

### **2. Re-tubing of all PIGS cartridges.**

Prior to deployment to the field, all latex rubber tubing was replaced in each PIGS cartridge to ensure there were no pinholes, cracks, or other leaks within the tubing that might have developed over time.

### **3. Re-bagging of cartridges.**

Prior to deployment to the field, new Tedlar® sample bags were added to each PIGS cartridge to replace older Tedlar® bags that were worn from extensive use. New Super PIGS cartridges, which were manufactured specifically just for JU03, received new Tedlar bags.

#### 4. Testing of all sample bags.

Each bag was checked for leakage after installation to each PIGS and Super PIGS cartridge to ensure there could be no mixing of outside air with the bag contents. All air was evacuated, the tubing was closed tightly and the bags were watched for slight re-inflation, which was the indicator of some kind of leak in the bag. Those found to leak were replaced and the new bag was re-tested.

#### 5. Pre-project cleaning and analysis checks of all PIGS and Super PIGS cartridge sample bags.

Prior to deployment to the field, all bags in approximately 700 PIGS cartridges and 300 Super PIGS cartridges were cleaned. The bags were cleaned by repeatedly filling them with UHP nitrogen and then evacuating on the cartridge cleaning apparatus seen in Fig. A-1. The apparatus consisted of a nitrogen tank and vacuum connected to a system that fills and evacuates the sample bags by the movement of a lever. Six cartridges were cleaned at one time. One side of the cleaning apparatus was used for the PIGS cartridges and the other was used for the Super PIGS cartridges. The computer mounted underneath the cleaning apparatus was used to create cartridge-cleaning records. This information was then uploaded to the ATGASs. The cleaning protocols (Fig. A-2) were developed after significant testing to ensure that bags containing concentrations in the expected high range of over 150,000 pptv could be cleaned to less than background levels. After cleaning, the bags were filled with UHP nitrogen and analyzed on the ATGAS to ensure there was no contamination from previous tests or from long-term storage. Any bags with a concentration greater than 2 pptv were re-cleaned and re-analyzed. All bags were stored evacuated until their use.



Figure A-1. Cartridge cleaning apparatus.

### Cardboard Cartridge Cleaning Procedure

1. Connect all tubes to the cleaning machine.
2. Open all clips.
3. Make sure the cleaning machine valves are set so that nitrogen can flow into all connect cartridges.
4. Evacuate bags.
5. Fill all bags with nitrogen and then evacuate. Repeat until all bags have been evacuated 5 times.
6. Fill 1 box with nitrogen for analysis.
7. Scan all cartridge bar codes with the bar code scanner.
8. Close all clips and remove cartridges.

### Plastic Cartridge Cleaning Procedure

1. Connect all cartridges to the cleaning machine.
2. Make sure the cleaning machine valves are set so that nitrogen can flow into all connect cartridges.
3. Evacuate bags.
4. Fill all bags with nitrogen and then evacuate. Repeat until all bags have been evacuated 3 times.
5. Fill all bags with nitrogen and disconnect from the cleaning machine.
6. Allow cartridges to stand for **AT LEAST 15 MINUTES**.
7. Connect cartridges to the cleaning machine again.
8. Evacuate bags.
9. Fill all bags with nitrogen and then evacuate. Repeat until all bags have been evacuated 3 times.
10. Fill 1 box with nitrogen for analysis.
11. Scan all cartridge bar codes with the bar code scanner.
12. Disconnect cartridges from the cleaning machine and remove them.

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Figure A-2. PIGS (cardboard) and Super PIGS (plastic) cartridge cleaning protocols.

6. Development of analysis protocols for the expected sample concentration ranges.

Analysis protocols were developed to optimize instrument performance, accuracy and efficiency during the project. Due to the magnitude of concentration ranges that were expected, and the complexity and carry-over issues resulting from measuring extremely low concentration samples immediately following extremely high concentration samples on the ATGASs, analysis parameters such as between bag purge times, injection length, and between cartridge purge times were tested and adjusted for the worst case scenario of analysis of the highest expected concentration followed by the analysis of the lowest expected concentration. Sample column volume and electron capture detector attenuation adjustments were also tested at different concentration levels to provide quick adjustments to the instruments in the case of unexpected concentration ranges.

7. Pre-project calculation of instrument limit of detection (ILOD) and instrument limit of quantitation (ILOQ).

Prior to packing the ATGASs for transportation to Oklahoma City, the ILOD and ILOQ were established for each ATGAS to provide information on instrument performance. The ILOD is the instrument's limit of detection and is defined as the lowest concentration that can be determined to be statistically different from zero. It is based upon the specific instrument's ability to differentiate a low level concentration standard from instrument noise. The ILOD was calculated as three times the standard deviation of a low level standard that was analyzed twelve times (one bag per cartridge). The ILOQ is the instrument's limit of quantitation and is defined as the lowest concentration that can be determined within 30% of the actual concentration. The ILOQ was calculated as ten times the standard deviation of the same low level standard analyzed 12 times. Since using different concentrations will yield different ILOD and ILOQs, the analyst selected the lowest concentration standard to meet as many of the following criteria as possible:

- Has a relative standard deviation (RSD) (the standard deviation divided by the mean multiplied by 100) of less than 15%.
- Has a signal to noise (the mean divided by the standard deviation) between 3 and 10 (a higher value does not invalidate the result; rather it indicates that a lower concentration standard should be used).
- Has a percent recovery (analyzed value divided by the certified value multiplied by 100) between 90% and 110%.

Also, to include possible carry-over issues, a 50,500 pptv standard was analyzed just prior to the analysis of each low level standard on each valve location (1-12). The final percent recovery and mean concentration data were graphed and visually inspected to indicate any trends or biases that might not be easily detected by looking at the raw numbers. Even though the results met the above criteria, a consistently increasing concentration result could provide evidence of carry-over issues. The results were documented and used as a reference point for



each ATGAS placed into the on-site laboratory facility (the TAF) in the Oklahoma University Health Sciences Building. Table A-1 shows the analyzed average, standard deviation, average recovery, signal to noise (S/N) ratio, RSD and the calculated ILOD and ILOQ. The average ILOD for all four ATGASs was 1 pptv while the average ILOQ was 3 pptv.

Table A-1. Pre-transport ILOD and ILOQ calculations for each ATGAS.

ATGAS Number	Certified Concentration (pptv)	Average (pptv)	Standard Deviation (pptv)	Average Recovery (%)	S/N Ratio	RSD (%)	ILOD (pptv)	ILOQ (pptv)
1	3.47	3.67	0.22	106	17	6	0.7	2.2
2	9.38	9.02	0.35	96	26	4	1.0	3.5
3	9.38	9.64	0.23	103	42	2	0.7	2.3
4	9.38	10.85	0.21	116	52	2	0.6	2.1
Avg.							1	3

#### 8. Pre-project estimation of method limit of detection (MLOD) and method limit of quantitation (MLOQ).

Prior to deployment to Oklahoma City, the MLOD and MLOQ were estimated for the PIGS to provide information on method performance and an estimation of the lowest field concentration level that can be determined with some degree of certainty (Table A-2). When samples are left outside in the weather, transported to and from the laboratory facility, and the bags opened and closed, many more chances of variability are added. Determination of the MLOD and MLOQ for the Super PIGS could not be established before field deployment due to time constraints. The MLOD is defined as the lowest concentration that can be determined to be statistically different from zero. It is based upon the method's ability to differentiate a low-level concentration standard from instrument and method noise. The MLOD and MLOQ are calculated exactly the same as the ILOD and ILOQ except that method variability is factored into the equation by using results generated by samples that have been put through the rigors of field sampling. The MLOD was calculated as three times the standard deviation of a low level standard. The MLOQ is defined as the lowest concentration that can be determined within 30% of the actual concentration. The MLOQ was calculated as ten times the standard deviation of the same low level standard. Three sets of seven PIGS, 21 cartridges in all, were deployed in Idaho Falls to mimic sampler movement in Oklahoma City. All cartridges were analyzed and an MLOD and MLOQ were estimated using the same guidance criteria as for the ILOD and ILOQ. The estimated MLOD was 1 pptv while the estimated MLOQ was 5 pptv. The results were used as reference points for field analysis in Oklahoma City.

The MLOD and MLOQ tend to increase over time due to tubing and bag deterioration. It is very important to establish these limits prior to project commencement in order to know the method capabilities of the materials and equipment that are going to be used. Changes can then be made, if necessary, to achieve needed method performance. Without this knowledge, the data quality may suffer and project objectives may not be met.

Table A-2. Pre-project estimation of MLOD and MLOQ.

Certified Conc. (pptv)	Analyzed Average (pptv)	Average Recovery (%)	Standard Deviation (pptv)	RSD (%)	S/N Ratio	MLOD (pptv)	MLOQ (pptv)	Number of Points
3.84	3.62	94	0.46	13	8	1	5	21

#### 9. ILOD and ILOQ re-determination after field deployment and prior to project initiation.

To verify that the ATGASs were functioning properly after being transported to and set up in a laboratory in Oklahoma City, the ILOD and ILOQ were once again determined just prior to initiation of the first IOP for each ATGAS (Table A-3). These results were compared to the results performed in the laboratory before transportation to the field (Table A-1). Any significant changes would require adjustments to the ATGASs to enhance their performance since all analysis protocols had been developed based upon results determined previously. No adjustments were needed since the results were consistent with those calculated prior to transport. The same certified standard could not be used to calculate the ILOD and ILOQ since the standard cylinder was empty upon arrival to Oklahoma City. The closest standard concentration was chosen to most closely mimic the prior analysis. The average ILOD was 1 pptv while the average ILOQ was 2 pptv.

Table A-3. Pre-project in-field calculation of ILOD and ILOQ.

ATGAS #	Certified Conc. (pptv)	Average (pptv)	Standard Deviation (pptv)	Average Recovery (%)	S/N Ratio	RSD (%)	ILOD (pptv)	ILOQ (pptv)
1	10.43	10.86	0.24	104	45	2	0.7	2.4
2	10.43	11.43	0.21	110	54	2	0.6	2.1
3	10.43	11.45	0.19	110	60	2	0.6	1.9
4	10.43	12.24	0.22	117	56	2	0.7	2.2
Avg.							1	2

#### 10. Re-analysis of 17% of cleaned cartridges used in previous IOP.

After every bag in every cartridge for a given IOP had been analyzed for SF<sub>6</sub>, all bags in each cartridge were cleaned with UHP nitrogen by following the cleaning protocols developed prior to the project (Fig. A-2). Personnel performing the cleaning had been trained on cleaning procedures prior to the field experiment. Seventeen percent (1 of every 6) of those cartridges were filled with UHP nitrogen and analyzed on the ATGAS to ensure there was no carry-over contamination from the previous IOP. If contamination was found in any bag, all six cartridges from that group were analyzed to ensure no contamination and all “dirty” cartridges were re-cleaned and re-analyzed.

## 11. Sampler Servicing Procedure and Handwritten Sampler Servicing Records.

During sampler servicing, sampler deployers were required to follow written procedures (Figs. A-3 and A-4). These procedures were developed after years of prior field experience. The sampler deployers received classroom and hands-on training in Idaho Falls prior to the experiment.

Cardboard Sampler Deployment Procedure	Cardboard Sampler Retrieval Procedure
<p>Repeat all steps for each sampler serviced.</p> <ol style="list-style-type: none"><li>1. Record the location number and time on the Sampler Servicing Record Sheet.</li><li>2. Open the lid and record the sampler number on the Sampler Servicing Record Sheet.</li><li>3. Place the <u>new cartridge</u> in the sampler and write its number on the Sampler Servicing Record Sheet.</li><li>4. Connect the cartridge to the sampler, making sure that:<ol style="list-style-type: none"><li>a. The tubes are securely connected.</li><li>b. The tubes are connected in the correct order.</li></ol></li><li>5. Open the clips on the cartridge, making sure that:<ol style="list-style-type: none"><li>a. The clips are opened and move freely on the tubes.</li><li>b. The tubing is fully opened. This may require you to push on the tube inside the clip with the blunt end of a pen.</li></ol></li><li>6. Check the sampler inlet tubes to make sure they have not been pushed back into the sampler. Pull out on the tubes if necessary.</li><li>7. If needed, replace the battery in the sampler. Normally, the batteries will be replaced after about 5 tests. You will be notified when to replace batteries.</li><li>8. Plug the TimeWand II cord into the sampler. Verify that the right LED is blinking and the left LED is out. If the left LED is still on, remove the battery for at least 2 minutes and replace it. If the right LED is not blinking, check the cable connections and the battery.</li><li>9. With the TimeWand II, scan the sampler serial number, the cartridge serial number, and the location serial number. These may be scanned in any order. Make sure you use the correct location number for each sampler. The TimeWand II will now download the program into the sampler. The left LED will light to indicate a successful download. Make sure the left LED is on before removing the cable!</li></ol> <p>NOTE: In emergencies only, the serial numbers may be entered with the keypad. (Type the 6-digit code and then press the "-" key.) Since this is very error prone, <u>do not use this method unless there is absolutely no other way!</u></p> <ol style="list-style-type: none"><li>10. Disconnect the TimeWand II.</li><li>11. Record any problems on the Sampler Servicing Record Sheet. If there are problems noted, place a mark on the metal bracket in the cartridge with a permanent marker so that lab analyst will know to check the Sampler Servicing Record Sheet.</li><li>12. Place the lid on the sampler and put it on the hanger.</li></ol>	<p>Repeat all steps for each sampler serviced.</p> <ol style="list-style-type: none"><li>1. Record the location number on the Sampler Servicing Record Sheet.</li><li>2. Retrieve the sampler from the hanger and remove the lid.</li><li>3. Record the sampler number on the Sampler Servicing Record Sheet.</li><li>4. Record the cartridge number of the <u>cartridge to be removed</u> on the Sampler Servicing Record Sheet.</li><li>5. Record the time on the Sampler Servicing Record Sheet.</li><li>6. Verify that the cartridge was connected correctly and the bags were filled. Record any problems on the Sampler Servicing Record Sheet. If there are problems noted, place a mark on the metal bracket in the cartridge with a permanent marker so that lab analyst will know to check the Sampler Servicing Record Sheet.</li><li>7. Close the clips on the cartridge and remove it from the sampler.</li><li>8. Scan the number of the <u>cartridge to be removed</u> with the TimeWand II. Then scan the "Pick Up" tag on the cord. If the tag is missing or damaged, enter PK0000 followed by the "-" key on the TimeWand II's keyboard. (Operator's manual Section III.)</li></ol>
	<h3>TimeWand II Data Retrieval Procedure</h3> <p>This procedure must be followed after completing each sampler servicing route. It loads information about the sampler servicing into the Gas Analysis System and insures the TimeWand II is charged. It also sets the clock in the TimeWand II.</p> <ol style="list-style-type: none"><li>1. Place the TimeWand II in the charger connected to the computer in the Tracer Analysis Lab.</li><li>2. Press any key on the TimeWand II. It will beep and display information about charge left and recharge time.</li><li>3. Double click the "Retrieve Data from TimeWands" icon on the computer and follow the instructions.<p>NOTE: Data may be retrieved from several TimeWand II's at the same time. Place as many as you have in the charger before retrieving data.</p></li><li>4. The retrieve software searches for TimeWand II's until it has retrieved data from all of them. If some are not present, it will search for about 70 seconds. Wait for the search to complete.</li><li>5. You will be prompted to insert a floppy disk into a specific drive. A labeled floppy disk will be available with the computer.</li><li>6. Place the Sampler Servicing Record Sheets in the notebook provided.</li><li>7. Leave the TimeWand II's in the charger to re-charge the batteries.</li></ol>

Figure A-3. PIGS (cardboard sampler) deployment and retrieval procedures.

### Plastic Sampler Deployment Procedure

Repeat all steps for each sampler serviced.

1. Open the cartridge lid. Place the sampler in the cartridge and press the wake up button on the sampler.
2. Turn on the downloader. DO NOT CONNECT THE DOWNLOADER TO THE SAMPLER BEFORE IT SAYS "Ready".
3. Record the installed cartridge number on the Sampler Servicing Record Sheet.
4. Record the sampler number on the Sampler Servicing Record.
5. Record the location number on the Sampler Servicing Record Sheet.
6. Record time on the Sampler Servicing Record Sheet.
7. Move the locking handles into lock position. Verify that the sampler and cartridge connect properly and that the cartridge tubes open correctly.
8. When the sampler has stopped "buzzing" and the downloader says "Ready", connect the downloader to the sampler and the location box.
9. Perform download by pressing F1 on the downloader and following the instructions on the screen. Download will take about 30 seconds. Download is complete when the downloader says "SUCCESSFUL" on the screen.
  - \* If a battery error occurs, replace the sampler batteries and repeat the download by pressing F1 again.
  - \* If other errors occur, try repeating the download (press F1 at Ready). If the error persists, use a different sampler or cartridge.
10. Disconnect the downloader from the sampler and location box and turn it off.
11. Record any problems on the Sampler Servicing Record Sheet. If there are problems noted, place a mark on the metal locking handles in the cartridge with a permanent marker so that lab analyst will know to check the Sampler Servicing Record Sheet.
12. Close the lid on the cartridge and put it on the hanger.

### Plastic Sampler Retrieval Procedure

Repeat all steps for each sampler serviced.

1. Record the location number on the Sampler Servicing Record Sheet.
2. Retrieve the cartridge from the hanger and open the lid.
3. Record the sampler number on the Sampler Servicing Record Sheet.
4. Record the cartridge number of the cartridge to be removed on the Sampler Servicing Record Sheet.
5. Record the time on the Sampler Servicing Record Sheet.
6. Verify that the cartridge was connected correctly and the bags were filled. Record any problems on the Sampler Servicing Record Sheet. If there are problems noted, place a mark on the metal locking handles in the cartridge with a permanent marker so that lab analyst will know to check the Sampler Servicing Record Sheet.
7. Open the metal locking handles and remove the sampler from the cartridge.

Figure A-4. Super PIGS (plastic sampler) deployment and retrieval procedures.

Hand written records for each removed or installed cartridge were entered on Sampler Servicing Record Sheets for every IOP. These records were created to provide the analyst with details pertaining to each cartridge and sample bag (Fig. A-5). These records were invaluable as a reference for sample check-in and later for QC flagging of data. These Sampler Servicing Records were filled out by field personnel and given to the laboratory analyst after sampler collection and delivery was performed. All record sheets were organized and placed in a binder for future reference. The metal plate of a cartridge was marked with a permanent marker if any problems were encountered during deployment or retrieval. If a mark was found, the analyst checked the sampler servicing record to determine the course of action for the analysis of that particular cartridge. The mark was then removed prior to the cartridge being used for the next IOP.

**Sampler Servicing Record Sheet**

Project: JU 2003 Route: CBD Paper Date: 7-19-03  
IOP(s): #7 TimeWand: C Name: Hoover

Location	Sampler	Cartridge Removed	Time	Cartridge Installed	Comments or Problems
LC 0027	GF 0031	SN 1208	19:15	SN	
LC 0032	GF 0014	SN 0225	19:19	SN	
LC 0033	GF 0300	SN 0268	19:26	SN	
LC 0133	GF 0998	SN 0513	19:28	SN	
LC 0023	GF 0008	SN 0233	19:35	SN	
LC 0037	GF 0092	SN 1062	19:38	SN	
LC 0047	GF 0059	SN 4344	19:43	SN	
LC 0042	GF 0211	SN 1272	19:49	SN	
LC 0051	GF 0045	SN 0215	19:52	SN	
LC 0052	GF 0022	SN 1065	19:55	SN	
* LC 0057	GF 0212	SN 4368	20:01	SN	Clip Broken #11 bag
LC 0067	GF 0085	SN 4336	20:05	SN	
LC 0062	GF 0048	SN 0328	20:15	SN	
LC 0061	GF 0207	SN 4307	20:18	SN	
LC 0161	GF 0319	SN 0164	20:20	SN	
LC 0072	GF 0073	SN 0469	20:23	SN	
LC 0073	GF 0309	SN 1226	20:27	SN	
* LC 0074	GF 0210	SN 1106	20:30	SN	#6 bag Flat
LC 0076	GF 0056	SN 4372	20:34	SN	
LC 0176	GF 0049	SN 4345	20:36	SN	
LC 0077	GF 0069	SN 0131	20:40	SN	
LC 0082	GF 0062	SN 1266	20:50	SN	
LC 0087	GF 0202	SN 0242	20:53	SN	
LC	GF	SN		SN	
LC	GF	SN		SN	
LC	GF	SN		SN	
LC	GF	SN		SN	

Figure A-5. Example Sampler Servicing Record.

## 12. Chain of custody procedures.

Chain of custody procedures were followed to ensure that a history of every field sample was generated. The process of sampler operation provided a computer generated chain of custody of each sample as well as automatically associating each sample with a sampling time and location. This process minimized the possibility of errors caused by mistakes in manually recording, copying or entering location information.

## 13. Sample check-in procedures.

All cartridges were checked-in prior to analysis. During this process each bag was inspected and the following flags were entered for each bag:

- B = Too big (overfilled)
- G = Good
- L = Low
- F = Flat
- D = Damaged clip or bag
- I = Improper hookup (tubes crossed, clip open, etc.)

These flags were used later for querying, flagging, and final data QC purposes.

## 14. Daily calibration of the ATGAS.

In order to quantitate the concentration of the samples, each ATGAS was calibrated at the beginning of each analysis day using six to twenty-four NIST-traceable SF<sub>6</sub> standards. The calibration standards ranged from 1.97 pptv to 210,700 pptv and covered the entire range of field sample concentrations. The calibration ranges were modified occasionally to accommodate the concentration ranges of samples being analyzed. Concentrations of samples were calculated using a quadratic equation fit to groups of three points. The calibration curve was examined for "wild fits" and an error message was displayed if such an event occurred so that the analyst could more closely examine the curve and decide if it was appropriate to use.

## 15. Initial ATGAS calibration verification (ICV).

After each calibration was completed, the curve was validated by analyzing the same calibration standards as samples. This validation was used to provide evidence that sample concentrations within the calibration range could be quantitated correctly. The recoveries were required to be within  $\pm 10\%$  of the certified value or the standards were re-analyzed. If the recoveries still did not meet the acceptance limits, the bags were refilled and analyzed again. If the recoveries were still not acceptable, the instrument was re-calibrated and ICV was attempted again.

#### 16. Continuing ATGAS calibration verification (CCV).

Approximately every 3 hours, the validity of the ATGAS instrument calibration curves were checked by re-analyzing calibration standards as samples. This procedure, called continuing calibration verification (CCV), was performed to provide evidence that instrument drift had not caused the calibration to be unable to correctly quantitate sample results within a reasonable acceptance level. Standards were chosen to cover the concentration range of samples that had been analyzed since the last calibration verification. The standards were required to have a recovery of  $\pm 20\%$  of the certified value for that section of the curve to be considered valid. If any of the standards were not within the acceptance window, the instrument was re-calibrated and the curves were re-validated. All data within the unacceptable concentration range, from the point of the last acceptable CCV, were flagged and re-analyzed.

#### 17. Atmospheric background checks of SF<sub>6</sub> in the TAF.

A background atmospheric check of SF<sub>6</sub> consisted of analyzing three samples of the air in the TAF on each ATGAS every analysis day. This information was used to determine if there was any leakage in the analysis system when compared to the instrument blanks that were subsequently analyzed. The data was also used for inter-comparison between ATGASs that were being used on the same day to check the between instrument precision. The results were also used to reveal discrepancies between ATGASs to indicate a problem that otherwise might go undetected. The average concentration for all background checks was 7 pptv. The standard deviation and RSD between all four ATGASs was 0.64 pptv and 8%, respectively, with no RSD over 15%. This indicates extremely good precision between the ATGASs. Figure A-6 shows the concentrations of the TAF background checks for each ATGAS for each analysis. The agreement between ATGASs is readily apparent. Data are shown only on those days when more than one ATGAS was in use and the checks were analyzed at approximately the same time.

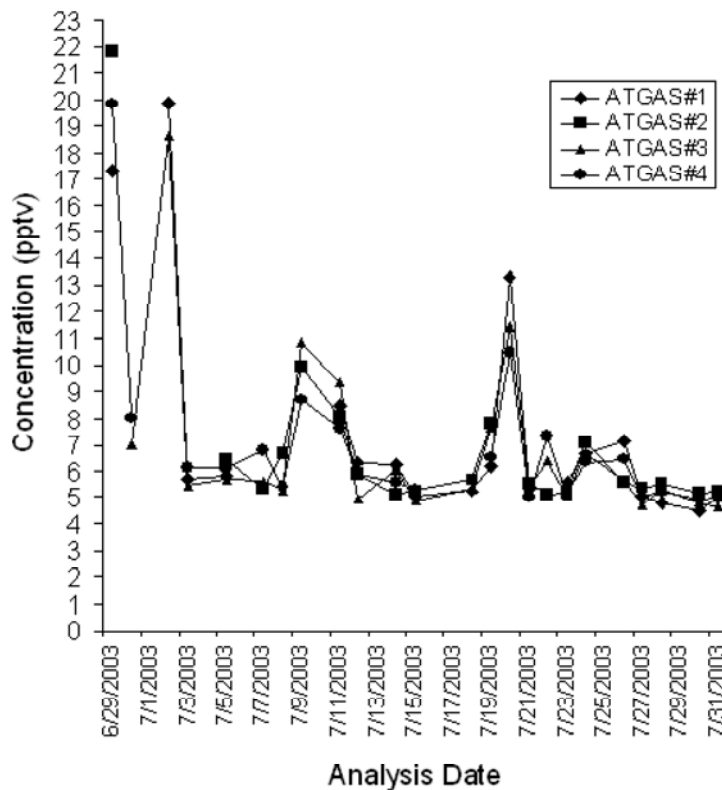


Figure A-6. Results of TAF background concentration checks on analysis days.

#### 18. Analysis of laboratory blanks.

A laboratory or instrument blank was analyzed on each ATGAS each analysis day to verify that there was no contamination or leaks within the analysis system as compared to the background checks analyzed that day, that there was no carry-over from previously analyzed high concentration standards, and to ensure carrier gas purity. The blank sample consisted of a cartridge of twelve bags that were each filled with ultra high purity (UHP) nitrogen. The concentration results of all bags were required to be less than the lowest calibration standard and close to a concentration of 0 pptv. If the concentration of one or more of the bags was higher than the acceptable range, the bag was re-filled and re-analyzed. If the concentration still was not within acceptable limits, the instrument was re-calibrated and re-verified or the samples were flagged and re-analyzed. If there were still indications of contamination, the problem was identified and fixed before analysis continued.

Table A-4 shows the laboratory blank results for each ATGAS and its corresponding ILOD and ILOQ. The average ILOD and ILOQ of 1 pptv and 5 pptv respectively are comparable to the two previously established limits using low concentration standards (Tables A-1 and A-3). The average concentration results of  $0.21 \text{ pptv} \pm 0.47 \text{ pptv}$  indicate no contamination or leakage problems within any of the ATGASs as well as no carry-over issues.



Table A-4. Laboratory blank sample results for each ATGAS.

ATGAS Number	Average Concentration (pptv)	Standard Deviation (pptv)	ILOD (pptv)	ILOQ (pptv)
1	0.25	0.36	1	4
2	0.29	0.47	1	5
3	0.28	0.44	1	4
4	0.00	0.60	2	6
Average	0.21	0.47	1	5

#### 19. Analysis of laboratory duplicates.

Analyses of laboratory duplicates was performed each day to provide evidence of instrument precision. Each day at least one PIGS and one Super PIGS cartridge was analyzed in duplicate on each ATGAS. The sample and its duplicate were analyzed at least 1-3 hours apart in order to ensure an appropriate estimation of instrument precision over time. The duplicate cartridges chosen for this process contained the greatest number of bags with concentration ranges within the calibration curve for that particular ATGAS. Relative percent differences (RPD), i.e. the difference of the results of the two analyses divided by their average, were calculated and were required to be within 20%. Any result not within the acceptable limits was flagged and re-analyzed. If the result was still not within acceptable limits, the analysis was terminated until the ATGAS precision could be re-established. The RPDs and RSDs can be seen in Table A-5. All RPDs and RSDs were below 5% indicating good instrument precision over time.

Table A-5. Laboratory duplicate results for each ATGAS.

ATGAS Number	Average RPD (%)	Average RSD (%)
1	0.8	1
2	0.2	2
3	0.2	2
4	4.9	4
Average	1.5	2

#### 20. Analysis of laboratory controls.

Laboratory controls were used to provide evidence of instrument precision and accuracy and were a product of all ICVs and CCVs. Table A-6 lists all ICVs and CCVs analyzed during the project along with their average results. All standards had less than 10% RSD except, understandably, for the 2.02 pptv standard which is at the ILOD. The average percent recoveries ranged from 98% to 101%. These two factors indicate extremely good instrument precision and accuracy. Again, the in-field calculated ILOD and ILOQ of 1 pptv and 4 pptv using the 3.48 pptv standard correspond well with the ILOD and ILOQs calculated previously (Tables A-1, A-3, and A-4).

Table A-6. Laboratory control results for all ATGASs.

Certified Concentration (pptv)	Average Concentration (pptv)	Average Recovery (%)	Standard Deviation (pptv)	RSD (%)	S/N Ratio	ILOD (pptv)	ILOQ (pptv)
2.02	2.00	99	0.30	16	7	1	3
3.48	3.41	98	0.35	10	10	1	4
9.00	8.81	98	0.55	6	16	2	6
10.43	10.53	100	0.57	5	18	2	6
20.18	19.97	99	1.2	6	17	4	12
38.7	38.5	99	2.0	5	19	6	20
77.4	75.9	98	4.5	6	17	14	45
82.9	82.1	99	3.9	5	21	12	39
284.6	280.0	98	17	6	17	51	170
291.4	289.6	99	17	6	17	51	170
514	506	98	23	5	22	69	230
779	767	98	48	6	16	144	480
796	790	99	45	6	18	135	450
1560	1542	99	96	6	16	288	960
3020	3003	99	178	6	17	534	1780
5100	5135	101	255	5	20	765	2550
5280	5212	99	453	9	12	1359	4530
7610	7572	100	365	5	21	1095	3650
8370	8374	100	313	4	27	939	3130
10120	10129	100	523	5	19	1569	5230
10440	10393	100	460	4	23	1380	4600
16310	16307	100	867	5	19	2601	8670
19430	19305	99	1035	5	19	3105	10350
21720	21681	100	771	4	28	2313	7710
36900	36662	99	1107	3	33	3321	11070
50500	50276	100	1568	3	32	4704	15680
75100	74932	100	2251	3	33	6753	22510
90000	89609	100	3059	3	29	9177	30590
103600	103506	100	2624	3	39	7872	26240
154900	154373	100	4315	3	36	12945	43150
179300	181594	101	2752	2	65	8256	27250
210700	211442	100	14582	7	14	43746	145820

## 21. Analysis of field blanks.

Field or method blanks were sampled and analyzed to indicate if there was any contamination or leakage within the entire sampling and analysis system. For example, isolated instances of high concentrations of SF<sub>6</sub> in the field blanks compared with acceptable results for the laboratory blanks indicate holes in the sampling bag, clips not properly closed, wrong location number, or other operational problems. Consistently high concentrations would indicate a sampling method that could not measure null concentrations accurately. The fifteen field blank samplers were set at 11 locations (Table A-7), several with two QC samplers, and each was used to check for any source of contamination or leaks within the sampler or in later handling of the cartridges. The PIGS blanks and controls were contained in one specially built sampler that housed two cartridges. One cartridge was the source cartridge and contained pre-filled bags of UHP nitrogen. The second cartridge was the receiver cartridge and captured the nitrogen that was transferred from the source cartridge via the pumping mechanisms during an IOP (Figs. A-7 and A-8). The total number of PIGS blanks analyzed for the entire project was 1200 with 1187 (99%) usable. The 13 unusable samples were either flat bags or did not meet all QC requirements.

Table A-7. Field locations of blank, control, and duplicate cartridges. Locations with an asterisk had two QC samplers stationed at that location.

Field Location	Cartridge Type	Position Number	Latitude deg. north	Longitude deg. west
CBD	blank	54	35.46974	97.5163
CBD	blank	056*	35.46969	97.5142
CBD	blank	57	35.46963	97.5129
CBD	blank	82	35.47293	97.5193
CBD	blank	086*	35.47279	97.5144
CBD	blank	87	35.47278	97.5128
CBD	control	23	35.46630	97.5178
CBD	control	42	35.46894	97.5197
CBD	control	043*	35.46890	97.5181
CBD	control	063*	35.47099	97.5180
CBD	control	65	35.47093	97.5154
CBD	control	72	35.47191	97.5193
CBD	duplicate	33	35.46742	97.5179
CBD	duplicate	053*	35.46977	97.5178
CBD	duplicate	61	35.47105	97.5210
CBD	duplicate	064*	35.47093	97.5165
CBD	duplicate	66	35.47072	97.5145
CBD	duplicate	76	35.47174	97.5142
1 km arc	blank	510	35.47512	97.5212
1 km arc	control	514	35.47667	97.5168
1 km arc	control	515*	35.47662	97.5158
1 km arc	duplicate	511*	35.47571	97.5204
1 km arc	duplicate	512	35.47630	97.5191
2 km arc	blank	537	35.47895	97.5319
2 km arc	blank	542*	35.48477	97.5207
2 km arc	control	540*	35.48373	97.5254
2 km arc	control	545	35.48598	97.5123
2 km arc	duplicate	543	35.48617	97.5180
4 km arc	blank	568*	35.49424	97.5456
4 km arc	blank	575	35.50328	97.5113
4 km arc	control	569	35.49760	97.5406
4 km arc	duplicate	567	35.49090	97.5492
4 km arc	duplicate	572*	35.50255	97.5254



Figure A-7. PIGS control or blank sampler showing source cartridge (right) and receiver cartridge (left).



Figure A-8. PIGS control or blank sampler with the covers on and bungee cords in place.

The Super PIGS blanks and controls had two samplers contained in separate cartridges connected by a filling tube and a data information line. The two cartridges were held together by bungee cords. One cartridge was the source cartridge and contained pre-filled bags of UHP nitrogen. The second cartridge was the receiver cartridge and captured the nitrogen that was transferred from the source cartridge via the pumping mechanism during the IOP (Fig. A-9). The total number of Super PIGS blanks analyzed for the entire project was 600 with 461 (77%) usable.



Figure A-9. Super PIGS control and blank cartridges.

Field blank results were visually scanned after completion of each IOP to ensure no obvious contamination or leakage problems. Every attempt was made to fix any problems before the initiation of the next IOP. Due to time constraints between IOPs, not every result could be reviewed closely or samples re-analyzed. After completion of the project, the blanks were graphed and scrutinized to determine if any flags should be added to the data.

Table A-8 below shows the PIGS average blank concentration result for each IOP. The average results of 1.1 pptv and standard deviation of 3.0 pptv indicate no evidence of contamination or leakage within the combined sampling and analysis system.

Table A-8. PIGS field blank results for each IOP.

IOP Number	Average Concentration (pptv)	Standard Deviation (pptv)
1	1.3	2.5
2	1.6	2.6
3	1.1	4.8
4	1.3	2.9
5	2.0	4.9
6	1.2	2.4
7	0.8	1.3
8	0.8	3.1
9	0.4	0.7
10	0.3	0.9
Average	1.1	3.0

Table A-9 shows the Super PIGS average concentration results for each IOP. The average results of 31 pptv and standard deviation of 46 pptv indicates evidence of contamination or leakage within the combined sampling and analysis system. Further discussion of this problem can be found in the Super PIGS QC Issues section of this report.

Table A-9. Super PIGS field blank results for each IOP.

IOP Number	Average Concentration (pptv)	Standard Deviation (pptv)
1	24	22
2	28	29
3	14	12
4	35	101
5	9	6
6	20	25
7	57	118
8	26	25
9	24	34
10	68	90
Average	31	46

## 22. Analysis of field duplicates.

Fifteen field duplicate samplers were placed at 11 locations, listed in Table A-7, in each IOP to check for imprecision and bias in the sampling, handling and storage of samples. These duplicate samplers were placed directly across from a regular field sampler on the same hanging

structures so that each set of samplers would collect similar air samples. All samples and their duplicates were downloaded with the same information from the same Timewand or downloader. Field duplicate results were visually scanned after completion of each IOP to ensure there were no obvious indications of imprecision or bias. Every attempt was made to fix any problems before the initiation of the next IOP. Due to time constraints between IOPs, not every sample result could be reviewed closely and samples re-analyzed. After completion of the project, RPDs were calculated and sample results greater than the MLOQ were graphed against their corresponding duplicate to determine method performance (Figs. A-10 and A-11). A regression analysis of all data above the MLOQ was performed on each duplicate data set. The intercept and slope were used as an indicator of bias. The correlation coefficient was used as an indicator of precision. Both the PIGS and the Super PIGS showed no significant bias with similar slope results of 0.913 and 0.929 respectively. The Super PIGS indicated slightly more bias with an increased intercept of 64 pptv compared with the PIGS intercept of 6.6 pptv. A lower correlation coefficient of 0.929 compared with the PIGS correlation coefficient of 0.984 indicated good precision although not as good as the PIGS. The PIGS results indicate no significant bias. The total number of PIGS duplicates analyzed was 1200 with 86% usable. The total number of Super PIGS duplicates analyzed was 600 with 70% usable.

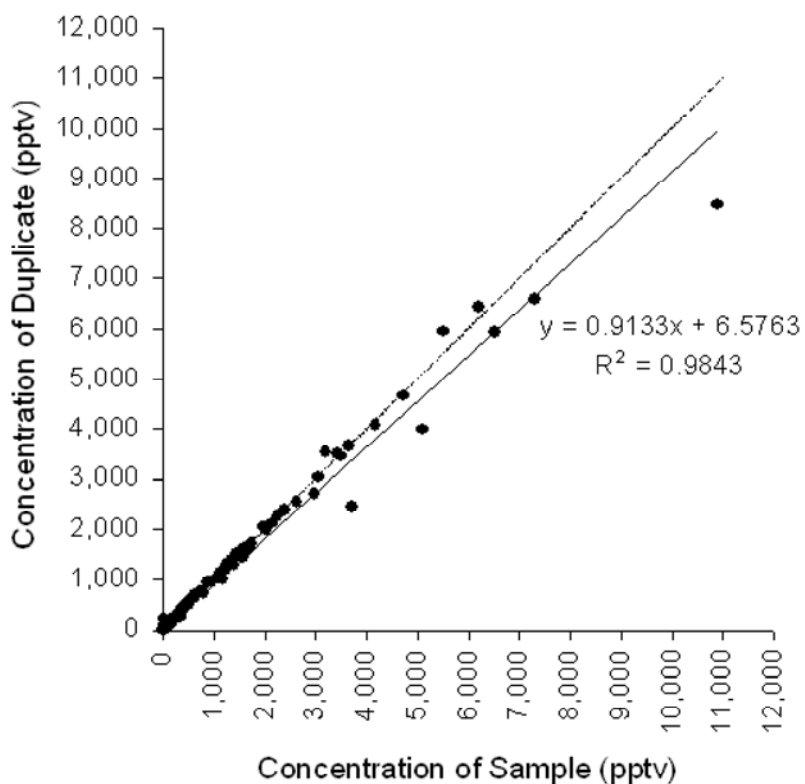


Figure A-10. Linear regression of PIGS field duplicates with concentrations greater than MLOQ (dashed line is 1:1).

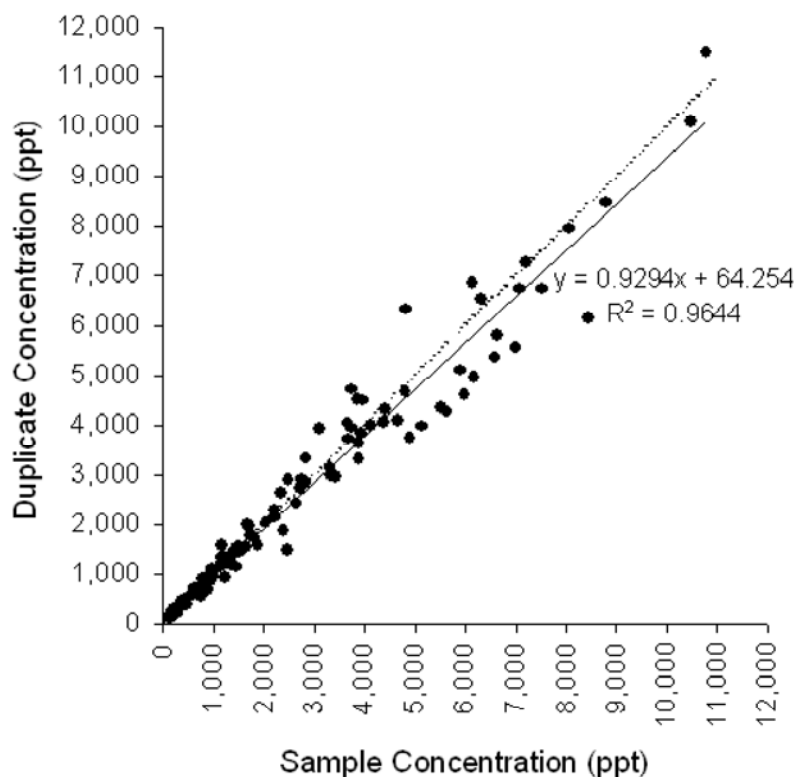


Figure A-11. Linear regression of Super PIGS field duplicates greater than the MLOQ (dashed line is 1:1).

The average duplicate RPD for the PIGS for each IOP was less than 15%. The average RSDs were all less than 10% (Table A-10). RPD and RSD less than 15% and 10%, respectively, indicate good precision and no bias.

Table A-10. PIGS field duplicate results.

IOP Number	Average RPD (%)	Average RSD (%)
1	7.4	5
2	6.5	5
3	6.7	5
4	9.5	7
5	12	8
6	12	8
7	5.9	4
8	6.6	5
9	6.9	5
10	4.7	3
Average	7.8	6

The average RPDs for the Super PIGS for each IOP were also less than 15% except for IOP 1 while the average RSDs were all less than 10%, except for IOP 1 (Table A-11). The PIGS average RPD was 7.8%, while the Super PIGS RPD was 9.3%. The PIGS average RSD was 6% while the Super PIGS average RSD was 7%. This indicates good precision with no bias and very comparable results with the PIGS.

Table A-11. Super PIGS field duplicate results.

IOP Number	Average RPD (%)	Average RSD (%)
1	17	12
2	9.6	7
3	12	8
4	2.6	2
5	9.4	7
6	5.0	4
7	8.0	6
8	8.6	6
9	13	9
10	8.2	6
Average	9.3	7

An insignificant number of samples, approximately 0.1%, had RPDs greater than 30% with either a sample or duplicate concentration of greater than four times the MLOQ. These results were closely investigated. If no problems could be found with the analysis, the sample and its duplicate were flagged as estimates and other samples within that batch were reviewed for trends.

### 23. Analysis of field controls.

Fifteen field control samplers were placed at 11 locations, listed in Table A-7, in each IOP to check for any bias and inaccuracy introduced during the sampling, handling, and storage of the samples. Each control sampler was placed alongside a regular field sampler. The controls were contained in specially built samplers that housed two cartridges and were identical in appearance to the field blank samplers (Figs. A-7 through A-9). One cartridge was the source cartridge and contained pre-filled bags of calibration gases. The second cartridge was the receiver cartridge and captured the calibration gas that was transferred from the source cartridge via the pumping mechanisms during the IOPs. Field control results were visually scanned after completion of each IOP to ensure there were no obvious recovery problems. Every attempt was made to fix any problems before the initiation of the next IOP. The estimated MLOD and MLOQ were calculated for each IOP and the flags for that IOP were set after each IOPs completion to give an indication of method performance. Due to time constraints between IOPs, these results could not be reviewed closely or samples re-analyzed. After completion of the project, the controls were graphed and scrutinized to determine if any flags should be added to the data and the final MLOD and MLOQ were calculated.



All PIGS controls had less than 15% RSD except, understandably, for the 2.02 pptv and 3.84 pptv standards which are at the MLOD and MLOQ, respectively, as seen in Table A-12. The average percent recoveries ranged from 89% to 108%. These two factors indicate good method precision and accuracy. The total number of PIGS controls was 1,200 with the percentage of usable data of 95%.

Table A-12. Field control results for the PIGS.

True Conc. (pptv)	Analyzed Conc. (pptv)	Recovery (%)	Standard Deviation (pptv)	RSD (%)	S/N Ratio	MLOD (pptv)	MLOQ (pptv)	Number of Points	Percent Usable
2.02	2.18	108	0.39	18	6	1	4	93	93
3.84	3.53	92	0.57	16	6	2	6	36	90
9.00	8.87	98	0.59	7	15	2	6	28	93
10.43	10.34	99	0.41	4	25	1	4	8	99
20.18	19.22	95	1.31	7	15	4	13	97	97
38.7	37.3	96	3.5	9	11	10	35	39	98
82.9	80.1	97	3.7	5	22	11	37	37	93
284.6	271.9	96	11.6	4	24	35	116	29	97
291.4	274.6	94	17.5	6	16	52	175	68	97
514	484	94	21.1	4	23	63	211	19	95
779	742	95	33	4	23	99	330	26	87
796	729	92	81	11	9	242	808	58	83
1560	1495	96	57	4	26	172	574	25	83
3020	2830	94	300	11	9	899	2995	95	95
5100	4978	98	122	2	41	366	1220	29	97
5280	4674	89	663	14	7	1990	6633	40	100
7610	7148	94	508	7	14	1525	5084	58	97
8370	8304	99	221	3	38	664	2212	10	100
10120	9723	96	551	6	18	1654	5513	26	87
16310	15049	92	1812	12	8	5438	18127	67	96
19430	18473	95	1006	5	18	3018	10059	70	100
21720	20850	96	878	4	24	2634	8779	29	97
36900	34181	93	3267	10	10	9800	32667	57	95
50500	47401	94	4436	9	11	13307	44357	57	95
75100	70826	94	3355	5	21	10065	33548	30	100

As seen in Table A-13, the Super PIGS controls had RSDs ranging from 2% to 91% with the highest results coming from standard concentrations near the MLOD and MLOQ. The average percent recoveries ranged from 77% to 629%. These two factors indicate method problems with precision and accuracy. Further discussion can be found in the Super PIGS QC Issues section of this report. The total number of Super PIGS controls analyzed was 600 with the average percentage of usable data of 60%.

Table A-13. Field control results for the Super PIGS.

True Conc. (pptv)	Analyzed Conc. (pptv)	Recovery (%)	Standard Deviation (pptv)	RSD (%)	S/N Ratio	MLOD (pptv)	MLOQ (pptv)	Number of Points	Percent Usable
2.02	12.7	629	12	91	1	34	115	32	64
3.84	5.95	155	2.9	49	2	9	29	10	50
9.00	16.9	187	83	49	2	25	83	10	67
20.18	28.3	140	13	47	2	40	132	32	64
38.7	40.2	104	9.6	24	4	29	96	11	55
82.9	77.6	94	6.8	9	11	20	68	10	50
284.6	250.8	88	15	6	17	45	151	11	73
291.4	273.0	94	32	12	8	97	323	23	66
514	457	89	47	10	10	142	472	6	60
779	666	86	82	12	8	247	822	10	67
796	713	90	79	11	9	237	789	18	51
1560	1454	93	85	6	17	255	851	9	60
3020	2543	84	494	19	5	1482	4939	33	66
5100	4486	88	156	3	29	469	1564	10	67
5280	4555	86	394	9	12	1183	3944	13	65
7610	6705	88	494	7	14	1482	4941	22	73
10120	9427	93	391	4	24	1172	3906	9	60
16310	13682	84	1883	14	7	5650	18835	21	60
19430	16993	87	1420	8	12	4259	14196	17	49
21720	15801	77	4752	28	4	14256	47521	8	53
36900	31855	86	1802	6	18	5406	18018	16	53
50500	40382	83	5394	13	8	16182	53941	21	70
75100	62803	84	1523	2	41	4572	15238	6	40

#### 24. Software quality control checks.

Several important quality checks were built into the software to efficiently aid the TAF analyst in ensuring that the ATGAS instruments were functioning correctly during analysis.

- Since the concentration is dependent upon the temperature of the ATGAS ovens, it is critical that the temperatures do not fluctuate widely during analysis. Temperature acceptance limits were set and the software produced a pop-up window to alert the analyst in case of unacceptable temperature readings. All samples obtained using the incorrect temperature were re-analyzed.
- To check for instrument drift, the software alerted the analyst to validate the calibration curve when more than three hours had elapsed from the last CCV. The analyst had the option of overriding the alert or checking the calibration and re-starting the 3 hour clock.

- In order to verify the calibration curve in the area of interest and to save time, the software produced on the computer screen a record of the highest and lowest concentrations measured since the last CCV. The analyst had only to re-analyze calibration samples within that range.
- Several data flags were shown immediately on the computer screen to aid the analyst in deciding whether the data for each bag was “good” or re-analysis was necessary.
- The software kept track of which ATGAS field duplicate was analyzed on and directed the analyst to use the same GC for the duplicate cartridge. This helped to quantitate the variability of the field analysis without adding the extra variability of analyzing on a separate ATGAS.
- The software alerted the analyst if any calibration points did not meet pre-determined acceptance criteria. The analyst could then review the calibration curve to determine the acceptable course of action.

## 25. Data verification.

Data verification was performed to ensure that the samples met all QC acceptance limits and that all samples had been analyzed for that particular IOP. Transcription and calculation errors were reduced by automated data reduction techniques such as automated flagging of results outside acceptable limits, auto-generated quality control sheets (Fig. A-12 and A-13), auto generation of chromatogram plots including calibration curves (Fig. A-14) and electronic transfer of data from the ATGAS's to Excel spreadsheets. The analyst and at least one other person familiar with the data analysis process reviewed all data packages. All data packages were batch processed per run on each ATGAS. All data packages included the raw data, a copy of the logbook pages for that analysis, the quality control sheet that summarized the results of all QC data generated for that batch (Fig. A-12 and A-13), plots of all chromatograms and calibration curves (Fig. A-14), and a data verification sheet (Fig. A-15) to ensure the verifier checked all QC parameters. Software produced an Analysis Summary (Fig. A-16) that was utilized to ensure that there was at least one acceptable result for each bag for each location that was downloaded for each IOP. Any samples rejected by the software were re-analyzed and the Analysis Summary report was re-run until all samples had been analyzed or a justifiable reason had been determined for a missing sample. Cartridges were not cleaned until all available samples had been analyzed.

