

## URBAN 2000 ${\rm SF}_6$ ATMOSPHERIC TRACER FIELD TESTS

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#### **ABSTRACT**

This report summarizes the release and measurement of the intentionally disseminated atmospheric tracer sulfur hexafluoride ( $SF_6$ ) by the Field Research Division during the URBAN 2000 field study. The URBAN 2000 study was conducted during October 2000 in Salt Lake City, Utah.  $SF_6$  was released during seven nocturnal Intensive Observation Periods (IOP) and was sampled by both continuous and bag samplers. Tracer releases included both point releases and line releases with release rates of 1-2 g s<sup>-1</sup>. Six continuous analyzers were deployed both as mobile and stationary units. Stationary bag samplers were positioned at 100 locations in a downtown urban sampling grid and on 1 km, 2 km, 4 km and 6 km arcs. Bag samplers were also placed on three building tops in the downtown area and on 2 and 4 km arcs upwind of the downtown sampling grid. Quality control samplers were placed at 30% of the sampling locations. A complete quality controlled data set was collected and is described along with a discussion of the quality control methods.

Tracer concentrations up to 245,000 parts per trillion by volume (pptv) were measured by the bag samplers with 4% of the samples having concentrations over 10,000 pptv. Most bag sampler tracer concentrations (35%) were below the method limit of detection (MLOD) of 14 pptv. An additional 17% of bag sample tracer concentrations ranged between the MLOD and the method limit of quantitation (MLOQ), which was 45 pptv. All other bag sample tracer concentrations ranged between 45 and 10,000 pptv. Significant tracer concentrations were measured at building tops in all IOPs. Building-top tracer concentrations appeared to be both cyclic (of same value) and periodic. On many occasions, the tracer was observed by the mobile real-time analyzers to be hugging the foot of the mountains along the NW 6 km arc, indicating very distinct topographic forcing of the tracer. Generally, the SF<sub>6</sub> tracer plume moved in a generally north-west direction from the downwind release site, as evidenced by both the bag sample and mobile real-time analyzer tracer concentrations. However, light winds observed during IOPs 2, 4, and 7 resulted in tracer concentrations being observed at 2 and 4 km arcs thought to be upwind of the release site. The tracer material during these IOPs did not rapidly disperse between tracer release periods, and significant quantities of the tracer remained to add to the concentrations from the subsequent releases. A mesoscale recirculation pattern back toward the downtown area was observed after sunrise during IOPs 5 and 7 and perhaps weakly during IOPs 2 and 4.

#### INTRODUCTION

In the autumn of 2000, scientists funded by the U. S. Department of Energy's (DOE) Chemical and Biological National Security Program (CBNP) of the National Nuclear Security Administration conducted a comprehensive field tracer study in an urban environment. That study has come to be known as URBAN 2000. The study was designed to measure multiple scales of motion, thereby allowing a nested system of atmospheric dispersion models