National Oceanic and Atmospheric Administration  
Air Resources Laboratory Field Research Division  
Quality Control Sheets

1

Analyst: Camille Edwin Debbie Looft Verified by: Roger Carter  
 Date: 07/11/2003  
 Project: JUT03  
 GC# 3 Date: 13 July 03  
 Parameter SF6  
 Data file: G3030711.r01

Calibration Verification(+/-10%)					Lab Blank (~lowest cal)		Calibration Check(+/-20%)				Background Level	
Bag	True Value	Result	%Recovery	area	Bag	Result	True Value	Result	%Recovery		Bag	Result
#01	2.02	2.19	109	3445	#01	.78	3.47	4.05	117		#1	9.16
#02	3.47	3.63	105	5290	#02	.63	20.18	21.30	106		#2	9.45
#04	20.18	20.28	100	24616	#03	.79	796.00	842.05	106		#3	9.37
#05	38.70	37.74	98	45170	#04	.81	5280.00	5705.80	108		Average	<del>9.40</del> 9.33
#06	82.90	81.65	98	95773	#05	.38	7610.00	7965.19	105		Sample	
#07	291.40	289.11	99	385102	#06	.41	16310.00	17390.03	107		Min=	.26
#09	796.00	789.28	99	1017609	#07	.40	19430.00	20835.45	107		Max=	19764.42
#10	1560.00	1552.75	100	1726576	#08	.60	2.02	2.27	112		Temperature	
#11	3020.00	3006.25	100	2684647	#09	.32	20.18	20.76	103		Min=	64.8
#12	5280.00	5340.60	101	3735608	#10	.47	291.40	306.29	105		Max=	66.4
#01	7610.00	7641.58	100	4634763	#11	.41	1560.00	1665.03	107			
#02	10120.00	10288.29	102	5740551	#12	.26	5280.00	5685.96	108			
#03	16310.00	16538.96	101	7562027			2.02	1.88	93			
#04	19430.00	19825.96	102	8284330			7610.00	8027.12	105			
							19430.00	20753.54	107			
							2.02	2.05	101			
							20.18	20.98	104			
							291.40	304.83	105			
							796.00	846.22	106			
							3020.00	3260.31	108			
							5280.00	5626.54	107			

Final Calibration Verification(+/-20%)					Comments/Corrective Actions	
Bag	True Value	Result	%Recovery			
#01	2.02	1.95	97		SN5366 #10 was low	
#02	3.47	3.67	106		SN 0279, #10 clip broken, but tube still shut so data OK.	
#04	20.18	20.73	103			
#05	38.70	39.95	103			
#06	82.90	85.07	103			

Figure A-12. Page 1 of a QC sheet.

Figure A-13. Page 2 of a QC sheet.

File=G3030711.R01

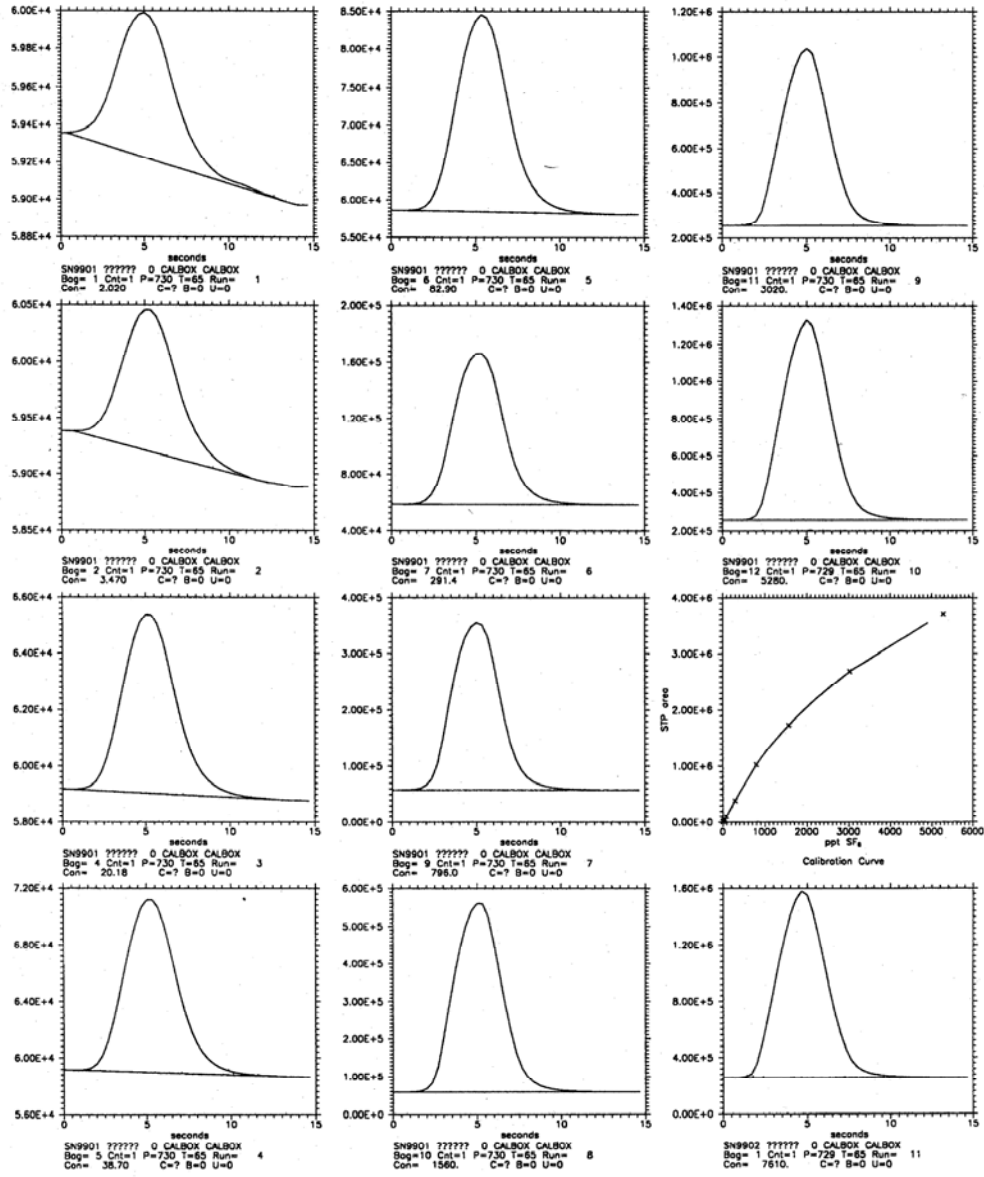


Figure A-14. Examples of chromatograms and calibration curve.

Figure A-15. Example of a data verification sheet.

Anlsum.out

Analysis Summary for JUT203 test 12  
start year=2003 start month= 7  
estimated results accepted as good.  
21-JUL-03 23:27:18

*Plastic  
IOPG*

*✓ de*

Cartridges downloaded, but analysis NOT complete

Cartridges with complete analysis that were NOT downloaded

SN1291	LC****	1	2	3	4	5	6	7	8	9	10	11	12	<i>} none downloaded</i>
SN5243	LC****	1	2	3	4	5	6	7	8	9	10	11	12	

Locations downloaded but NOT listed as project locations

LC8043  
LC8044  
LC8045  
LC8046  
LC8053  
LC8055  
LC8056  
LC8063  
LC8064  
LC8065  
LC8066  
LC8083  
LC8084  
LC8086  
LC8153  
LC8164  
LC8166  
LC8254  
LC8256  
LC8286  
LC8343  
LC8363  
LC8365  
LC8940  
LC8945  
LC8946  
LC8950  
LC8954  
LC8956  
LC8963  
LC8964  
LC8965  
LC9043  
LC9044  
LC9045  
LC9046  
LC9053  
LC9054  
LC9055  
LC9056

Figure A-16. Example of an Analysis Summary sheet.

## 26. Post Determination of Method of Limit Detection.

Although the PIGS MLOD and MLOQ were estimated prior to deployment to Oklahoma City, the final MLOD and MLOQ for the PIGS and the Super PIGS was re-established after completion of the project. The MLOD and MLOQ were determined to provide a concentration result with a defined level of confidence to be statistically different from zero. All concentrations were compared with these values and QC flags were generated accordingly. All data were later flagged according to these values. The method limit is dependent upon method performance and should be established using the same variables such as location, time, and weather conditions as was used for the data collection. The PIGS MLOD and MLOQ were calculated based upon the analysis of field controls (Table A-12), the procedure stated in the pre-project MLOD and MLOQ determination section. Table A-14 shows the results from the 2.02 pptv field control used to calculate the final PIGS MLOD of 1 pptv and MLOQ of 4 pptv.

Table A-14. Post-project determination of PIGS MLOD and MLOQ.

Certified Conc. (pptv)	Analyzed Average (pptv)	Average Recovery (%)	Standard Deviation (pptv)	RSD (%)	S/N Ratio	MLOD (pptv)	MLOQ (pptv)	Number of Points
2.02	2.18	108	0.39	18	6	1	4	93

The Super PIGS MLOD and MLOQ however, could not be calculated in the same way as the PIGS using the field control results (Table A-13). The MLOD and MLOQ were calculated based upon testing that was done later at the FRD laboratory facility. A total of 97 points were used to calculate the final MLOD as 33 pptv and the final MLOQ as 111 pptv. The final MLOD and MLOQ values for both the PIGS and Super PIGS were used to set QC flags in the database.

## 27. Method verification.

All field data were verified to make sure there was a result for every location, cartridge and sample bag and that all results were flagged appropriately. Every quality control sheet (Figs. A-12 and A-13) for each data package was reviewed to ensure proper flagging of final data. Dot plots (Fig. A-17) were created and reviewed to ensure all data were reasonable with respect to each release. Any suspicious data point was traced back through the analysis and deployment records to determine if it was indeed a valid result. The sampler servicing record (Fig. A-5), which was used by all field deployers to note any problems was used to check any outliers or anomalies in the data. Time history plots (Fig. A-18) were also reviewed as well as chromatograms (Fig. A-14) to determine any suspicious data points. Any suspicious data point was traced back through the analysis and deployment records to determine if it was indeed a valid result. All field QC was scrutinized. All suspicious data were appropriately flagged.



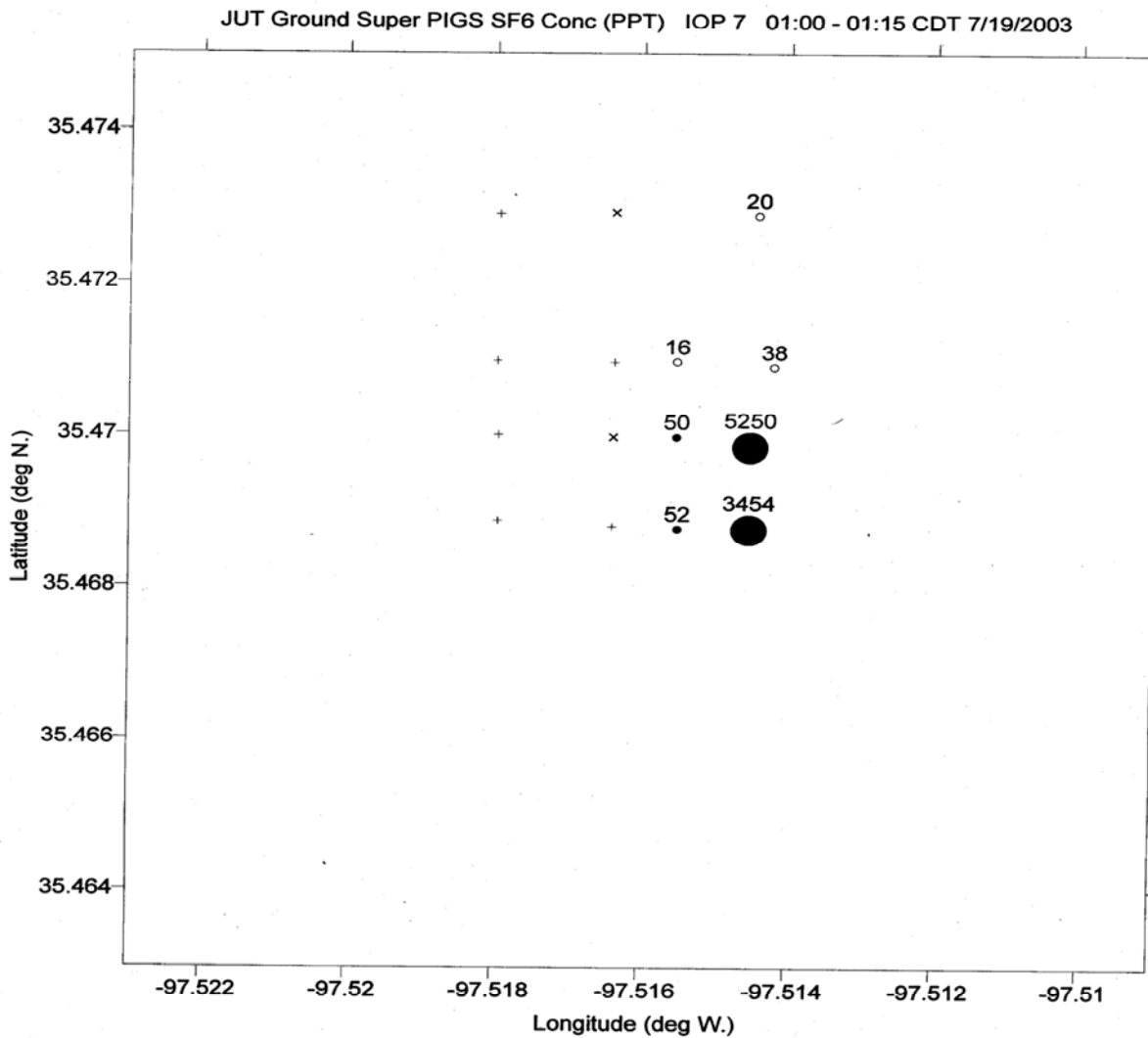


Figure A-17. An example of a dot plot where “+” means less than MLOQ, “x” indicates no data, and the dot size is proportional to bag concentration.

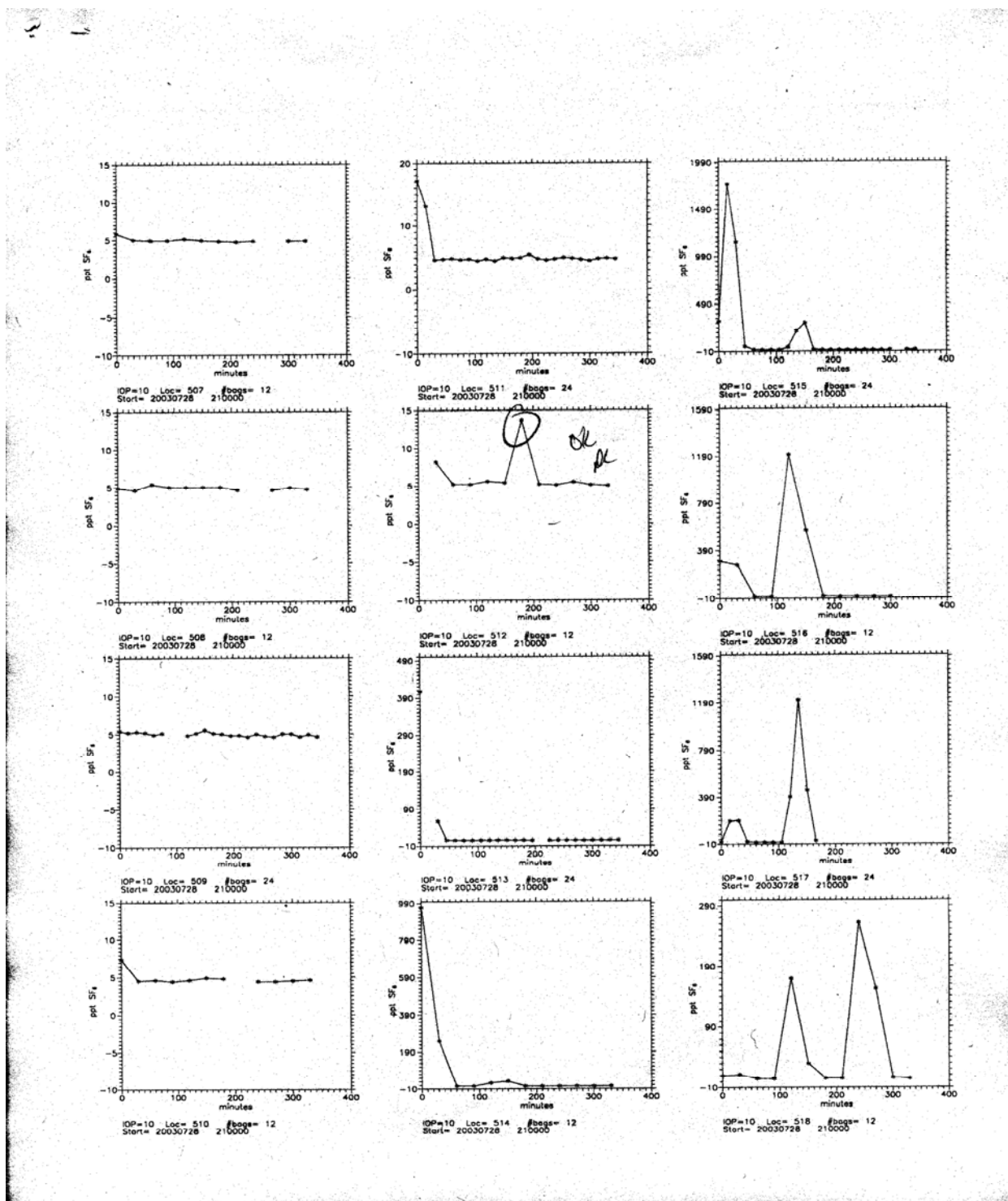


Figure A-18. Example of a tracer concentration time history plot for 12 selected locations in IOP 10, with each dot representing results from one sample bag.

## 28. Data handling.

All results were printed on hard copy as a backup in case of loss of the data files and to aid in the data verification process. The data packages were filed for future reference and to be readily available during the project for immediate review. Backup copies of the raw ATGAS data were made occasionally and at the end of the project to prevent total loss of data in the case of a computer failure. All final QC and sample results were printed on hard copy and placed in a binder to be stored with any reference materials for the project.

## 29. Holding time studies.

Holding time studies are determinations of the length of time a sample can be held in its container before the sample concentration changes appreciably. Holding time studies should be conducted whenever the method or sampling container is changed in any way prior to commencement of a project. These studies should be used to determine what effect degradation of the materials will have on sample results. Knowledge of the length of time the samples can be held will help in planning the analysis schedule for the samples in the field. Due to time constraints, holding time studies for the PIGS and the Super PIGS could not be performed prior to commencement of the project. Although holding time studies had been conducted on the PIGS previously, replacement of the tubing and new Tedlar® bags necessitated completion of new studies to determine the length of time that the samples could be held before degradation of the data results. These studies were performed upon return from the project and showed that holding the samples for 3-4 days, as was sometimes needed in the field, did not have any detrimental effect on sample results.

## **Super PIGS QC Issues**

During field deployment, some of the results from the Super PIGS field control QC samplers were sub-standard compared with those collected using the PIGS. On the other hand, Super PIGS field sample results compared well to their neighboring PIGS samplers. Adding to the confusion was the observation that the results from duplicate or collocated Super PIGS samplers were very similar and exhibited none of the problems observed in the field blanks and field controls. The discrepancies surfaced immediately after the first IOP and the samplers were examined for mechanical problems. Operational tests were conducted periodically as time permitted throughout the rest of the study. Randy Johnson, the FRD engineer who designed the samplers, flew to Oklahoma City for several days to help with this process. Several defects were found and repaired, but these failed to completely solve the problem with the QC samples. Time constraints imposed by the Super PIGS construction schedule did not permit any pre-deployment sampler performance studies to be conducted. Additional time constraints imposed by the schedule of IOPs during the field study prevented more intensive testing required to fully identify the problems. To meet the schedule of the field study, there was no choice but to continue using the Super PIGS without complete confidence that all of the sampling problems were resolved.

A comparison of the blank, control, and duplicate results for the laboratory, PIGS, and Super PIGS are seen in Table A-15. As can be seen, all results increased slightly when the added variability of the sampling method is included. However, the large increase in the Super PIGS blank and control results along with only a slight increase in duplicate results make it apparent that more than just normal random variations occurred with the QC samplers.

Table A-15. Comparison of blanks, controls and duplicates.

Source Type	Blanks	Control	Duplicates
	Average Concentration (pptv)	Average RSD (%)	Average RSD (%)
Laboratory	0.21	5	2
PIGS	1.1	7	8
Super PIGS	31	14	9

As a result of the problems observed with the Super PIGS QC samplers, a sampler testing program was conducted at the FRD office in the months following the JU03 project. The testing entailed operating the samplers using the same control program as was used in the field. Several PIGS and Super PIGS were placed inside a large, insulated test box. A high concentration standard was injected into the test box containing the PIGS and Super PIGS samplers. The injection was timed to coincide with the sampling of the third bag with the final concentration calculated to mimic concentrations most seen in the field. Fourteen tests were conducted with the Super PIGS in the test box. These trials tested the QC sampler handling methods, the effect of elevated temperatures on the samplers, the effect of humidity on the samplers, the effect of sample holding times, the effect of high concentrations of SF<sub>6</sub> on field blanks, using direct comparisons of PIGS and Super PIGS in controlled concentration of SF<sub>6</sub>.

During the testing, two of the Super PIGS samplers used for QC purposes during the field experiment were found to be assembled incorrectly. The inlet tubing to the sample pump inside the sampler was not connected. This was likely the result of a manufacturing process defect. Thus, these two samplers really did not sample from the source bags as intended. When the analyzed sample data from these two samplers were removed from the QC database, the overall results improved greatly and showed reasonable values of MLOD and MLOQ. However, MLOD and MLOQ were still much higher than those calculated for the PIGS. Following the discovery of the missing tubing in the two QC samplers, all remaining Super PIGS samplers were also inspected and none were found to have the manufacturing defect.

Although the missing inlet tubing was the major problem identified to have caused the poor Super PIGS field QC performance in two samplers, other minor problems were discovered with the Super PIGS during post deployment test box testing. For example, it was found that all Super PIGS samples tracked very well and were extremely comparable to their PIGS counterparts, but there was leakage into bags from the outside air when the cartridge was connected to the sampler. Test box studies showed that blanks operated in an atmosphere where SF<sub>6</sub> was present had higher levels of SF<sub>6</sub> in the sample bags. Consequently, the field blanks co-

located with samplers showed blanks tracking the concentrations of samplers in some cases and verified the test box results (Fig. A-19). The field controls also showed high concentration levels in the low concentration bags and exhibited variability especially at the lower concentrations as seen in Fig. A-20.

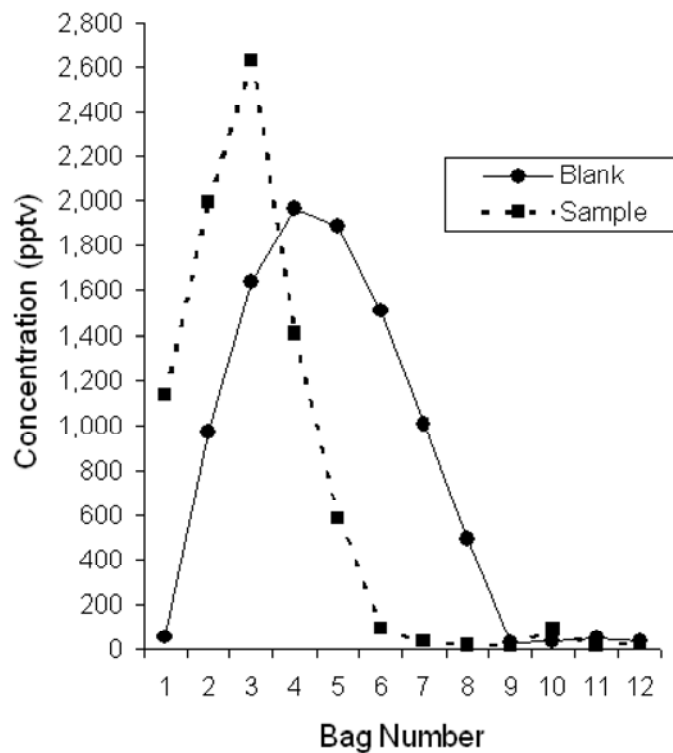


Figure A-19. Example of a Super PIGS field blank tracking the collocated sampler.

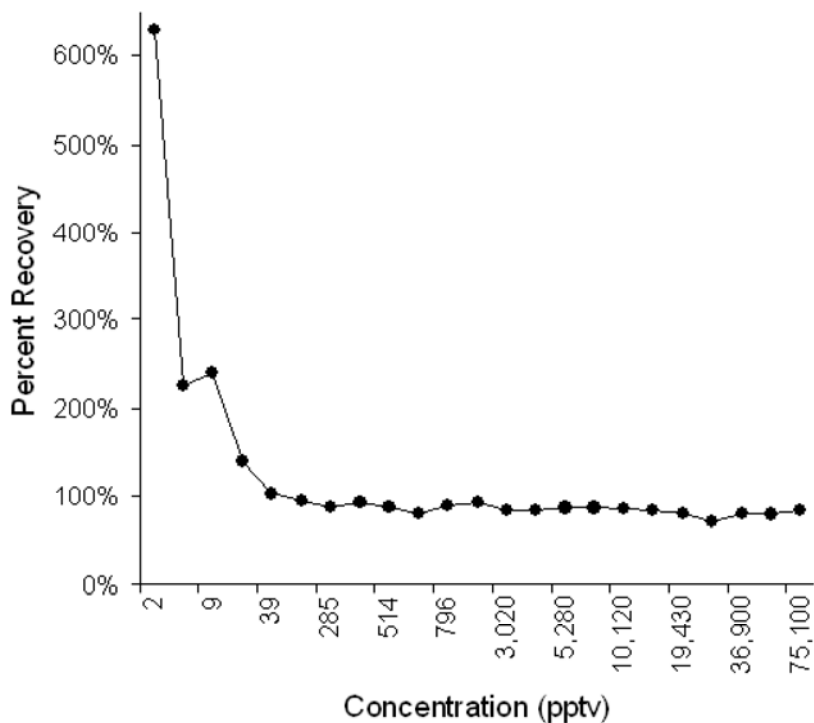


Figure A-20. Percent recoveries of Super PIGS field controls.

The test box and field results clearly indicated that the Super PIGS QC samplers were mixing air from the environment with the air being drawn into the sampler inlet tube as the sample bags were being filled. For a QC sampler which is pulling in air from source bags filled with known concentrations of  $\text{SF}_6$ , the environmental air usually contains a much different concentration of  $\text{SF}_6$  than the intended sample in the source bag. Thus, mixing the two together significantly changes the results. For a regular Super PIGS that is filling the bags with environmental air, mixing additional environmental air with the incoming air does not change the concentration of the sample at all. Obviously, the Super PIGS QC samplers did not represent actual sampler performance and could not be used to subsequently calculate the MLOD and MLOQ. The MLOD and MLOQ were therefore calculated based on the results of the first two bags in each sampler used in the test box sampler tests at the FRD office. These should have had concentrations of 0 pptv. However, due to the leakage and diffusion issues, these bags always contained some concentration of  $\text{SF}_6$  with an average concentration of 12 pptv. A total of 97 data points were used to calculate the final MLOD as 33 pptv and the final MLOQ as 111 pptv. These results also compared favorably to the results in Table A-13 where the 38.7 pptv standard exhibited an RSD of 24%, an MLOD of 29 pptv, and an MLOQ of 96 pptv.

None of these effects appear to be large enough to significantly reduce the usability of the JU03 field data. Still, the discrepancies were quantified so that the reported MLOD and

MLOQ values for the Super PIGS accurately reflected the true quality of the field data collected during JU03.

## Summary

All calculations for the ILOD and ILOQ both before and during the field deployment, (shown in Table A-16) were comparable. The calculated ILOD for each determination was 1 pptv while the ILOQ ranged slightly from 2 to 4 pptv using low level standards and up to 5 pptv using laboratory blanks. The MLOD and the MLOQ estimated prior to the project and the final calculated results after the project for the PIGS and Super PIGS are shown in Table A-17. The estimated PIGS MLOD and MLOQ results calculated prior to the project were nearly identical to the final project calculation indicating good method performance (Table A-18). Super PIGS MLOD and MLOQ results were discussed in a previous section.

Table A-16. Instrument limit of detection (ILOD) and instrument limit of quantitation (ILOQ) calculations.

	ILOD (pptv)	ILOQ (pptv)
Pre transport (low level standard)	1	3
Pre project (low level standard)	1	2
Project laboratory (blanks)	1	5
Project laboratory (low level standard)	1	4

Table A-17. Method limit of detection (MLOD) and method limit of quantitation (MLOQ) calculations.

	MLOD (pptv)	MLOQ (pptv)
Pre-project estimation PIGS (field controls)	1	5
Post- project PIGS (field controls)	1	4
Post-project Super PIGS (laboratory studies)	33	111
Post-project Super PIGS (field controls)	29	96

Table A-18. Target QC limits and QC results for the ATGAS instrument, PIGS and Super PIGS samplers.

	Target Limits	Average Instrument Results	Average PIGS Results	Average Super PIGS Results
Between Instrument Precision (background checks)	<10% RSD	8% RSD $\pm$ 4%		
Instrument Bias (lab blanks)	< 1 pptv	0.21 pptv $\pm$ 0.49 pptv		
Instrument Precision (lab duplicates)	<5% RPD	2% RPD $\pm$ 2%		
Instrument Accuracy and Precision (Lab control)	<10% RSD	5% RSD $\pm$ 3%		
Method Bias (field blanks)	<5 pptv		1.1 pptv $\pm$ 3 pptv	31 pptv $\pm$ 46 pptv
Method Precision (field duplicates)	<15% RPD		8% RPD $\pm$ 11%	10% RPD $\pm$ 9%

A summary of the project statistics are shown in Table A-19. The average percentage of good data greater than the MLOQ was 71%, the percentage of good data less than the MLOD was 16%, and the percentage of good data greater than the MLOD but less than the MLOQ was 5.3%. The percentage of good data, that data with no known analytical or field sampling problems, is the sum of the percentage of good data greater than the MLOQ, data less than the MLOD and data greater than the MLOD but less than the MLOQ. This average percentage was 92%. The percentage of data with analysis QC problems was 0.23%, the percentage of data with field problems was 7.4%, and the percentage of data with analysis problems was 0.39%. The percentage of data with problems includes data with analysis QC problems, field problems, and analysis problems were 8% for the project.



Table A-19. Detailed summary statistics for PIGS and Super PIGS final data.

IOP	Good Data							
	Good Data > MLOQ (%)	Good Data < MLOD (%)	> MLOD but < MLOQ (%)	Good Data (%)	Analysis/ QC Problems (%)	Field Problems (%)	Analysis Problems (%)	Data Problems (%)
1	54	12	4.3	70	0.06	29	0.06	30
2	69	17	4.0	90	2	7.7	0.06	10
3	72	13	4.8	90	0	10	0.17	10
4	71	16	5.0	92	0	6.3	1	8
5	69	19	4.4	92	0.11	7.3	0	8
6	76	14	5.4	95	0	4.1	0.67	5
7	71	22	4.6	97	0.06	2.6	0.28	3
8	77	10	9.9	97	0	3.3	0.06	3
9	76	15	6.9	98	0.11	1.7	0.72	2
10	73	20	3.7	97	0	2.2	0.89	3
Ave	71	16	5.3	92	0.23	7.4	0.39	8

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## APPENDIX B. TGA QA/QC

Continuous SF<sub>6</sub> concentration measurements were made by ten van mounted, ARLFRD-built mobile tracer gas analyzers (TGA). The analyzer is based on a modified TGA-4000 (Sciencetech Inc. of Pullman, Washington) which has been integrated with a controlling computer, a GPS system, a dilution system, an automated cleaning system and a computer controlled calibration system. These analyzers measure atmospheric SF<sub>6</sub> concentrations with a response time of just under one second (Benner and Lamb, 1985).

The TGA tags each concentration measurement with sampling time and location from the GPS system. These were collected by the computer at the rate of 2 Hz, stored for later post-processing and simultaneously displayed for operator interpretation and control. Using this display, operators performed real-time monitoring of plume concentrations, and used software controls to mark the beginning and ending of the plume trace. The operator then communicated this information to personnel directing the test.

### Calibration

Calibration of the TGA was accomplished by allowing it to sample calibration mixtures with known concentrations of SF<sub>6</sub> and recording the output corresponding to each concentration. SF<sub>6</sub> concentrations of sample air are then determined by linearly interpolating between the calibration concentrations whose output values bracket the sample output. The calibration functions are all controlled by the integrated computer when initiated by the operator.

The SF<sub>6</sub> calibration standards were stored in Tedlar® bags identical to those used in the PIGS, which are described in Appendix A. The bags were connected to the TGA sample stream by a series of electrically operated three-way valves. The computer switched the sample stream from outside air to a given calibration mixture by activating the corresponding valve. Eight calibration standards were used ranging in concentration from pure air (0 pptv) to over 10,000 pptv SF<sub>6</sub>. The calibration standards were manufactured by Scott-Marrin, Inc. of Riverside CA and had a manufacturer listed concentration uncertainty of  $\pm 5\%$  and were NIST traceable. A full set of eight calibrations was run on each analyzer both before the release began and after sampling was completed. Operators also ran calibration verification sets during the tests as needed. Usually, these were complete sets, but in some cases lack of time forced these to be partial sets.

Two quantities that are useful for evaluating instrument performance are the method limit of detection (MLOD) and the method limit of quantitation (MLOQ). The MLOD is the lowest concentration level that can be determined to be statistically different from a blank or a 0 pptv SF<sub>6</sub> sample (Keith et. al., 1983). The MLOQ is typically defined to be the level at which the concentration may be determined with an accuracy of  $\pm 30\%$ . The recommended values for these are  $3\sigma$  for MLOD and  $10\sigma$  for MLOQ, where  $\sigma$  is the standard deviation for measurements made on blanks or low standards (Keith et. al., 1983). The MLOD differs from the instrument limit of

detection (ILOD) in that it includes all variability introduced by the sampling method. MLOD/MLOQ are used in this report because they are based on the variability observed during sampling operations.

Since the TGA is measuring continuously, every point may be viewed as a measurement of a blank so long as it is sampling clean air. The standard deviation of the baseline signal then defines  $\sigma$ .

A second method of determining the MLOD and MLOQ is to calculate the standard deviation of the instrument's response to a calibration gas. This deviation may then be used as  $\sigma$  in the MLOD/MLOQ calculations.

Both methods were used for the real-time analyzers. After data collection for an IOP was completed, the data analyst followed a written procedure and calculated each instrument's MLOD and MLOQ from the baseline noise and from the variation of instrument response to each calibration gas used during the testing. The procedure called for comparing the MLOD from the lowest concentration calibration with a signal to noise ratio between 3 and 10 with the MLOD from the baseline calculation. The larger of these two values was generally selected as the instrument MLOD for that IOP. However, other factors such as number of calibrations available for the calibration variation calculation, consistency of the calculated numbers from different calibration concentrations and availability of good calibrations in the MLOD range were also considered. In some cases, adjustments were made or another value selected. Every effort was made to ensure that the selected MLOD accurately represented instrument performance or registered an error by being higher than necessary. Setting the MLOD too low allows some data to be flagged as valid when it should not be and is unacceptable by FRD standards.

The MLOD/MLOQs for each instrument and each IOP are listed in Table 6. The MLODs for this project were noticeably higher than the 10 pptv specification for the instrument. This was largely because the analyzers were adjusted to cover 0 to 10,000 pptv which was a much larger range than typically used. Some low-end sensitivity was sacrificed thereby making the MLODs higher. There were also some cases of exceptionally high MLODs. These were due to instrument problems. Often, operational problems first affect low-end sensitivity of the instrument which causes the calculated MLOD to be much higher. Generally speaking, an MLOD of 150 pptv or greater indicates that the analyzer was experiencing difficulties during that IOP.

## **Accuracy Verification Tests**

To determine the overall accuracy and precision of the real-time analyzer measurements, calibrated analyzers were allowed to sample gas mixtures with known SF<sub>6</sub> concentration. The percent recovery (i.e., 100% multiplied by the measured concentration divided by the actual concentration) for each test was recorded. Ninety-seven tests were made and are summarized in Table B-1. These tests were made over a period of two months during the year 2000 on multiple

analyzers. Most of these tests were made in the laboratory, but some were made with the analyzers mounted in minivans. The test conditions were designed to mimic the actual field operations as closely as possible. The calibration procedures were exactly the same as those used in the field and the times between calibration and test varied from a few minutes to several hours, just as they do in actual operations. Measurements were made both with and without the dilution system operating. The sampled mixtures were not the same as the calibration mixtures. A second set of tests was conducted during the summer of 2004. The measurements were made the same way except all instruments were in the laboratory and no dilution system was used.

Table B-1. Percent recovery of SF<sub>6</sub> concentrations by real-time analyzers sampling known mixtures as unknowns.

SF <sub>6</sub> Concentration (pptv)	Average Recovery (%)	Standard Deviation (%)	Number Of Trials
<u>year 2000</u>			
514	98	8.7	20
2065	110	4.1	17
2087	105	6.7	15
2065 and 2087 combined	107	5.9	32
4095	101	8.7	45
<u>year 2004</u>			
504	105	5.0	54
1593	105	7.3	46
8300	106	2.8	73

Since both the calibration mixtures and the sampled mixtures were listed by the manufacturer as  $\pm 5\%$ , it is reasonable to expect accuracy variations up to  $\pm 10\%$ . All of the average recovery values are within this range. The standard deviations for all of the groups reported were less than 8.7%, which should be a reasonable estimate of instrument precision.

## Quality Control

The quality control (QC) procedure for the real-time analyzers included 12 steps that ensure the real-time analyzer data is as reliable as possible. During field operations, operators were required to follow written checklists that included all QC steps. A written procedure was also followed during post-test processing. The QC steps are:

1. Pre-project preparation.
2. Monitoring of key operational parameters during the study.
3. Daily instrument calibrations.
4. Real-time monitoring of QC parameters during testing.
5. Operator logging of all measurements.
6. Post-test screening of calibrations.
7. Post-test determination of MLOD/MLOQ.

8. Post-test screening of data.
9. Verification of all calculations and data by a second analyst.
10. Identification of data problems and setting of QC flags.
11. Identification of latitude/longitude for stationary analyzers.
12. Review of final data files.

1. Pre-project preparation.

Before the experiment, each analyzer was thoroughly tested to be sure that all systems were in good working order. Any necessary repairs were made. The analyzers were then conditioned by running them for several weeks, which was required for optimum performance. During this period, each one was adjusted to provide the best response to the range of concentrations expected during the study.

Operator training occurred several weeks before field deployment. Dedicated binders were prepared for each analyzer that contained all procedures, phone numbers, safety and Nuclear Regulatory Commission (NRC) requirements. All operators were trained on the operation of the TGAs, including troubleshooting and data handling. They were each required to complete at least one day of hands-on training plus attend one training class at the FRD office in Idaho Falls. In Oklahoma City, operators were expected to run the analyzers for several days prior to the first IOP as part of the required training.

2. Monitoring of key operational parameters.

Analyzer operators filled out a Settings Record as they ran the real-time analyzers (Fig. B-1). They recorded 17 instrument parameters at key times during the operation. These included gas pressures, flow rates, temperatures, electrometer settings, etc. The Settings Record, constructed in table form, contained several days of entries. These sheets were reviewed for any large changes in the parameters that could indicate a problem with the analyzer. Any changes were investigated and the required maintenance was performed. Each TGA operator also maintained a dedicated logbook during the experiment and recorded the measured SF<sub>6</sub>, location of the analyzer, and any problems with the analyzer. Operators ran their analyzers between IOPs to ensure optimum instrument performance.

TEL number: 3

[illegible]

Figure B-1. A TGA-4000 settings record.

### 3. Daily instrument calibrations.

All analyzers were calibrated at the beginning and end of each measurement period and between releases. Typically, there was ample time to run a complete set of calibrations between releases, but in a few instances, between release calibrations were limited to a few selected bags because of time constraints. This allowed a calibration curve to be generated using calibrations that bracketed the testing period. It also provided a check on analyzer sensitivity drift.

### 4. Real-time monitoring of QC parameters during testing.

Calibration verifications were performed throughout the IOP to monitor instrument drift. After the first set of calibrations was completed, the calibration curve was checked every time additional calibrations were performed. This was done by treating the new calibrations as unknowns and calculating their concentration based on the calibration curve generated from the first set of calibrations. Due to the nature of the instrument and the need for almost instantaneous measurements, when the calculated concentrations were more than 20% different than the actual concentrations, the operator first ensured that a complete set of calibrations was run then immediately continued with sampling. Appropriate calibrations for each measurement period were selected later during the post-test screening of calibrations. The analyzer also calculated and displayed an MLOD from the baseline noise. Operators were required to display and record this value after every set of calibrations. If large variations were observed, the cause was investigated and corrected.

### 5. Operator logging of all measurements.

To help ensure that noise spikes, analyzer adjustments, and extraneous features were not reported as valid measurements, operators were required to mark all SF<sub>6</sub> peaks on the computer using the software marking function. They also recorded details of each peak, e.g., time, concentration, latitude and longitude, together with other pertinent observations in a notebook. Any signals that could be mistaken for SF<sub>6</sub> were also recorded in the notebooks.

### 6. Post-test screening of calibrations.

After an IOP was completed, the TGA operators delivered a copy of their logbook entries as well as a disk containing all data for the IOP to the data analyst. The entire data file including the calibrations from each analyzer was then carefully reviewed by the data analyst on a laptop. To ensure that concentration calculations were as accurate as possible, any calibration points with problems such as significant baseline drift, contamination, accidental instrument adjustments, etc., were identified and eliminated. The recovery for each calibration was calculated and examined. This was done by treating the calibration as an unknown and calculating the concentration using the calibration curve. The recovery was defined as the calculated concentration divided by the actual concentration converted to a percent. The recoveries for all calibrations above the MLOQ were expected to be between 80% and 120%. If they were not, they were re-examined for problems and the logbook entries were reviewed. In



cases where the calibrations showed evidence of significant sensitivity drift during the test, the calibrations could be divided into two groups, typically an “early” group and a “late” group. Each group was used to calculate concentrations for peaks within the time frame they encompassed. If the calibrations still failed to meet the recovery limits, all data in the concentration ranges that were out of limits were flagged as estimates.

#### 7. Post-test determination of MLOD/MLOQ.

The MLOD and MLOQ were determined for each analyzer for each day’s operation. These values define the lower limit of valid measurements. Concentrations below these levels are flagged with appropriate QC flags so users of the data are aware of its limitations. The MLOD and MLOQ were calculated by two methods: calculations based on the baseline noise and calculations based on the variation in response to calibrations of the same concentration. The data analyst then compared these two calculations and selected the instrument MLOD/MLOQ following the guidelines in a written FRD procedure. Typically, the value calculated from the lowest concentration calibration with a signal to noise ratio in the 3 to 10 range was compared to the value calculated from the baseline noise and the larger of the two selected. However, other factors such as number of calibrations available, instrument problems, behavior on other calibration levels, etc. were considered in the selection.

#### 8. Post-test screening of data.

After a test, the data analyst reviewed the marked peaks and compared them with the notebook to ensure that marked peaks were above the MLOD and that they were not false peaks caused by extraneous factors such as altitude changes, bumps, interfering chemicals in the air, etc. The peaks were checked for correct identification of instrument baseline on leading and trailing sides of each peak. The entire data set was examined for possible peaks that may have been missed. Once necessary corrections were made, the peaks were converted to concentrations, plotted and reviewed.

#### 9. Verification of all calculations and data by a second analyst.

During steps 5, 6, and 7, the data analyst generated a QC sheet (Figs. B-2 and B-3), plots of the calibrations curves, results from the MLOD/MLOQ calculations, and plots of all peaks. The QC sheet was annotated with notes explaining problems that were identified, corrective actions taken, and justification for all data processing decisions that were made by the analyst. A second person familiar with the data processing procedures reviewed and verified this entire data package. If any errors were discovered or if the verifier did not agree with the decisions made, the problems were discussed with the data analyst and a resolution agreed on and implemented.

Figure B-2. Page 1 of a TGA-4000 QC sheet.

27	291.4	321.2	110.2	299.7	102.9
28	796.0	867.8	109.0	817.2	102.7
29	1560.0	1747.2	112.0	1616.8	103.6
30	5280.0	5941.0	112.5	5405.5	102.4
31	10120.0	10375.6	102.5	10131.6	100.1
32	0.0	-0.0		0.0	
33	38.7	45.6	117.9	41.8	108.1
34	82.9	98.1	118.4	90.9	109.6
35	291.4	324.4	111.3	302.8	103.9
36	796.0	868.4	109.1	817.8	102.7
37	1560.0	1751.8	112.3	1621.4	103.9
38	5280.0	6036.8	114.3	5507.6	104.3
39	10120.0	10447.6	103.2	10208.4	100.9

Calibration curve errors (for all calibrations averaged):

	RMS error	percent of range center
all cals	77.26 ppt	1.5%
< 544	6.13 ppt	2.3%
> 544	112.1 ppt	2.1%

comments/corrective actions:

*all < 26 should be marked as estimates.  
corrected portion should be added to all.*

Figure B-3. Page 2 of a TGA-4000 QC sheet.

## 10. Identification of data problems and setting of QC flags.

The operator logbooks and concentration plots were carefully reviewed for any anomalies that required the QC flags to be set. The review focused specifically on instrument over range, dilution system usage that was not detected, starting or stopping of the dilution system during a peak, and van movements during a peak. Any other problems were also noted. From this review, a list of flags that needed to be set was generated and entered into the computer. These were combined with the data during the generation of final data files so that users would be aware of any questionable data. The flags values are defined as:

- 0 Good data.
- 1 Concentration less than MLOQ but greater than MLOD; treat as an estimate. (See note on dilution system below.)
- 2 Concentration less than MLOD; not statistically different than 0; treat as 0 or null value. (See note on dilution system below.)
- 3 Concentration is greater than 115% of the highest calibration; treat as an estimate.
- 4 Instrument over ranged its output; concentration is unusable.
- 5 Null values. Analyzer was in position and operating correctly and no SF<sub>6</sub> was found. Treating these concentrations as 0 is appropriate.
- 6 Analyzer was not in use. No data available. Do NOT treat these as 0. Flag 6 indicates a human decision to not operate. For example: leave and do calibrations, move to a new place, we don't need you this test, etc.
- 7 Analyzer was broken. No data available. Do NOT treat these as 0 values. Concentrations are unknown.
- 8 Analyzer was operating, but was experiencing problems. Treat all concentrations as estimates.
- 9 Concentrations are unusable because of instrument problems, but are included for qualitative indications only. In this case, the instrument was operating and collected data, but problems discovered later made it impossible to have any confidence at all in the concentrations. Since the data was available it was included and may be useful for some purposes such as determining arrival times, etc. Calculations should not be done with these concentrations.
- 10 Concentrations unusable because of external problems. For example: fugitive sources, noise caused by trucks passing, etc.
- 11 Concentrations are estimates because of external problems. This flag indicates that something external to the analyzer had a small effect on the data, making it less certain but not totally unreliable. For example: a passing truck creating a small amount of noise during a high concentration peak.

### Comments on QC flags

In most cases, concentrations flagged as unusable were set to -999 in the data files. In some cases, data was included with a flag that indicates missing or unusable data, the most common example being instrument over range, (flag 4). In these cases, the data were there for qualitative indications only and should not be used for calculations.

In a few cases, the MLOD/MLOQ for an analyzer was calculated to be an abnormally high value. The indication was that the instrument was not measuring low concentrations correctly. Flags 8 and 9 were then used instead of 1 and 2 to indicate less than MLOD (flag 9) and less than MLOQ (flag 8) since these more accurately reflect what was happening.

Note on dilution system use: When the dilution system was used, the incoming sample stream was mixed in equal parts with ultra pure air. This reduced the concentration to half the actual concentration in the air. The concentrations measured by the analyzer are doubled before reporting to reflect the actual air concentration. However, the MLOD and MLOQ levels reflect instrument operation and must be based on instrument levels, which are 50% of reported concentrations. While the dilution system was in use, the levels at which flags 1 and 2 are set will be twice the reported MLOD/MLOQ values (i.e., 1 indicates a data value less than  $2 \times \text{MLOQ}$ ; 2 indicates a data value less than  $2 \times \text{MLOD}$ ).

#### 11. Identification of latitude/longitude for stationary analyzers.

Each analyzer was equipped with a GPS unit and the attached computer automatically tagged each measurement with a time and position. However, close to the tall buildings in the central business district, the GPS signals were not reliable. For stationary vans, the positions included in the final data files were determined as follows:

For every  $\text{SF}_6$  peak marked by the operator at a given location, the median latitude and longitude from the “good” GPS positions in the file was determined. “Good” GPS positions were defined to be all those with horizontal dilution of precision (HDOP) less than or equal to 3.0 and the number of satellites in use greater than or equal to 4.

The operator notebooks were then carefully reviewed to determine which peaks were measured at the same location. Once a group of peaks was identified with a particular location, the median values of latitude and longitude were plotted on a map. If the medians appeared to make a tight group at the appropriate location, it was assumed that the GPS worked reasonably well and the reported position was the average of these medians. If the medians exhibited significant scatter (more than a few car lengths), appeared to be in the wrong location or there were too few to determine if the grouping was good, it was assumed that the GPS did not work well in that location and the GPS locations were not used. In these cases, the positions were read off of high-resolution satellite photos available from Terraserver.com. These photos had resolutions of about 6 inches per pixel and readily showed sidewalks, crosswalks, parking spaces, vehicles on the roads, etc. The positions read off of Terraserver.com did not include altitudes, so the altitude was reported as -999 in the data files while those taken from GPS positions have an altitude reported in meters. If the altitude is -999, it should be assumed that the analyzer van was at street level. (All vans were at street level except when analyzer 7 was parked on the top of the Main Street Parking Garage. A GPS position was reported in this case.)

When the analyzer vans were mobile, the GPS positions read by the van were reported in the data files. Some caution is advised when using the data since they will contain some spikes and erroneous readings. There are also a few instances where the GPS lost its position and took

several minutes to regain it. These are most easily detected by looking at the HDOP (horizontal dilution of precision) and the number of satellites the GPS used. Both of these values are included in the data files. HDOP decreases as the reliability of the position value improves. Typically, reliable readings will have HDOP values of 4 or less. Higher HDOP values indicate that the position is questionable and anything with an HDOP over 10 is generally very bad. The reliability of the position values also improve as the number of satellites increases. At least 4 satellites are required for a good GPS position and more are better. Any position with less than 4 satellites should be regarded as unreliable. These rules of thumb apply only to the mobile vans. Stationary vans that have averaged GPS positions or positions read off of Terraserver.com have HDOP=0 and number of satellites= -1 in the data files.

Van 5 was always mobile. Other vans were inadvertently mobile for one peak measurement on three occasions: van 3 in IOP 4, van 2 in IOP 5, and van 8 in IOP 5. These occurred when the analyzer unexpectedly encountered an SF<sub>6</sub> plume while driving to or leaving a stationary position.

## 12. Review of final data files.

After the final data files were created, they were carefully reviewed for any problems. Each of the 390 data files were read into Excel and each column plotted versus time. The concentrations were compared to the earlier peak plots to verify that all the peaks were included at the correct time. The position variables (longitude, latitude, altitude, HDOP, number of satellites) were plotted and reviewed to verify that van movements were accurately reflected in the data files. Longitudes and latitudes were checked to verify that the correct ones were being included. The QC flags were checked visually by plotting and by computer programs that listed start and stop times for each flag and the range of concentrations flagged with a 1 or 2. These lists were then compared with the lists generated earlier in the QC process. Any problems were fixed and the files regenerated using the updated information. The process was repeated until no discrepancies were found.

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## **APPENDIX C. LIST OF ACRONYMS**

ACS – American Chemical Society  
AGL -- above ground level  
ARO – Army Research Office  
ARL – Air Resources Laboratory  
ARLFRD – Air Resources Laboratory Field Research Division  
ASCII – American standard code for information interchange  
ASU – Arizona State University  
ATDD – Atmospheric Turbulence and Dispersion Division  
ATGAS – Automated Tracer Gas Analysis System  
CBD – central business district  
CBRD – Chemical, Biological and Radiological Defense  
CCV – continuing ATGAS calibration verification  
CD – compact disk  
CDT – Central Daylight Time  
CFR – Code of Federal Regulations  
DHS – Department of Homeland Security  
DOT – Department of Transportation  
DPG – Dugway Proving Ground  
DRDC – Defence Research and Development Canada  
DSTL – Defence Science and Technology Laboratory  
DTRA – Defense Threat Reduction Agency  
ECD – electron capture detector  
EPA – Environmental Protection Agency  
FRD – Field Research Division  
GC – gas chromatograph  
GPS – global positioning system  
HDOP – horizontal dilution of precision  
ICV – initial ATGAS calibration verification  
ILOD – instrument limit of detection  
ILOQ – instrument limit of quantitation  
IOP – intensive operating period  
ISO – International Standards Organization  
IU – Indiana University  
JU03 – Joint Urban 2003 Experiment  
LLNL – Lawrence Livermore National Laboratories  
LOD – limit of detection  
LOQ – limit of quantitation  
MLOD – method limit of detection  
MLOQ – method limit of quantitation  
MSL – (above) mean sea level  
NELAC – National Environmental Laboratory Accreditation Conference

NOAA – National Oceanic and Atmospheric Administration  
NRC – Nuclear Regulatory Commission  
OCS – Oklahoma Climatological Survey  
OU – Oklahoma University  
PIGS – programmable integrating gas samplers  
pptv – parts per trillion by volume  
ppt - parts per trillion by volume  
PVC – polyvinyl chloride  
QC – quality control  
RPD – relative percent differences  
RSD – relative standard deviation  
SF<sub>6</sub> – sulfur hexafluoride  
S/N – signal to noise (ratio)  
sodar – sound direction and ranging  
SUV – sports utility vehicle  
TAF – tracer analysis facility  
TGA – trace gas analyzer  
TKE – turbulent kinetic energy  
TP9 – Technical Panel 9  
TTCP – The Technical Cooperation Program  
UHP – ultra high purity  
UTC – coordinated universal time  
UU – University of Utah  
PA – public affairs  
PNNL – Pacific Northwest National Laboratory  
WS – wind speed



## **Keywords**

ARLFRD, joint urban, sulfur hexafluoride sampling, Oklahoma City, atmospheric tracer, Field Research Division, total gas analyzer, TGA, PIGS, Super PIGS, SF<sub>6</sub> dissemination, SF<sub>6</sub> sampling, programmable integrating gas samplers, urban dispersion.

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## APPENDIX D. RELEASE QC PLOTS

Actual release rates differed only slightly from the target release rates. The release rates through the mass flow meter ranged anywhere from 4% under to 12% greater than intended. Graphs of the point source release rates for each IOP are shown in Figs. D-1 through D-10. Release rates for the point source were designed to be constant throughout each release period. The standard deviations of the actual flow rates, with a maximum value of  $0.083 \text{ g s}^{-1}$ , indicate very steady flow rates. Tracer dissemination summary, including location, release date and time, type of release (continuous or puff), target release rate, actual average release rate from the mass flow meter and the total mass of  $\text{SF}_6$  released for each period are listed in Tables 2 and 3 in the body of this report.

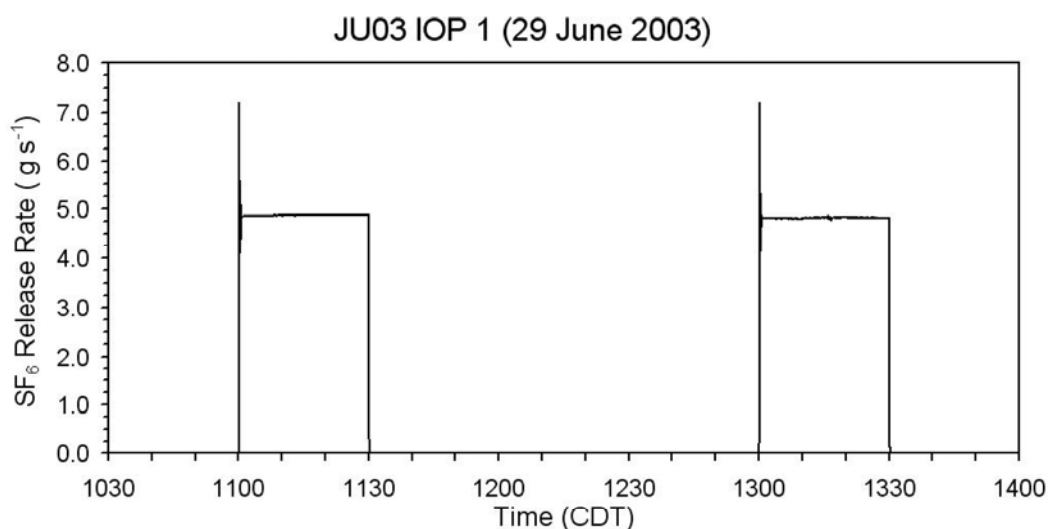


Figure D-1.  $\text{SF}_6$  release rates for two release periods of IOP 1.

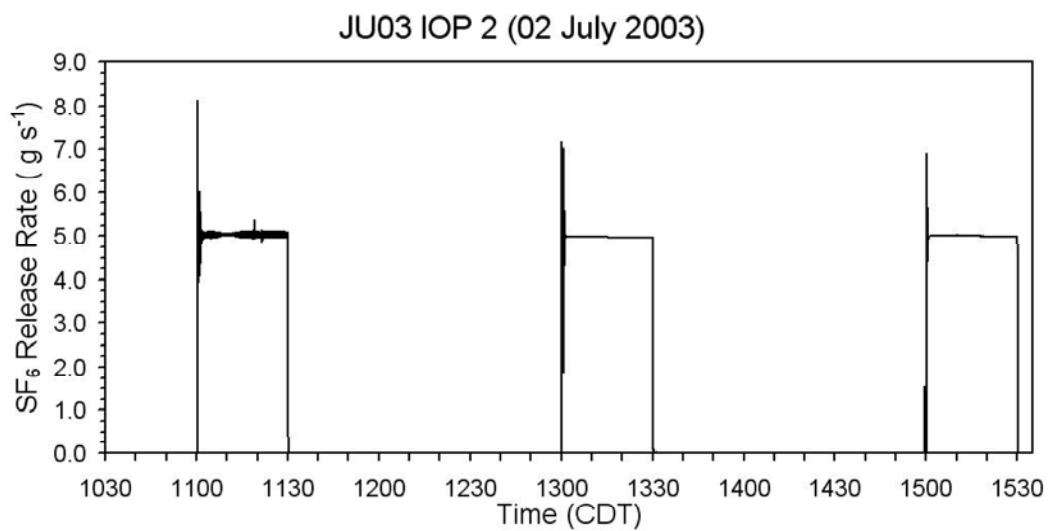


Figure D-2.  $\text{SF}_6$  release rates for three release periods of IOP 2.

Figure D-3.  $\text{SF}_6$  release rates for three release periods of IOP 3.

Figure D-4. SF<sub>6</sub> release rates for the three release periods of IOP 4.

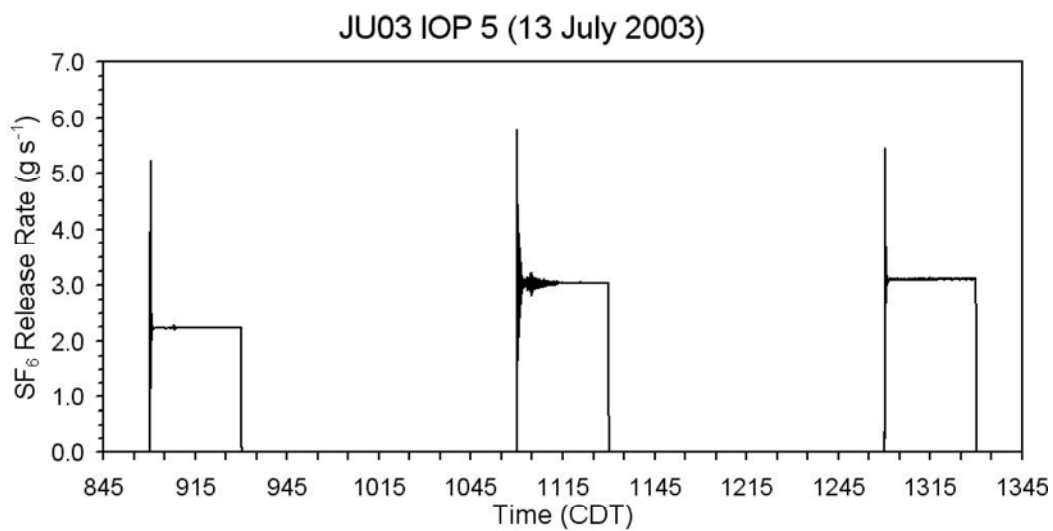


Figure D-5. SF<sub>6</sub> release rates for three release periods of IOP 5.

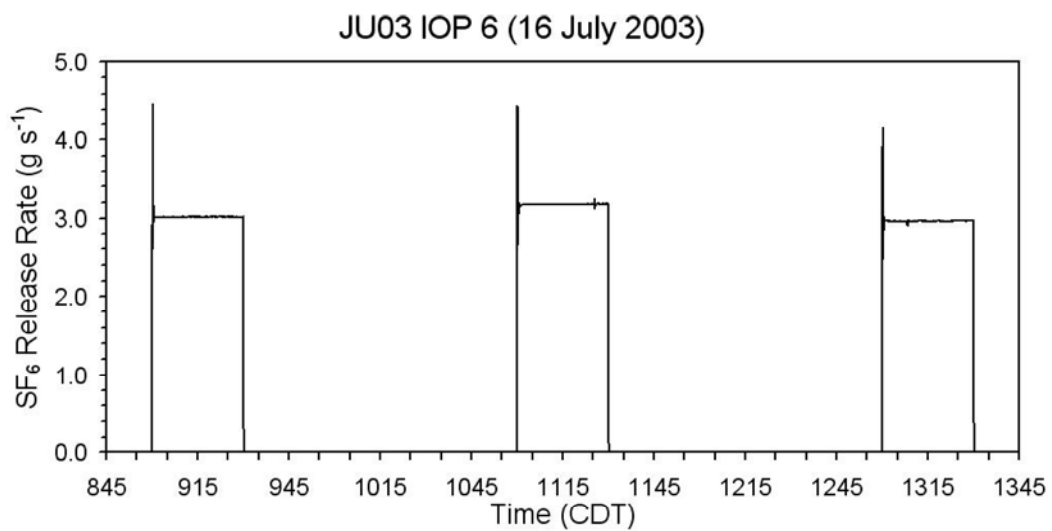


Figure D-6. SF<sub>6</sub> release rates for three release periods of IOP 6.

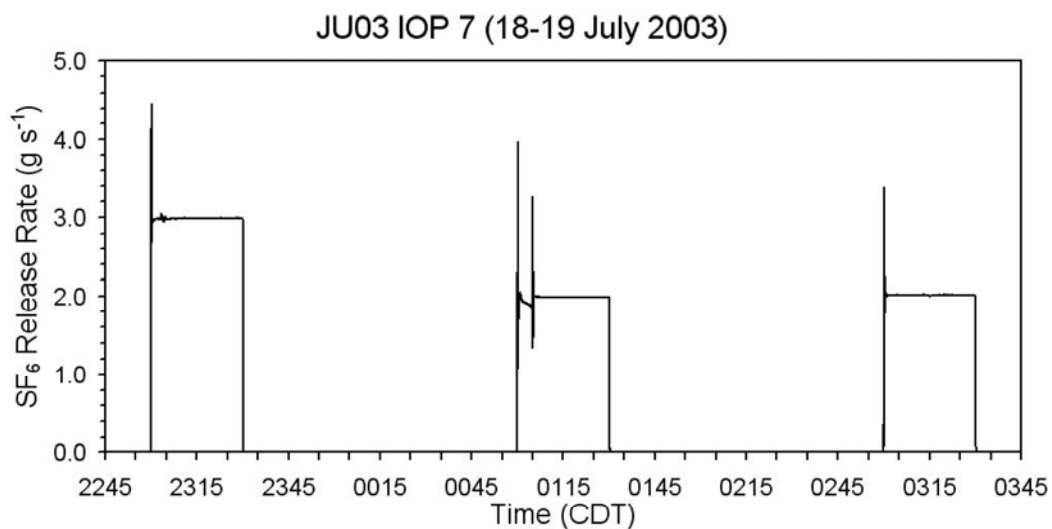


Figure D-7. SF<sub>6</sub> release rates for three release periods of IOP 7.

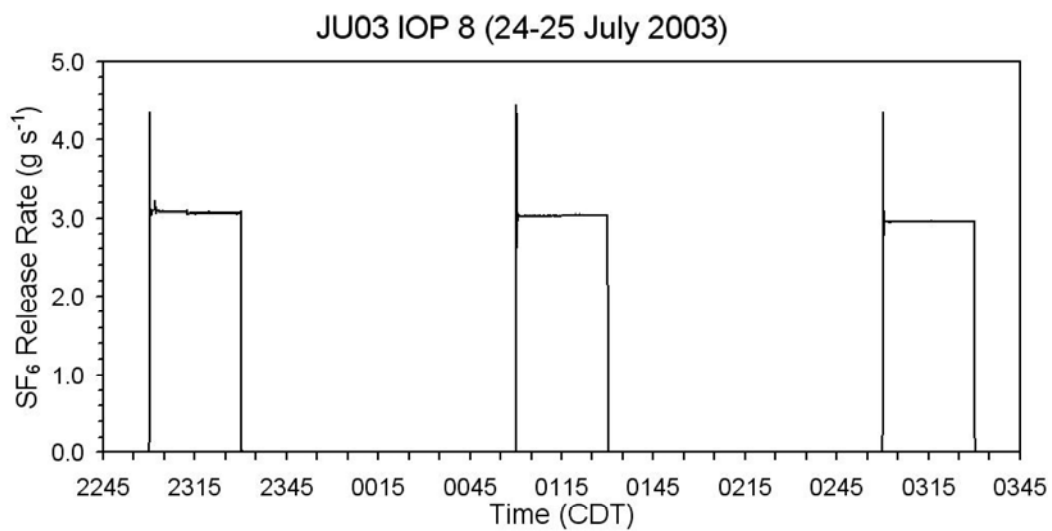


Figure D-8. SF<sub>6</sub> release rates for three release periods of IOP 8.

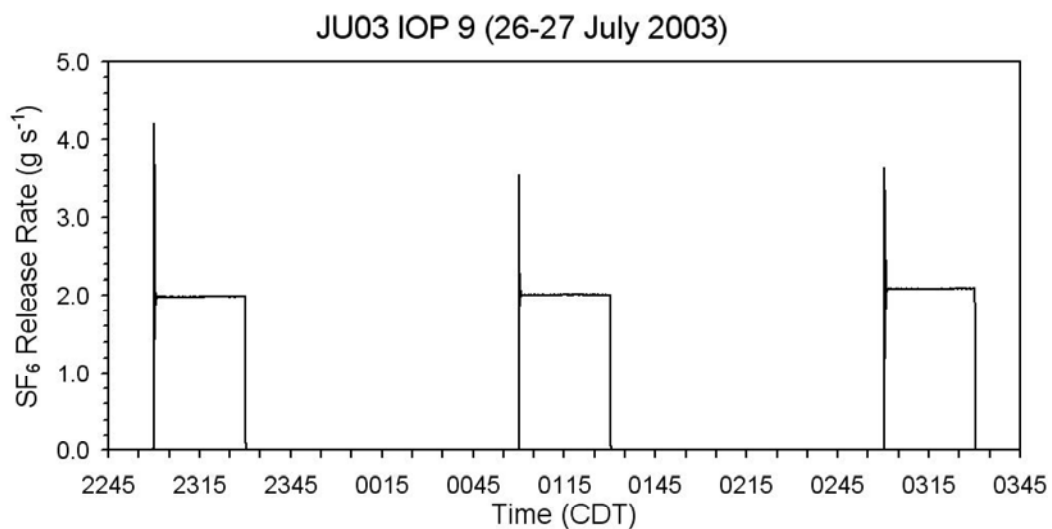


Figure D-9. SF<sub>6</sub> release rates for three release periods of IOP 9.

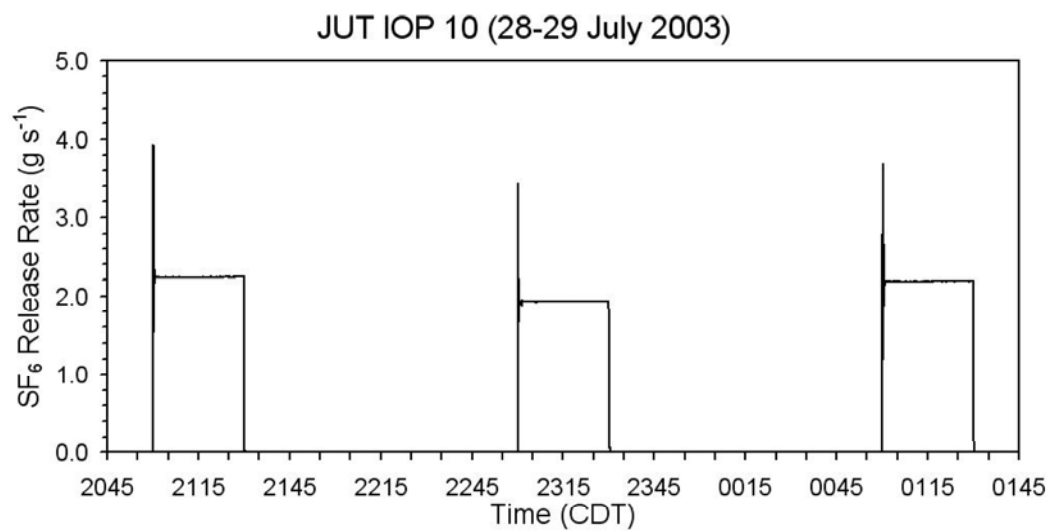


Figure D-10. SF<sub>6</sub> release rates for three release periods of IOP 10.



## **APPENDIX E: RELEASE SITE TEMPERATURE AND RELATIVE HUMIDITY PLOTS**

A Visalia HMP-45AC probe recorded temperature and relative humidity measurements at the release site during each IOP of JU03. The probe was positioned approximately 1.9 meters AGL on a tripod housing the continuous point source dissemination device and sonic anemometer (Fig. 6). Exact locations of the probe during each IOP can be found in the SF<sub>6</sub> Tracer Release System section of the report. This appendix contain time history plots of both the temperature and relative humidity during each IOP (Figs. E-1 to E-20). Temperature graphs are plotted air temperature (C°) vs. the time (CDT) while relative humidity time history graphs are plotted relative humidity (%) vs. time (CDT). Temperatures during the IOPs ranged between 24-38 (C°). The relative humidity which decreased during the day and increased at night ranged between 25-73%.

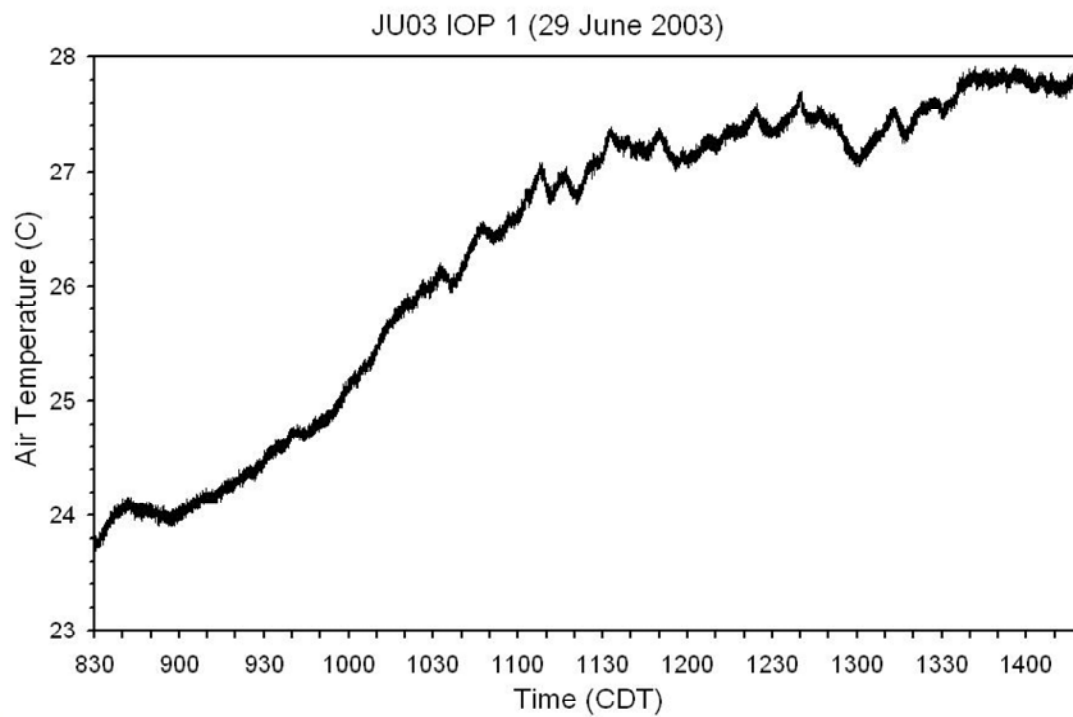


Figure E-1. Time history plot of the release site air temperature during IOP 1.

Figure E-2. Time history plot of the release site relative humidity during IOP 1.

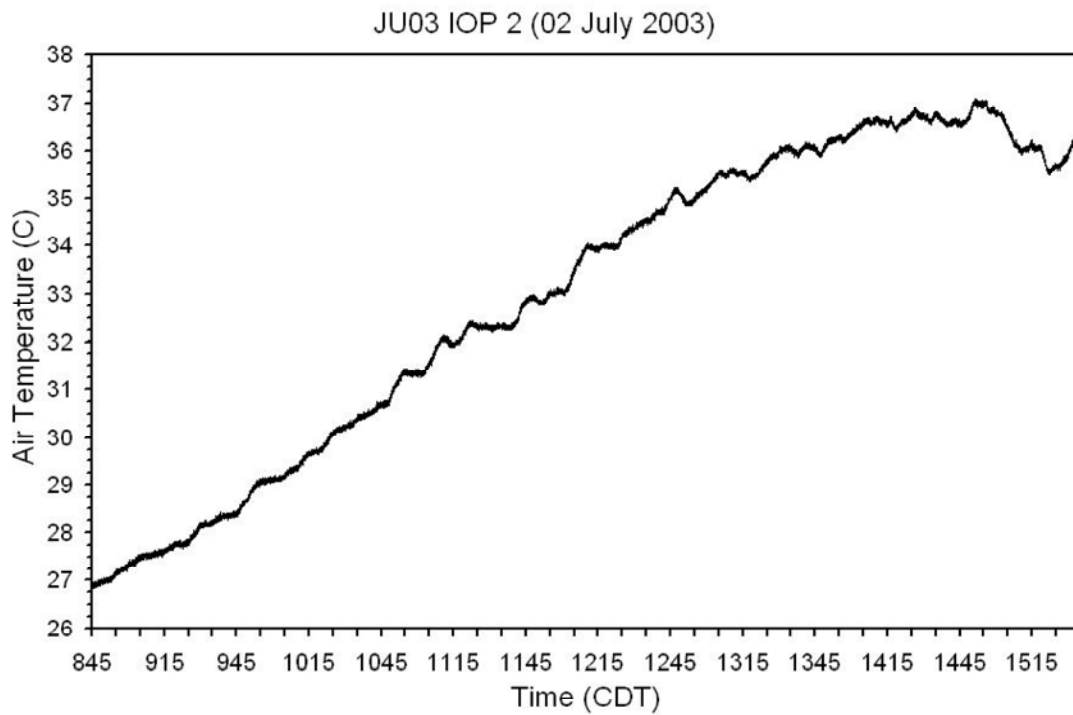


Figure E-3. Time history plot of the release site air temperature during IOP 2.

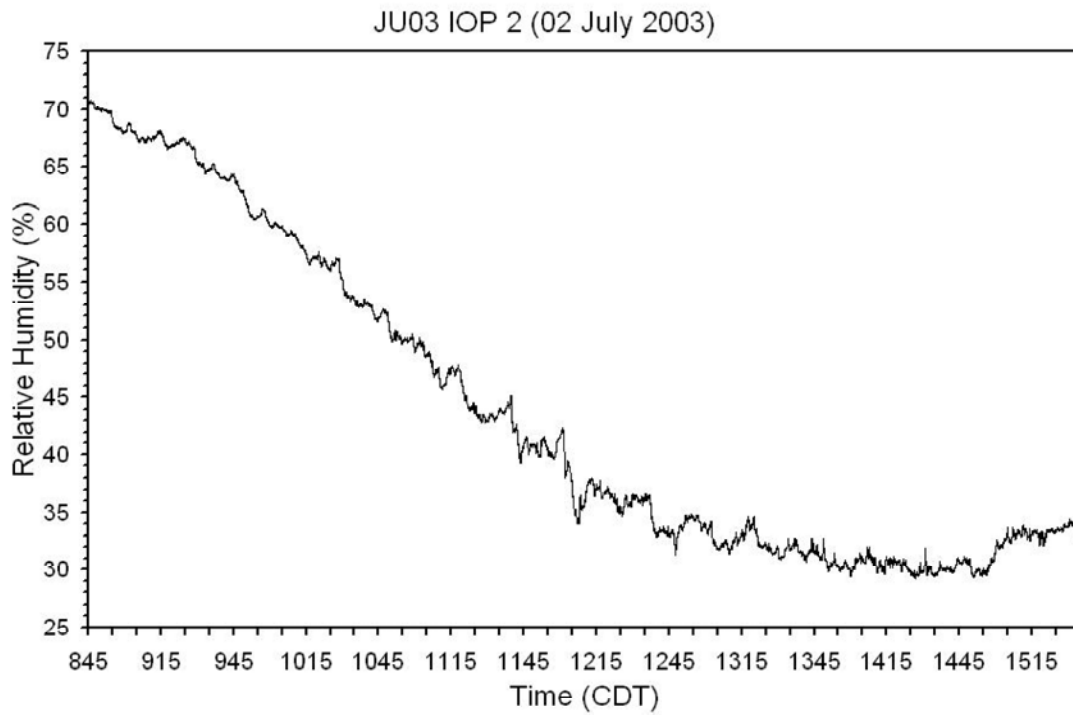


Figure E-4. Time history plot of the release site relative humidity during IOP 2.

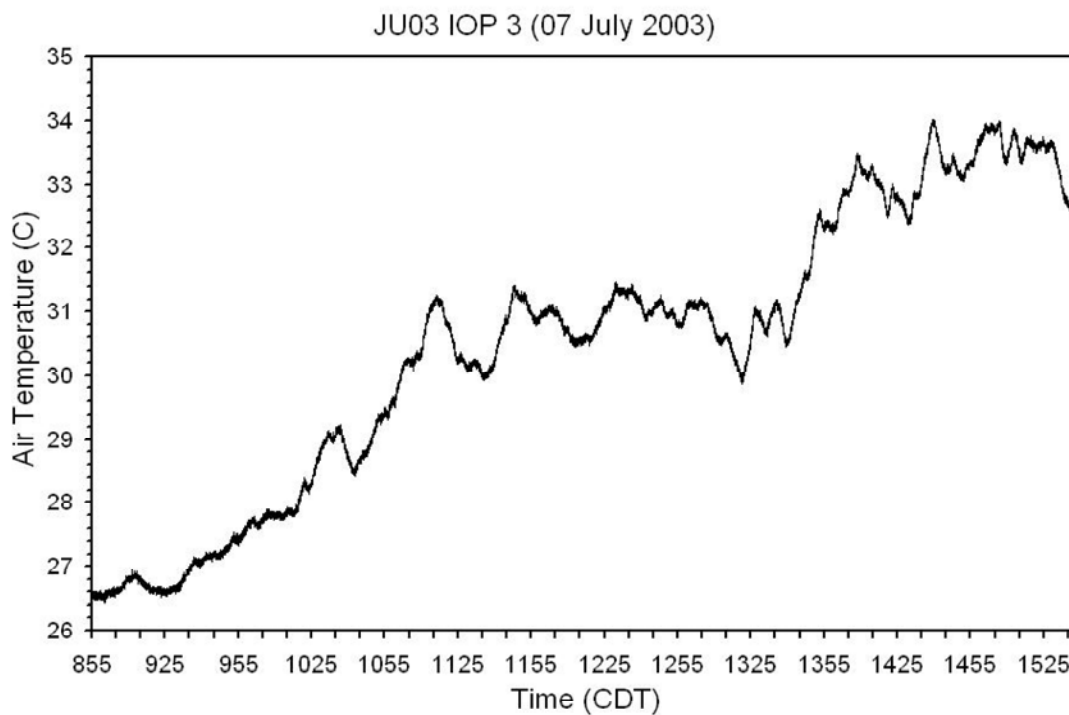


Figure E-5. Time history plot of the release site air temperature during IOP 3.

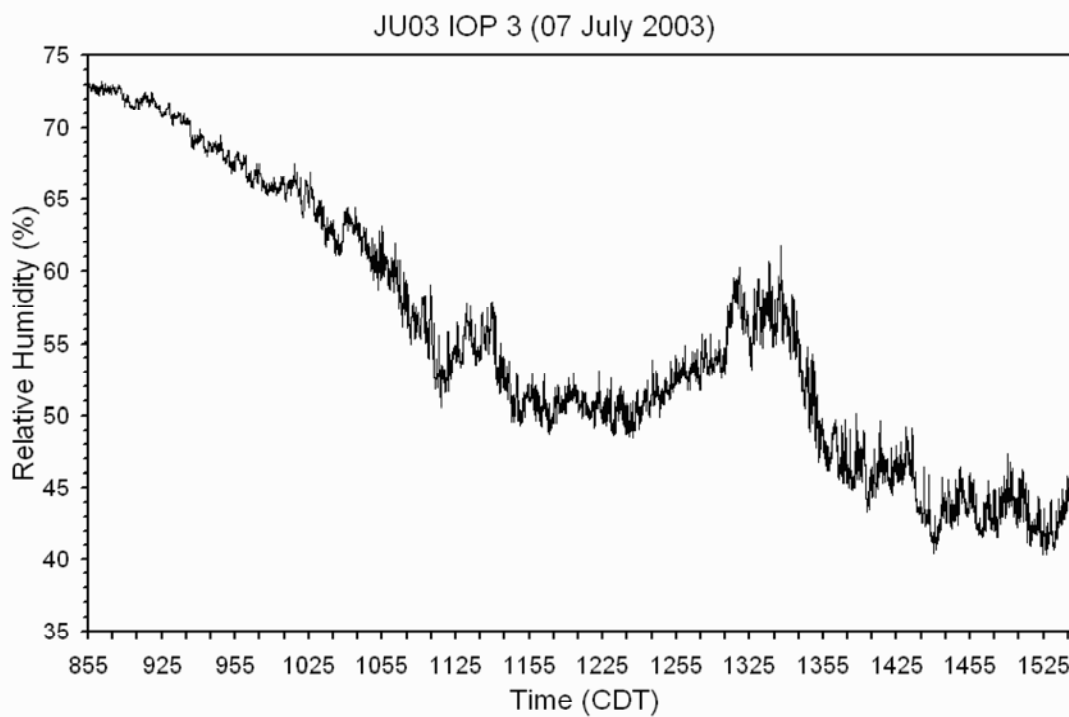


Figure E-6. Time history plot of the release site relative humidity during IOP 3.

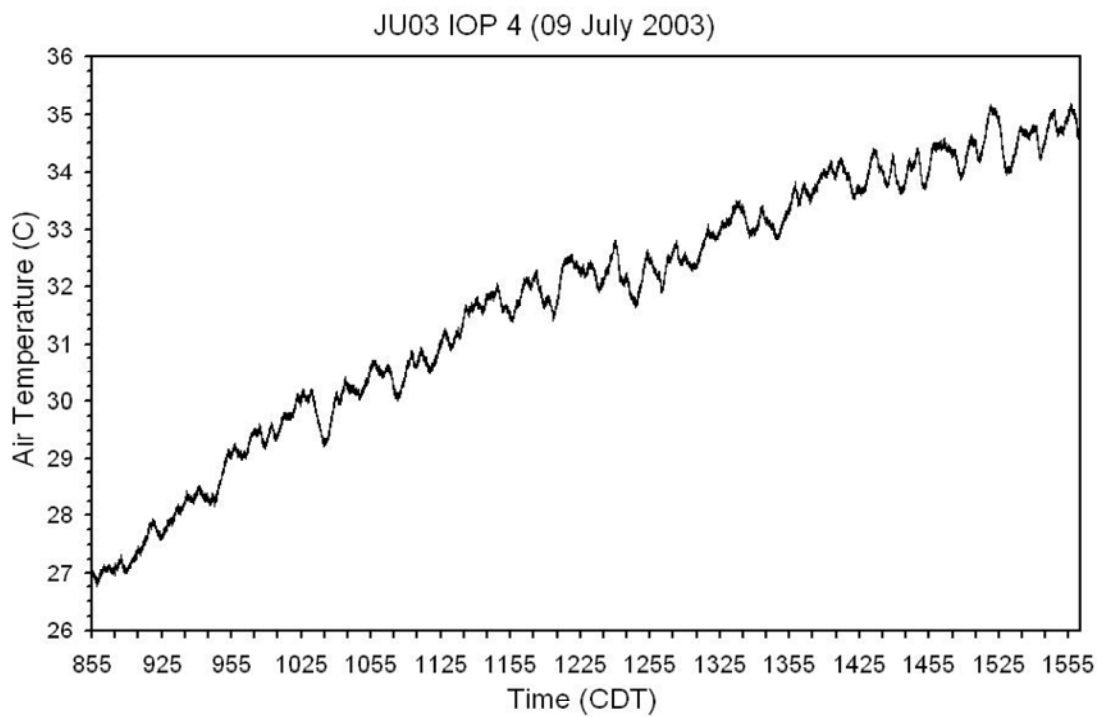


Figure E-7. Time history plot of the release site air temperature during IOP 4.

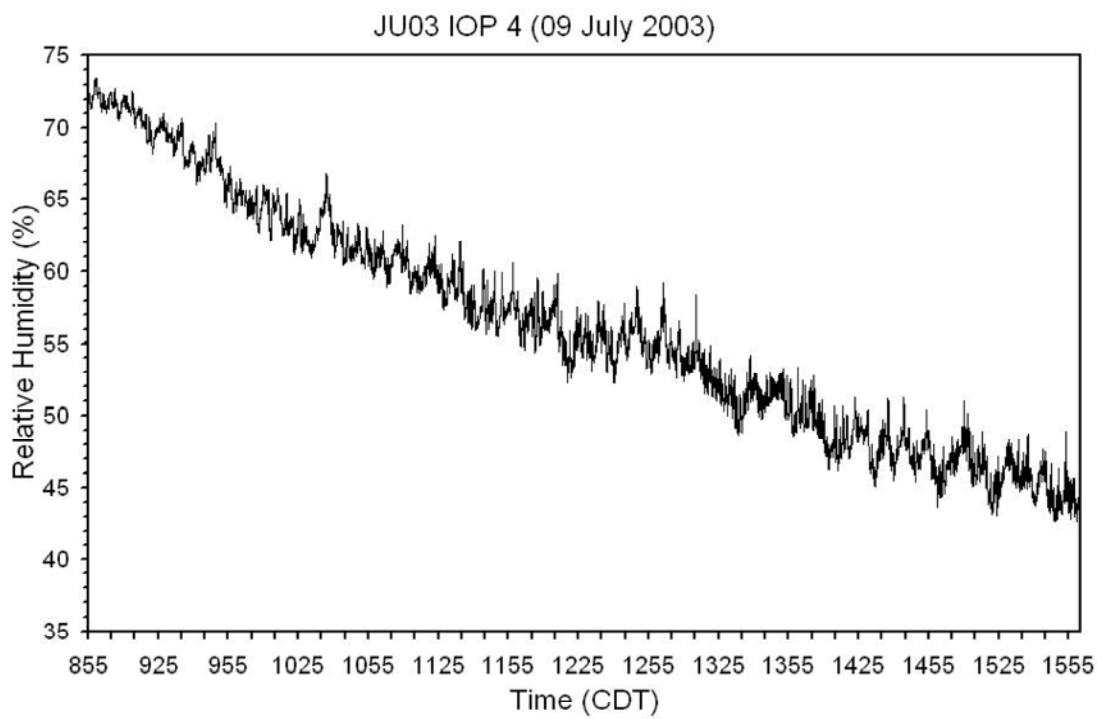


Figure E-8. Time history plot of the release site relative humidity during IOP 4.

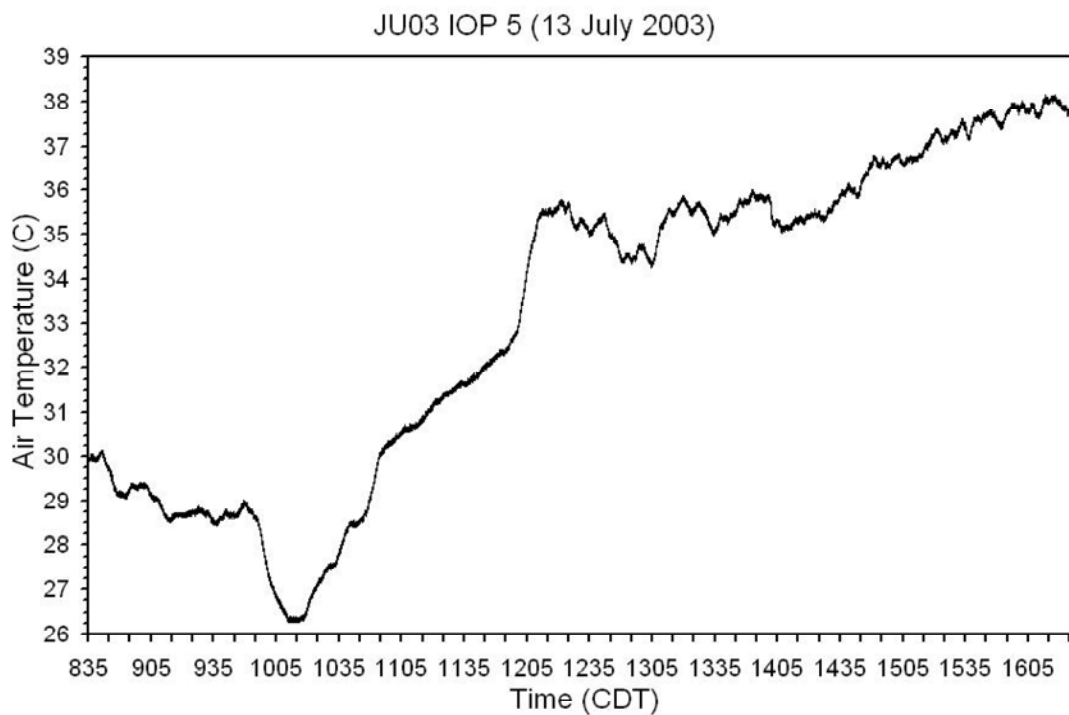


Figure E-9. Time history plot of the release site air temperature during IOP 5.

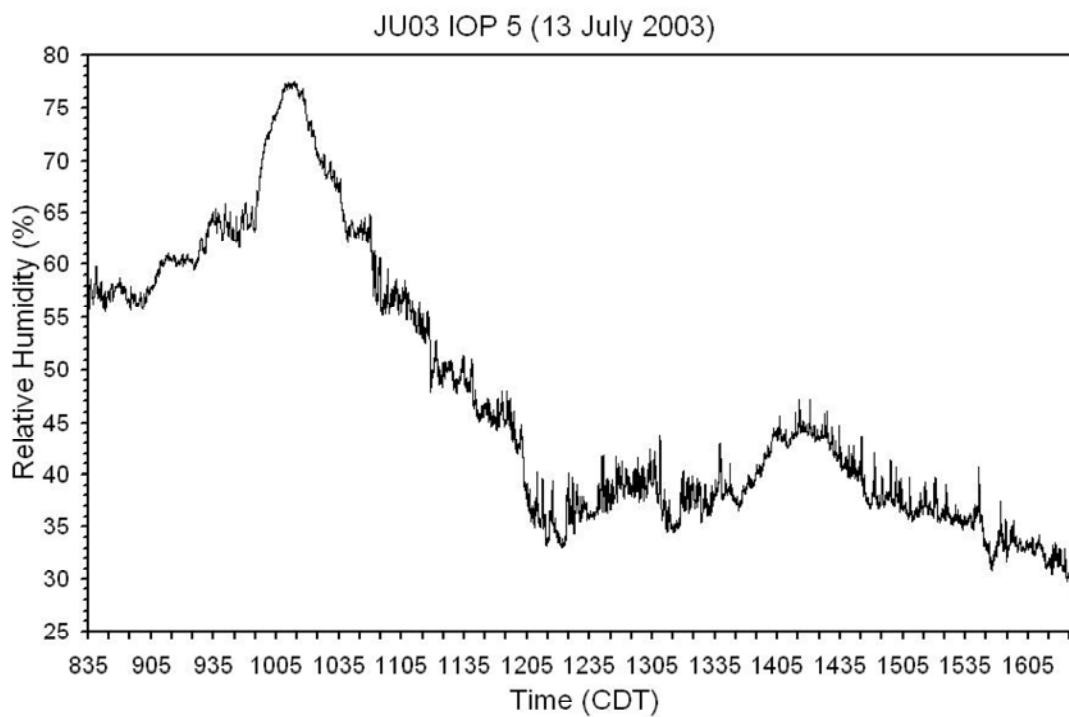


Figure E-10. Time history plot of the release site relative humidity during IOP 5.

Figure E-11. Time history plot of the release site air temperature during IOP 6.

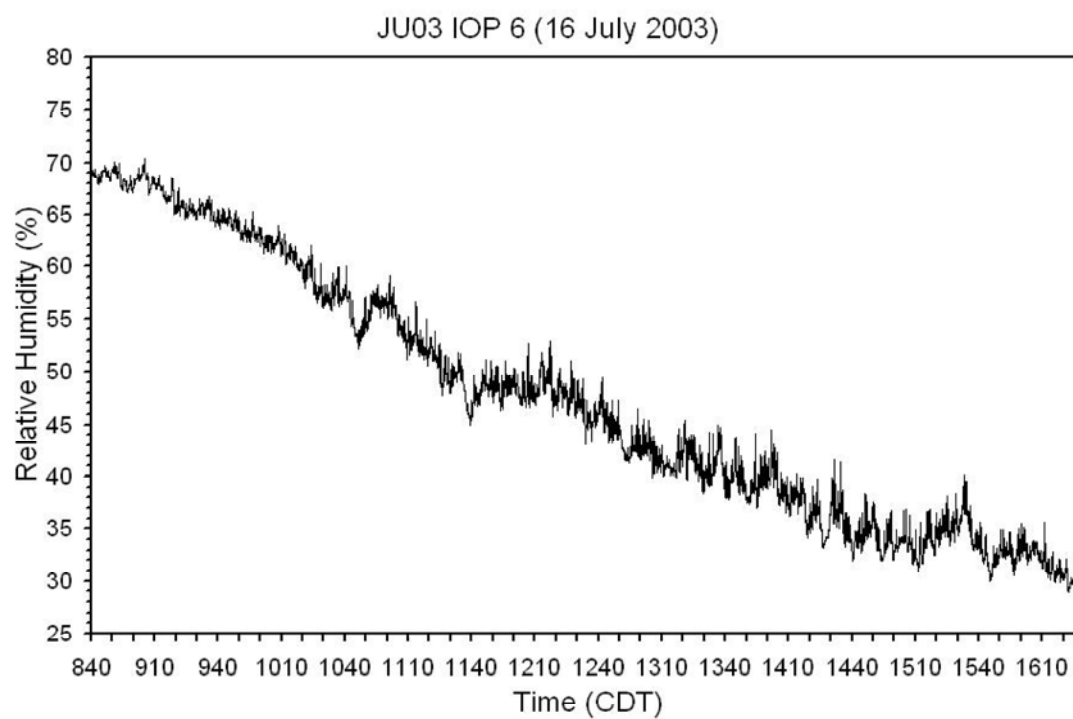


Figure E-12. Time history plot of the release site relative humidity during IOP 6.

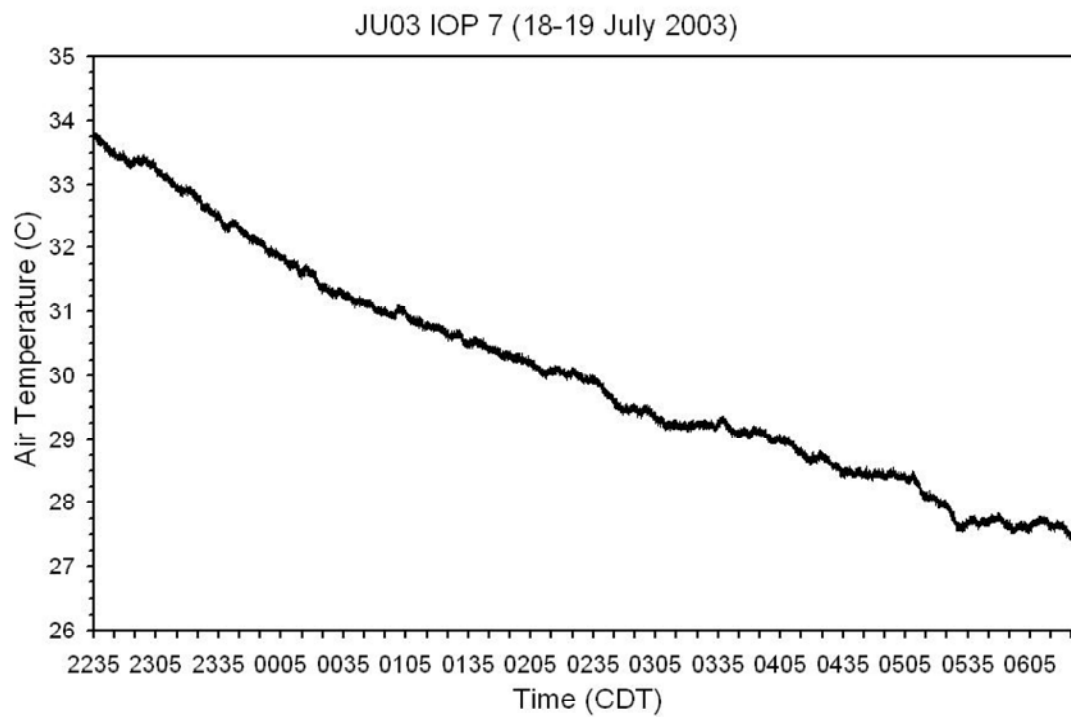


Figure E-13. Time history plot of the release site air temperature during IOP 7.

Figure E-14. Time history plot of the release site relative humidity during IOP 7.



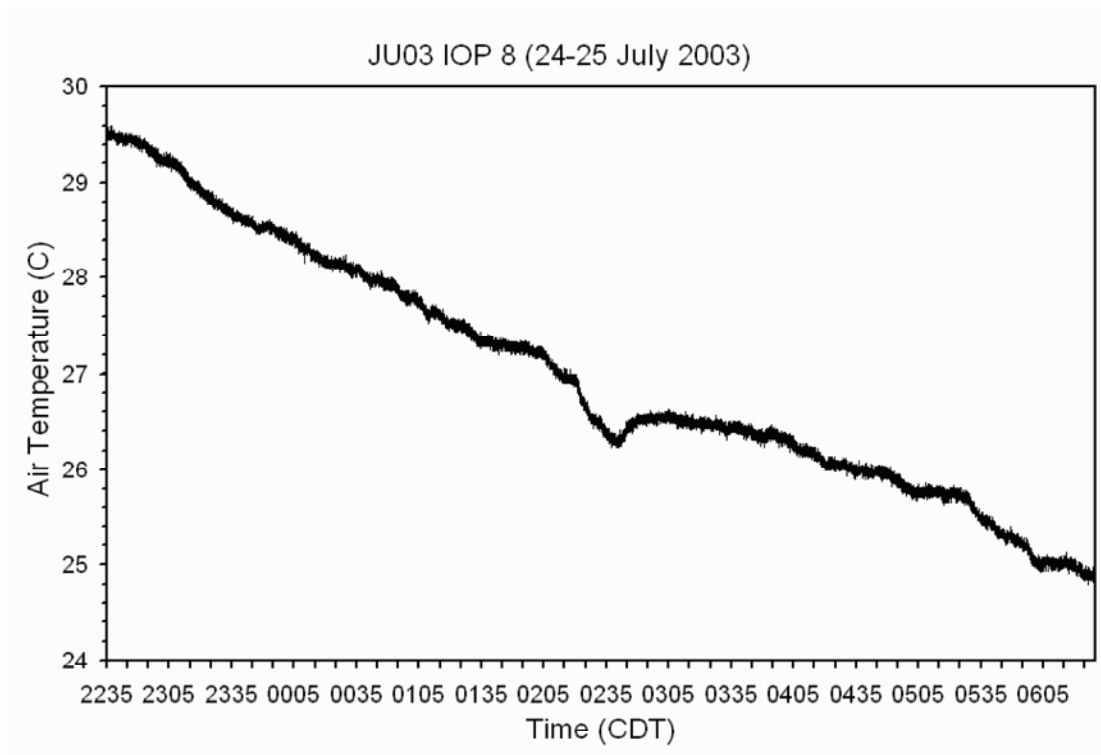


Figure E-15. Time history plot of the release site air temperature during IOP 8.

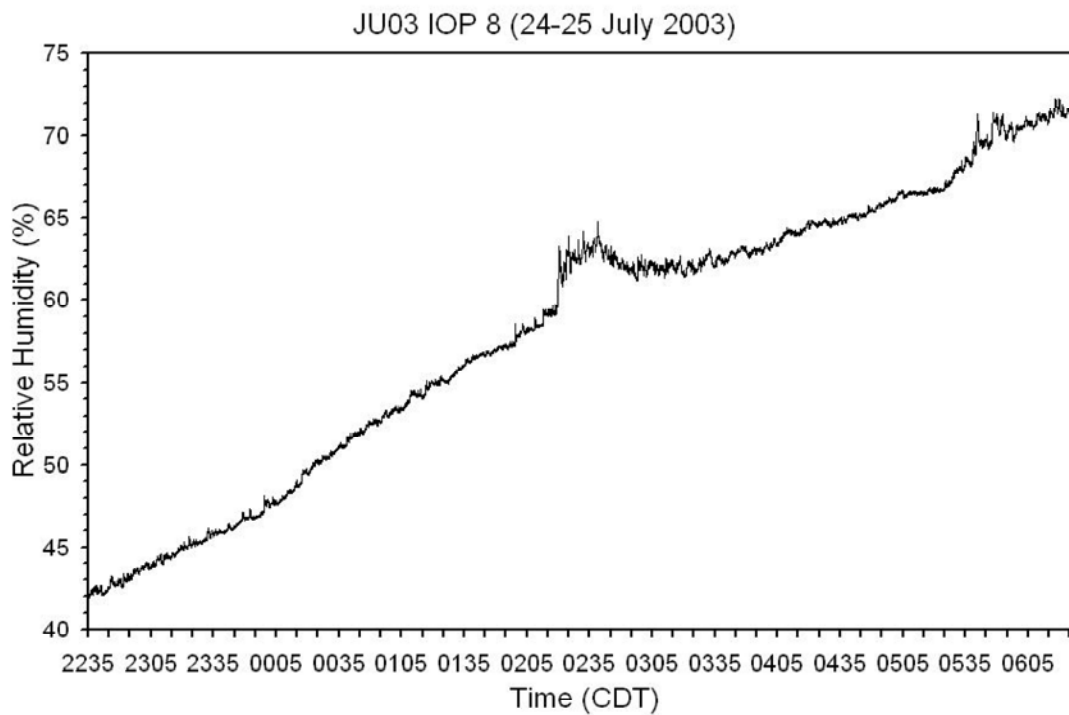


Figure E-16. Time history plot of the release site relative humidity during IOP 8.

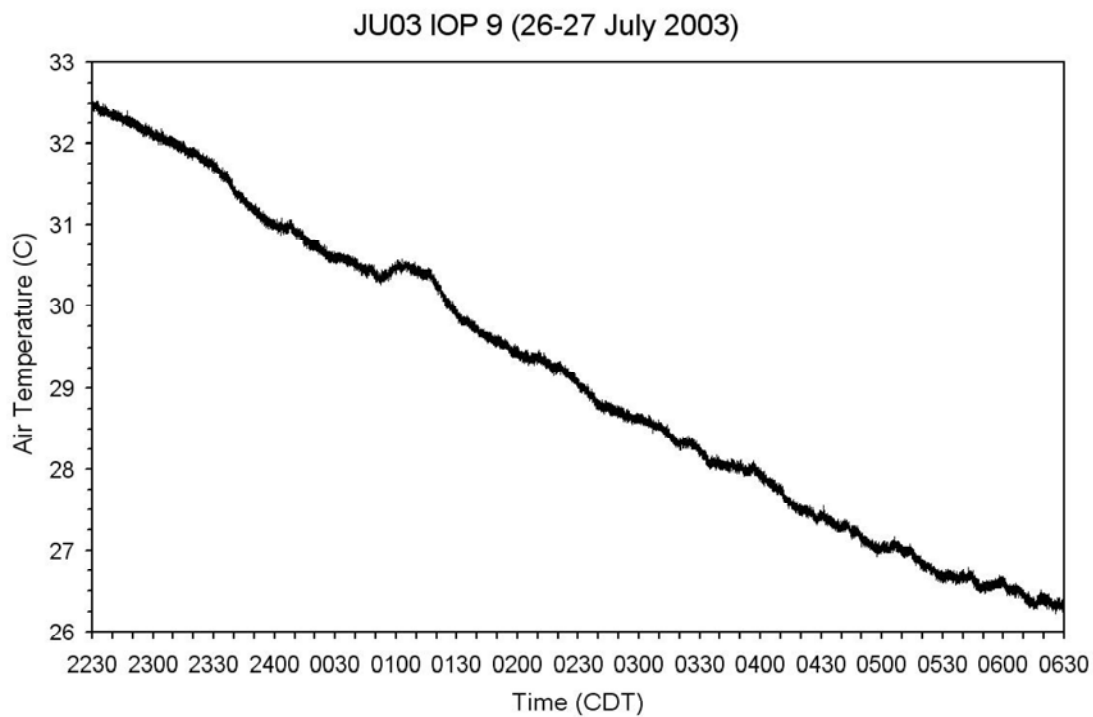


Figure E-17. Time history plot of the release site air temperature during IOP 9.

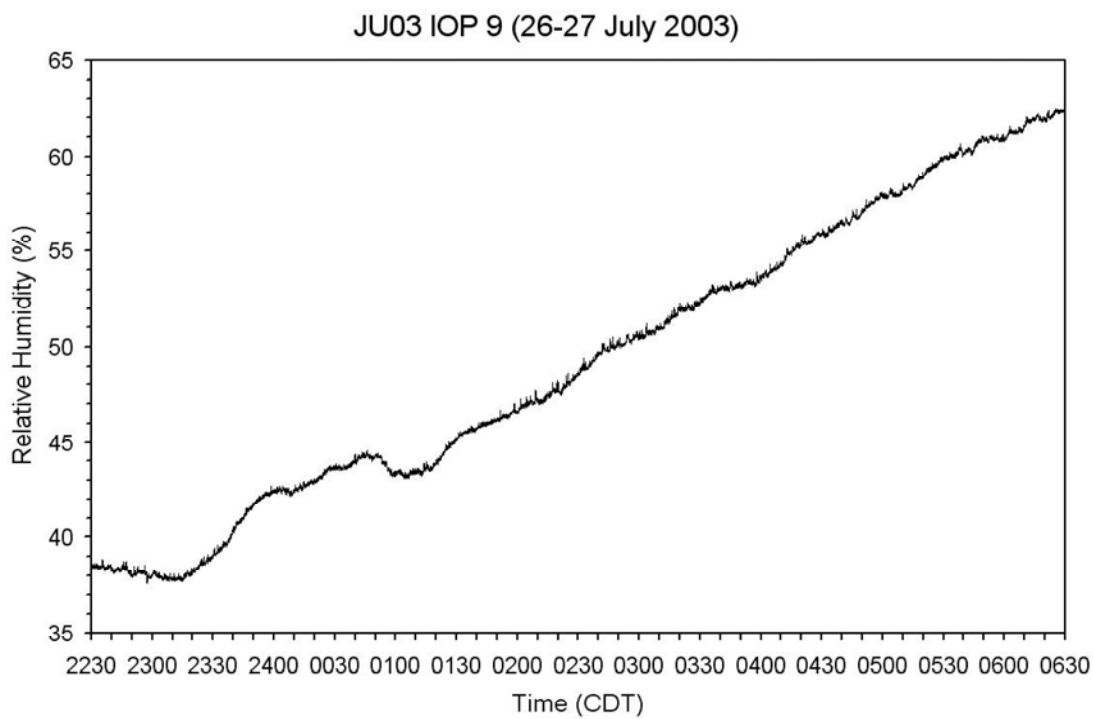


Figure E-18. Time history plot of the release site relative humidity during IOP 9.

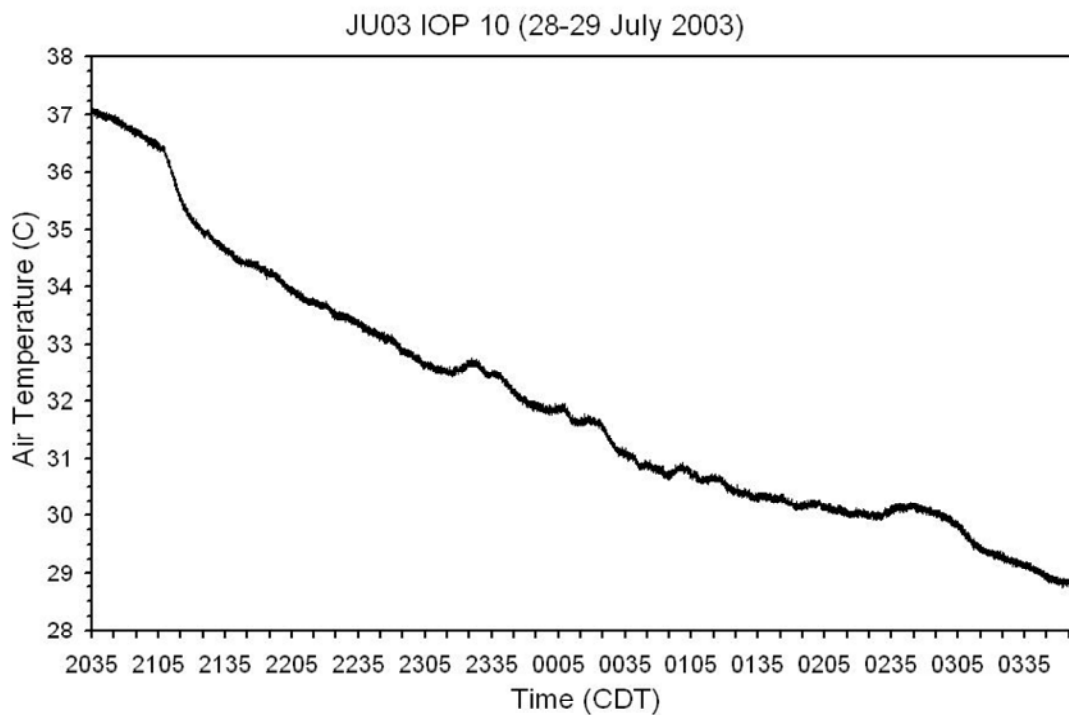


Figure E-19. Time history plot of the release site air temperature during IOP 10.

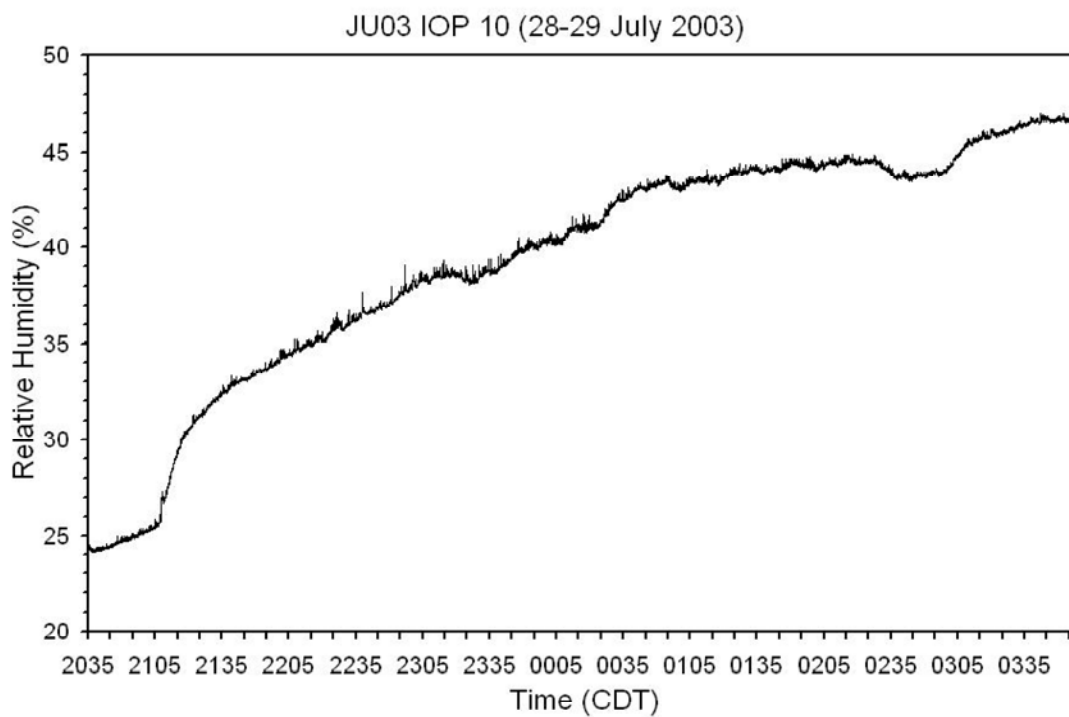


Figure E-20. Time history plot of the release site relative humidity during IOP 10.

# **APPENDIX F: ROOFTOP SAMPLER PLOTS**

Samplers were deployed on the rooftops of ten buildings across the CBD. Exact locations and building top information can be found in the Dissemination and Sampling section of the report. The rooftop samplers in this appendix are plotted by one of the three east-west streets (Park Ave, Robert S. Kerr, or Dean A. McGee) that it was positioned on. The last plot in each IOP combine all of the rooftop samplers into a single plot. The time history graphs (Figs. F-1 to F-40) are plotted by SF<sub>6</sub> concentration (pptv) vs. time (CDT).

Figure F-1. Time history plots of the rooftop samplers located on Park Ave during IOP 1.

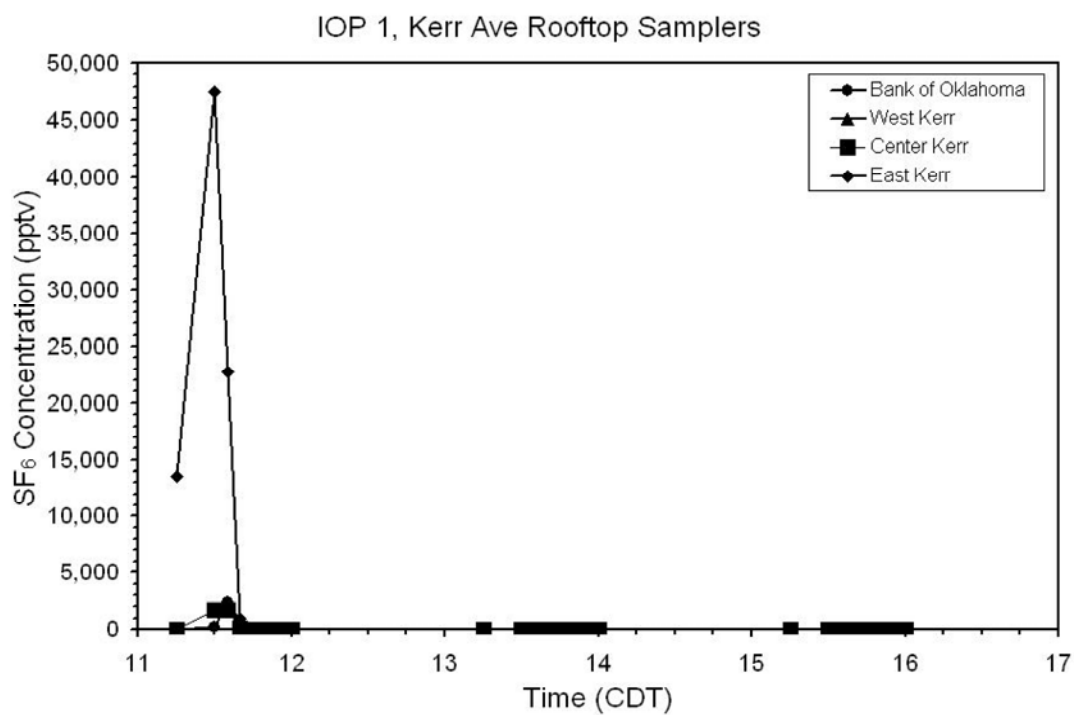


Figure F-2. Time history plots of the rooftop samplers located on Robert S. Kerr Avenue during IOP 1.

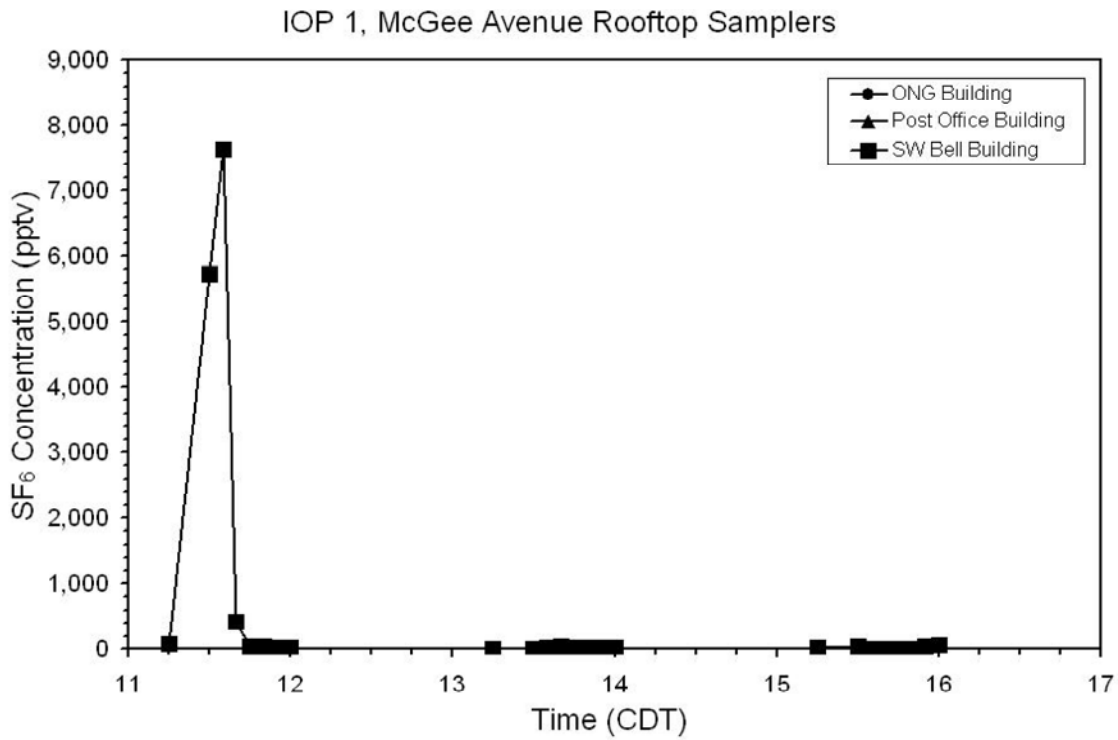


Figure F-3. Time history plots of the rooftop samplers located on Dean A. McGee Avenue during IOP 1.

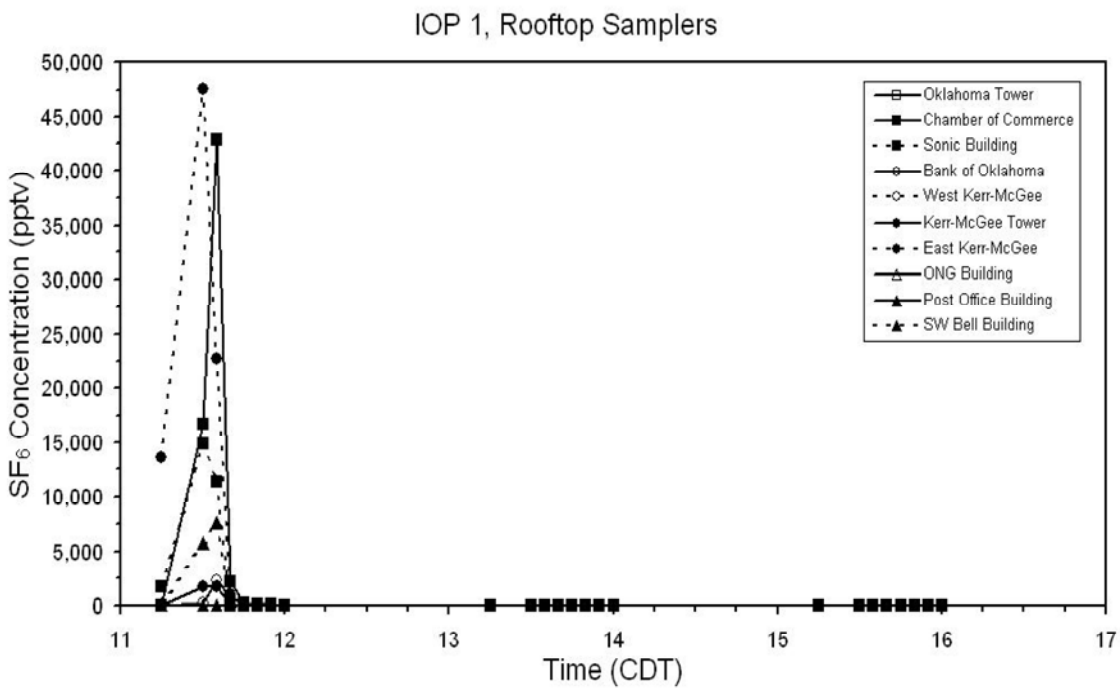


Figure F-4. Time history plots of all of the rooftop samplers during IOP 1.

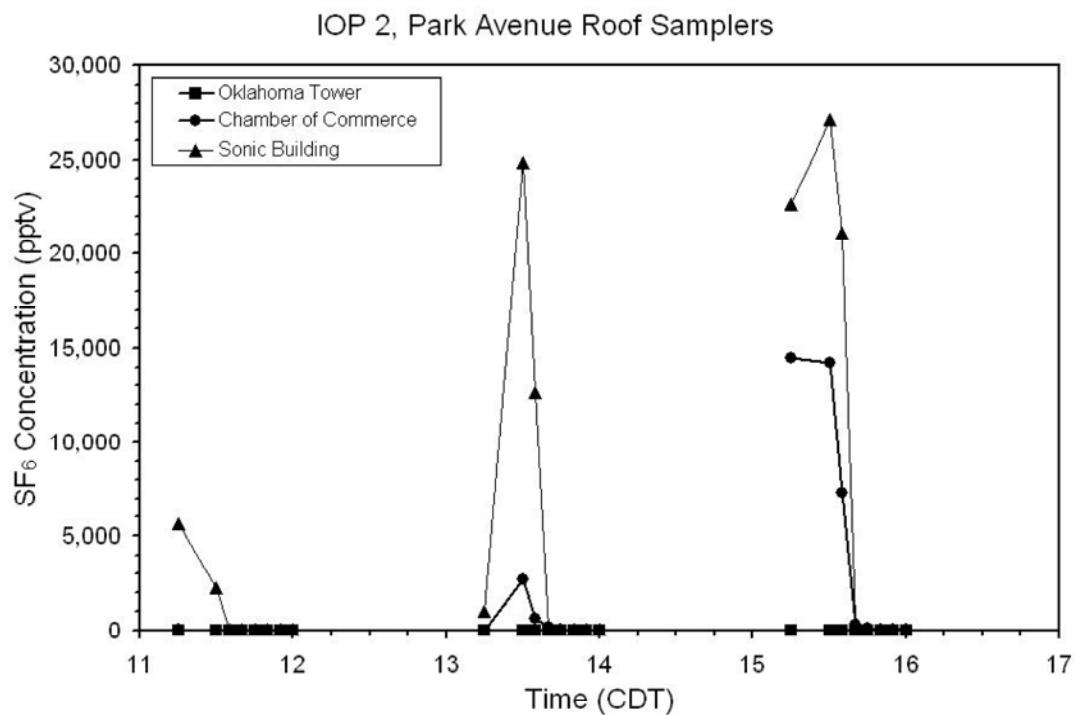


Figure F-5. Time history plots of the rooftop samplers located on Park Ave. during IOP 2.

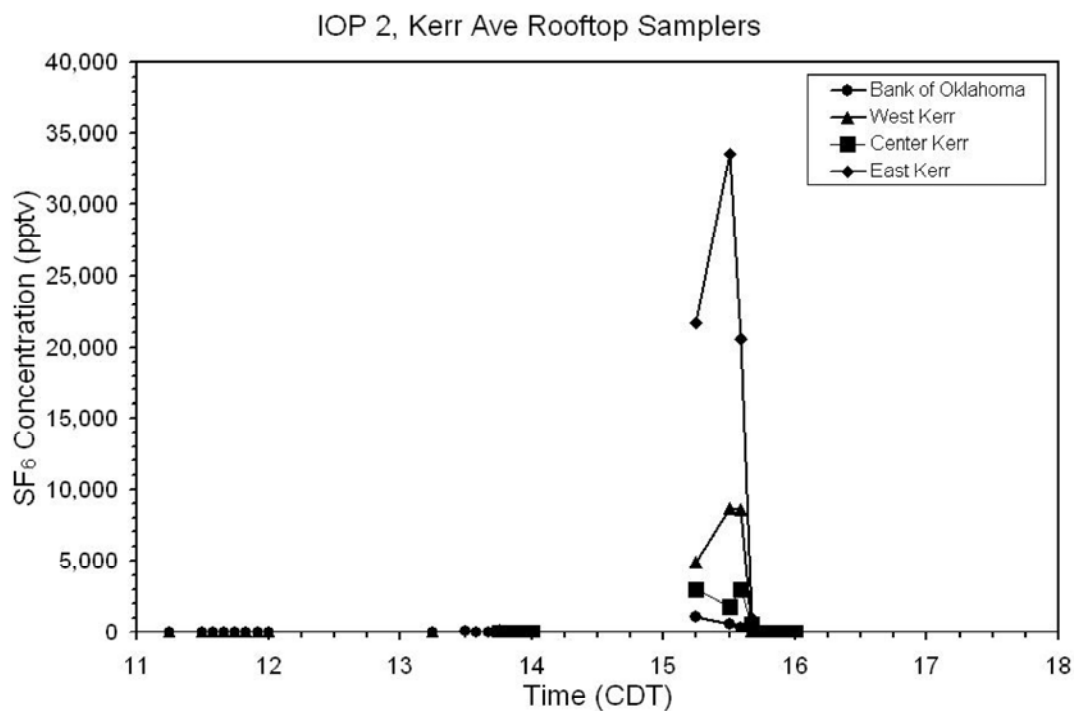


Figure F-6. Time history plots of the rooftop samplers located on Robert S. Kerr Avenue during IOP 2.

Figure F-7. Time history plots of the rooftop samplers located on Dean A. McGee Avenue during IOP 2.

Figure F-8. Time history plots of all of the rooftop samplers during IOP 2.



Figure F-9. Time history plots of the rooftop samplers located on Park Avenue during IOP 3.

Figure F-10. Time history plots of the rooftop samplers located on Robert S. Kerr Avenue during IOP 3.

Figure F-11. Time history plots of the rooftop samplers located on Dean A. McGee Avenue during IOP 3.

Figure F-12. Time history plots of all of the rooftop samplers during IOP 3.

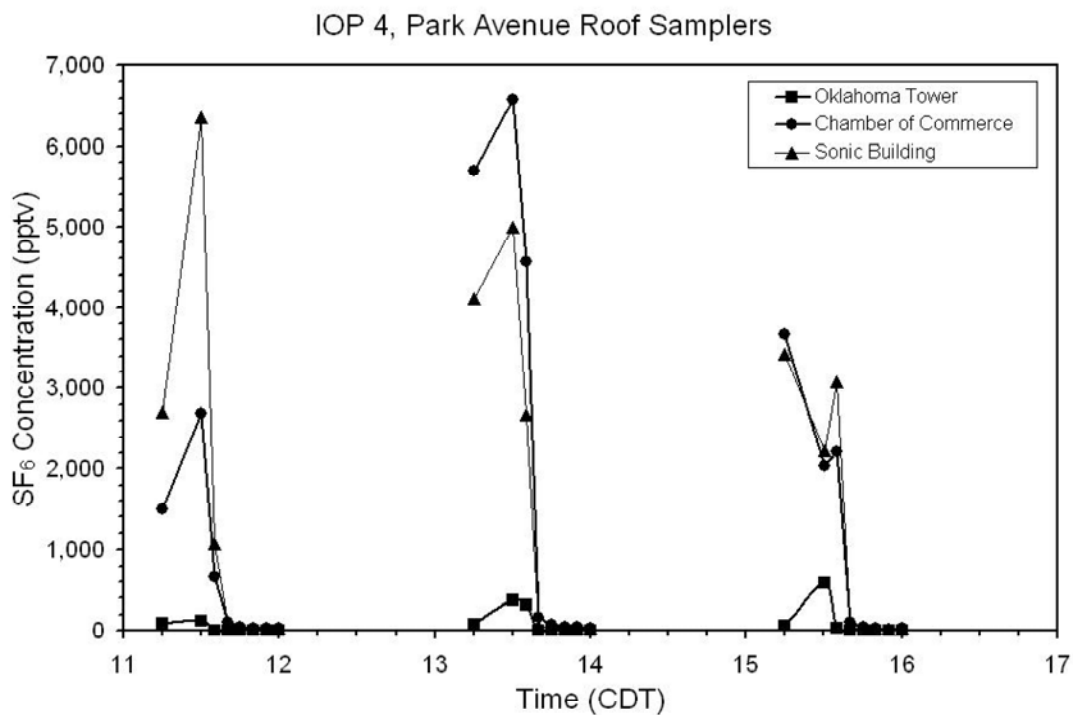


Figure F-13. Time history plots of the rooftop samplers located on Park Avenue during IOP 4.

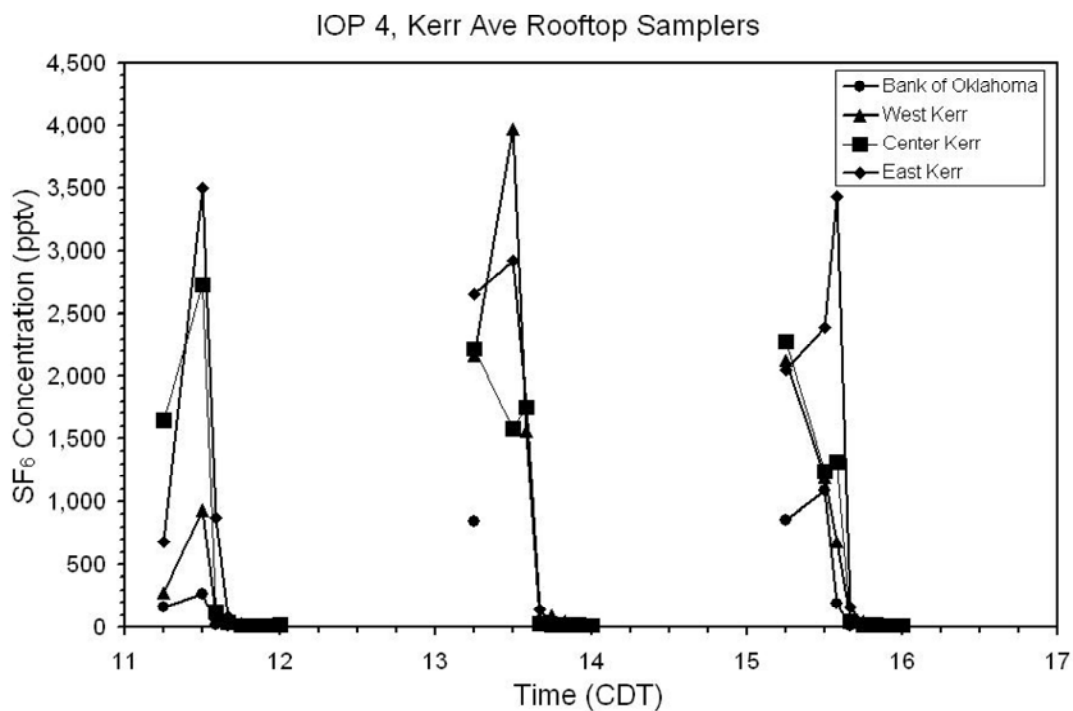


Figure F-14. Time history plots of the rooftop samplers located on Robert S. Kerr Avenue during IOP 4.

Figure F-15. Time history plots of the rooftop samplers located on Dean A. McGee Avenue during IOP 4.

Figure F-16. Time history plots of all of the rooftop samplers during IOP 4.

Figure F-17. Time history plots of the rooftop samplers located on Park Avenue during IOP 5.

Figure F-18. Time history plots of the rooftop samplers located on Robert S. Kerr Avenue during IOP 5.

Figure F-19. Time history plots of the rooftop samplers located on Dean A. McGee Avenue during IOP 5.

Figure F-20. Time history plots of all of the rooftop samplers during IOP 5.

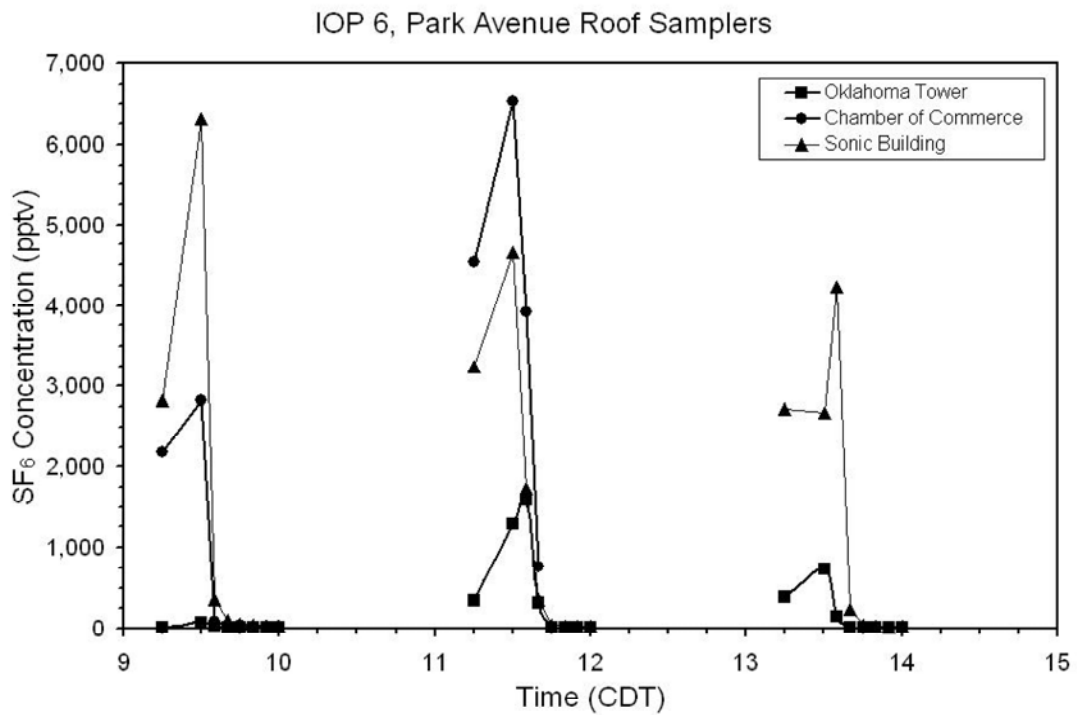


Figure F-21. Time history plots of the rooftop samplers located on Park Avenue during IOP 6.

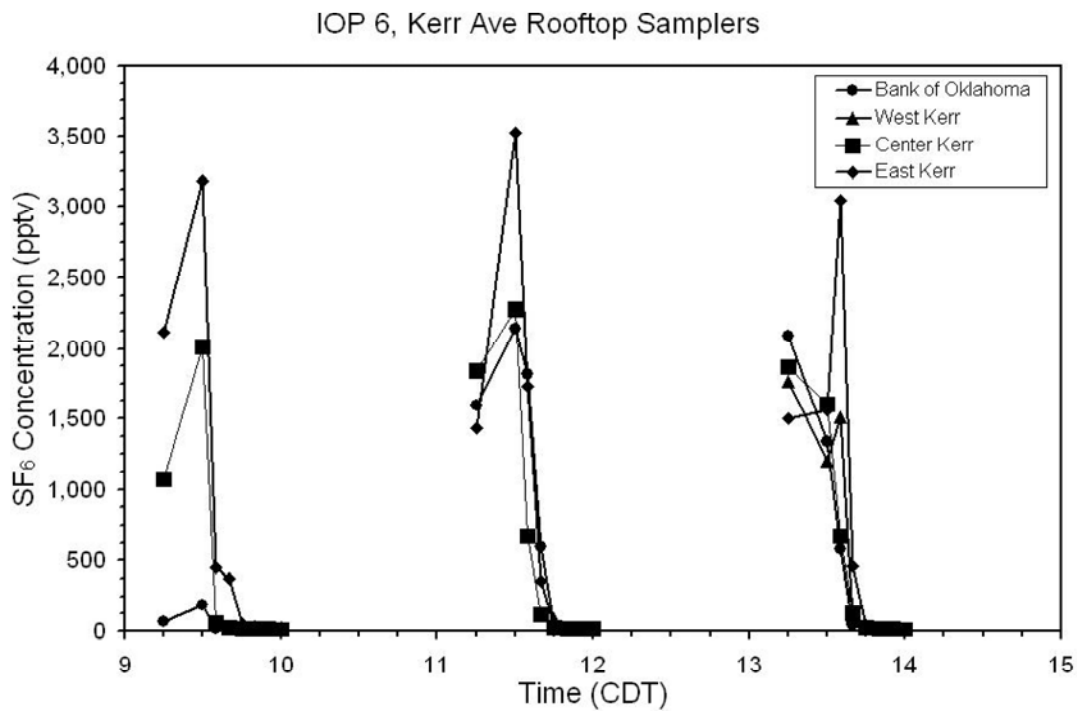


Figure F-22. Time history plots of the rooftop samplers located on Robert S. Kerr Avenue during IOP 6.

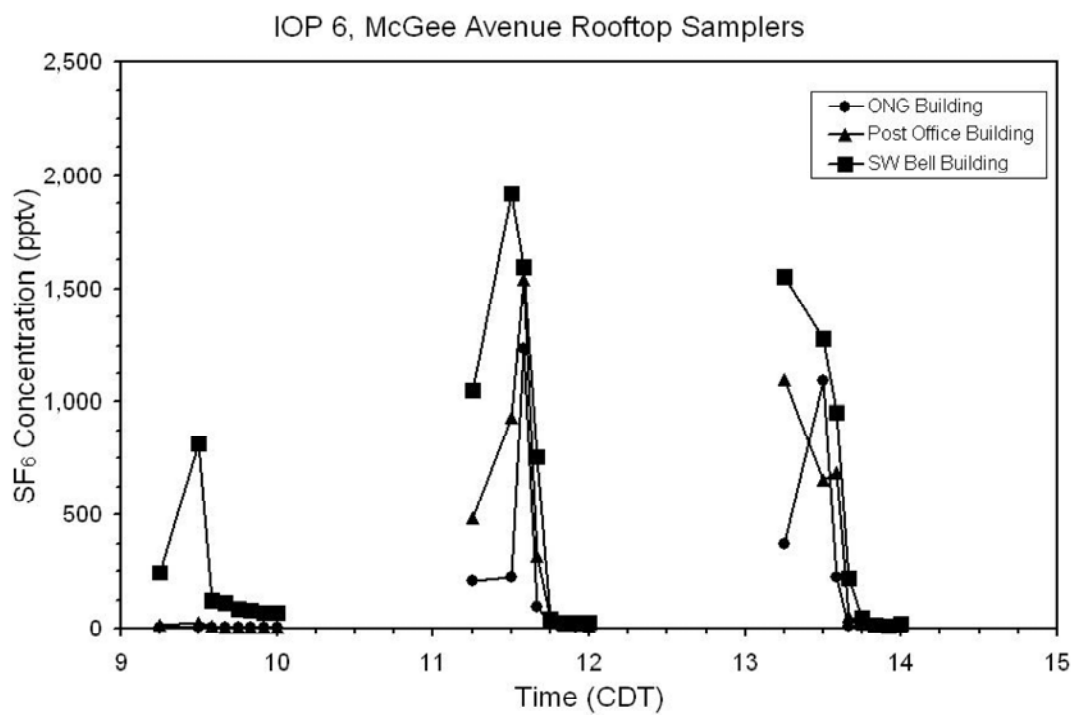


Figure F-23. Time history plots of the rooftop samplers located on Dean A. McGee Avenue during IOP 6.

Figure F-24. Time history plots of all of the rooftop samplers during IOP 6.



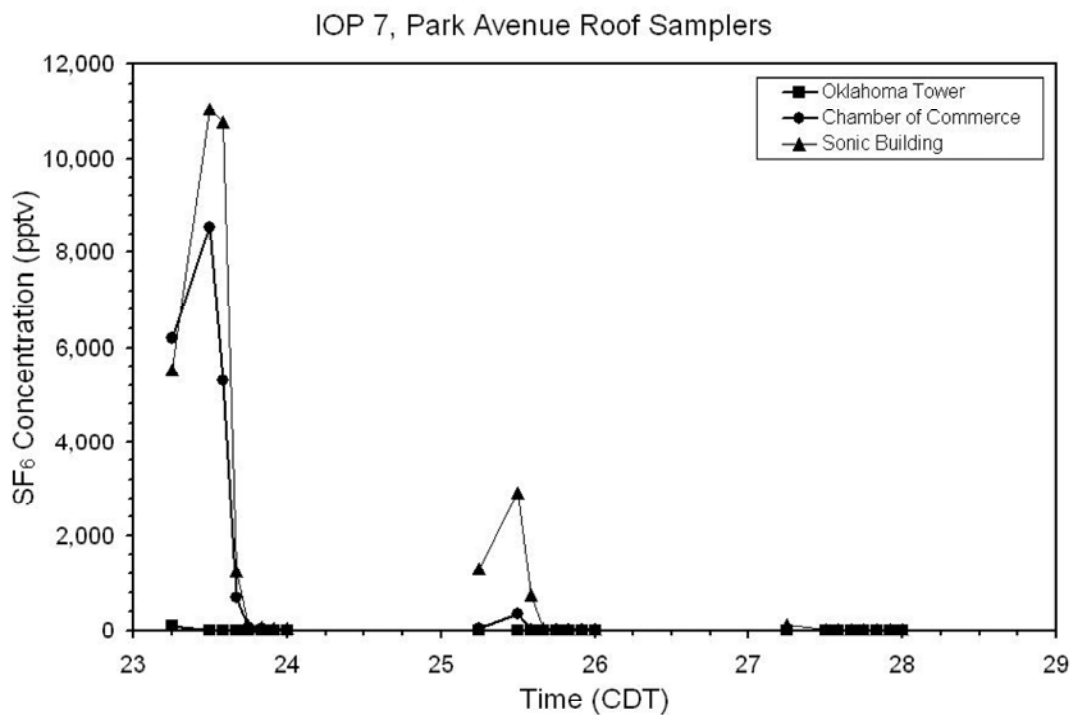


Figure F-25. Time history plots of the rooftop samplers located on Park Avenue during IOP 7.

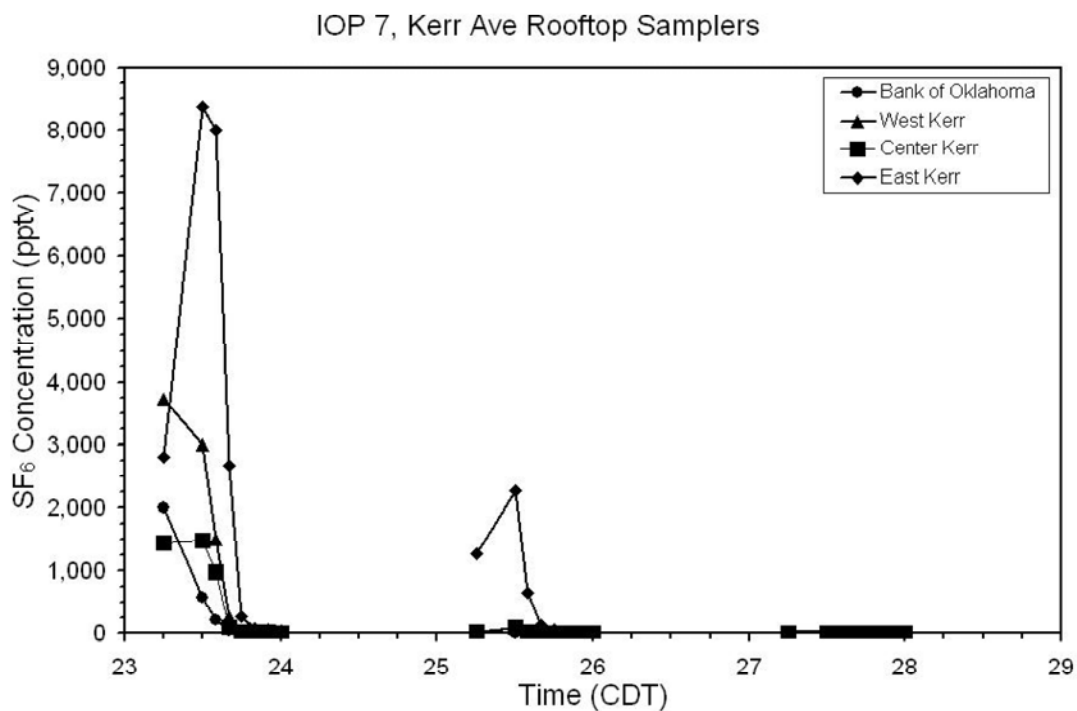


Figure F-26. Time history plots of the rooftop samplers located on Robert S. Kerr Avenue during IOP 7.

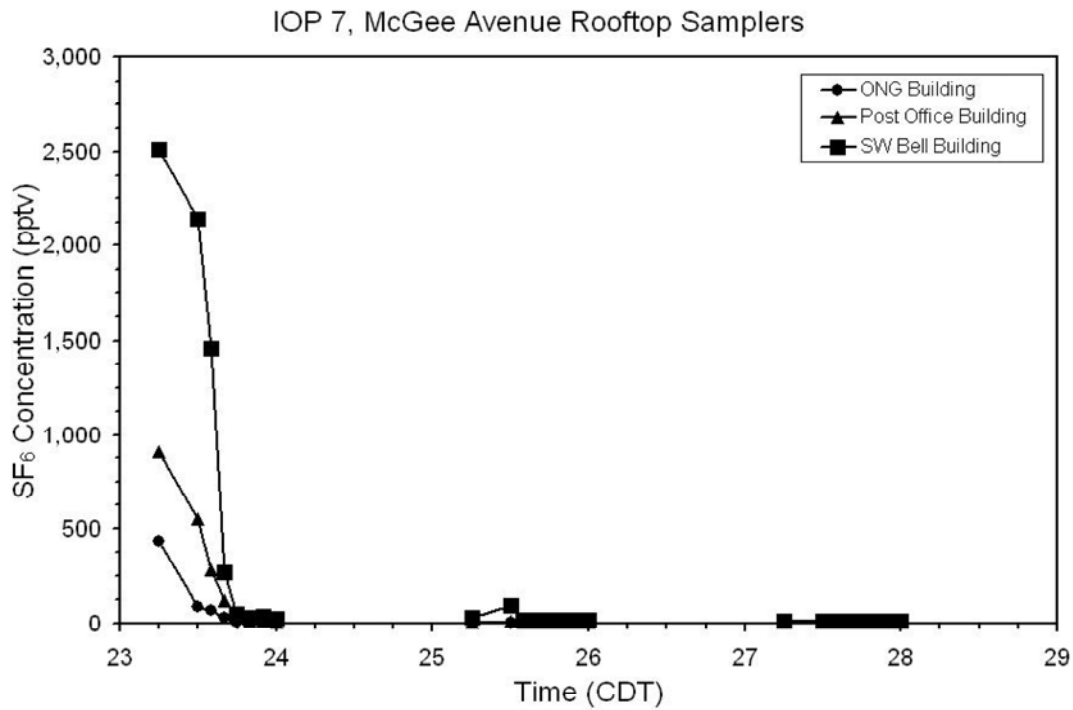


Figure F-27. Time history plots of the rooftop samplers located on Dean A. McGee Avenue during IOP 7.

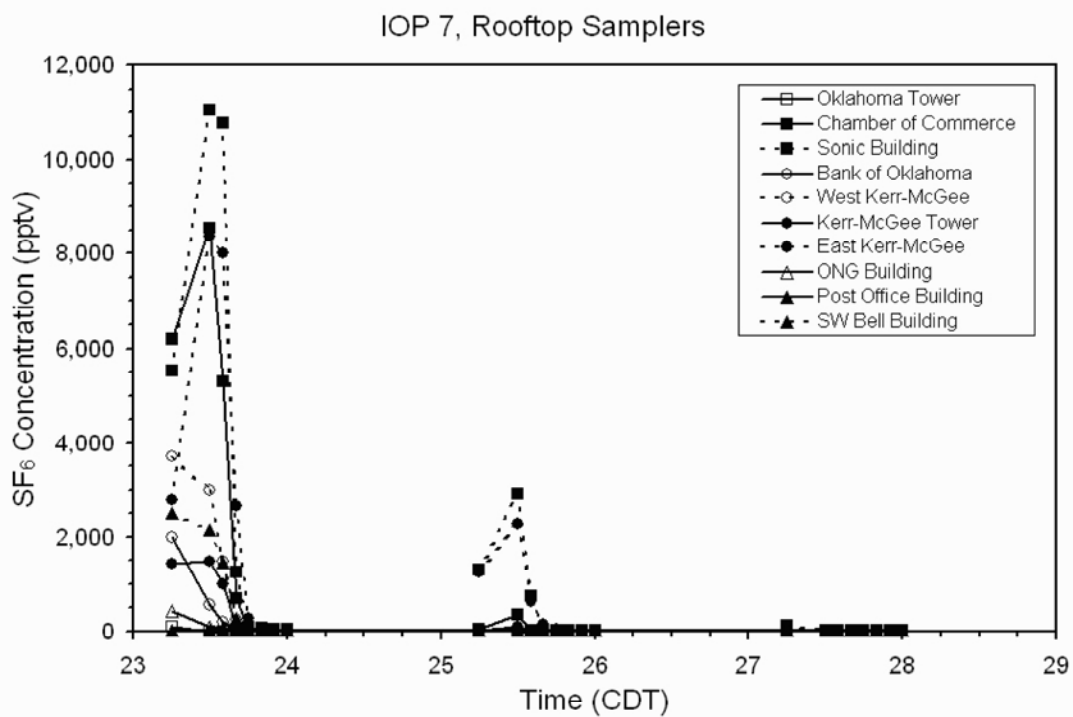


Figure F-28. Time history plots of all of the rooftop samplers during IOP 7.

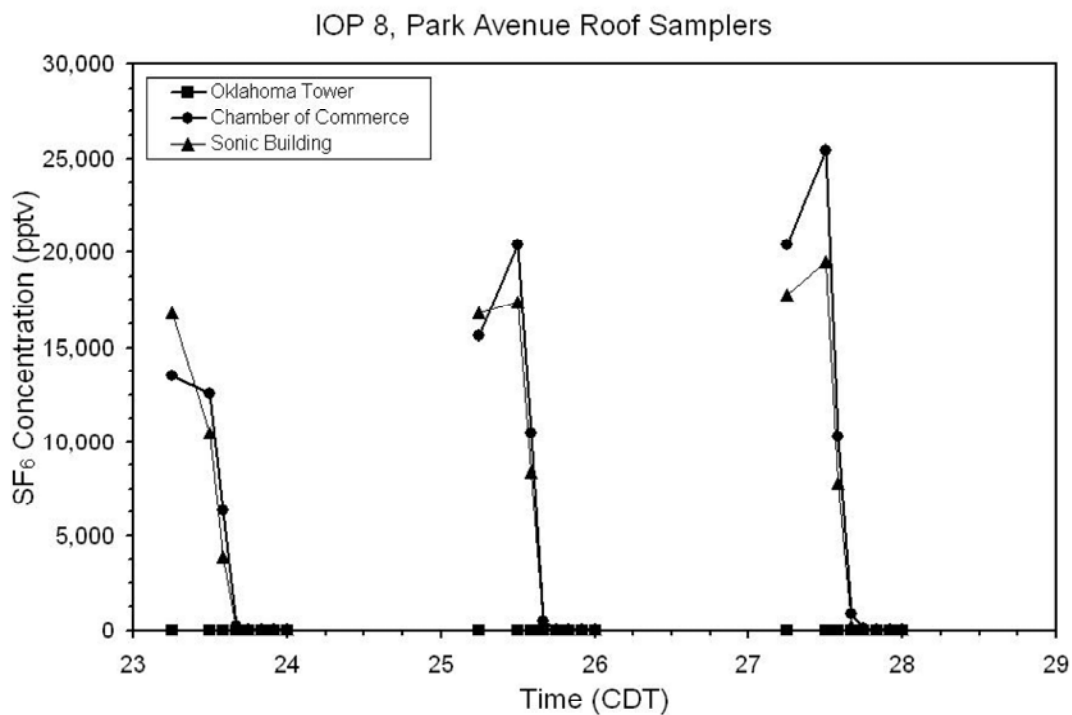


Figure F-29. Time history plots of the rooftop samplers located on Park Avenue during IOP 8.

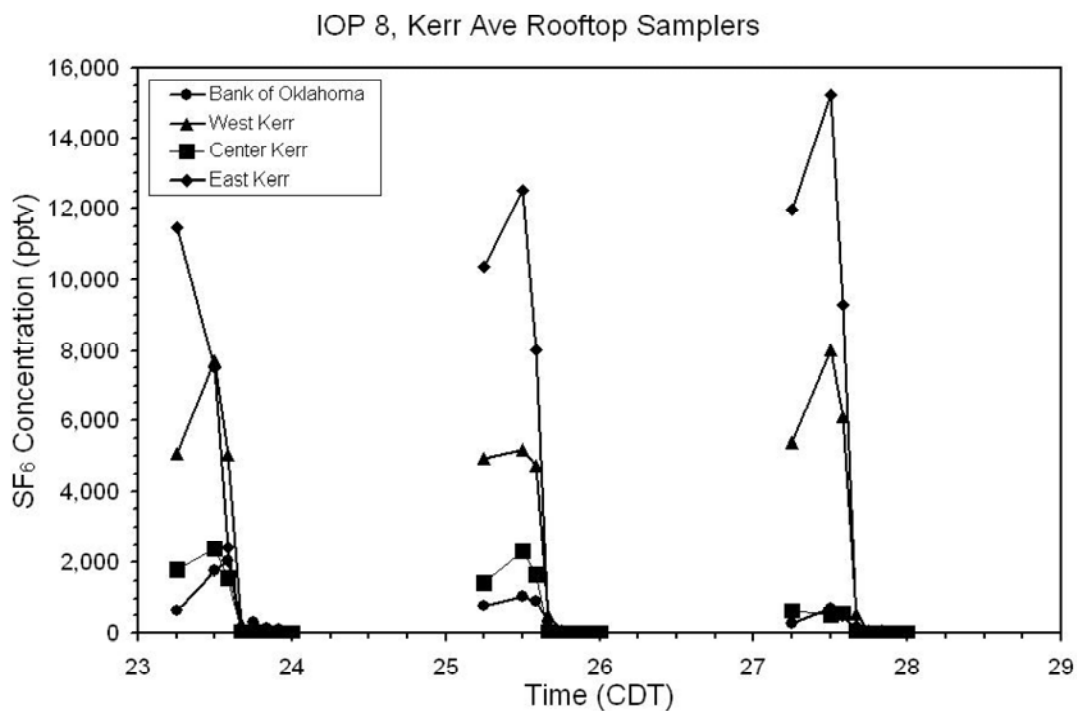


Figure F-30. Time history plots of the rooftop samplers located on Robert S. Kerr Avenue during IOP 8.

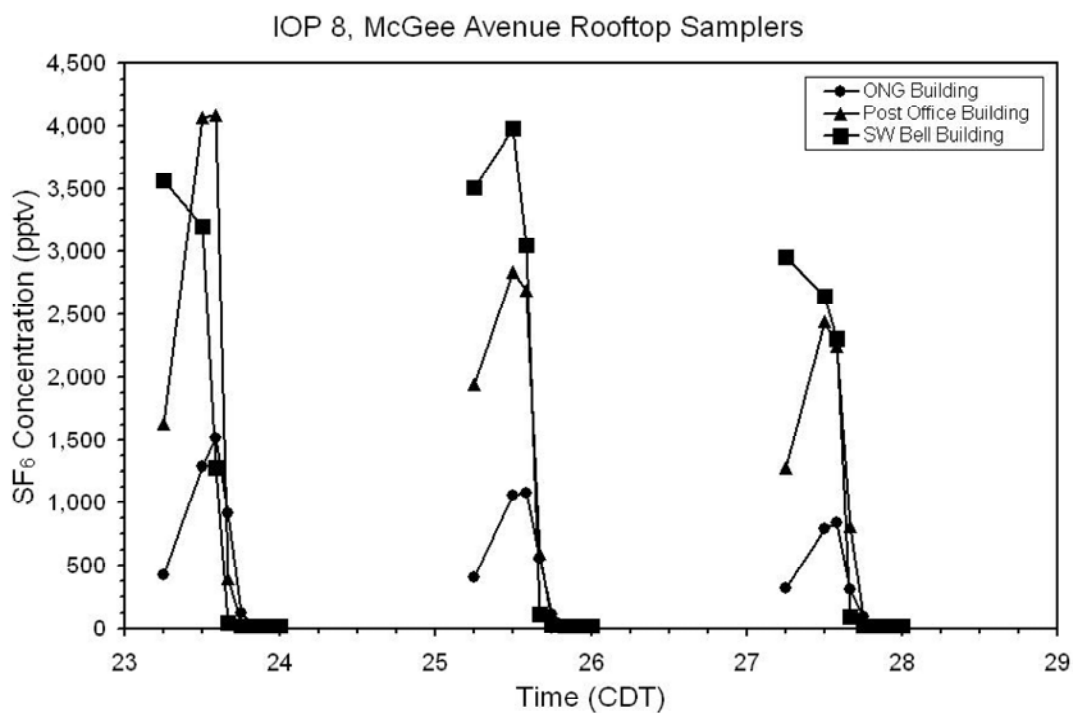


Figure F-31. Time history plots of the rooftop samplers located on Dean A. McGee Avenue during IOP 8.

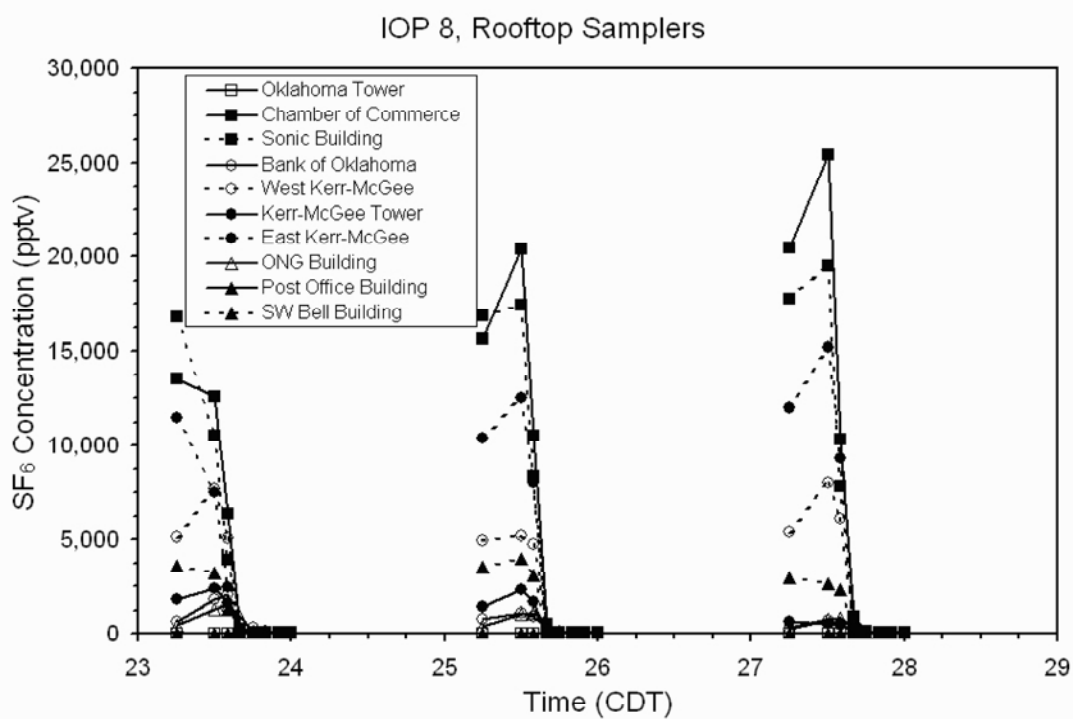


Figure F-32. Time history plots of all of the rooftop samplers during IOP 8.

Figure F-33. Time history plots of the rooftop samplers located on Park Avenue during IOP 9.

Figure F-34. Time history plots of the rooftop samplers located on Robert S. Kerr Avenue during IOP 9.

Figure F-35. Time history plots of the rooftop samplers located on Dean A. McGee Avenue during IOP 9.

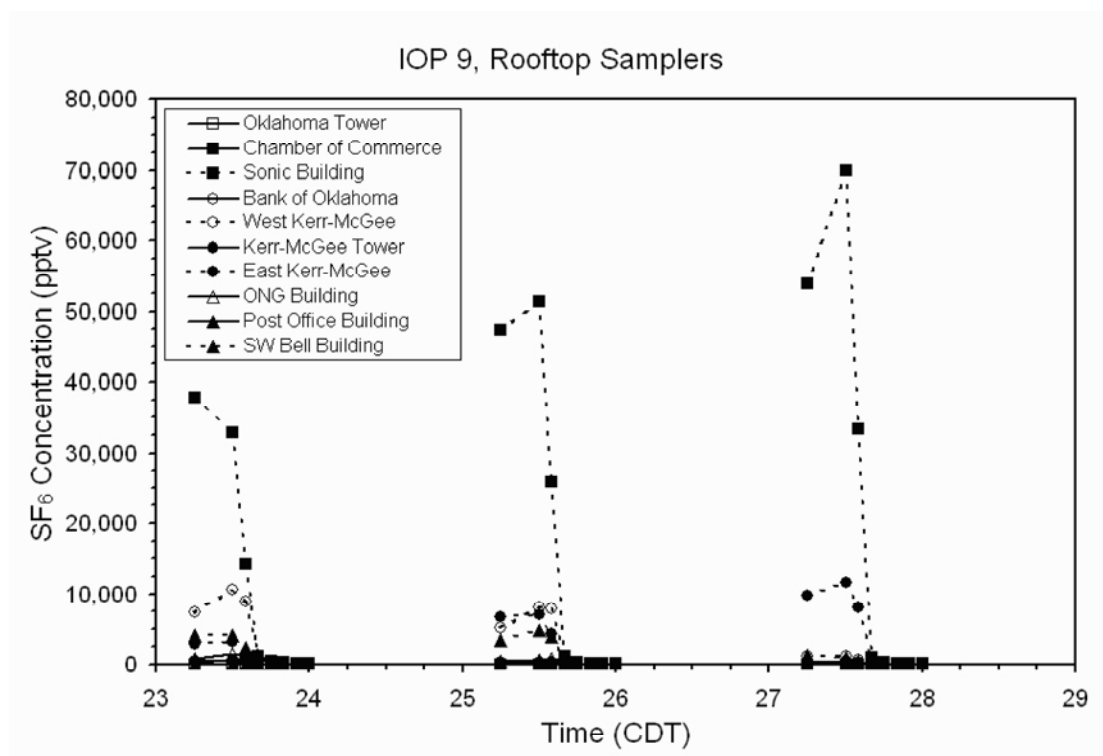


Figure F-36. Time history plots of all of the rooftop samplers during IOP 9.

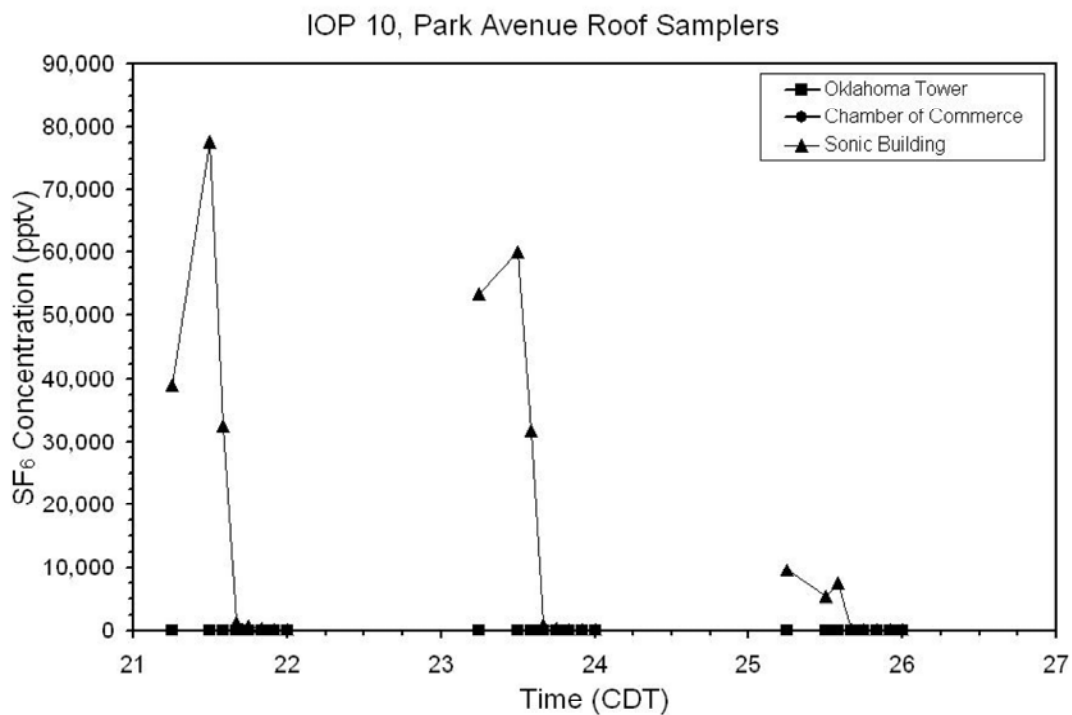


Figure F-37. Time history plots of the rooftop samplers located on Park Avenue during IOP 10.

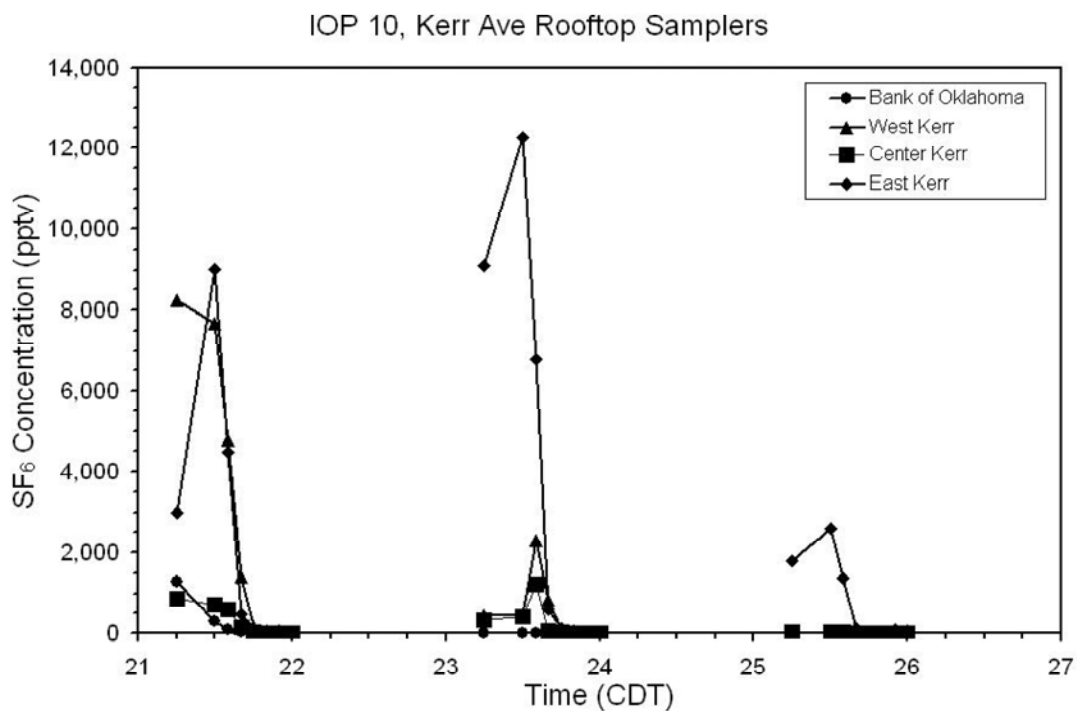


Figure F-38. Time history plots of the rooftop samplers located on Robert S. Kerr Avenue during IOP 10

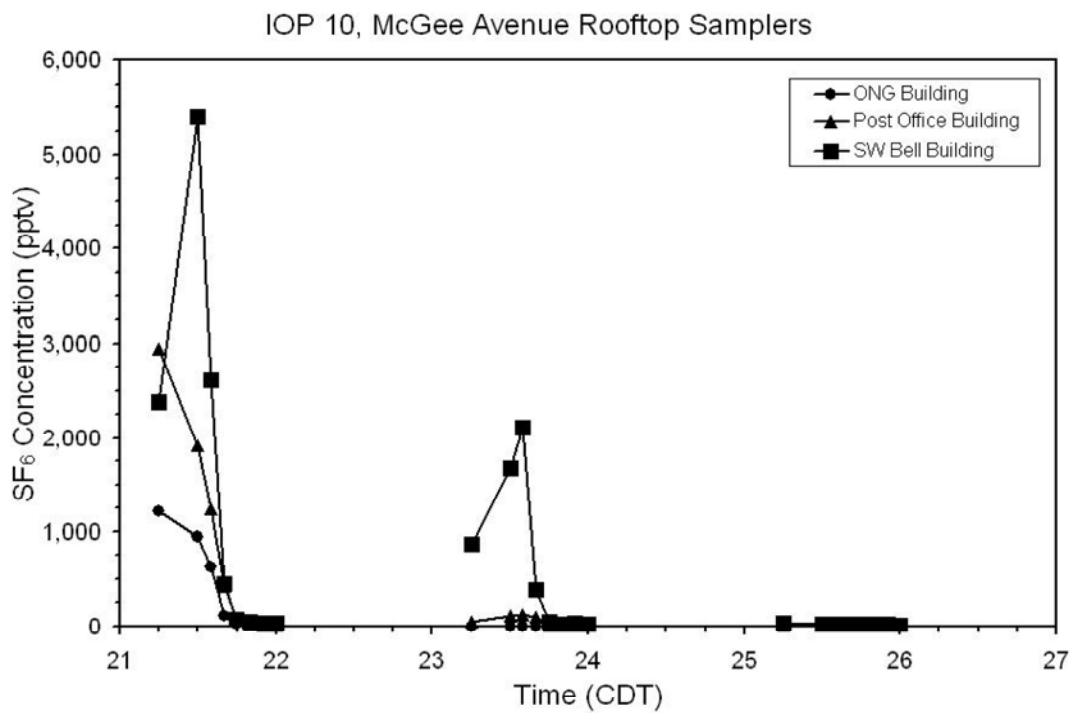


Figure F-39. Time history plots of the rooftop samplers located on Dean A. McGee Avenue during IOP 10.

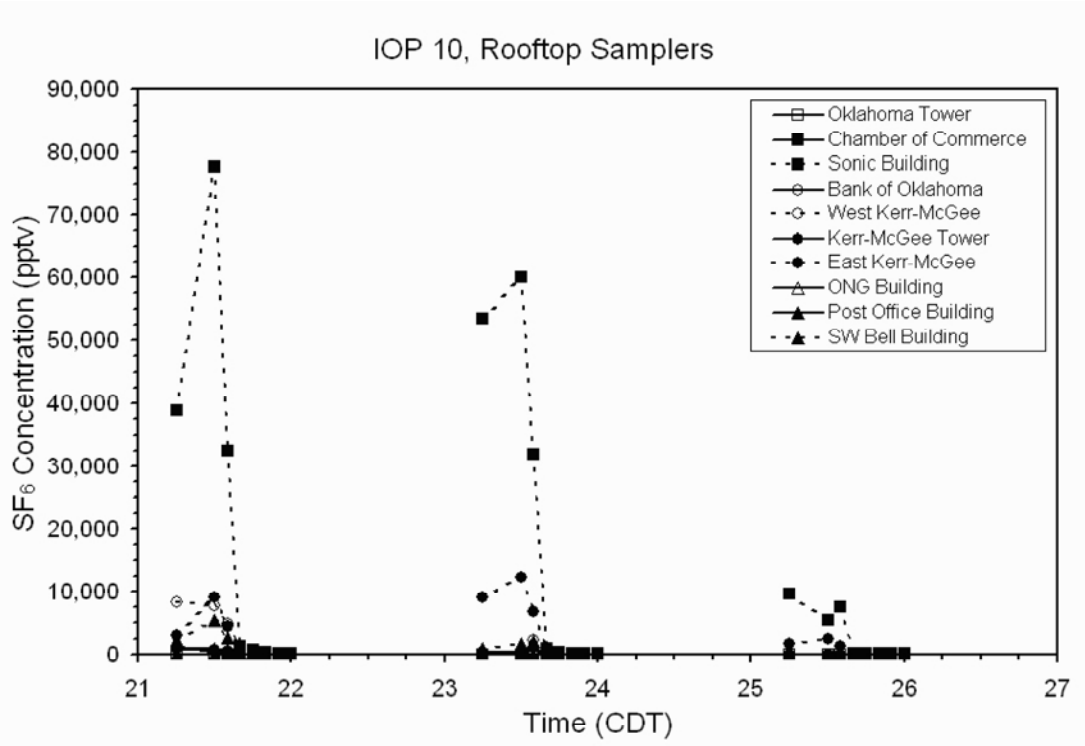


Figure F-40. Time history plots of all of the rooftop samplers during IOP 10.



## **APPENDIX G: SURFACE VS. ROOFTOP SAMPLER PLOTS**

Samplers were placed on the top of ten buildings across the CBD to measure the vertical transport of the SF<sub>6</sub> plume as it moved downwind of the release site. The ten rooftop samplers were placed on buildings where access was permitted and safe. The most desirable locations were building tops where samplers were already placed on the surface. Exact locations and building height information can be found in the Dissemination and Sampling section of the report. The paired surface and rooftop sampler time history plots for each IOP (Figs. G-1 to G-100) are graphed by SF<sub>6</sub> concentration (pptv) vs. time (CDT).

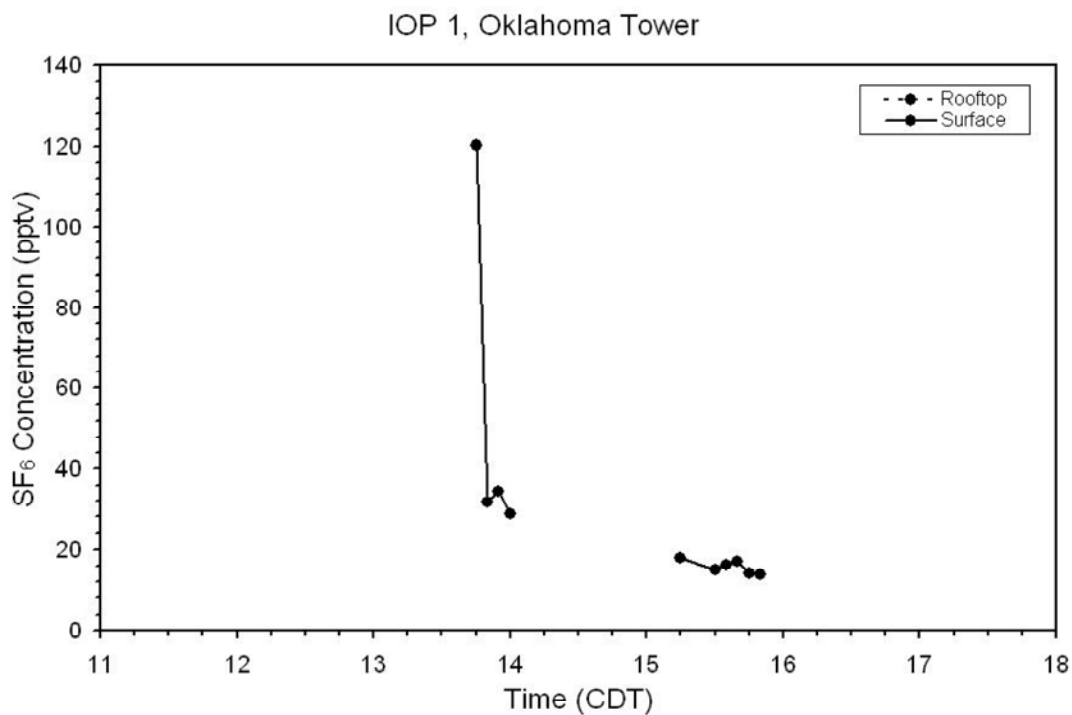


Figure G-1. Surface vs. rooftop time history plot of samplers located at the Oklahoma Tower during IOP 1.

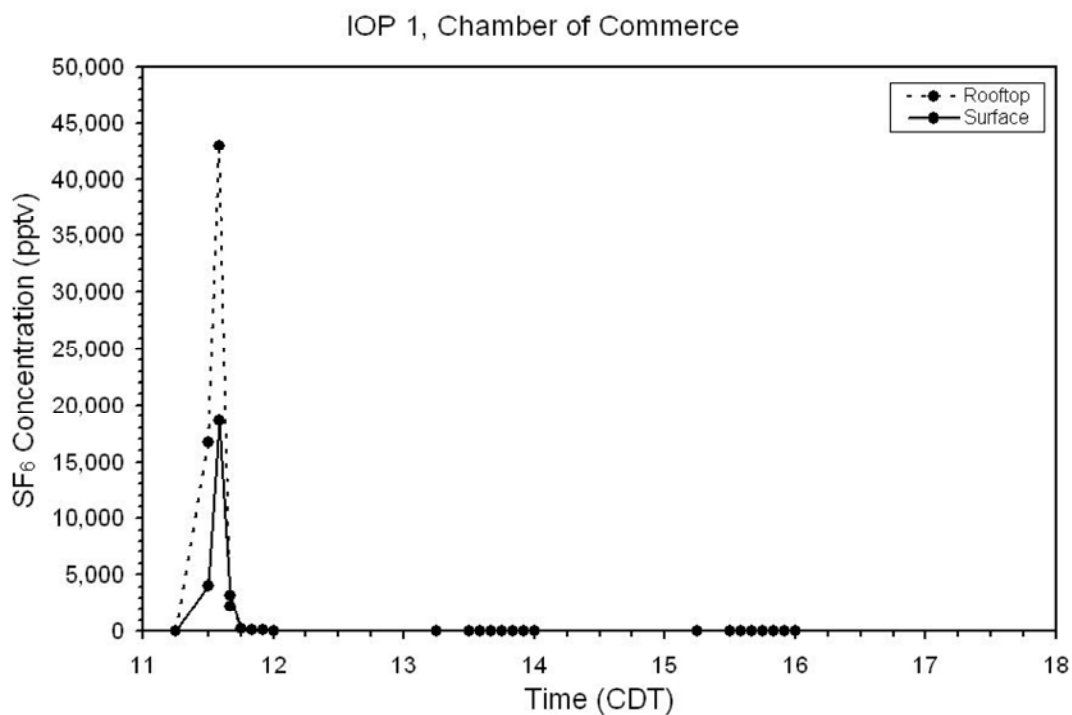
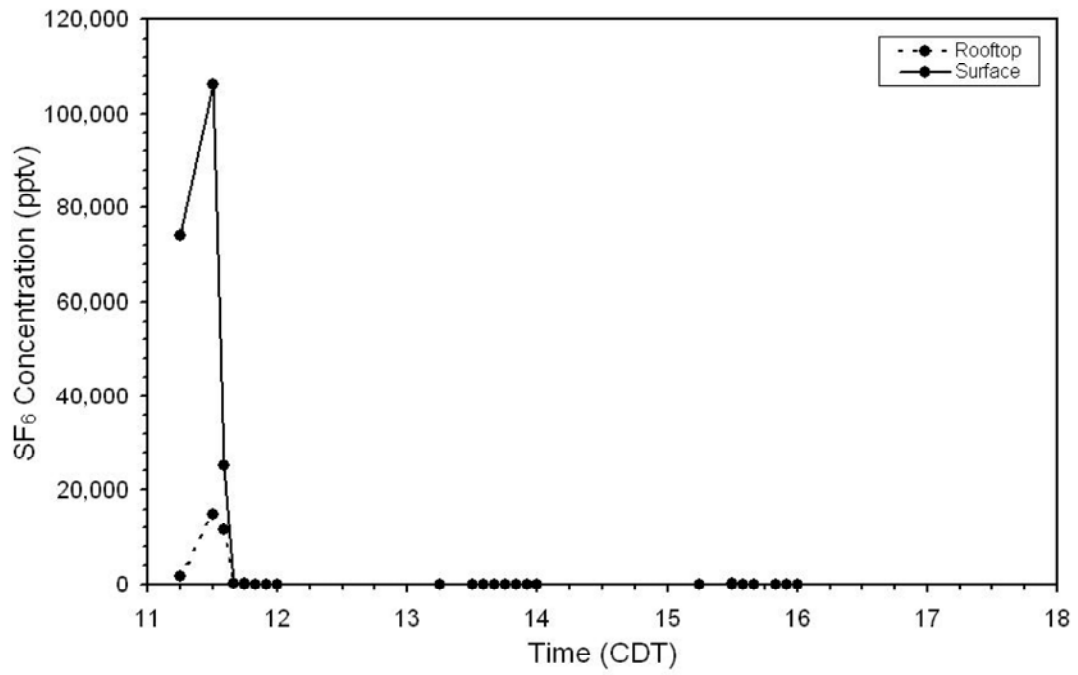
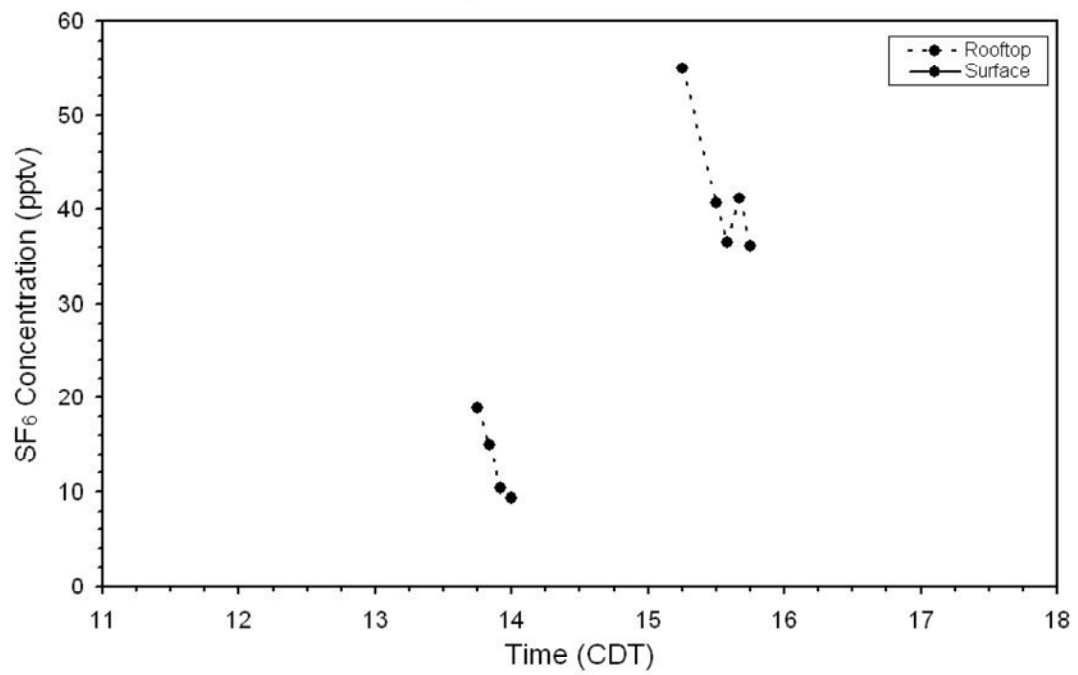


Figure G-2. Surface vs. rooftop time history plot of samplers located at the Chamber of Commerce during IOP 1.

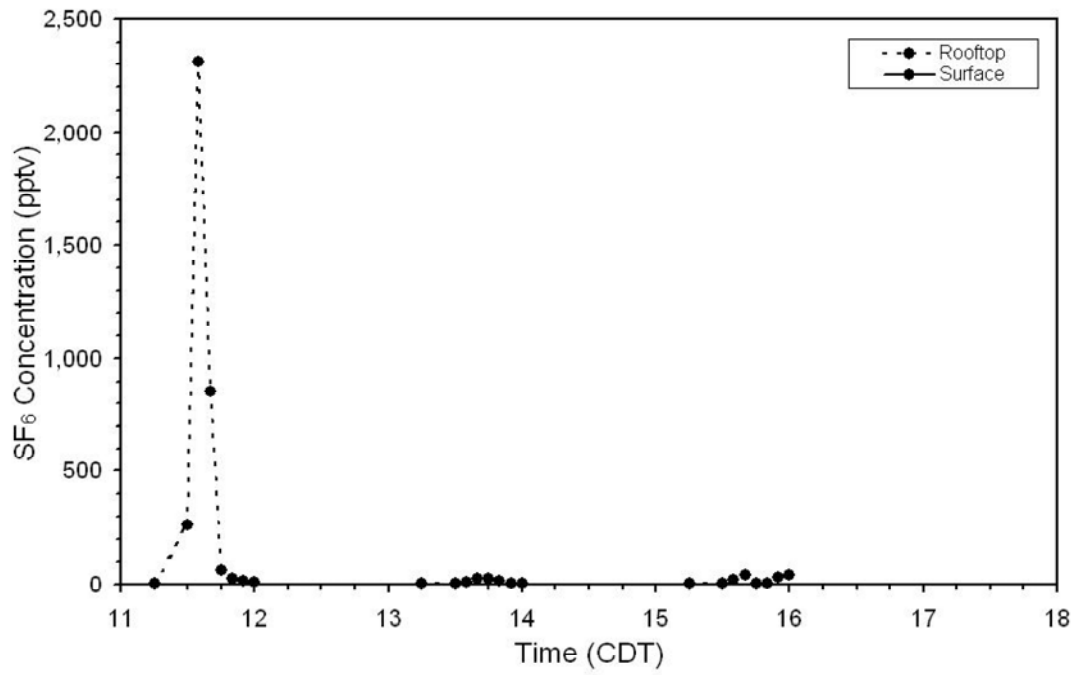
IOP 1, Sonic Building



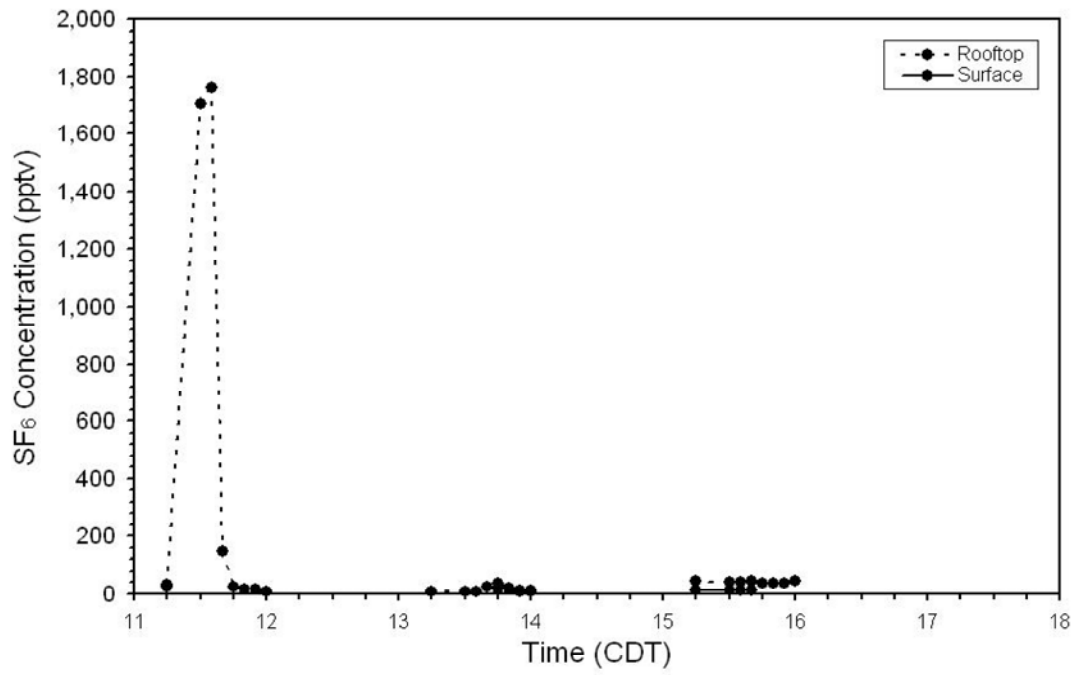
IOP 1, West Kerr Tower



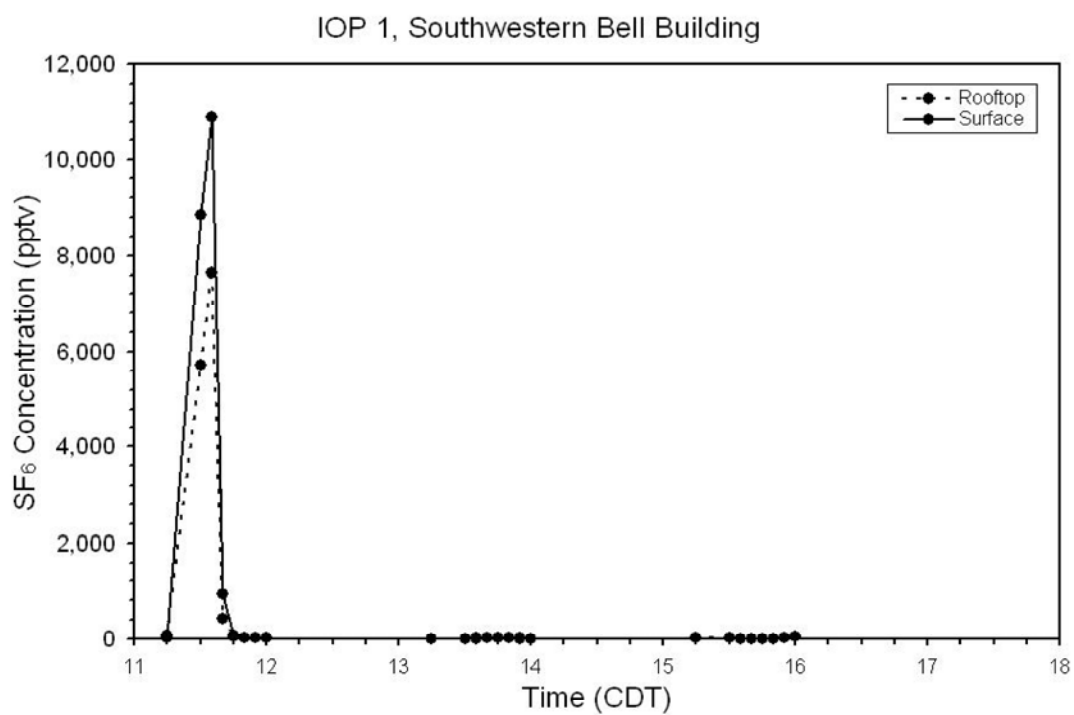
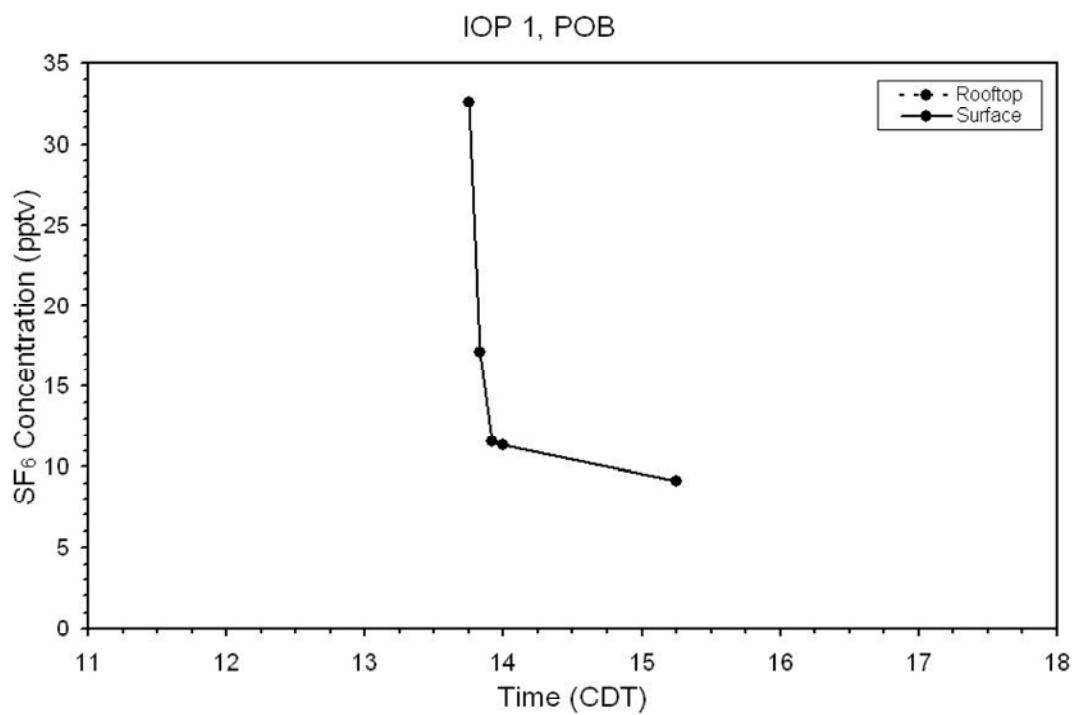
IOP 1, Bank of Oklahoma



IOP 1, Center Kerr Tower

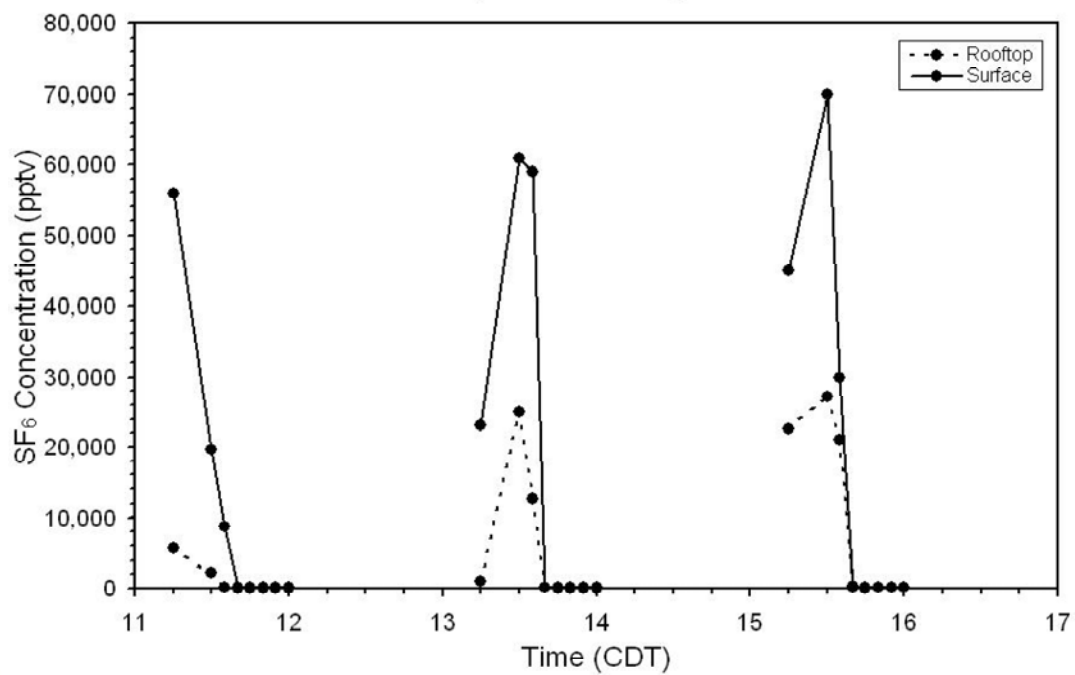




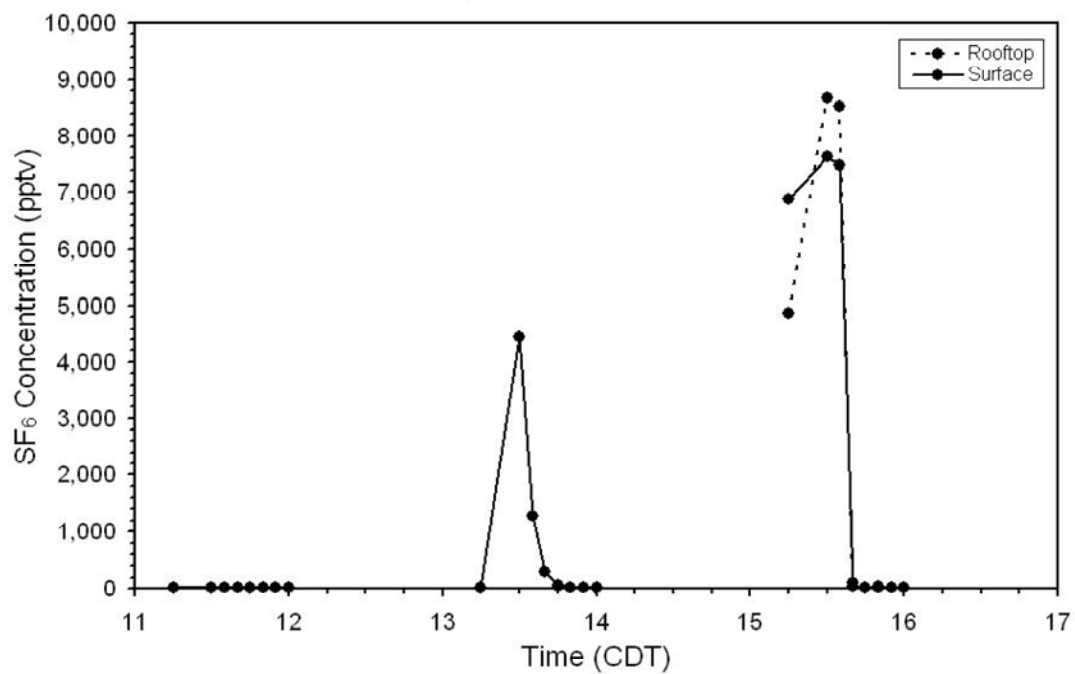




IOP 2, Sonic Building

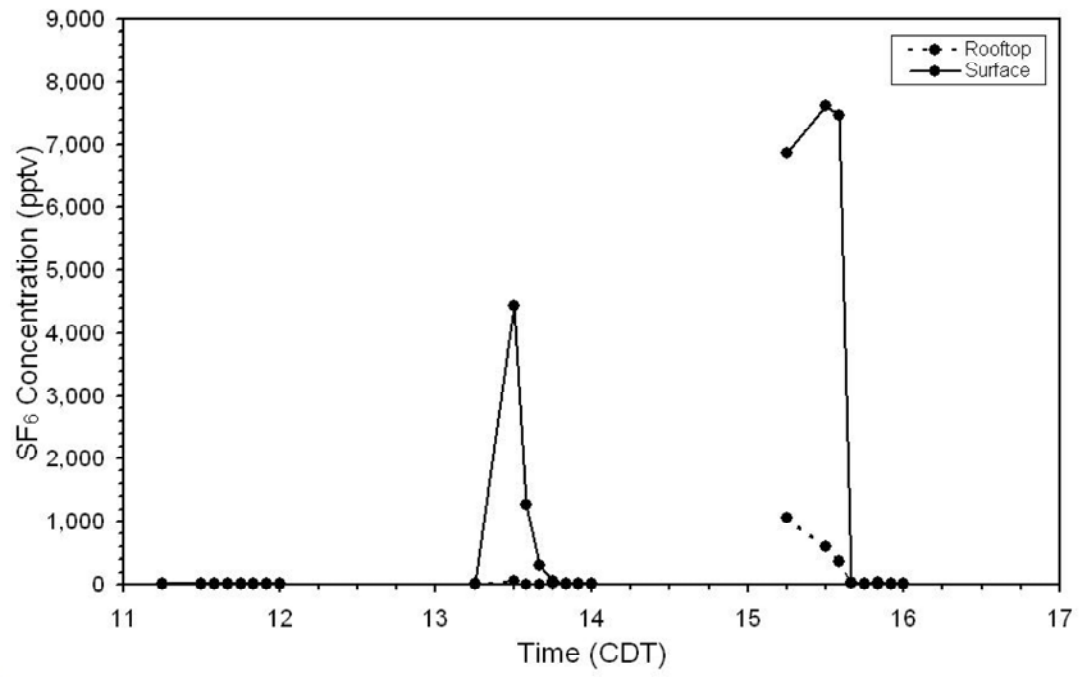


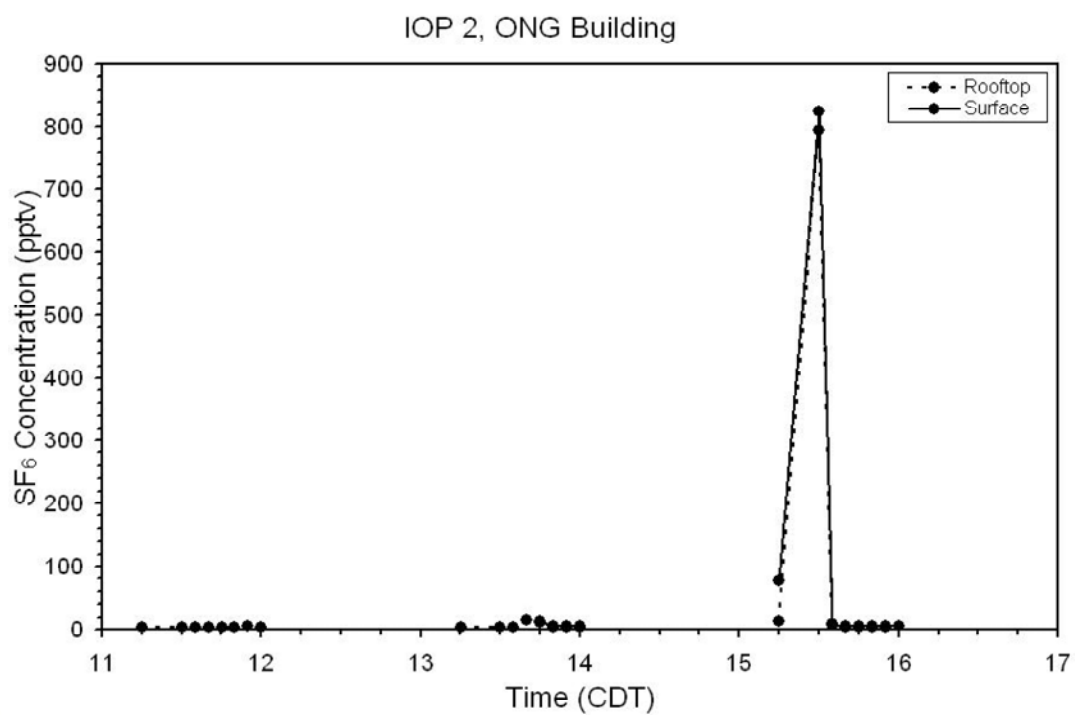
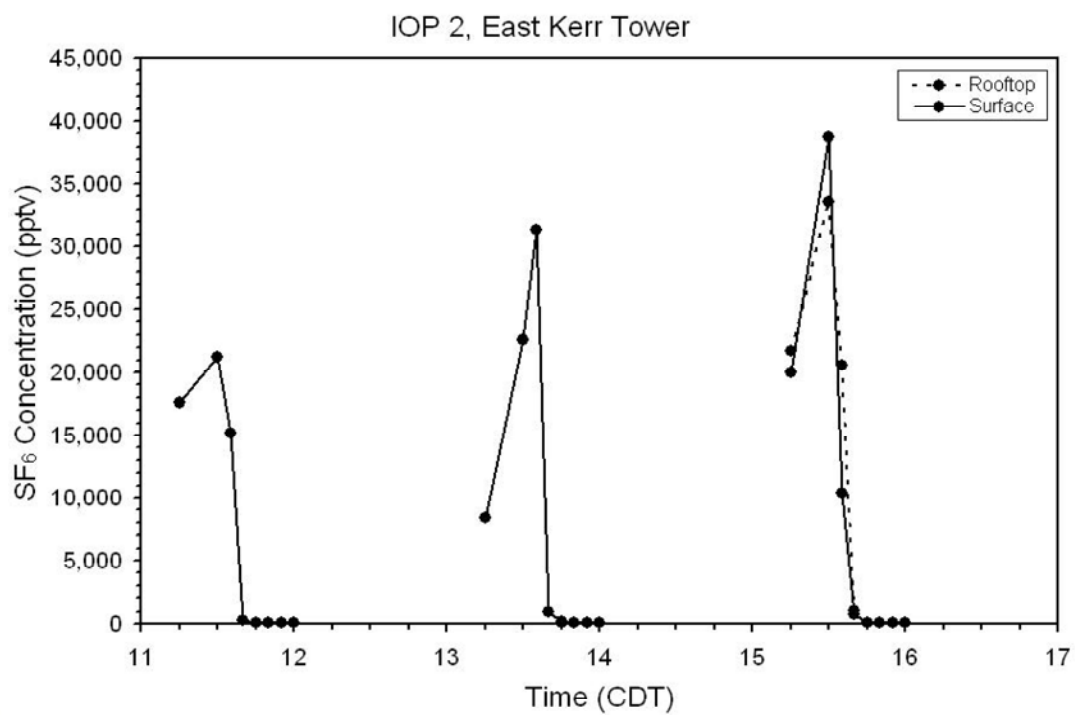
IOP 2, West Kerr Tower



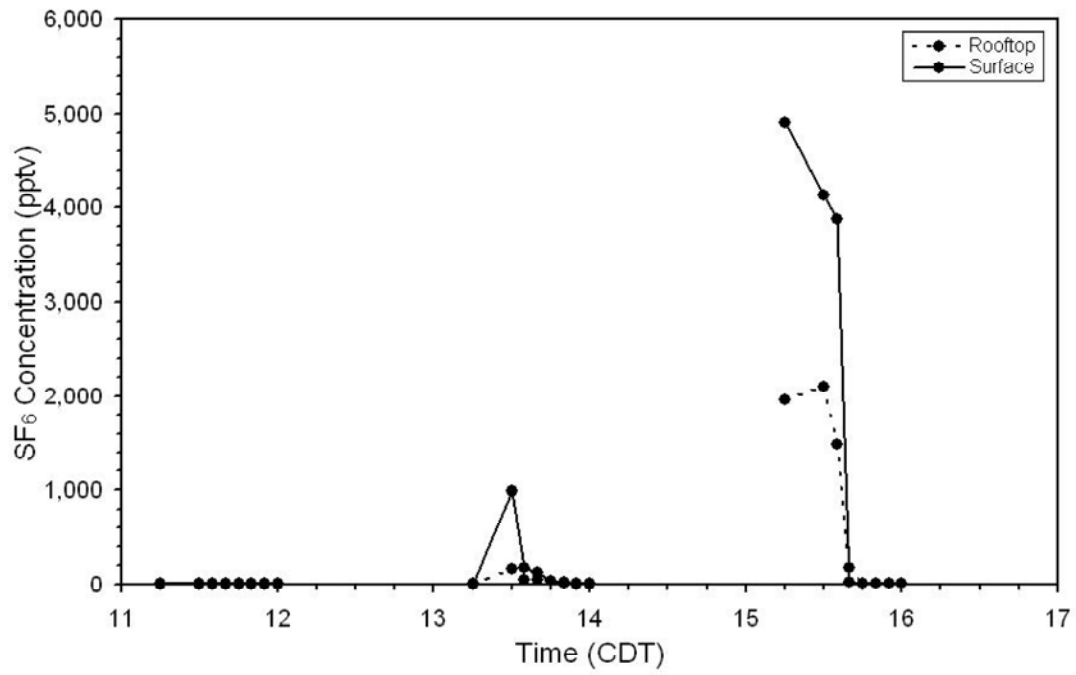


IOP 2, Bank of Oklahoma

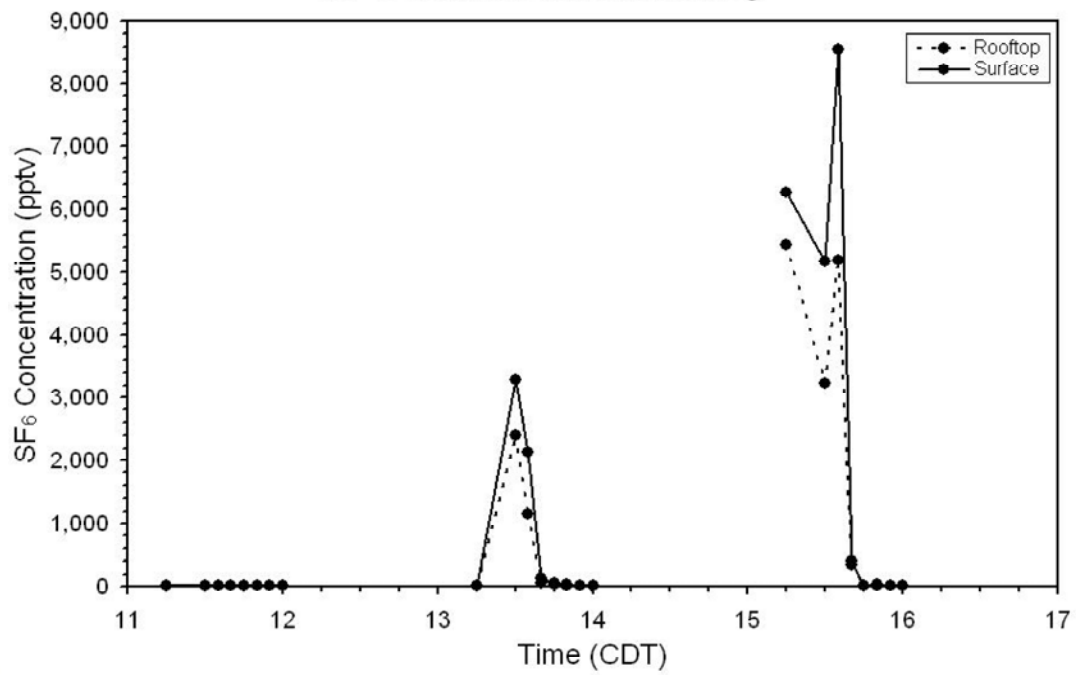


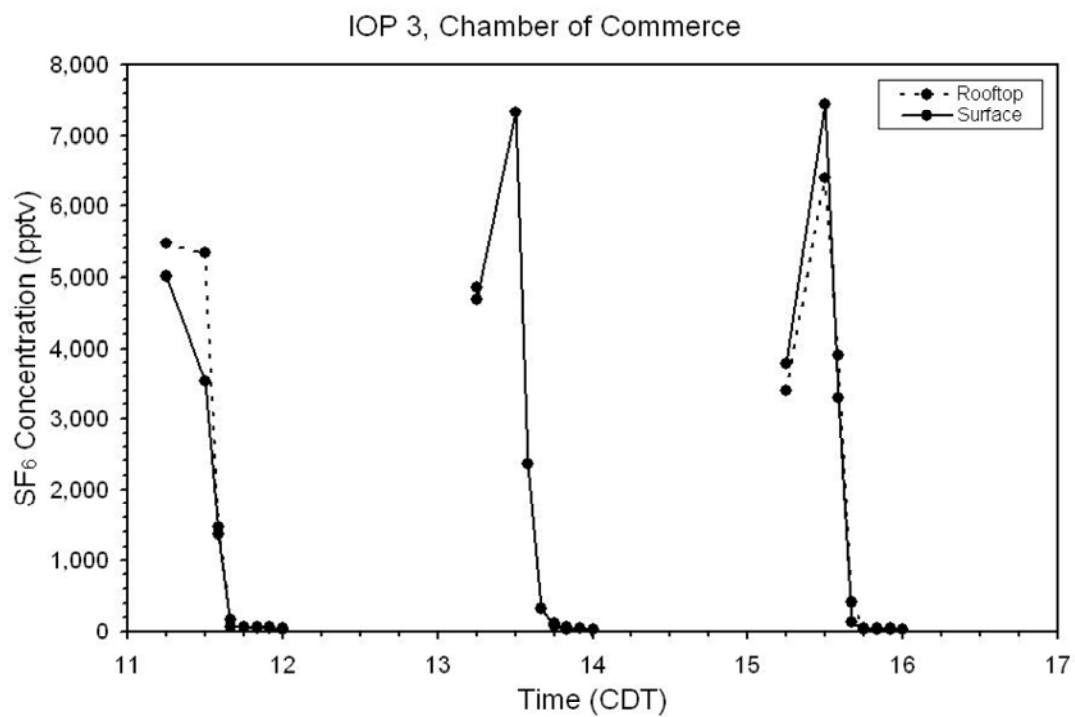
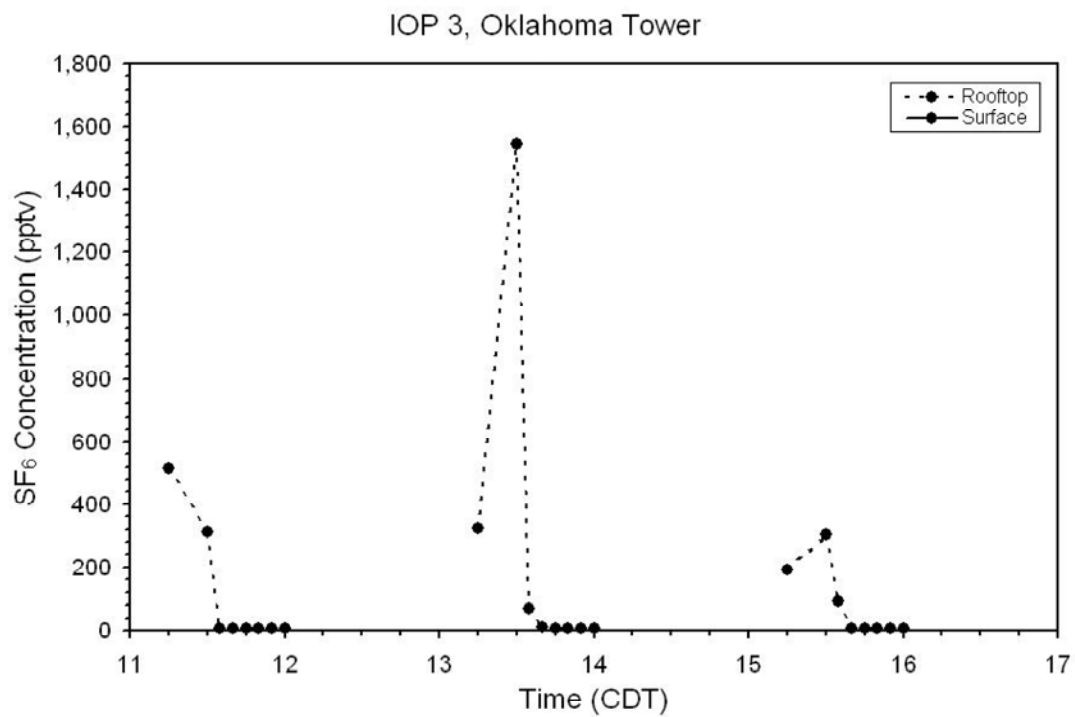


IOP 2, POB

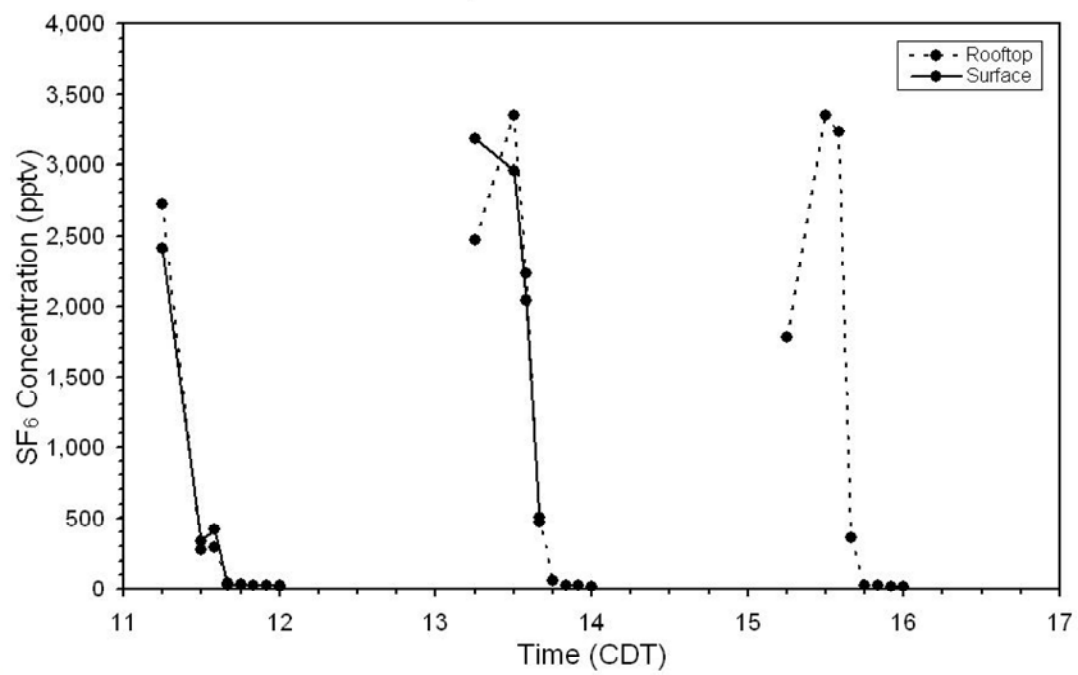


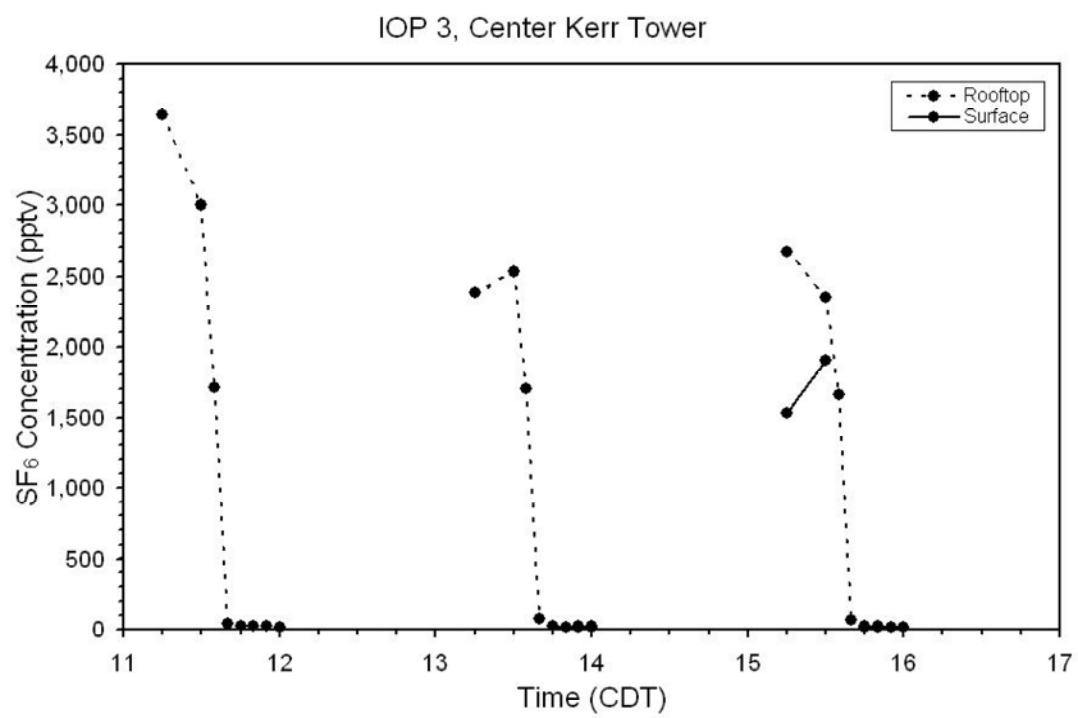
IOP 2, Southwestern Bell Building



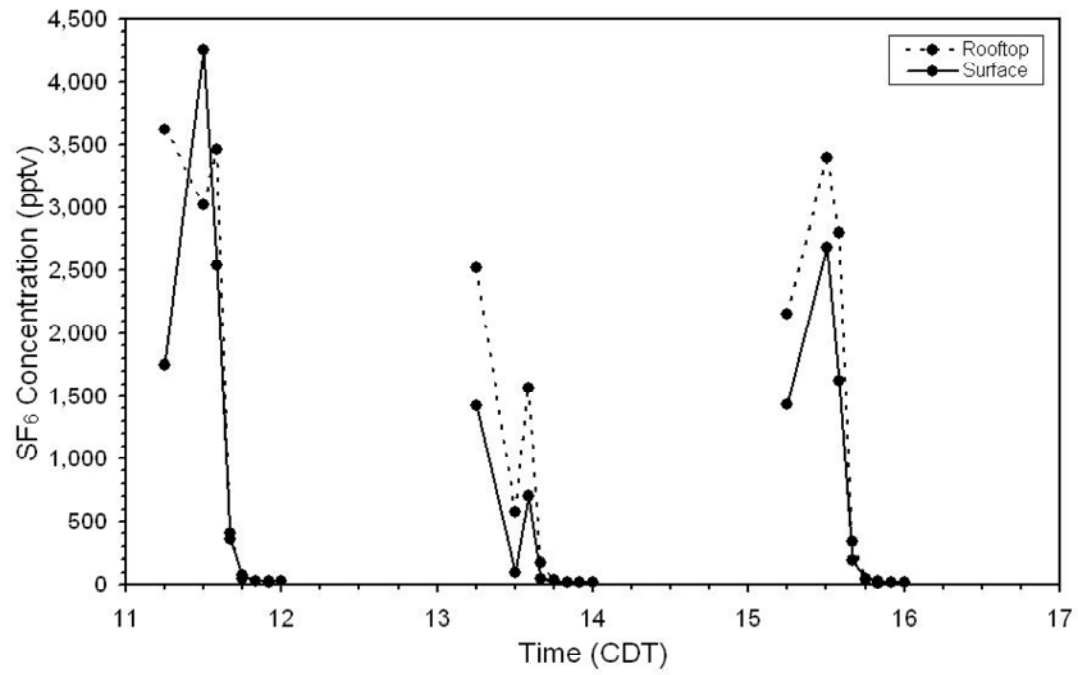


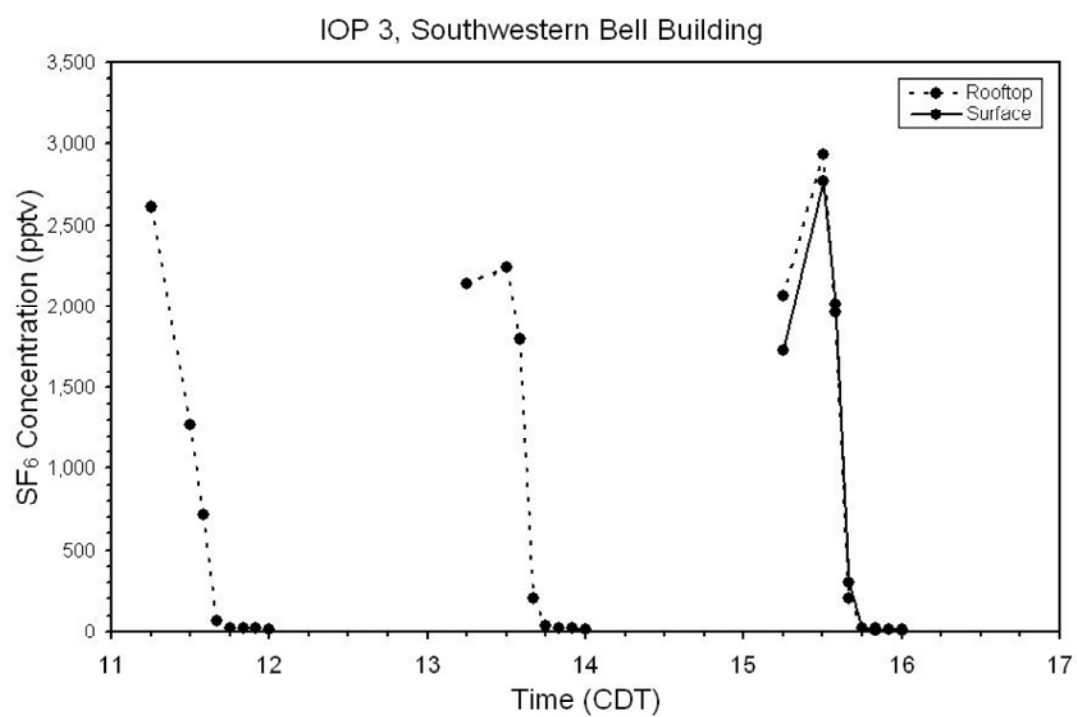
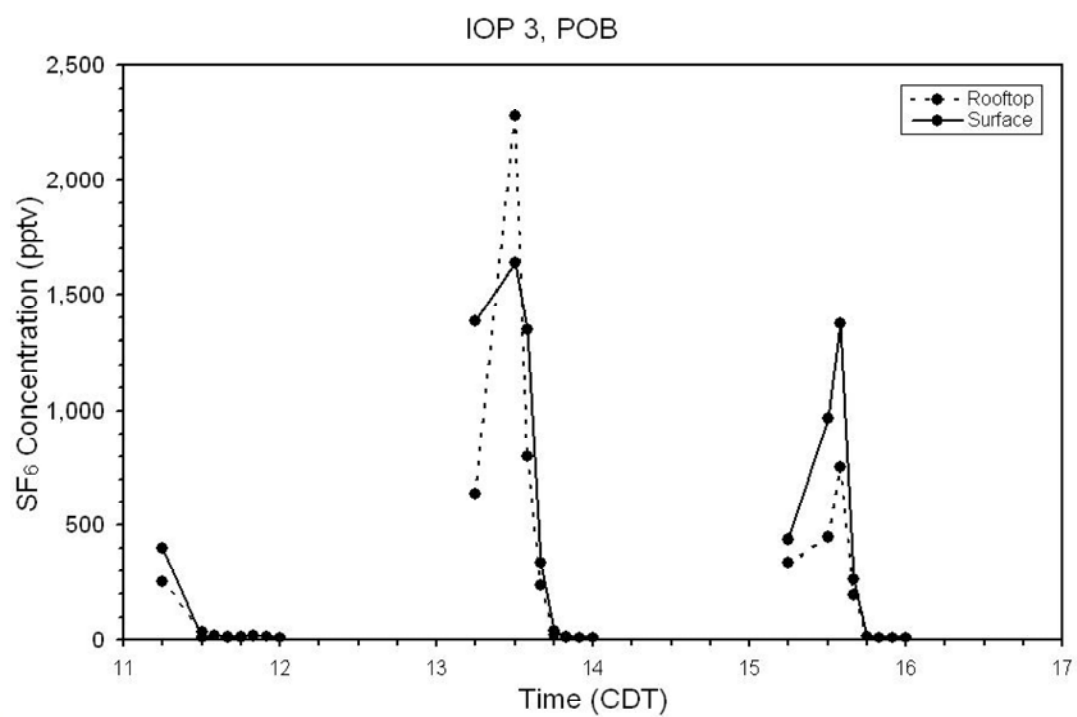
IOP 3, West Kerr Tower





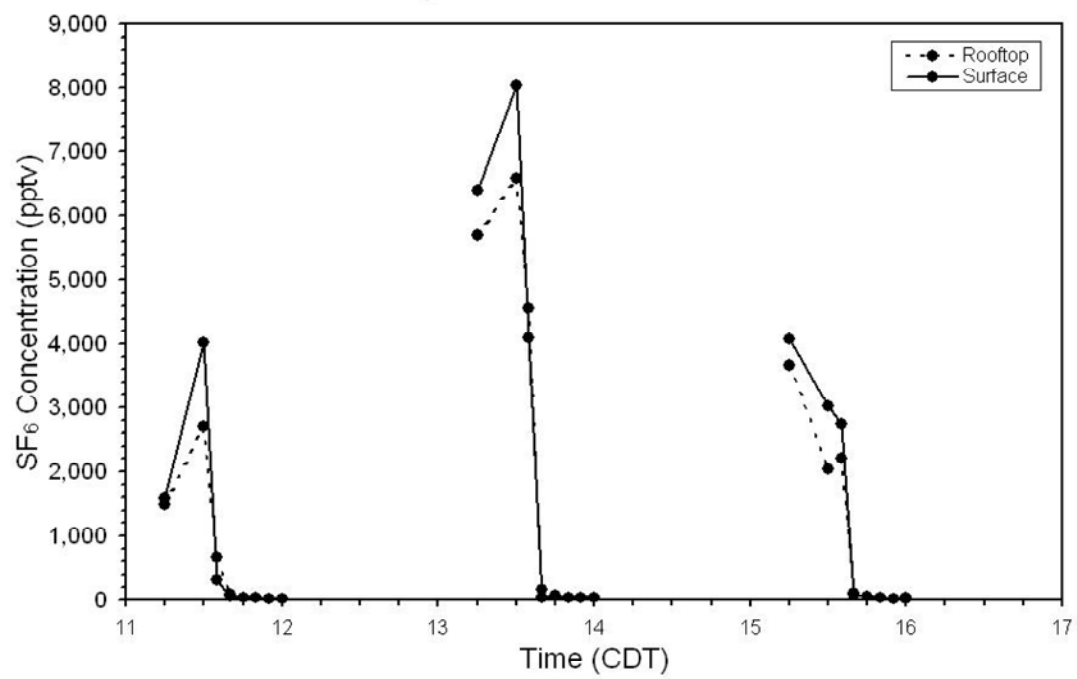
IOP 3, East Kerr Tower



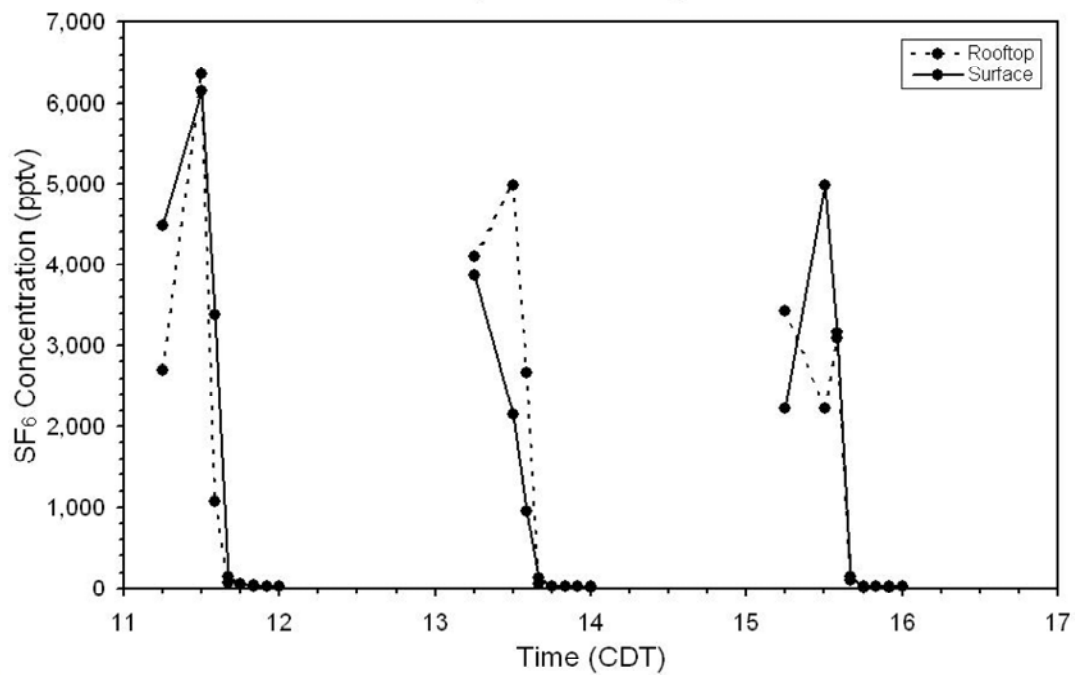




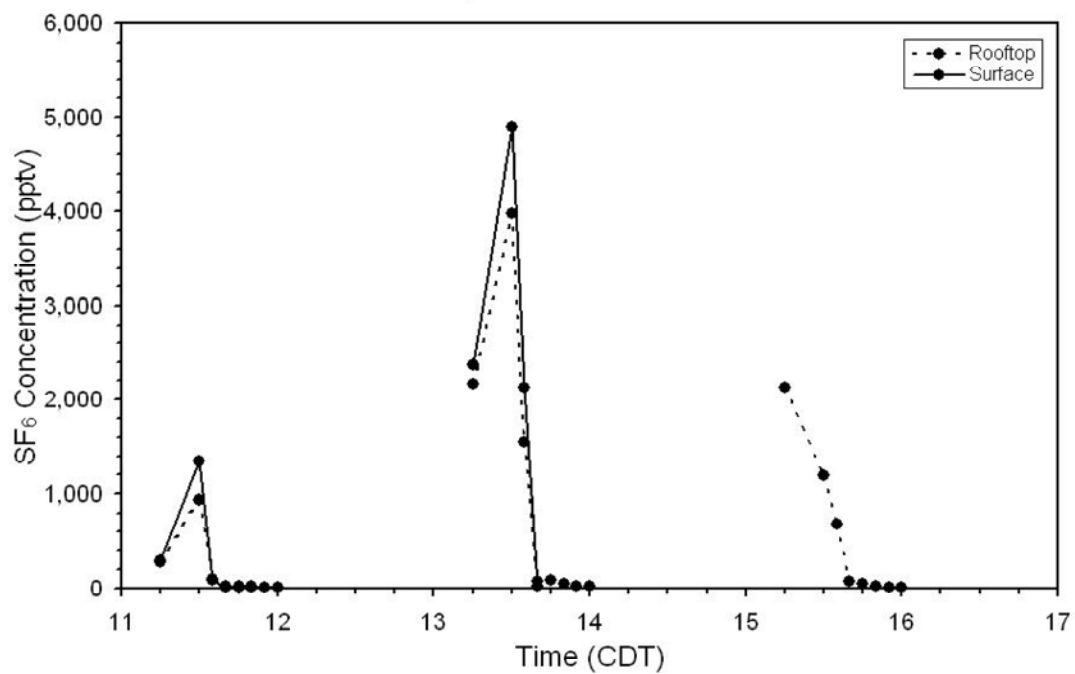
IOP 4, Chamber of Commerce



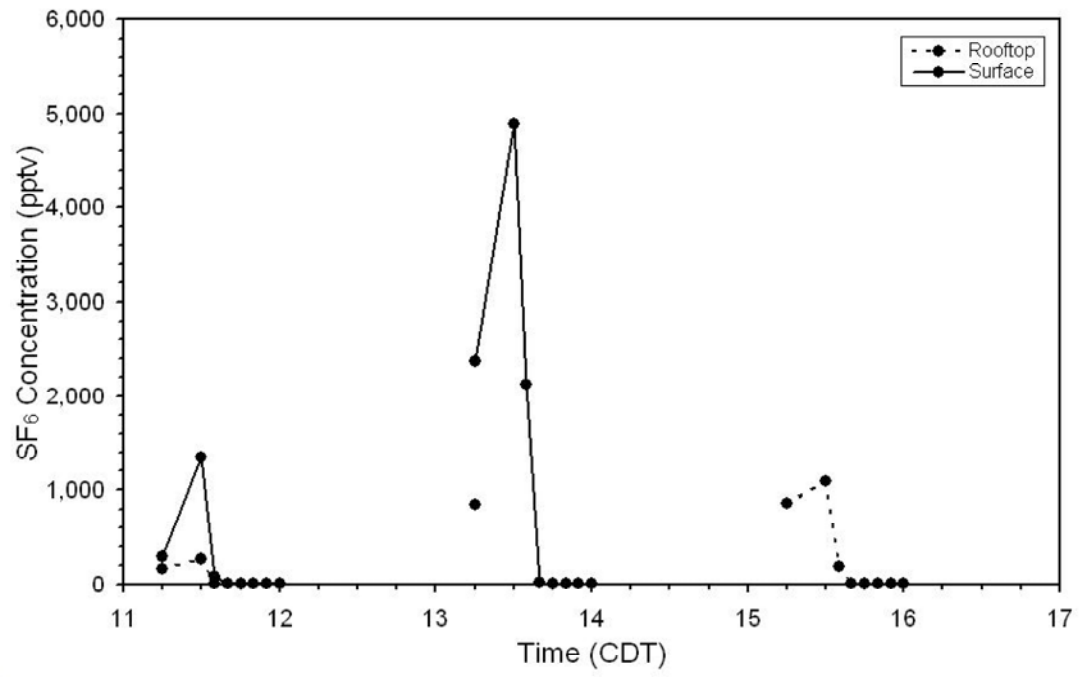
IOP 4, Sonic Building



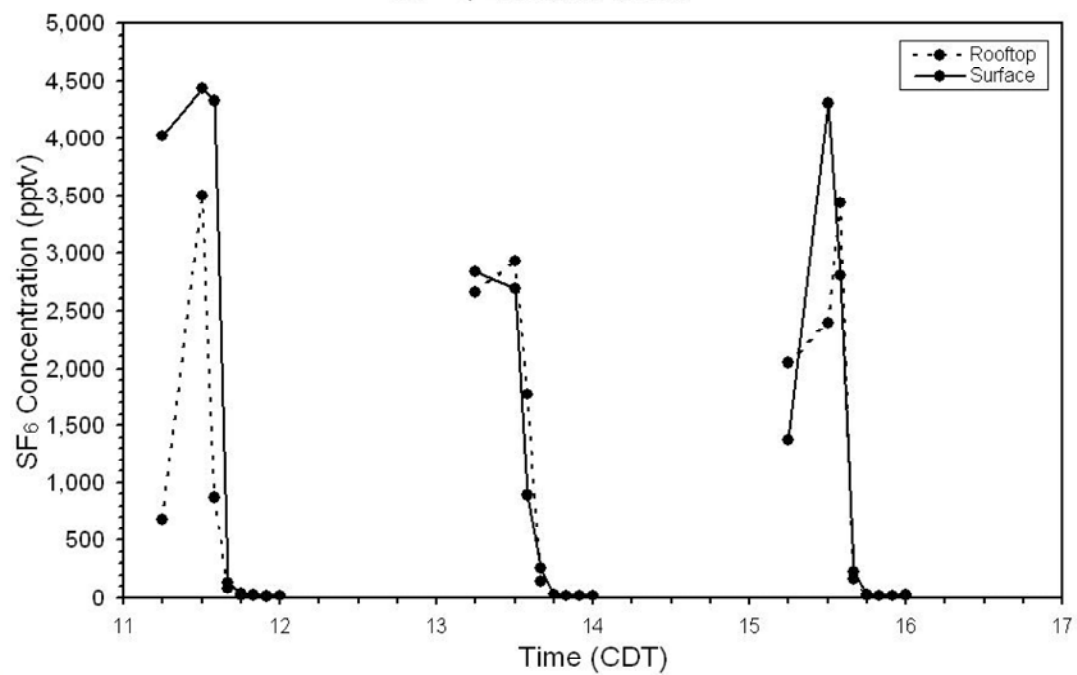
IOP 4, West Kerr Tower



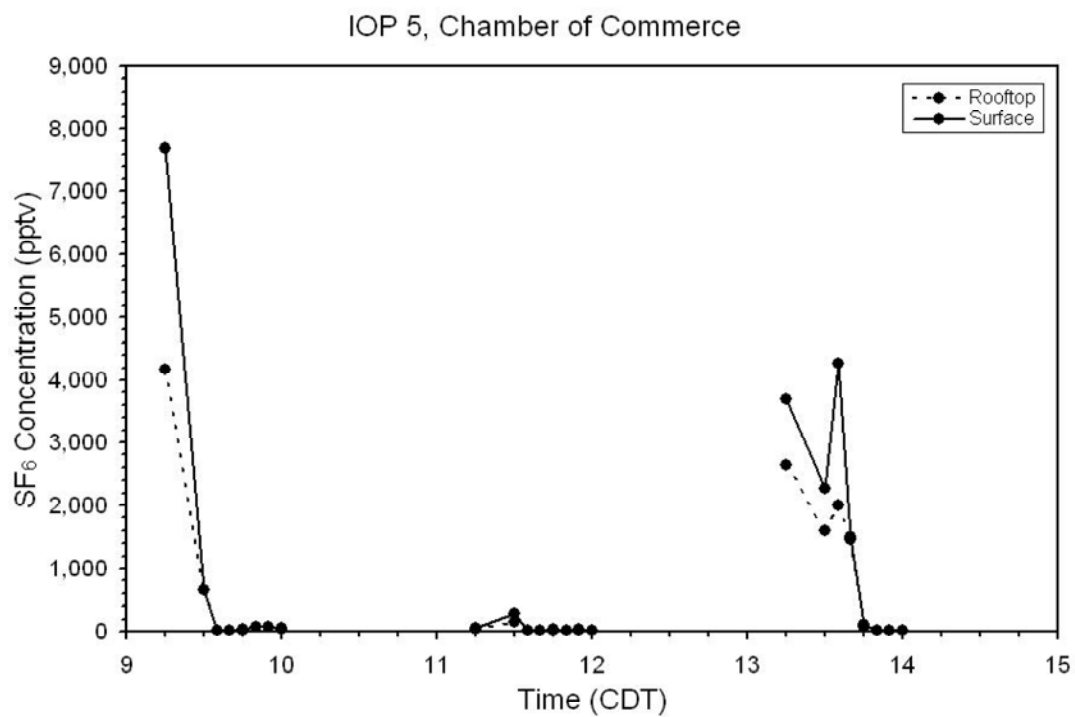
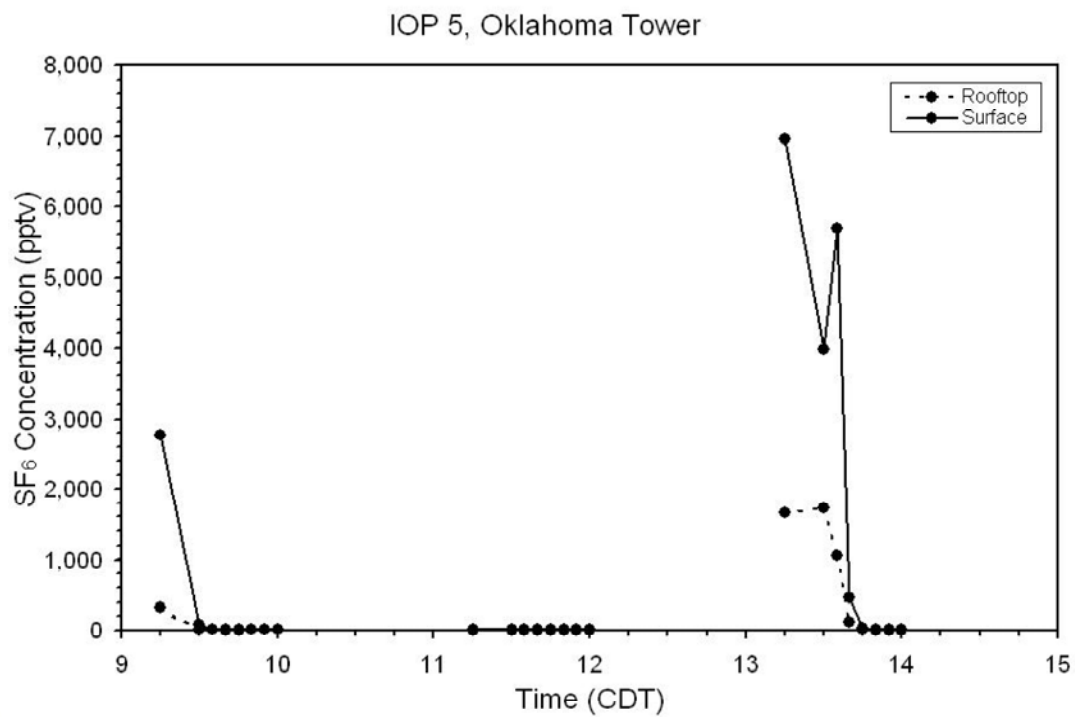
IOP 4, Bank of Oklahoma



IOP 4, East Kerr Tower

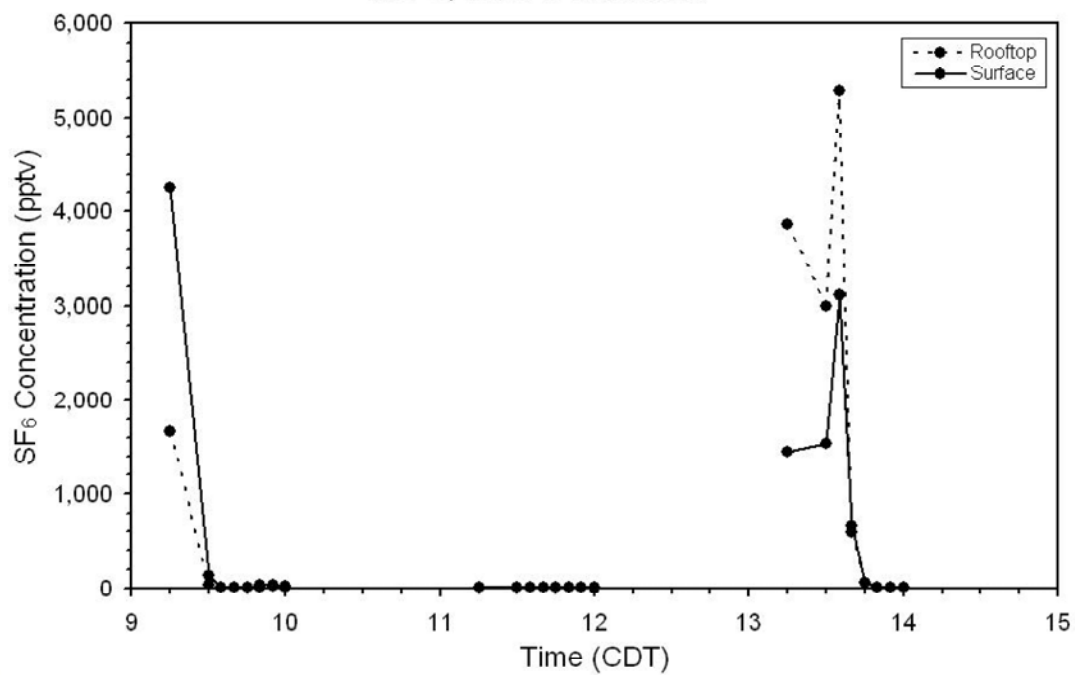




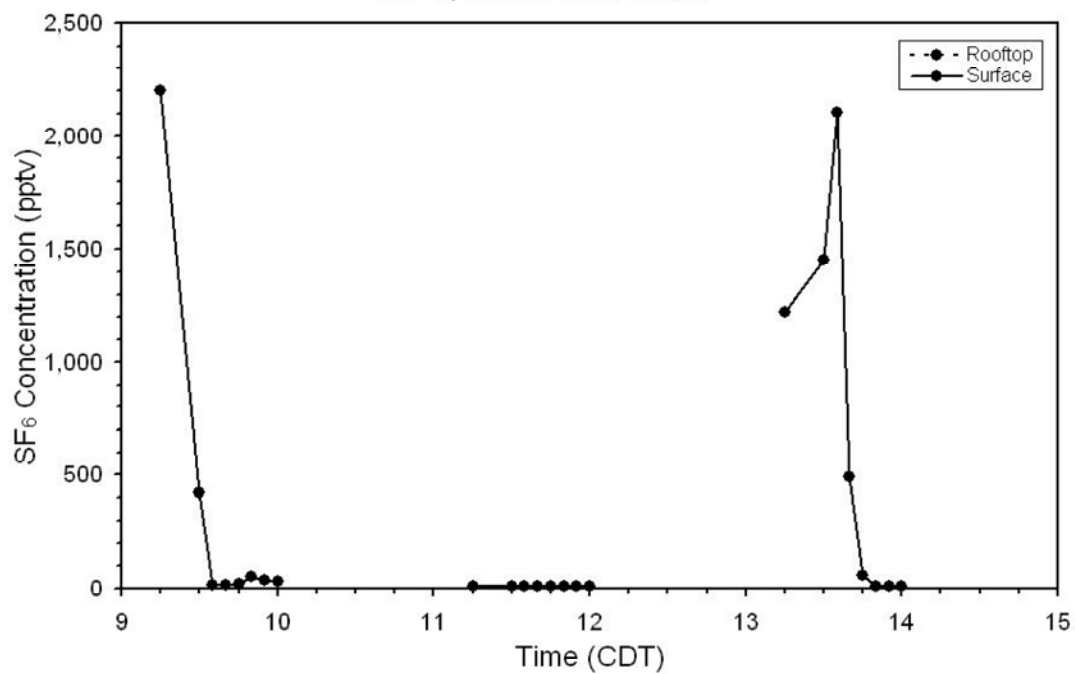




IOP 5, Bank of Oklahoma



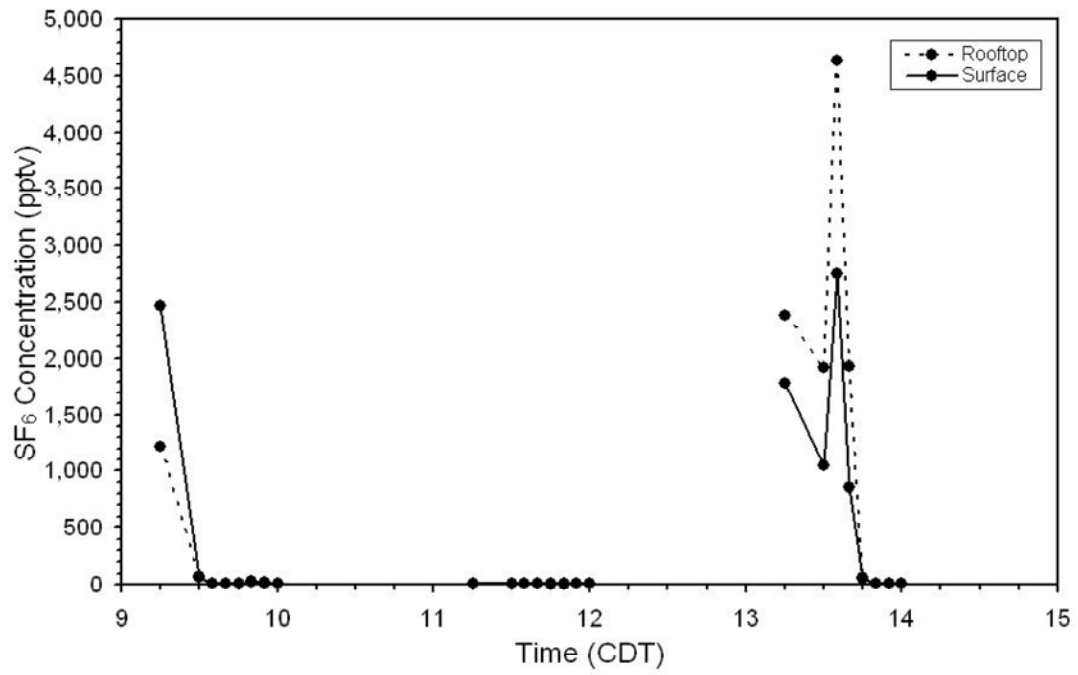
IOP 5, Center Kerr Tower



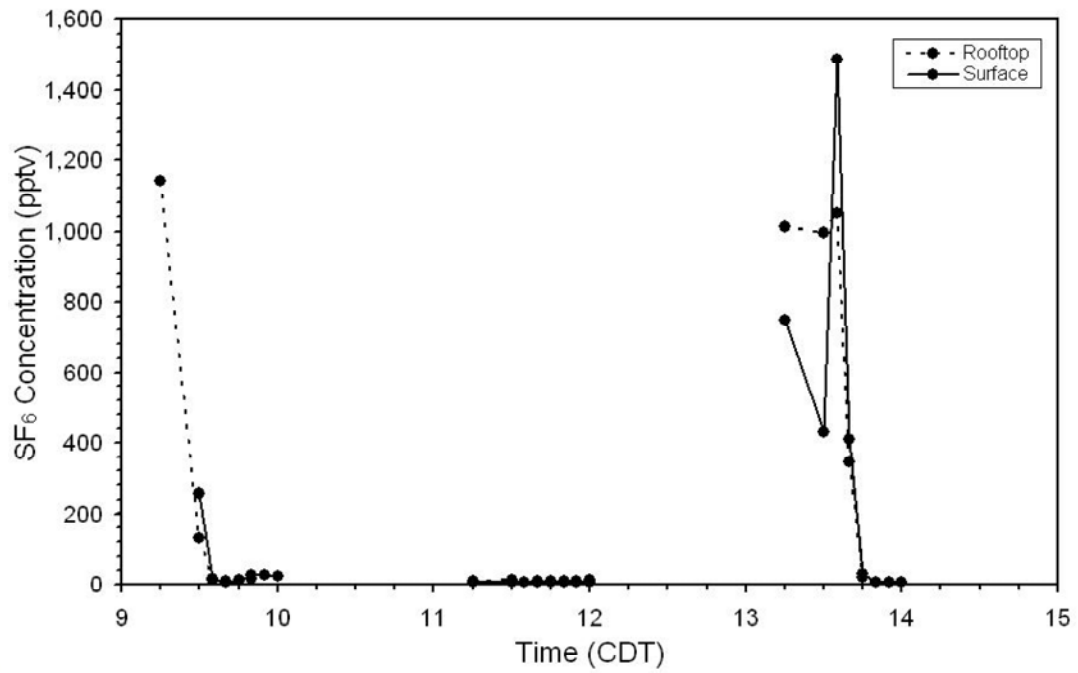




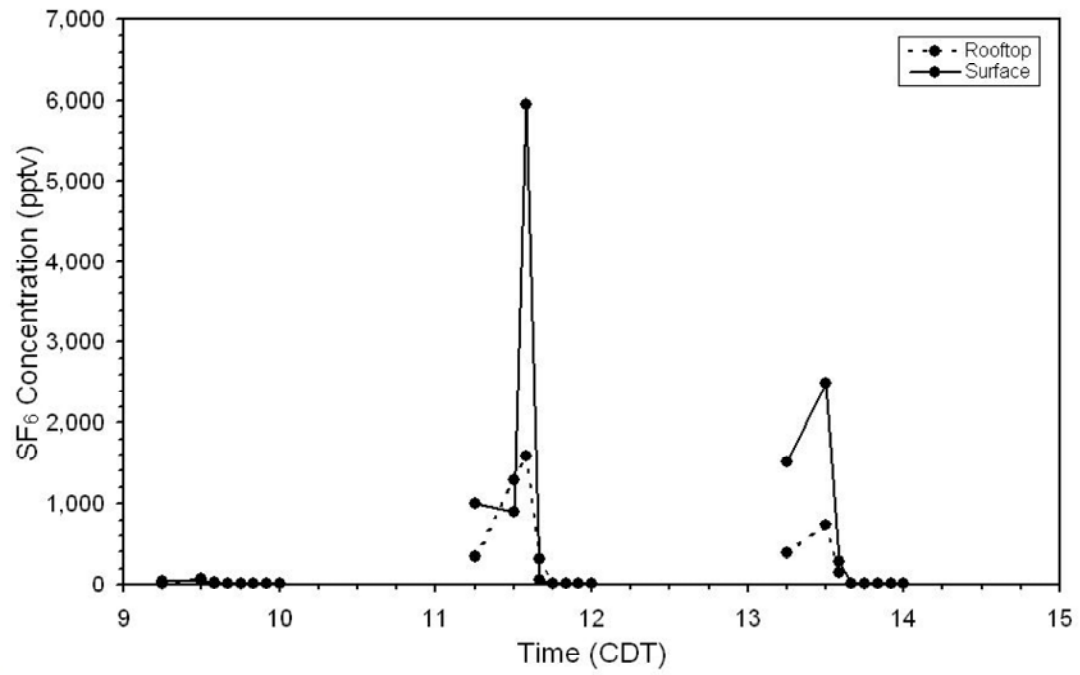
IOP 5, POB

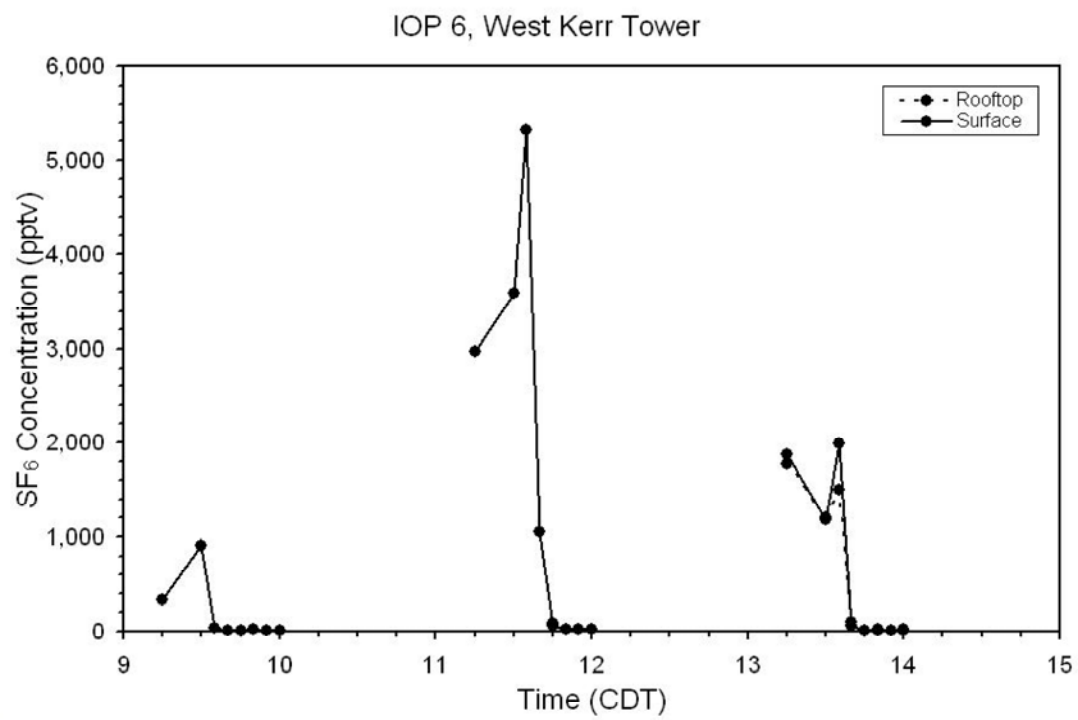


IOP 5, Southwestern Bell Building



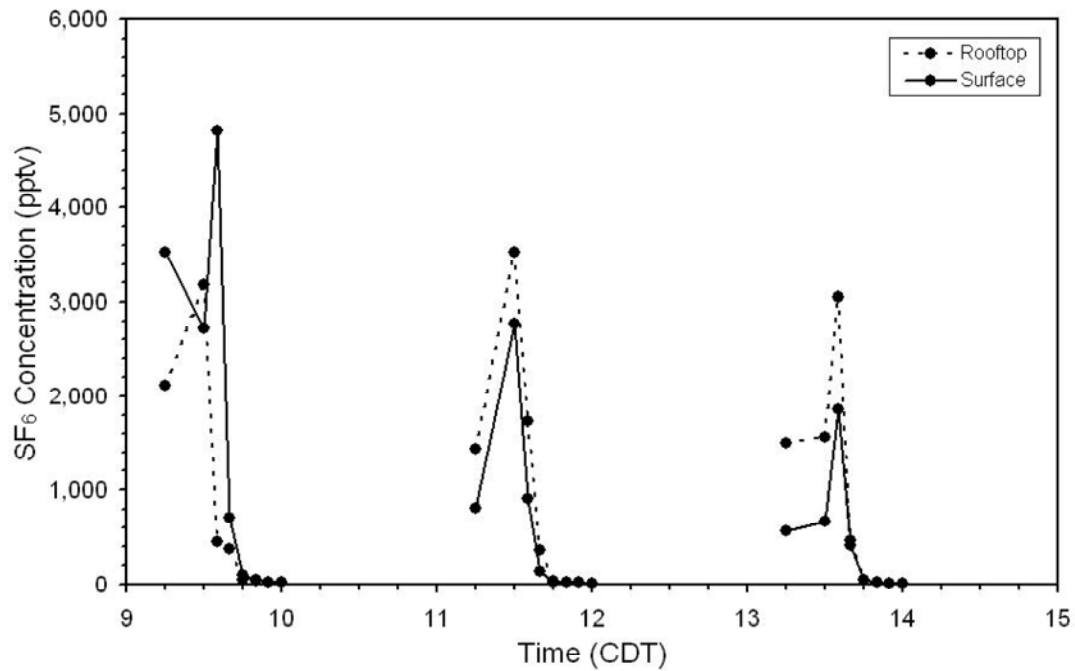
IOP 6, Oklahoma Tower



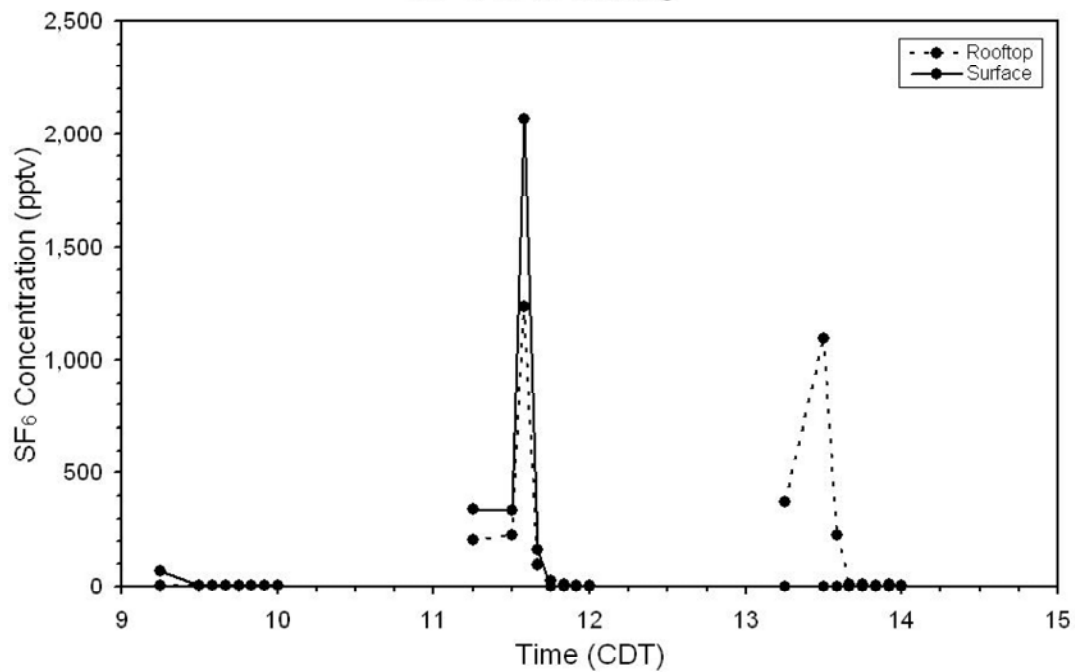


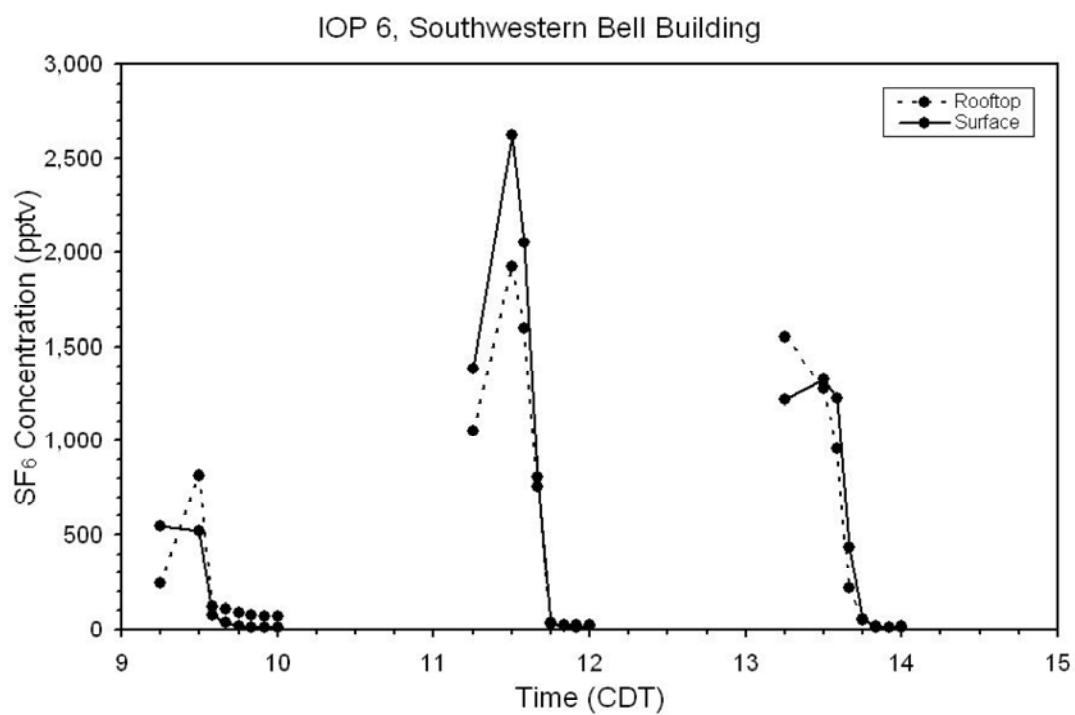
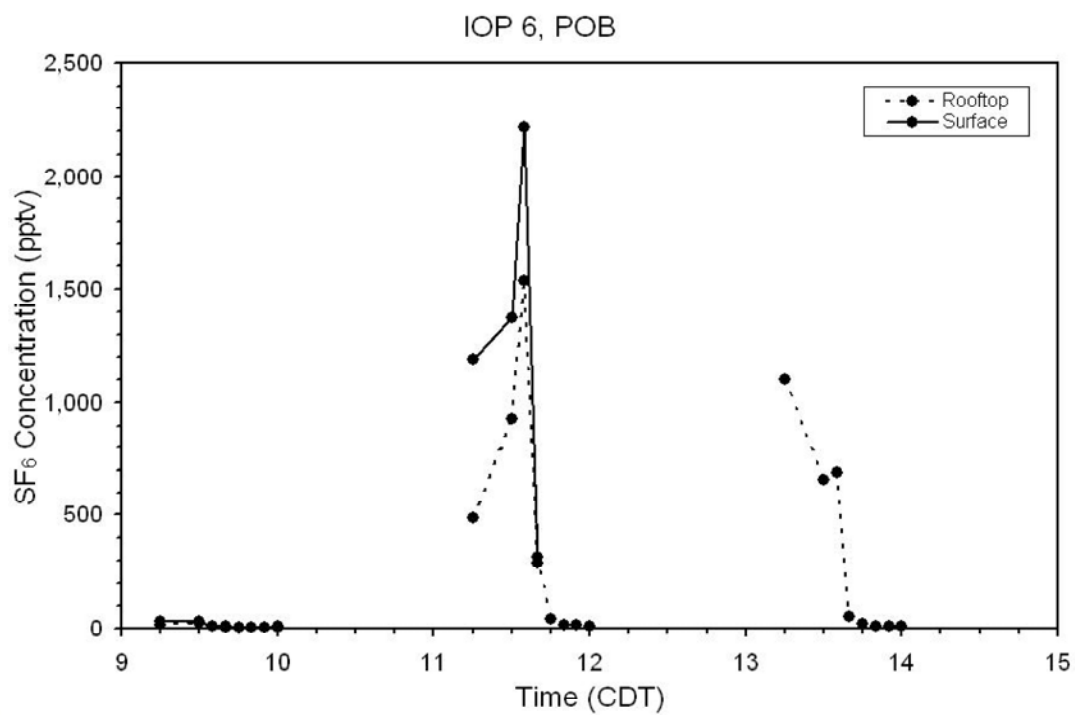


IOP 6, East Kerr Tower



IOP 6, ONG Building

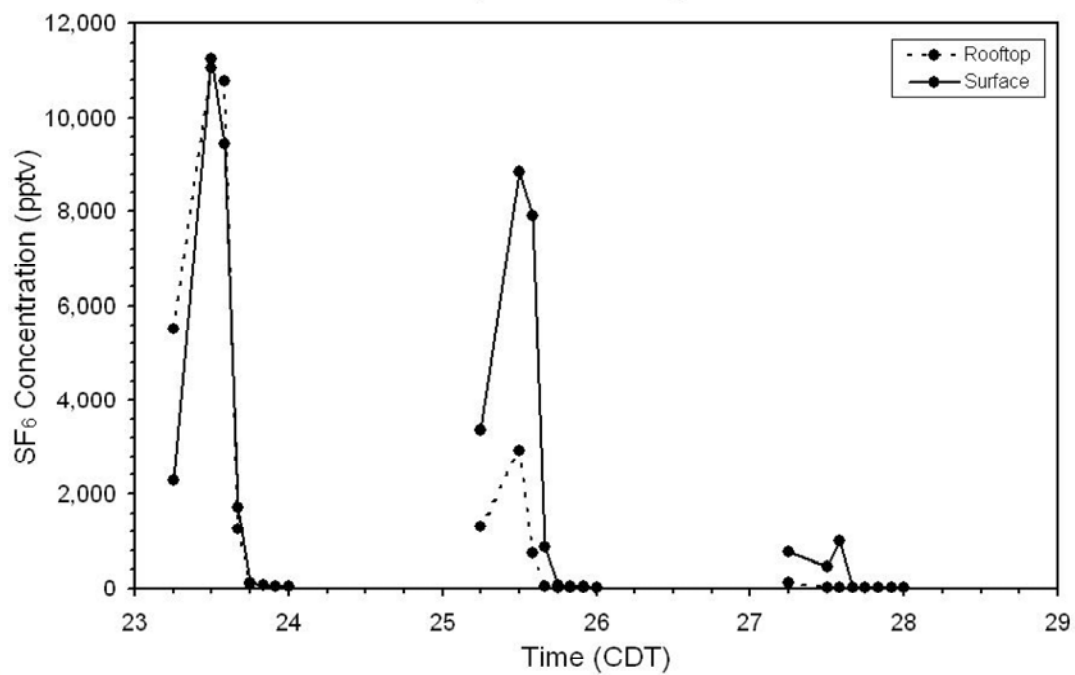




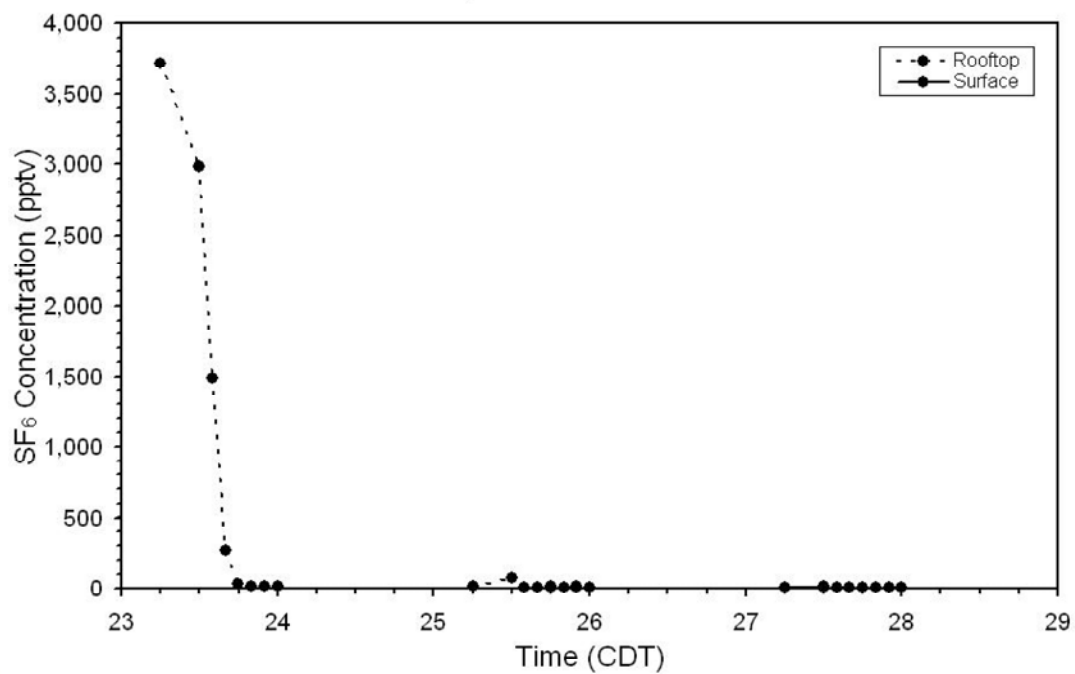




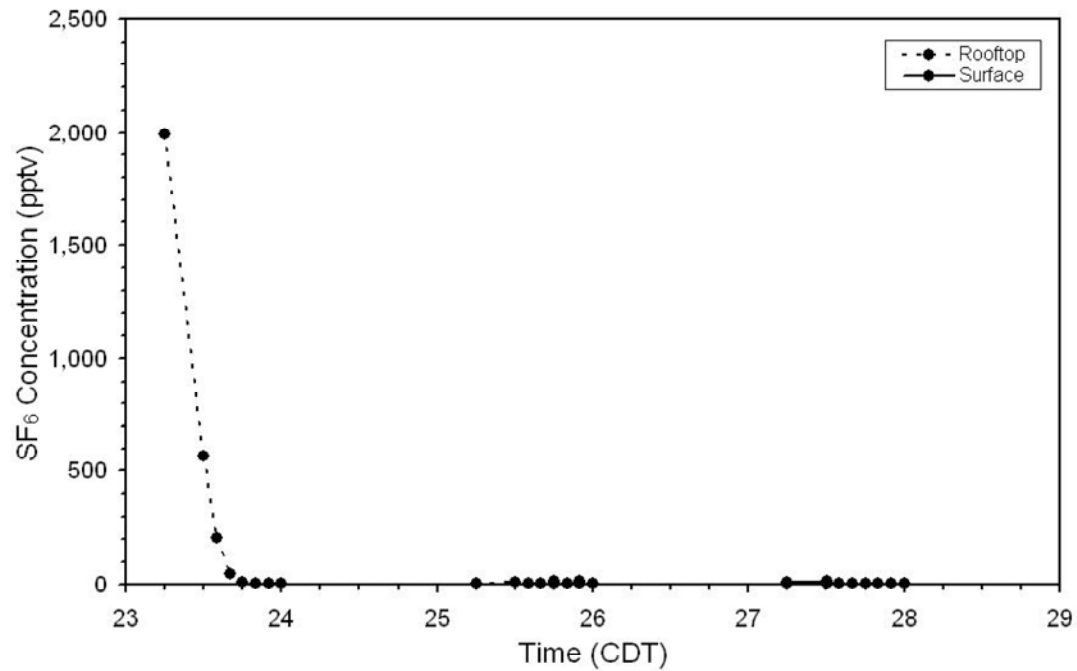
IOP 7, Sonic Building



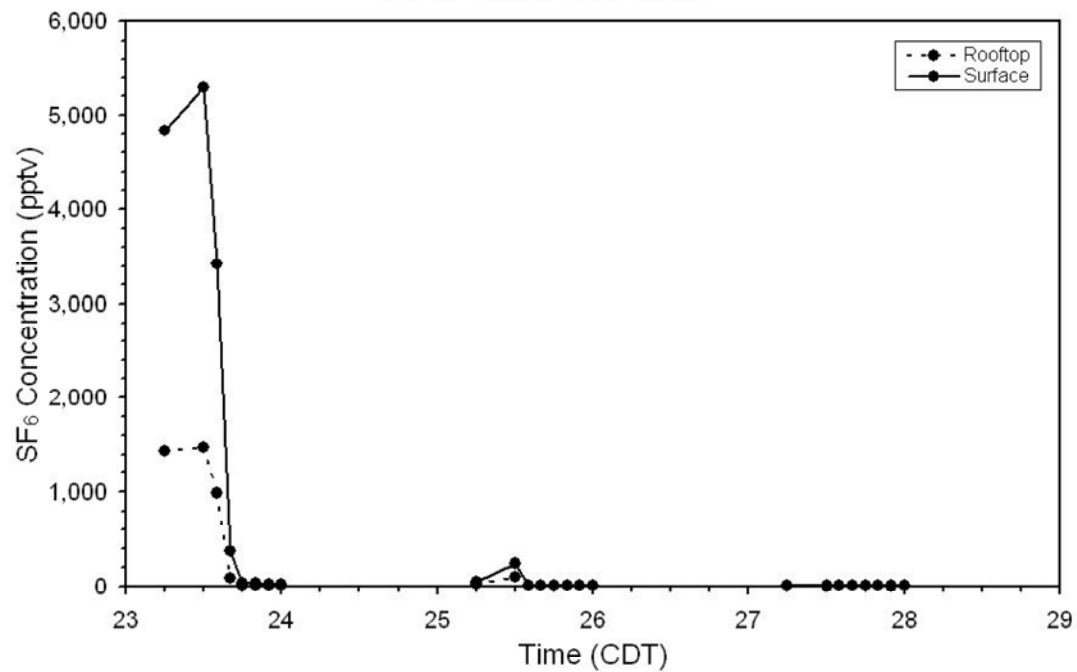
IOP 7, West Kerr Tower

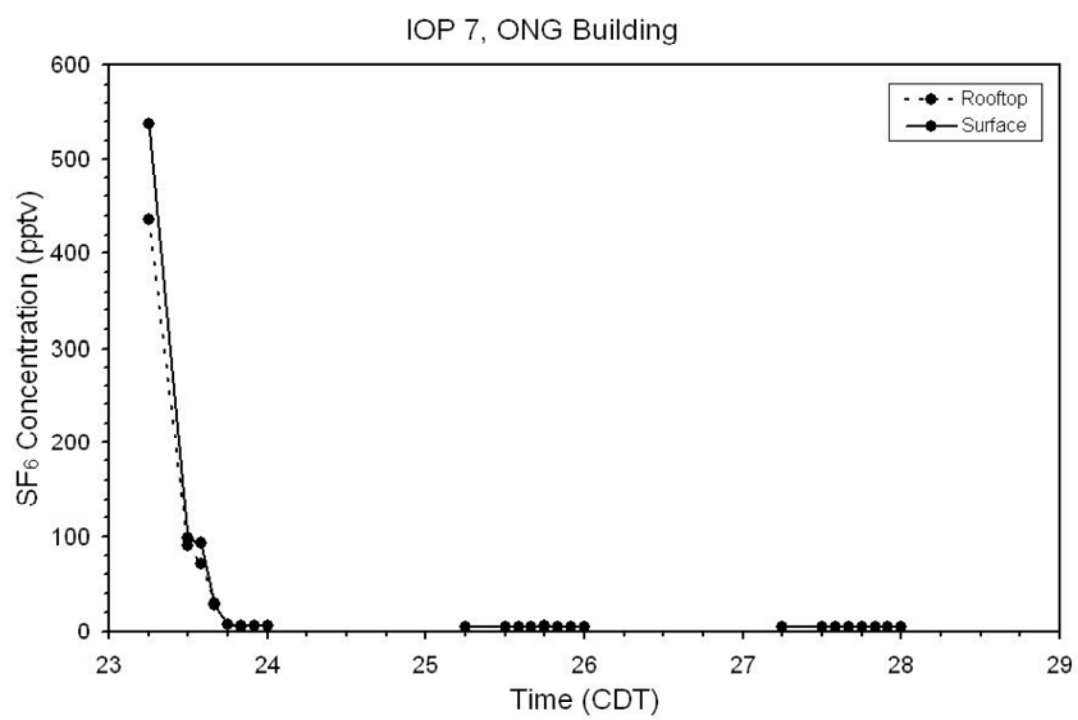


IOP 7, Bank of Oklahoma

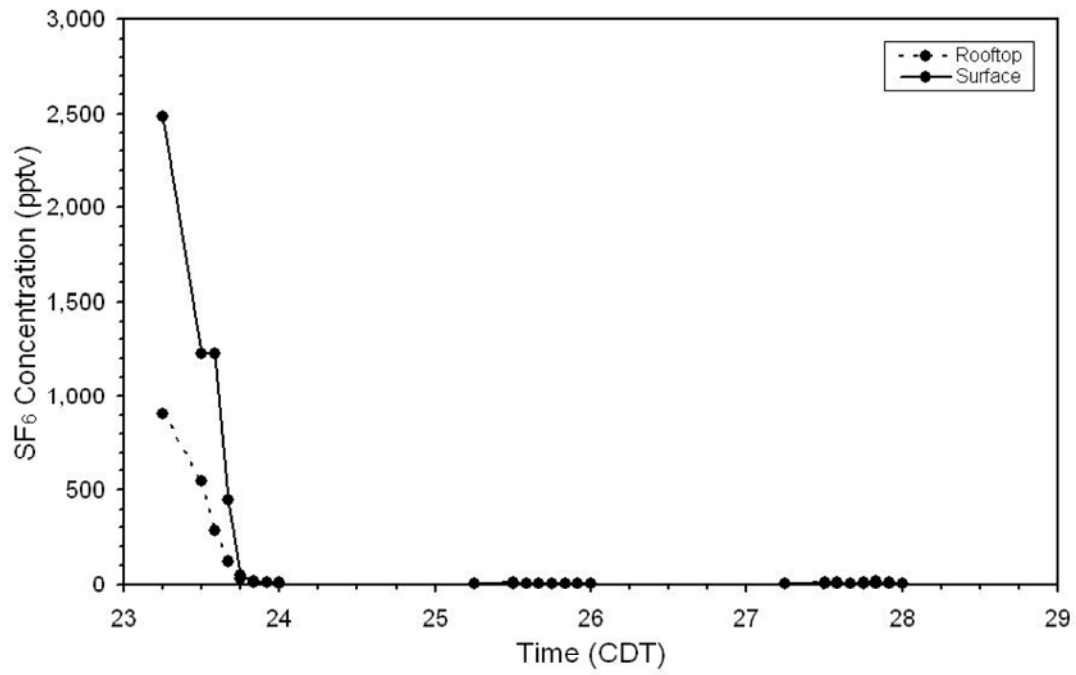


IOP 7, Center Kerr Tower

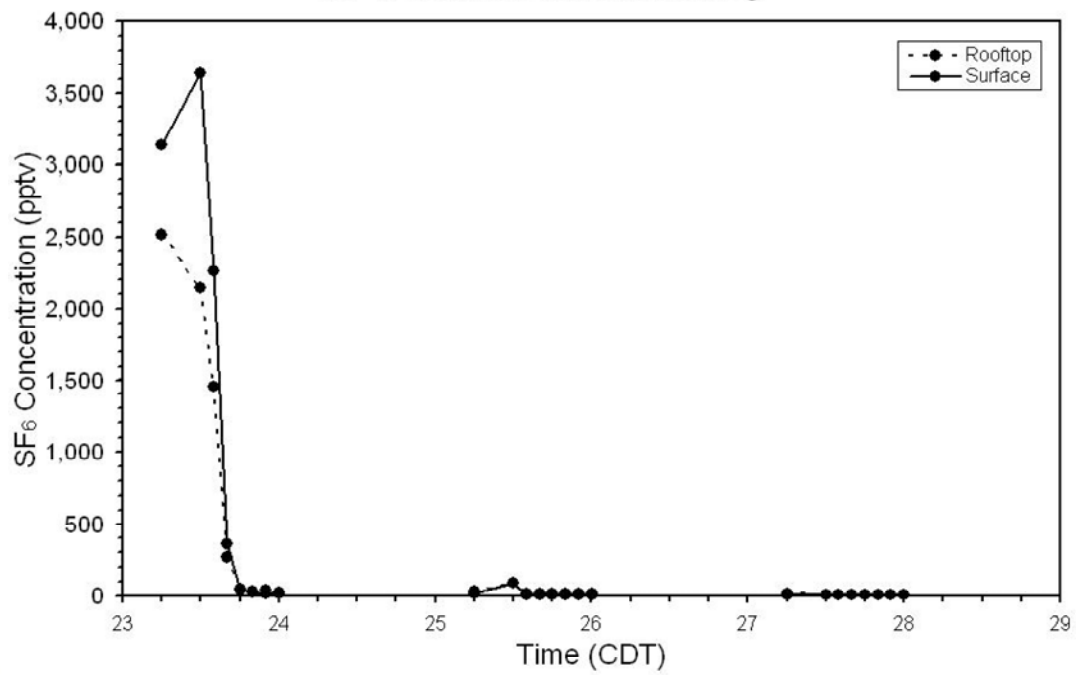




IOP 7, POB

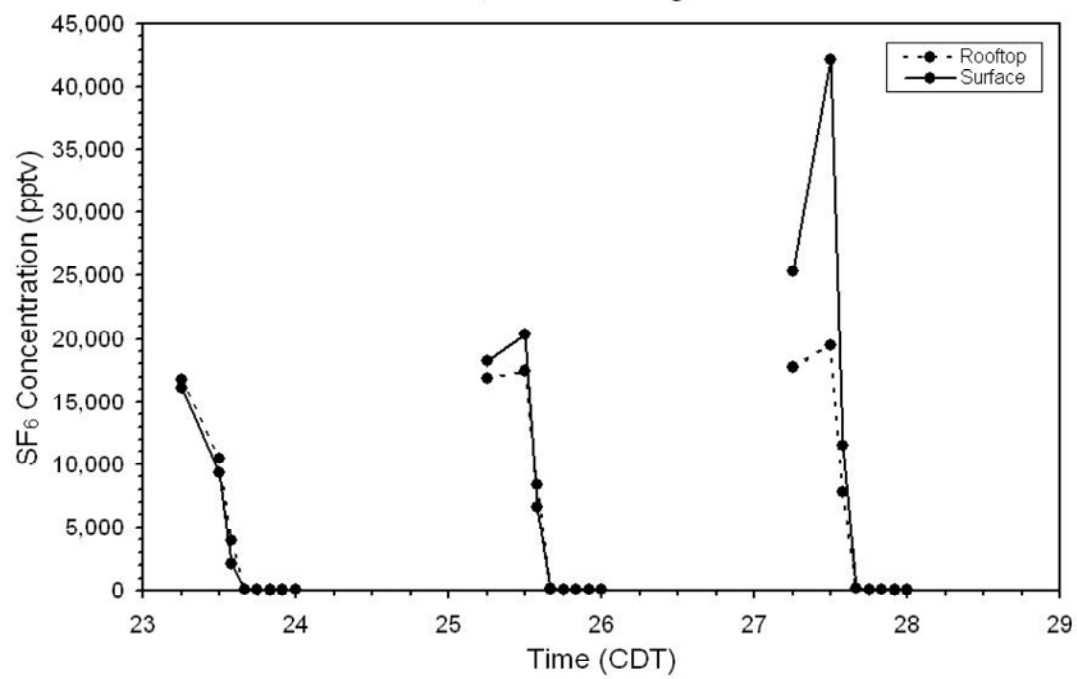


IOP 7, Southwestern Bell Building

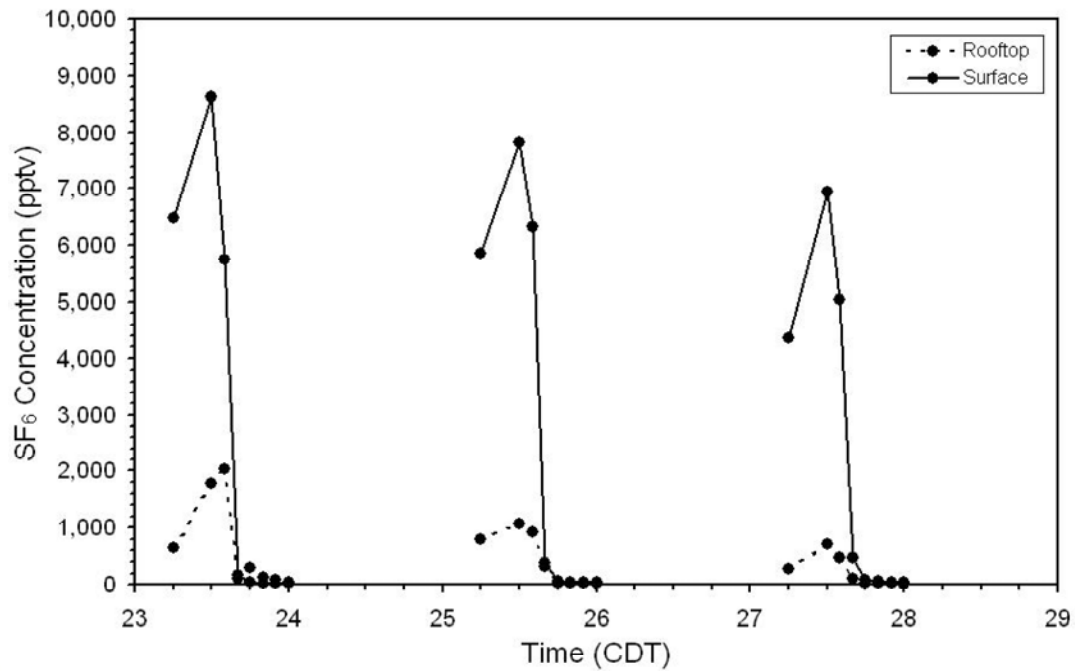




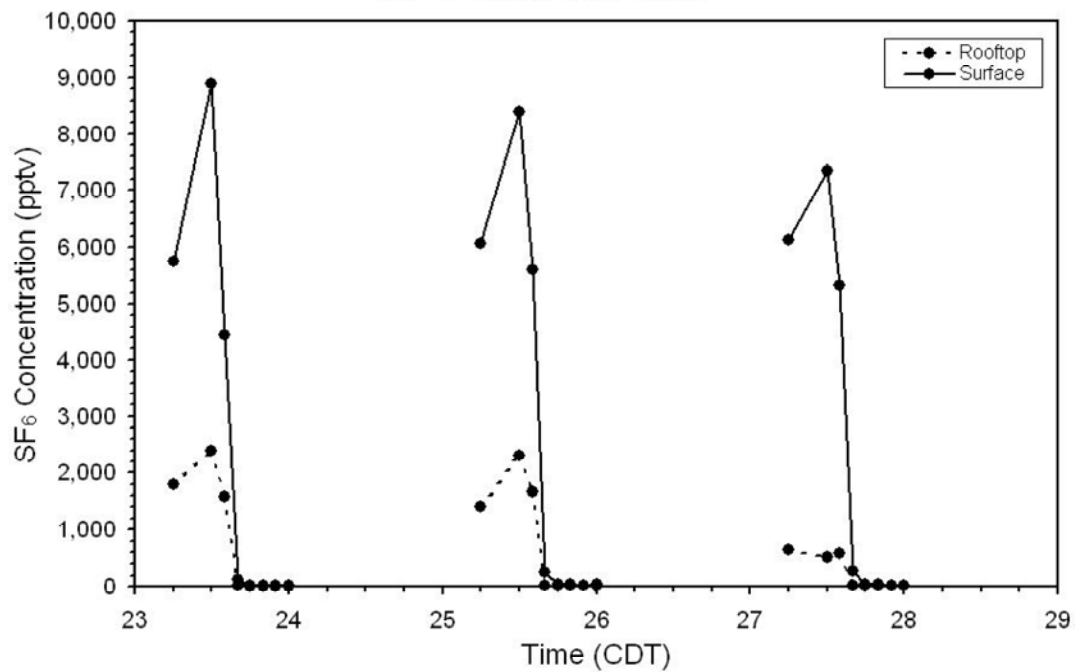
IOP 8, Sonic Building



IOP 8, Bank of Oklahoma



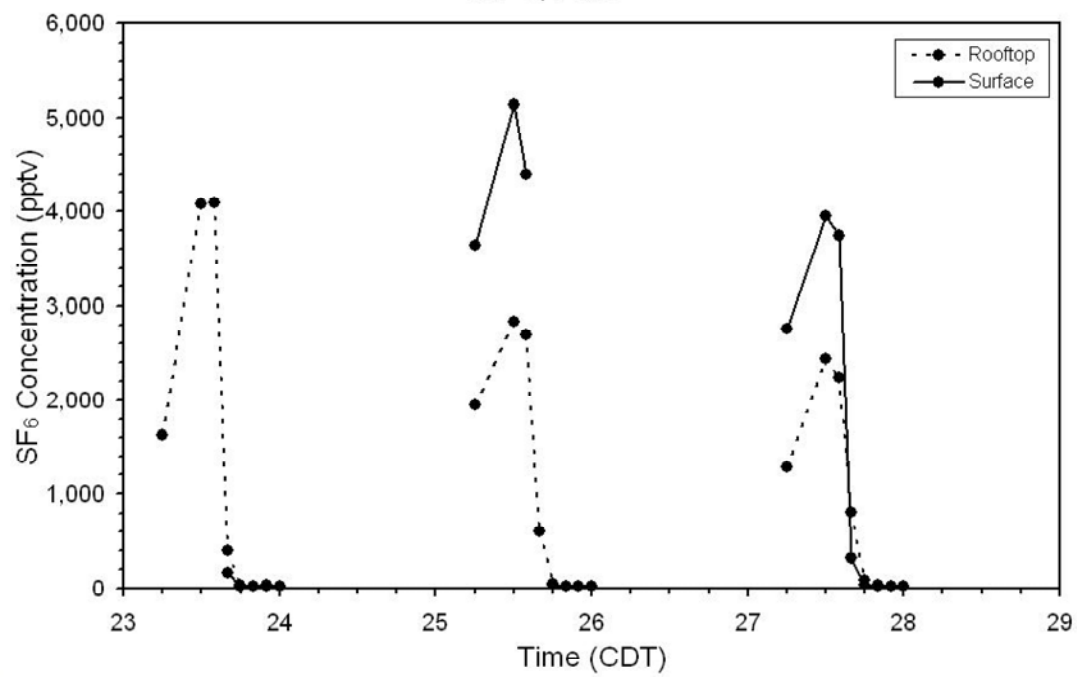
IOP 8, Center Kerr Tower

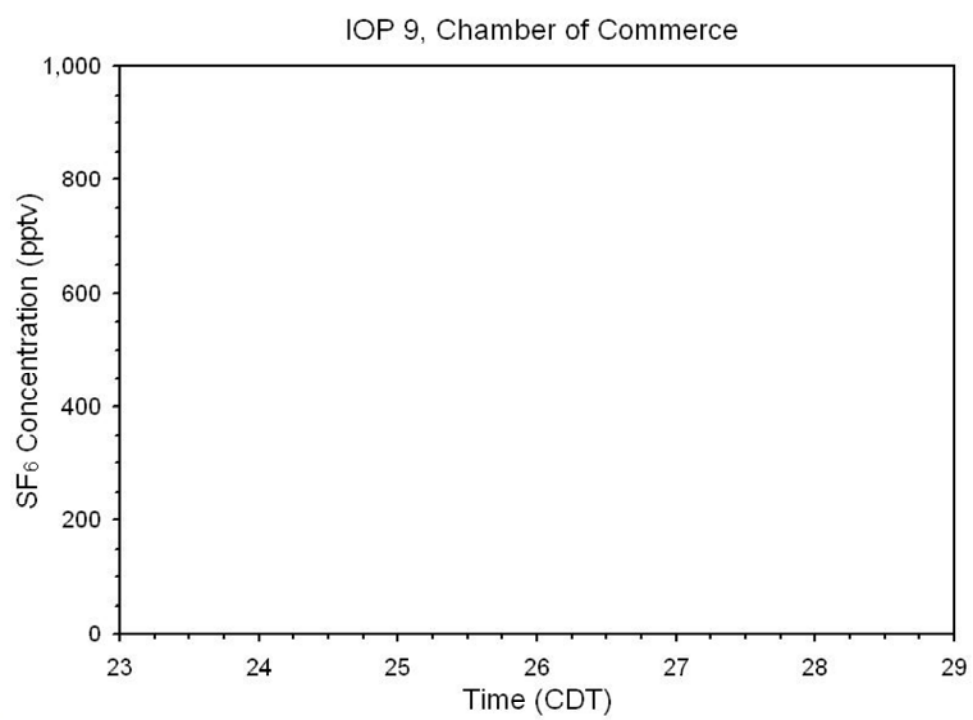




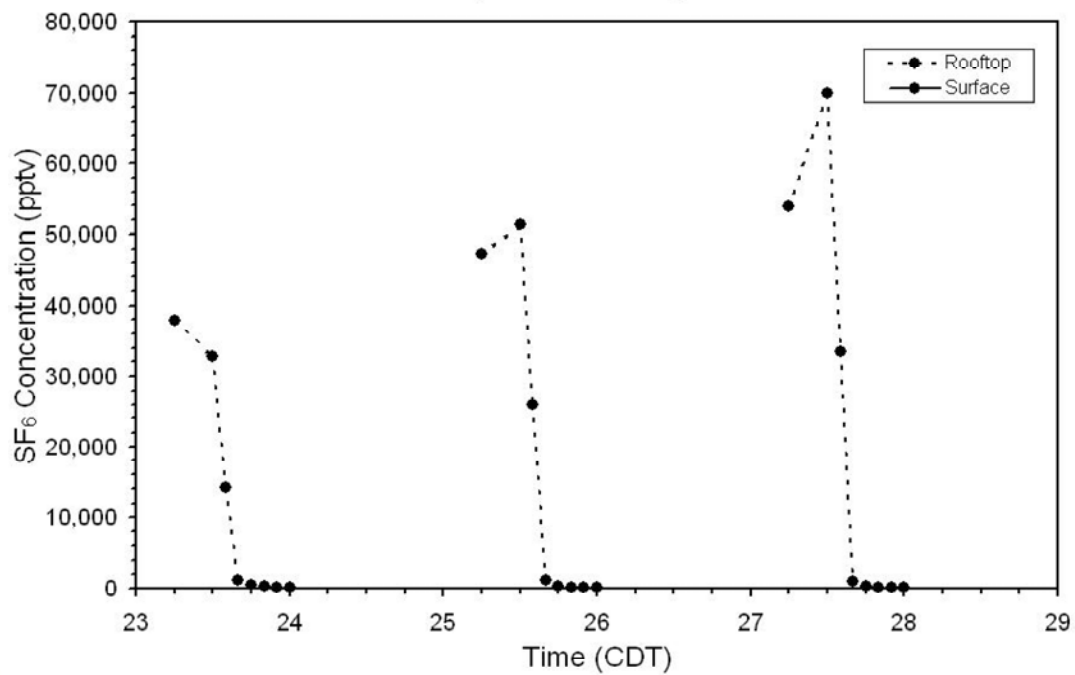


IOP 8, POB

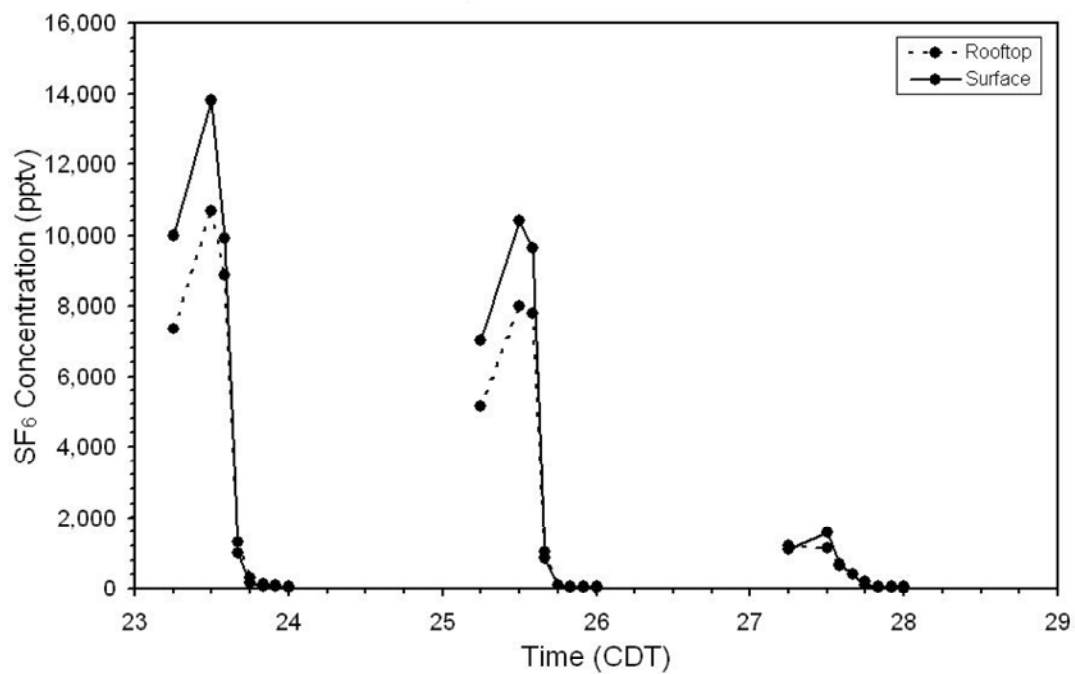




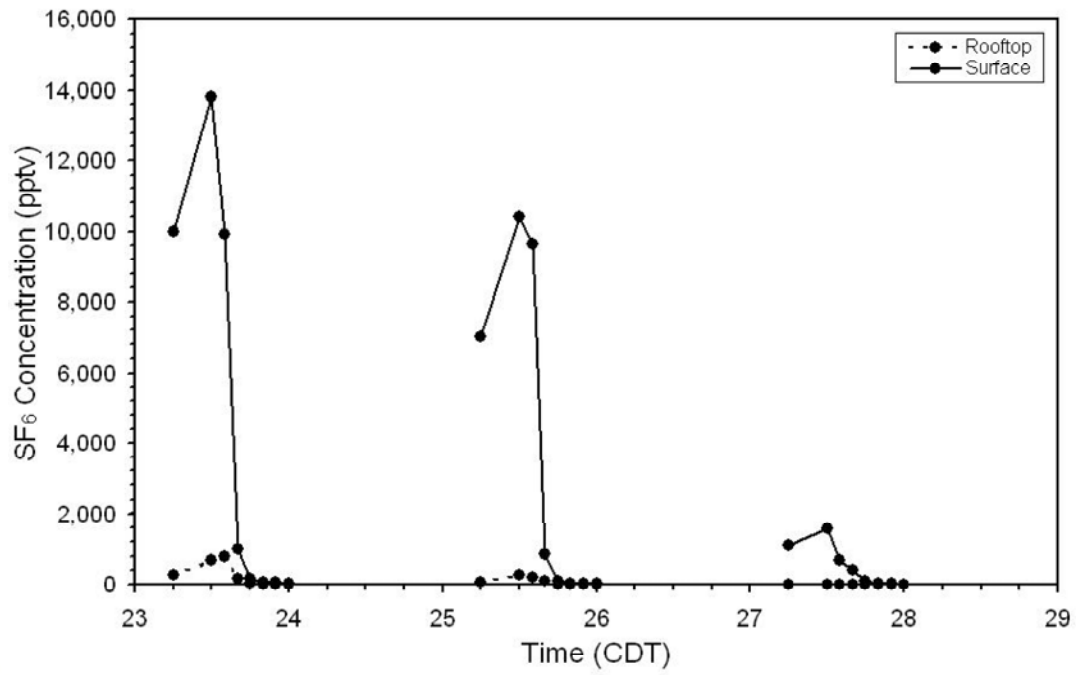
IOP 9, Sonic Building



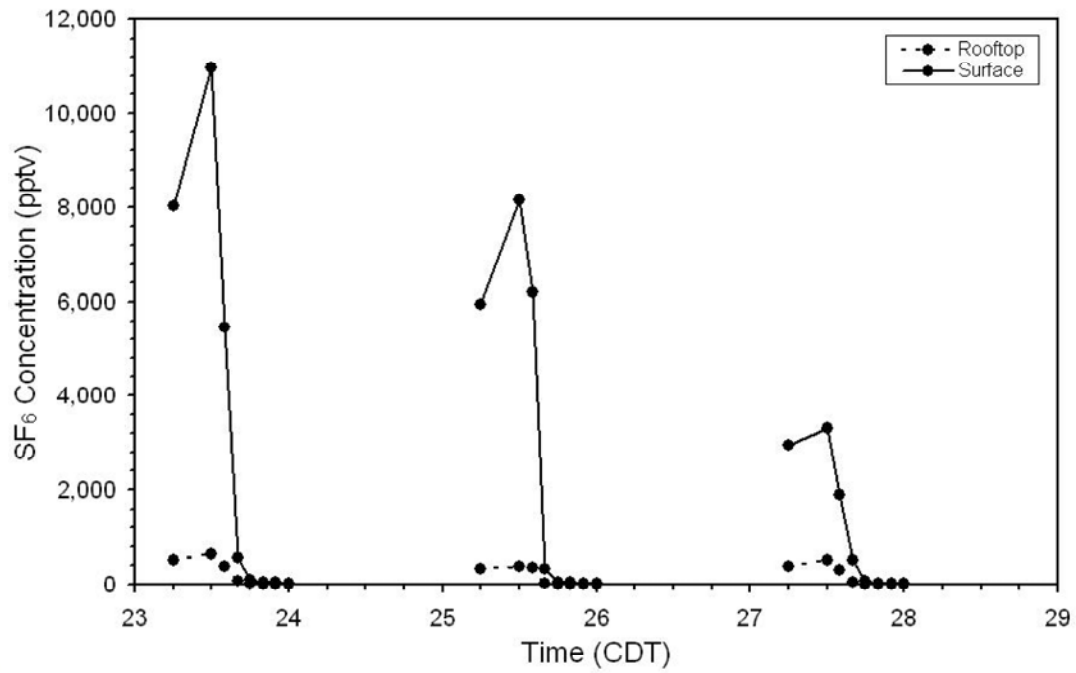
IOP 9, West Kerr Tower



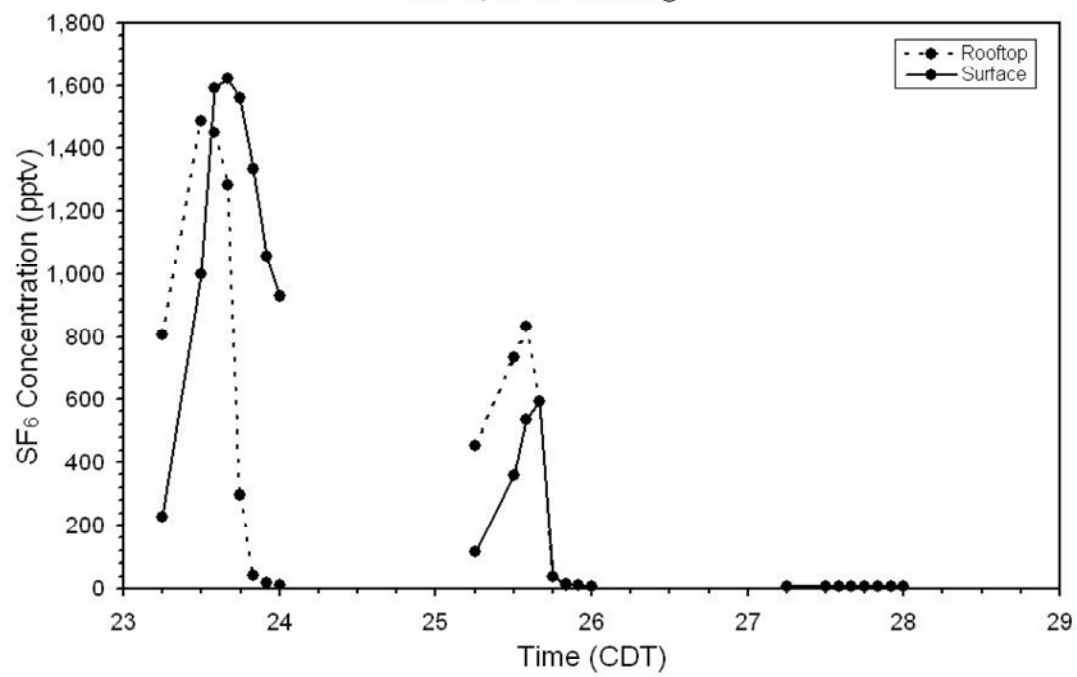
IOP 9, Bank of Oklahoma



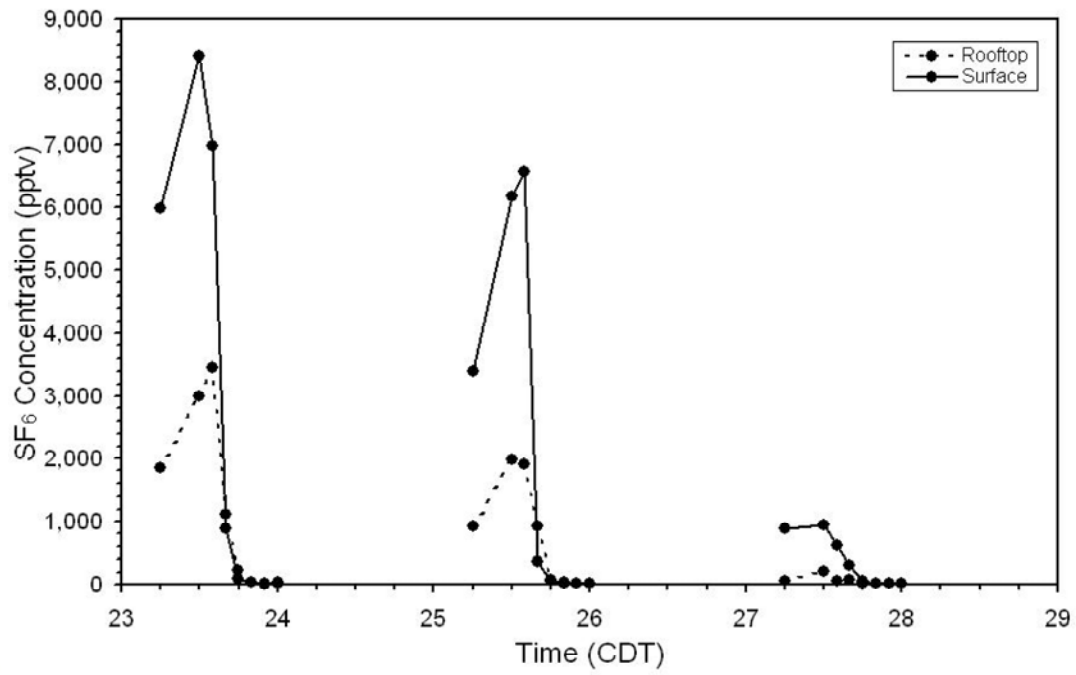
IOP 9, Center Kerr Tower



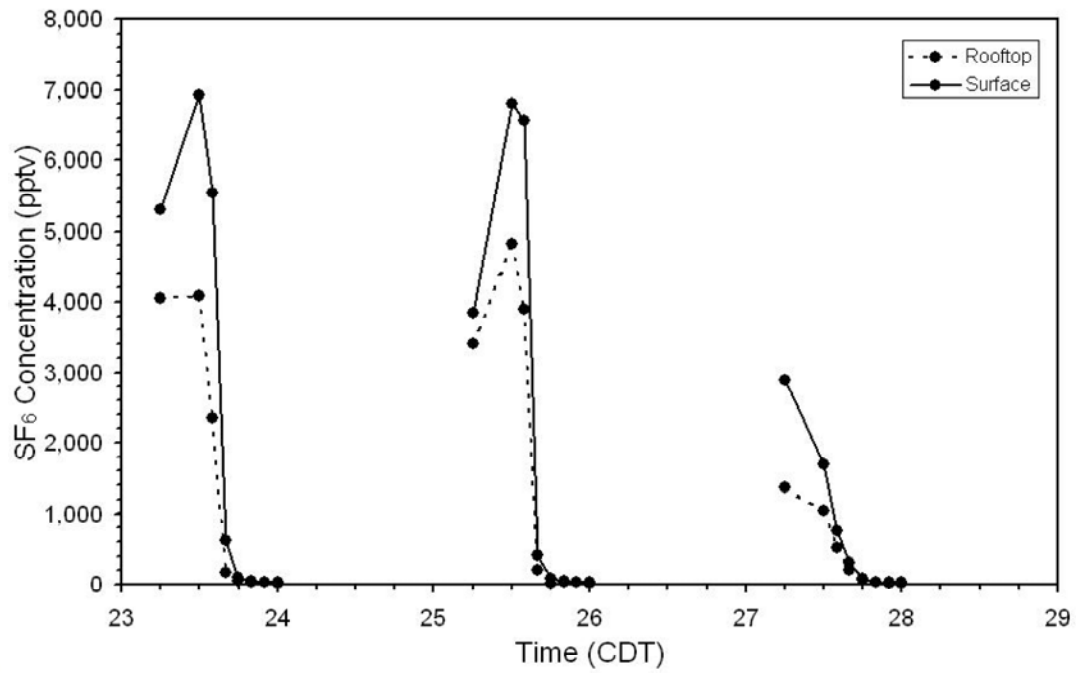
IOP 9, ONG Building

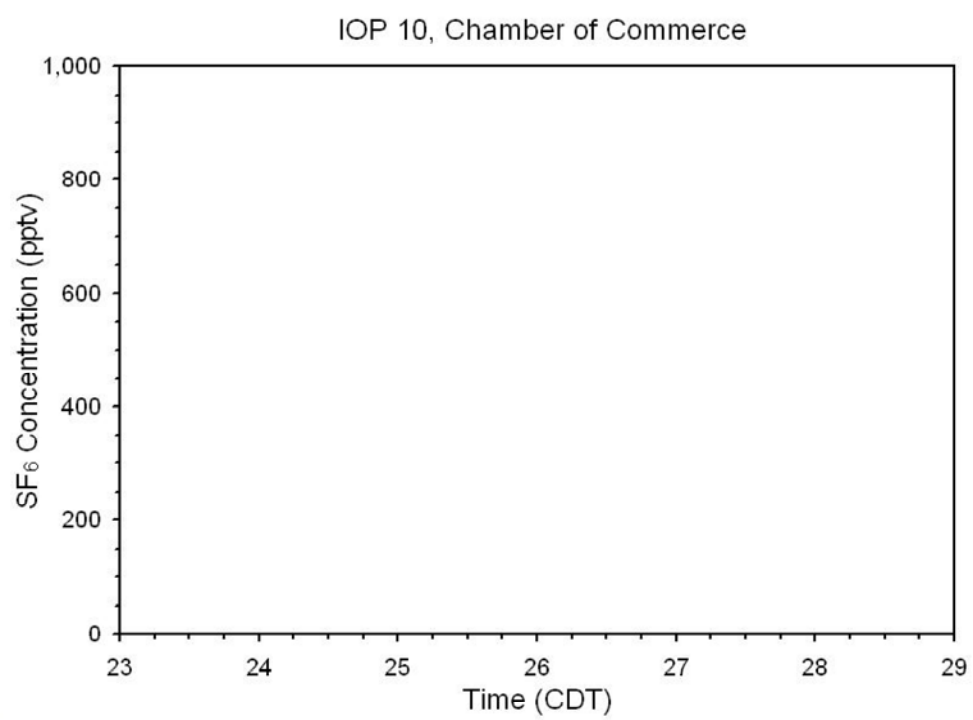


IOP 9, POB

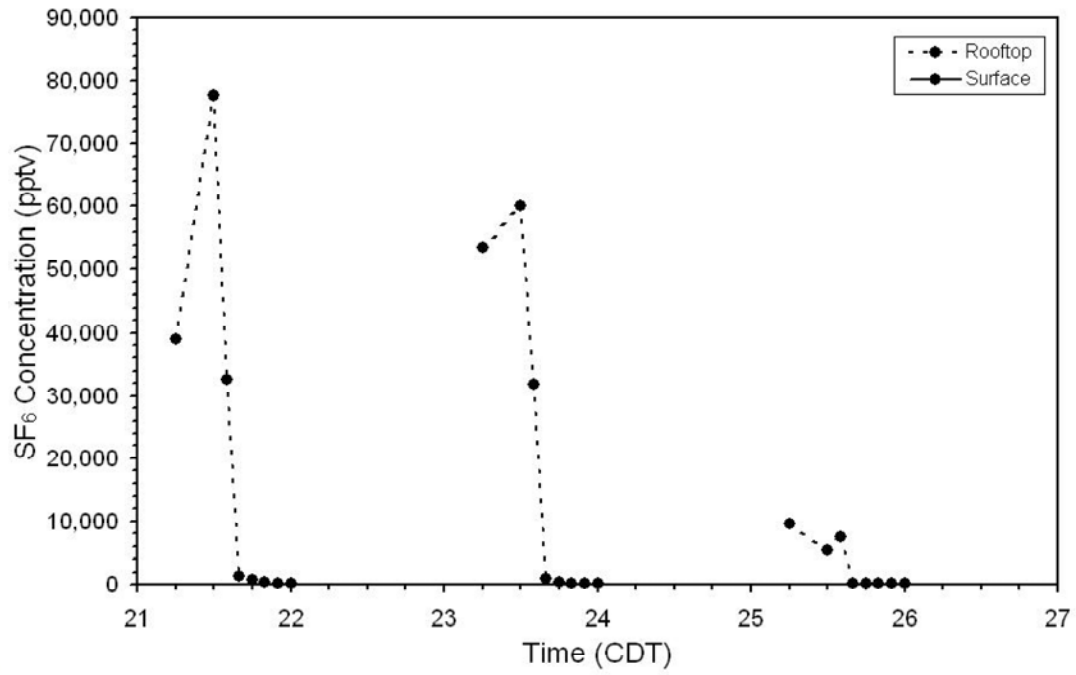


IOP 9, Southwestern Bell Building

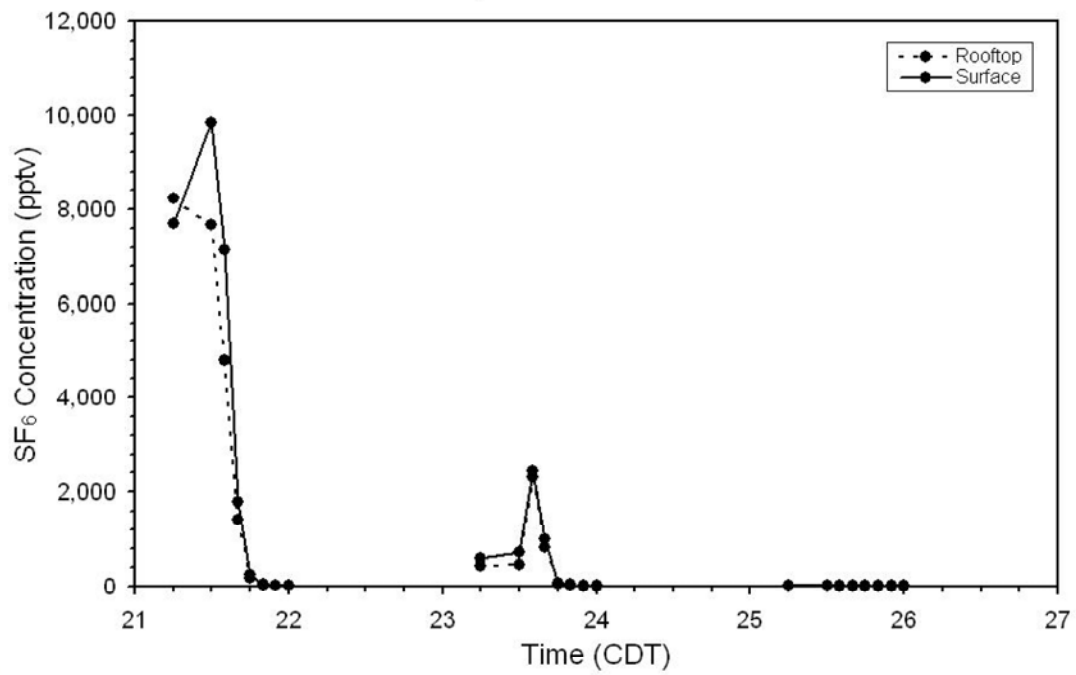




IOP 10, Sonic Building

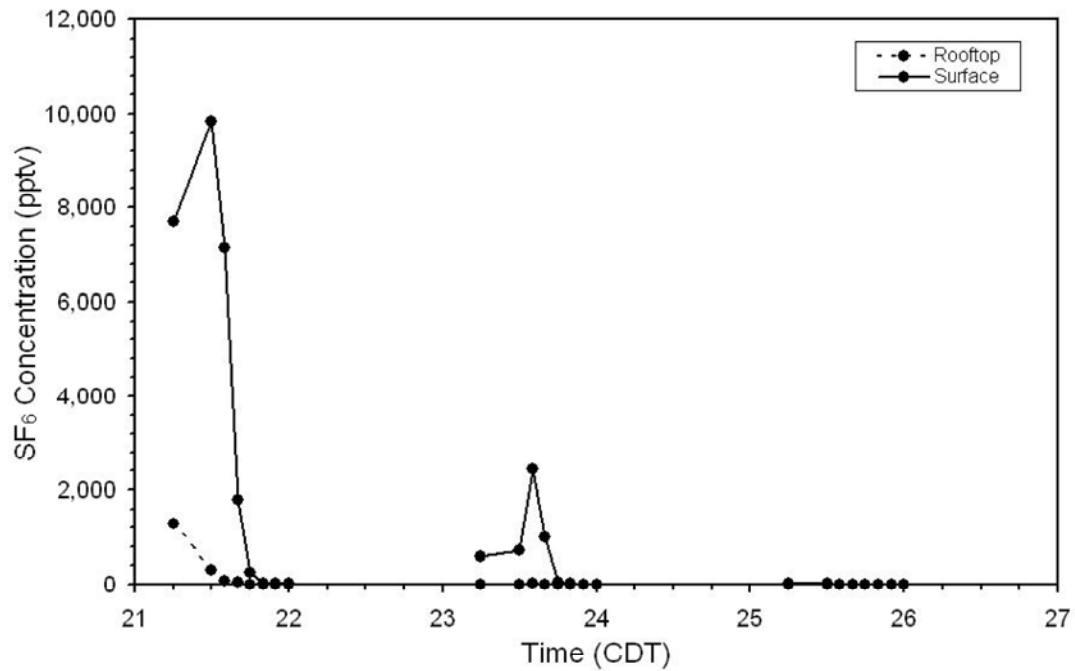


IOP 10, West Kerr Tower

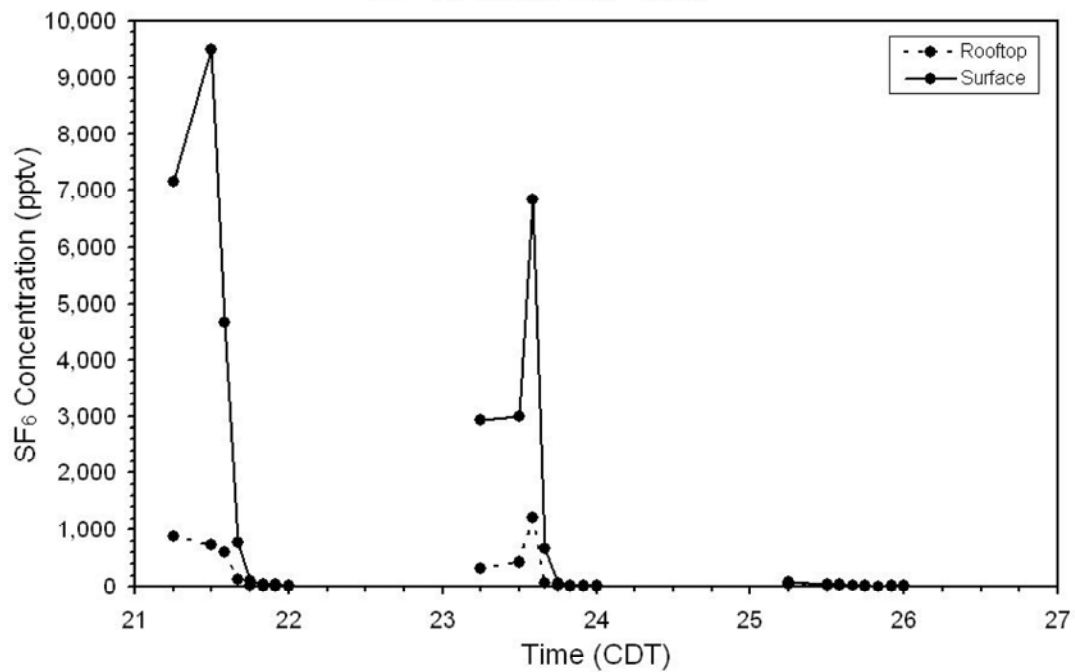




IOP 10, Bank of Oklahoma



IOP 10, Center Kerr Tower







# APPENDIX H: SURFACE VS. ROOFTOP TGA PLOTS

The mobile real-time tracer analyzers provided instantaneous readings of the SF<sub>6</sub> plume during each IOP of JU03. Two of the TGA vans were paired together to measure the real-time vertical transport of the plume as it moved downwind of the waste site. Van 7 was placed on top of the 7-Main Street parking garage while TGA 6 was deployed at roof level of the Main Street parking garage. Exact locations of these vans are found in the final IOP summaries. These TGAs were paired together during IOPs 1, 3, 4, 5, 6, and the first 3 continuous releases of IOP 7. Time histories of the plume are plotted by SF<sub>6</sub> concentration (pptv) vs. time (CDT) and shown in Figs. H-1 to H-20.

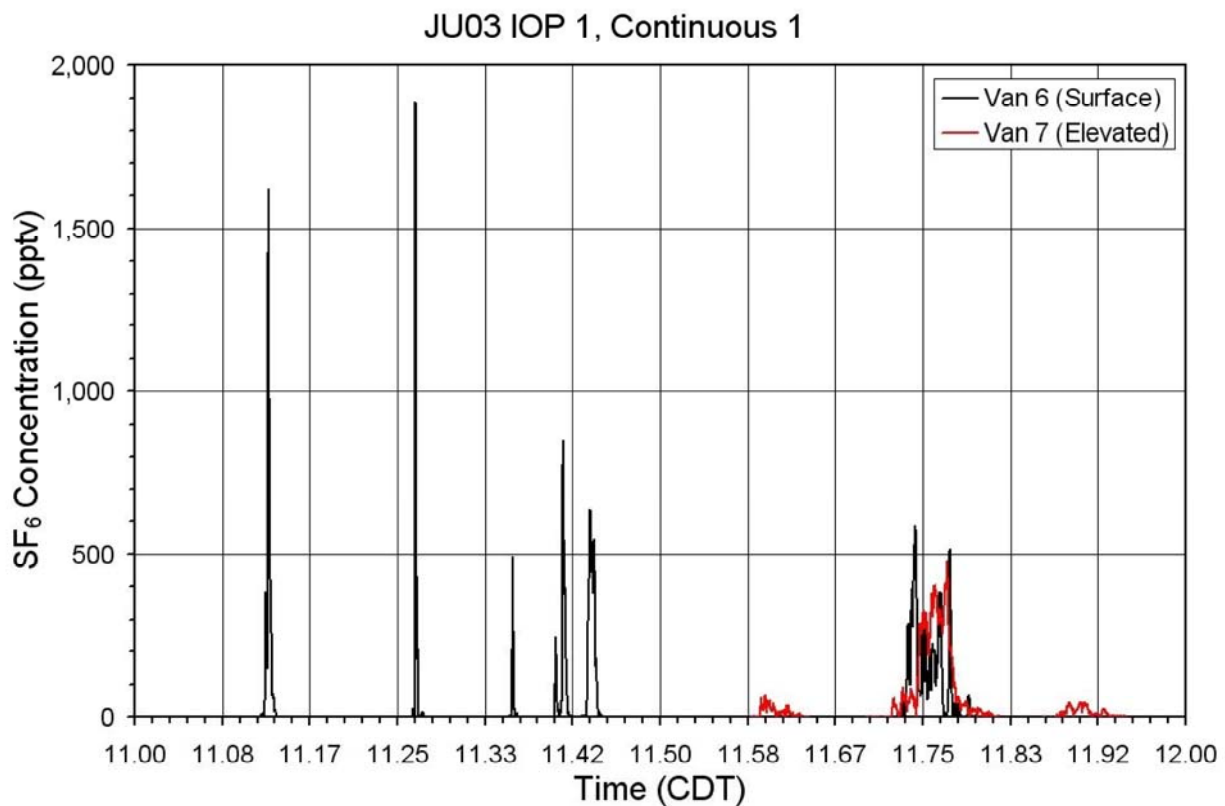


Figure H-1. Surface (van 6) vs. (van 7) time history plots of plume SF<sub>6</sub> during the 1<sup>st</sup> continuous release of IOP 1.

Figure H2. Surface potential (mV) vs. time (s) of the SF plane during the continuous rise of IOP 1.

Figure H3. Surface potential (mV) vs. time (s) of the SF plane during the puff release of IOP 1.

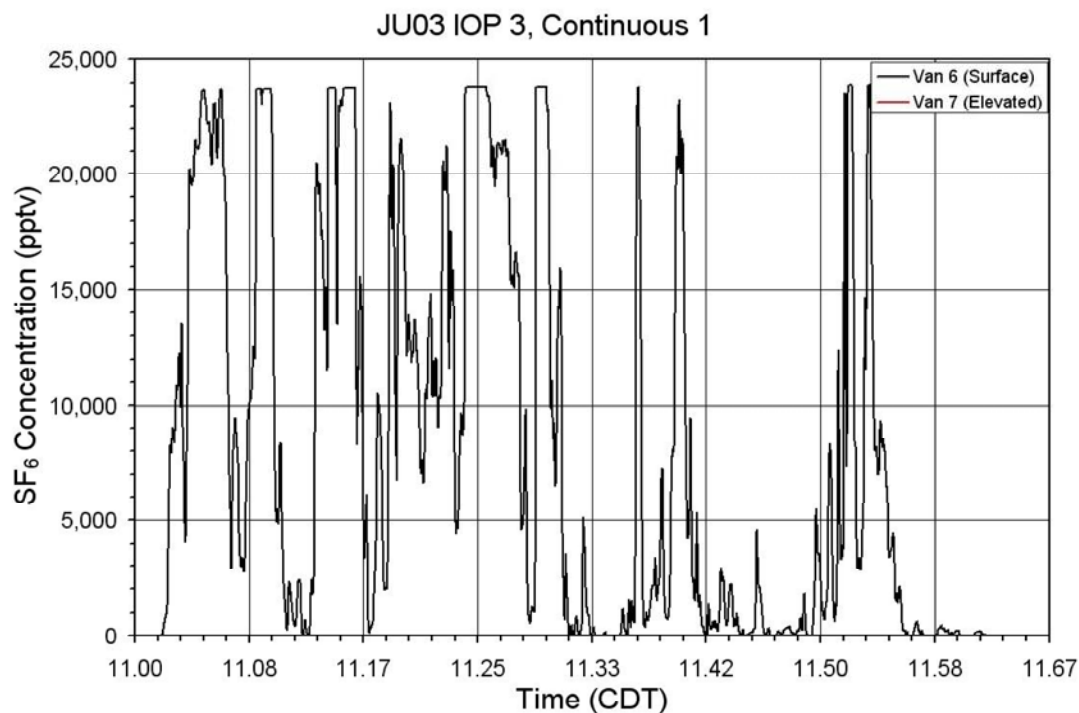


Figure H4. Surface van 6 and elevated van 7 time history plots of the SF<sub>6</sub> plume during the continuous release of IOP 2.

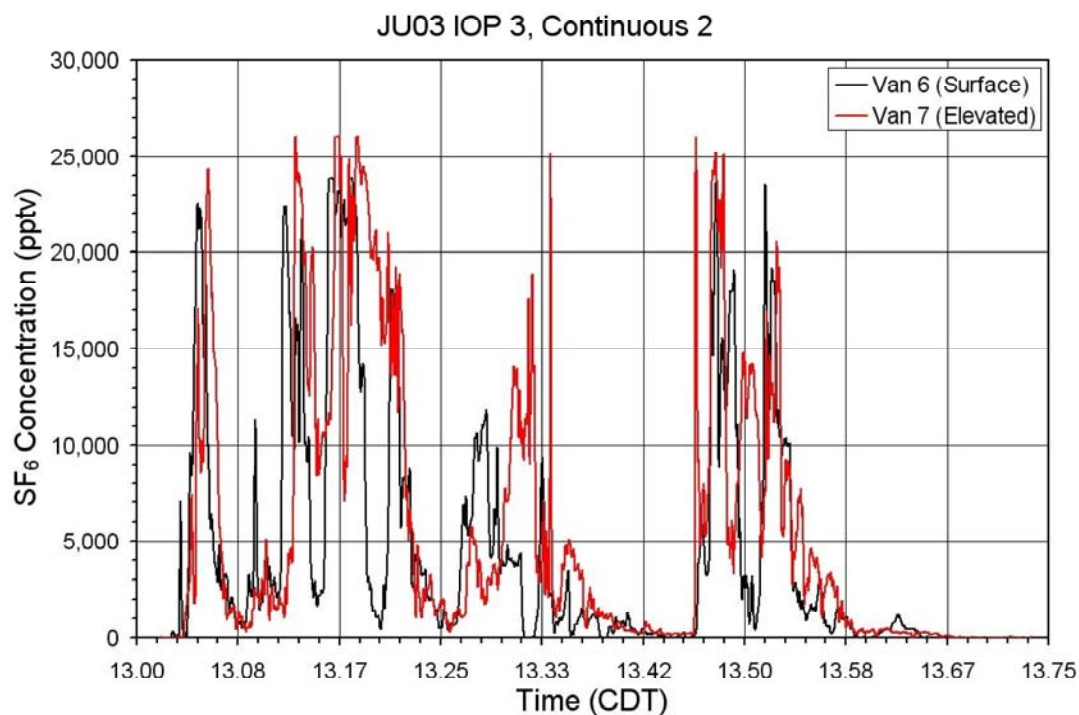


Figure H5. Surface van 6 and elevated van 7 time history plots of the SF<sub>6</sub> plume during the continuous release of IOP 3.

Figure H6. Since van  $\delta$  is elevated (an 7) the history plot of the SF pulse during the continuous use of IOP 3.

Figure H7. Since van  $\delta$  is elevated (an 7) the history plot of the SF pulse during the puff release of IOP 3.

Figure H8. ~~Since van 6 s. elevated (an 7) the histry p0s of the SF pime~~  
during the ~~continuous~~ <sup>rise</sup> of IOP 4.

Figure H9. ~~Since van 6 s. elevated (an 7) the histry p0s of the SF pime~~  
during the ~~continuous~~ <sup>rise</sup> of IOP 4.



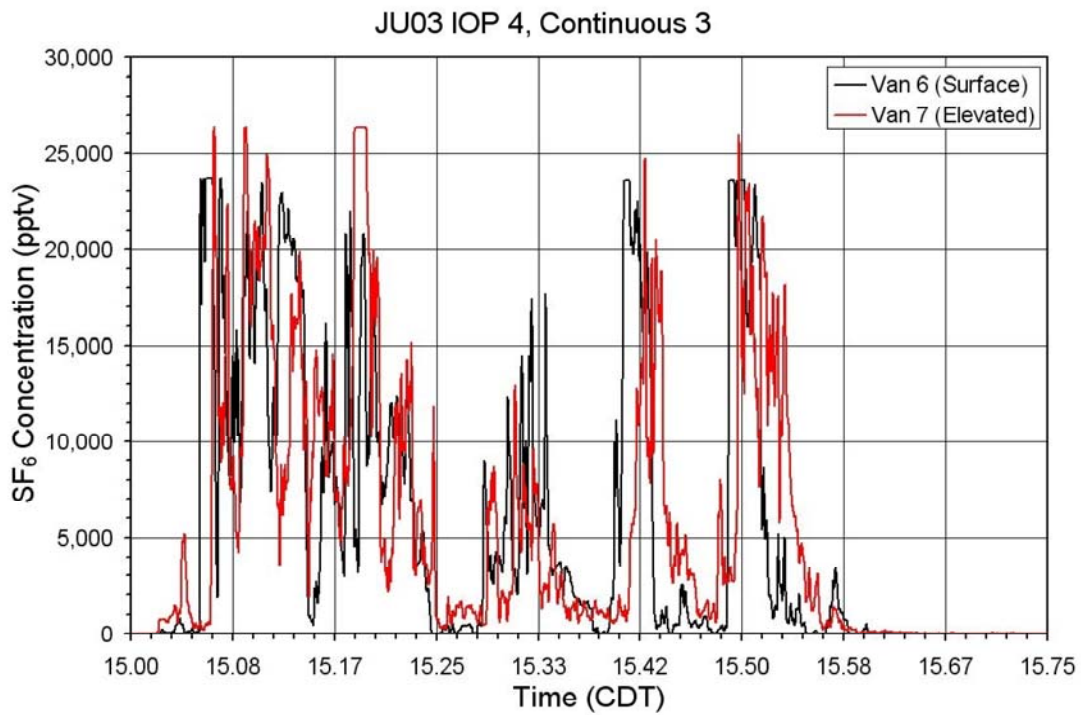


Figure H10. Surface van 6 and elevated (van 7) time history plots of the SF<sub>6</sub> plume during the continuous release of IOP 4.

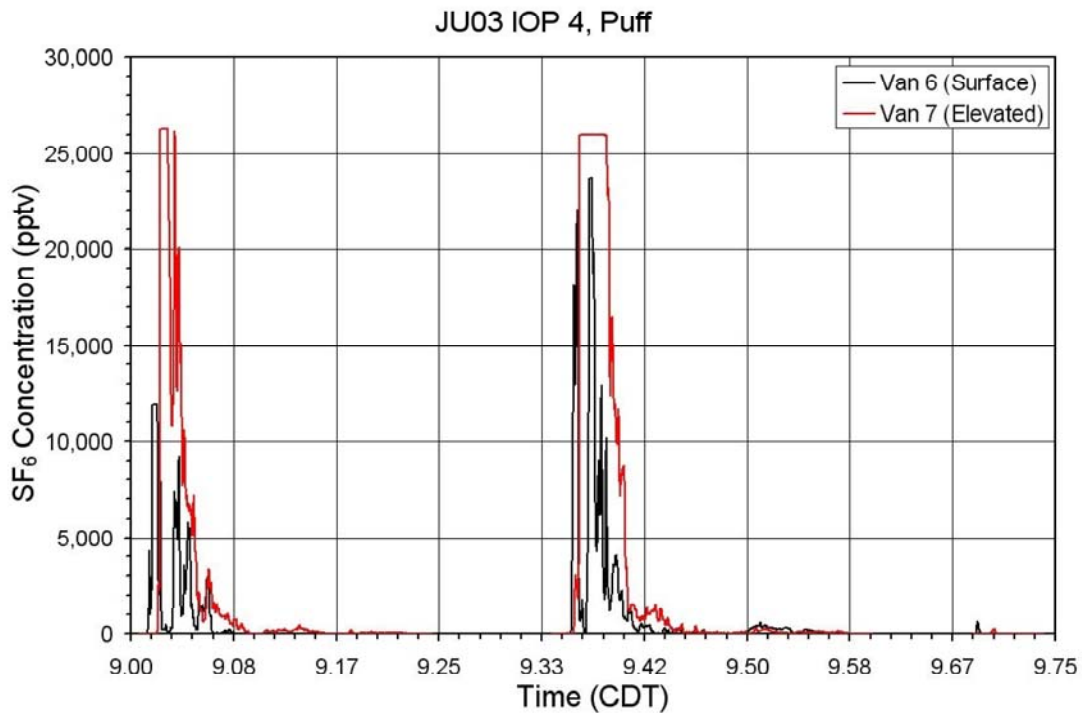


Figure H11. Surface van 6 and elevated (van 7) time history plots of the SF<sub>6</sub> plume during the puff release of IOP 4.

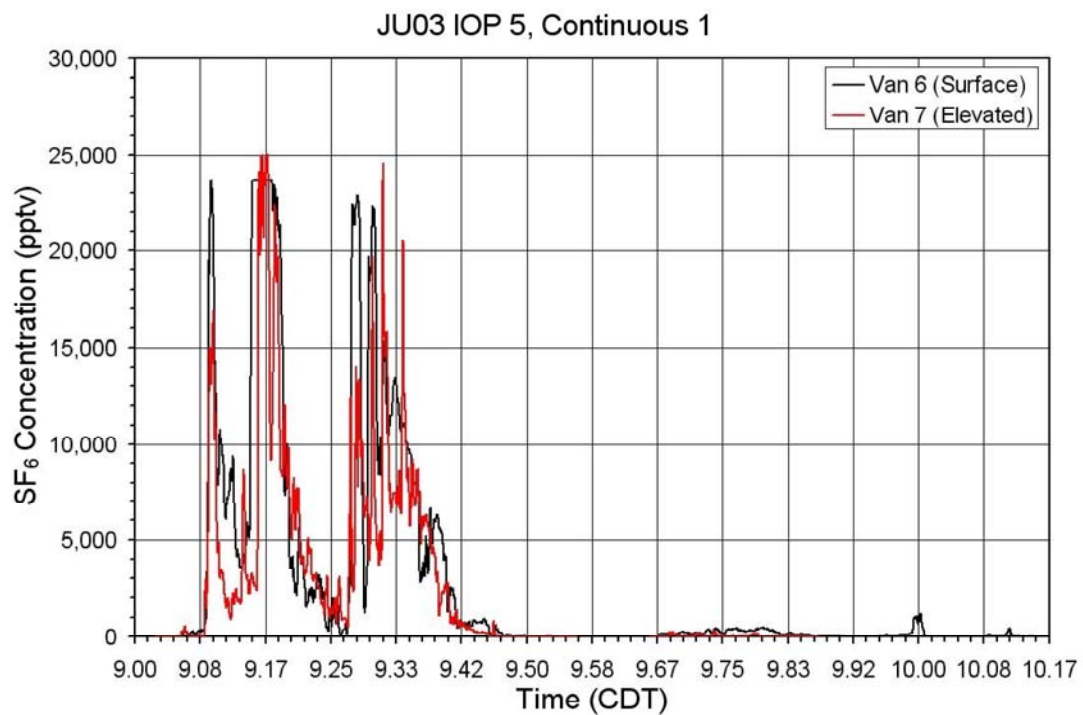


Figure H12. Surface van 6 and elevated (van 7) time history plots of the  $\text{SF}_6$  plume during the continuous release of IOP 5.

Figure H13. Surface van 6 and elevated (van 7) time history plots of the  $\text{SF}_6$  plume during the continuous release of IOP 5.

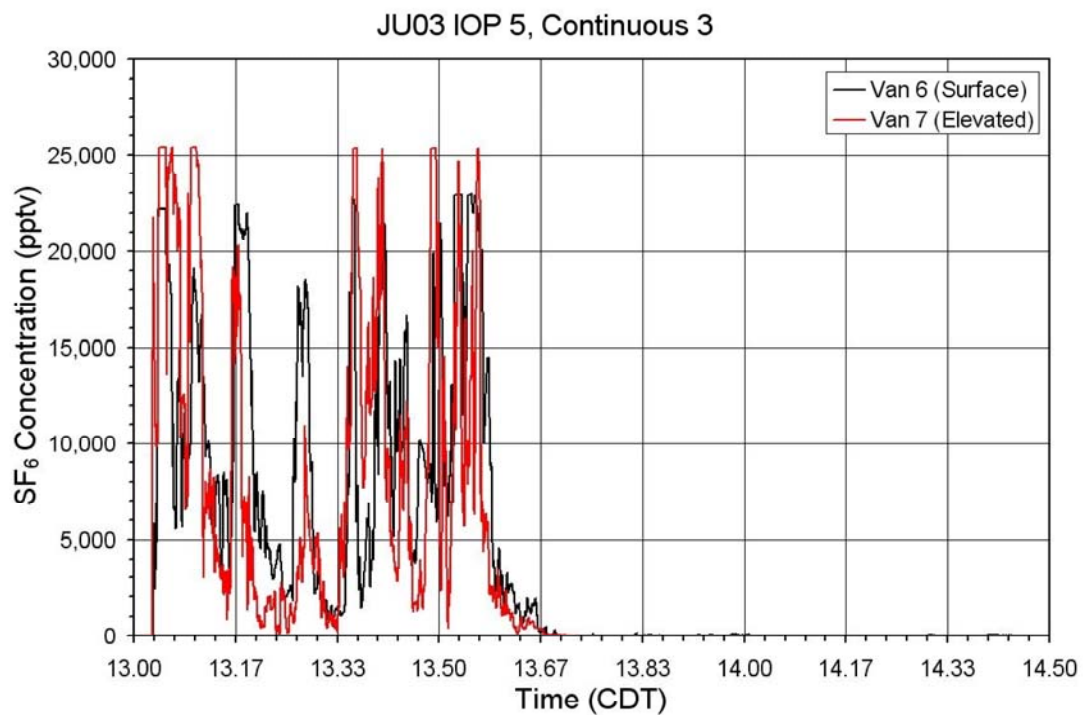


Figure H14. Surface van 6 and elevated (van 7) time history plots of the SF<sub>6</sub> plume during the continuous release of IOP 5.

Figure H15. Surface van 6 and elevated (van 7) time history plots of the SF<sub>6</sub> plume during the puff release of IOP 5.

Figure H16. Surface elevation (m) of the hybrid of the SF pipe during the continuous use of IOP 6.

Figure H17. Surface elevation (m) of the hybrid of the SF pipe during the continuous use of IOP 6.

Figure H18. Surface and elevated (Van 7) time history plots of the SF<sub>6</sub> plume during the continuous release of IOP 6.

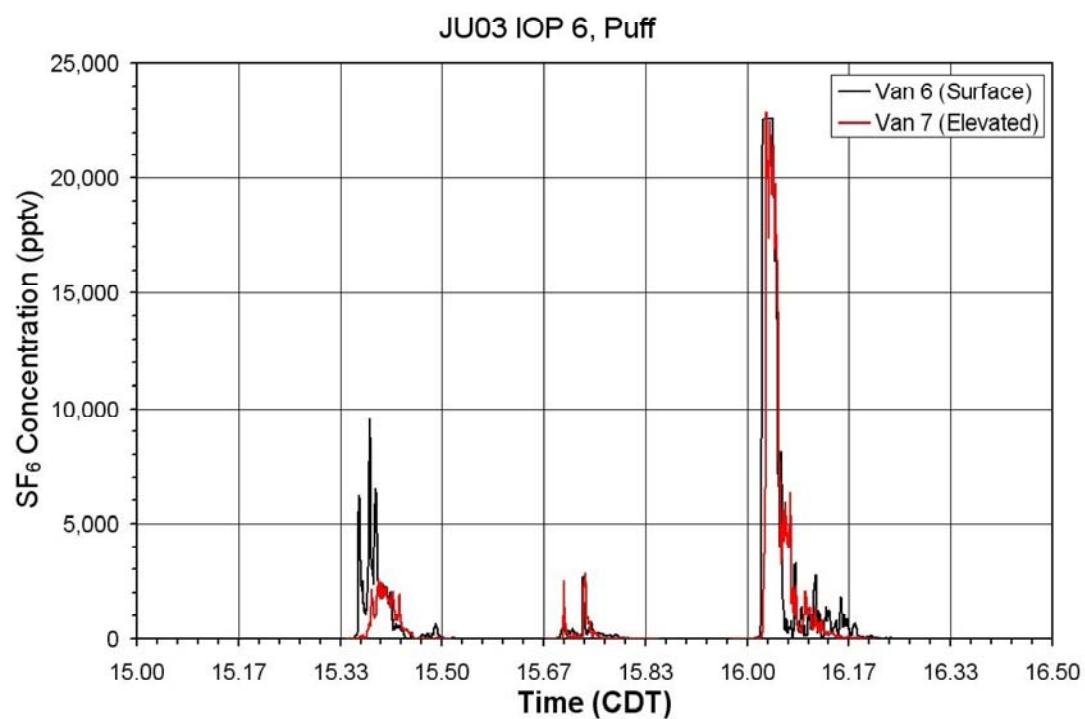


Figure H19. Surface and elevated (Van 7) time history plots of the SF<sub>6</sub> plume during the puff release of IOP 6.

Figure H20. Surface elevation (m) vs. time (hr) of the SF pipe during the continuous rise of IOP 7.

Figure H21. Surface elevation (m) vs. time (hr) of the SF pipe during the continuous rise of IOP 7.

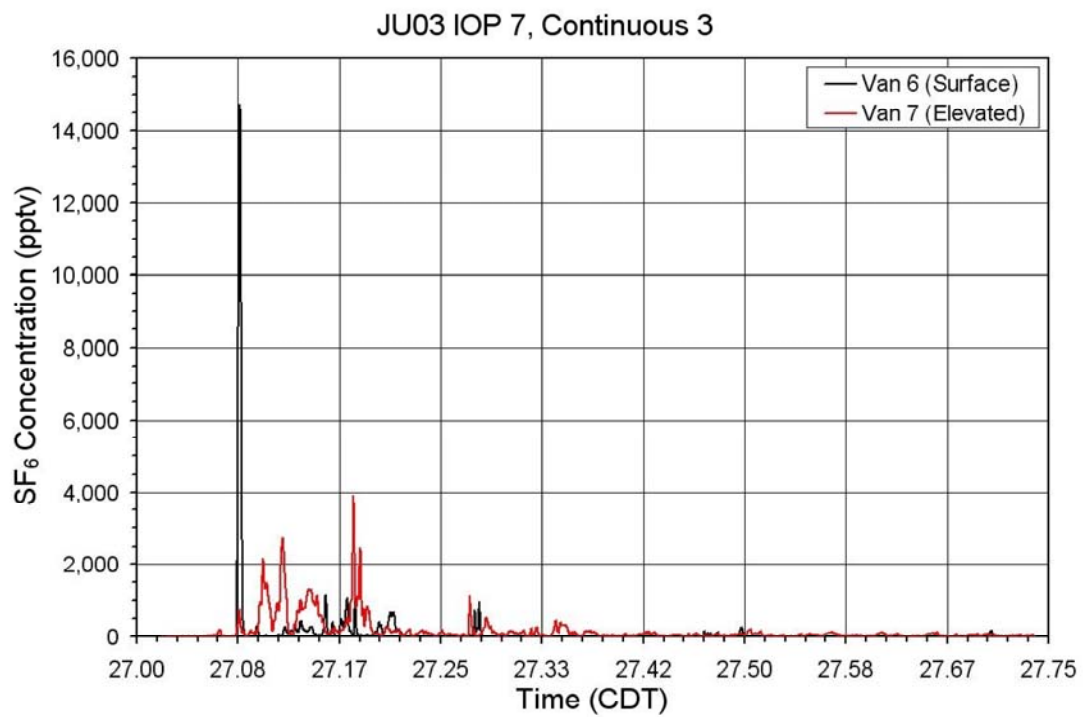


Figure H22. Surface van 6 and elevated (van 7) time history plots of the  $\text{SF}_6$  plume during the continuous case of IOP 7.

## APPENDIX I: ECAY SAMPLER PLOTS

The Super PIGS, as outlined earlier in the report, had the capability of program different sampling times and pause sampling between bags. The samples which started sampling at the station were sampled 2 15-minute cycles followed by 6 5-minute cycles. The 5-minute cycles were not measured until the concentration dispersed or decayed after the release had ended. After the 5-minute sampling period is paused for an hour before the process of sampling repeated at the station for the next continuous release. Figures I-1 to I-39 display the footprints of each of the Super PIGS bags. The rooftop samplers (small circles) represent a certain range of concentration. Gray (<33 pptv, blue (33 to 100 pptv), green (100 to 1,000 pptv), brown (1,000 to 10,000 pptv), and red (> 10,000 pptv). An excessive concentration is missing.



Figure I-1. CBD Superfund Site Concentration footprints, DOP 1 from 1100-1150 CDT. Traces released from 1100-1130. CD





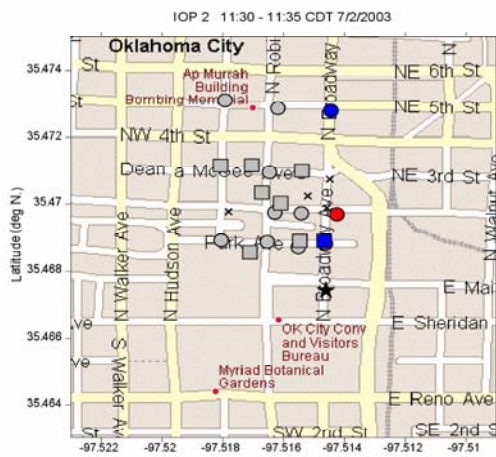




Figure I-5. CBD Superfund site footprint, IOP 2 from 1150-1200 and 1300-1340 CDT. Treasures from 1100-1130 and 1300-1330 CDT.



Figure I-6. CBD Superfund site footprint, IOP 2 from 1340-1400 and 1500-1530 CDT. Treasures recovered from 1300-1330 and 1500-1530 CDT.



Figure I-7. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 2 from 1530-1600 CDT. Tracer release occurred from 1500-1530 CDT.

Figure I-8. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 3 from 1100-1150 CDT. Tracer release occurred from 1100-1130 CDT.



Figure I-9. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 3 from 1150-1200 and 1300-1340 CDT. Tracer releases occurred from 1100-1130 and 1300-1330 CDT.

Figure I-10. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 3 from 1340-1400 and 1500-1530 CDT. Tracer releases occurred from 1300-1330 and 1500-1530 CDT.

Figure I-11. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 3 from 1530-1600 CDT. Tracer release occurred from 1500-1530 CDT.

Figure I-12. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 4 from 1100-1150 CDT. Tracer release occurred from 1100-1130 CDT.

Figure I-13. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 4 from 1150-1200 and 1300-1340 CDT. Tracer releases occurred from 1100-1130 and 1300-1330 CDT.

Figure I-14. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 4 from 1340- 1400 and 1500-1530 CDT. Tracer releases occurred from 1300-1330 and 1500-1530 CDT.

Figure I-15. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 4 from 1530-1600 CDT. Tracer release occurred from 1500-1530 CDT.

Figure I-16. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 5 from 0900-0950 CDT. Tracer release occurred from 0900-0930 CDT.



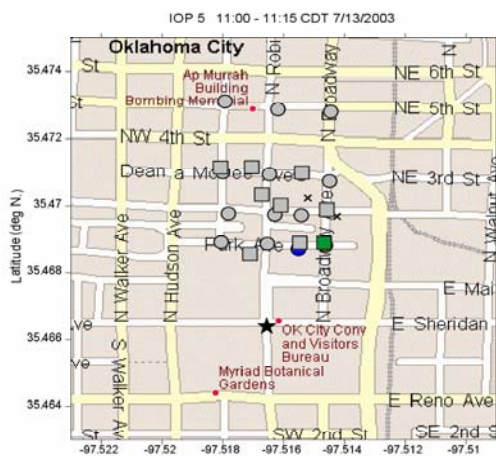


Figure I-17. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 5 from 0950-1000 and 1100-1140 CDT. Tracer releases occurred from 0900-0930 and 1100-1130 CDT.

Figure I-18. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 5 from 1140-1200 and 1300-1330 CDT. Tracer releases occurred from 1100-1130 and 1300-1330 CDT.

Figure I-19. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 5 from 1330-1400 CDT. Tracer release occurred from 1300-1330 CDT.

Figure I-20. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 6 from 0900-0950 CDT. Tracer release occurred from 0900-0930 CDT.

Figure I-21. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 6 from 0950-1000 and 1100-1140 CDT. Tracer releases occurred from 0900-0930 and 1100-1130 CDT.

Figure I-22. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 6 from 1140-1200 and 1300-1330 CDT. Tracer releases occurred from 1100-1130 and 1300-1330 CDT.

Figure I-23. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 6 from 1330-1400 CDT. Tracer release occurred from 1300-1330 CDT.

Figure I-24. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 7 from 2300-2350 CDT. Tracer release occurred from 2300-2330 CDT.



Figure I-25. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 7 from 2350-2400 and 0100-0140 CDT. Tracer releases occurred from 2300-2330 and 0100-0130 CDT.

Figure I-26. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 7 from 0140-0200 and 0300-0330 CDT. Tracer releases occurred from 0100-0130 and 0300-0330 CDT.

Figure I-27. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 7 from 0330-0400 CDT. Tracer releases occurred from 0300-0330 CDT.

Figure I-28. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 8 from 2300-2350 CDT. Tracer release occurred from 2300-2330 CDT.

Figure I-29. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 8 from 2350-2400 and 0100-0140 CDT. Tracer releases occurred from 2300-2330 and 0100-0130 CDT.

Figure I-30. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 8 from 0140-0200 and 0300-0330 CDT. Tracer releases occurred from 0100-0130 and 0300-0330 CDT.

Figure I-31. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 8 from 0330-0400 CDT. Tracer release occurred from 0300-0330 CDT.

Figure I-32. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 9 from 2300-2350 CDT. Tracer release occurred from 2300-2330 CDT.



Figure I-33. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 9 from 2350-2400 and 0100-0130 CDT. Tracer releases occurred from 2300-2330 and 0100-0130 CDT.

Figure I-34. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 9 from 0140-0200 and 0300-0330 CDT. Tracer releases occurred from 0100-0130 and 0300-0330 CDT.

Figure I-35. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 9 from 0330-0400 CDT. Tracer releases occurred from 0300-0330 CDT.

Figure I-36. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 10 from 2100-2150 CDT. Tracer releases occurred from 2100-2130 CDT.

Figure I-37. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 10 from 2150-2200 and 2300-2340 CDT. Tracer releases occurred from 2100-2130 and 2300-2330 CDT.

Figure I-38. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 10 from 2340-2400 and 0100-0130 CDT. Tracer releases occurred from 2300-2330 and 0100-0130 CDT.

Figure I-39. CBD Super PIGS SF<sub>6</sub> tracer concentration footprints during IOP 10 from 0130-0200 CDT. Tracer releases occurred from 0100-0130 CDT.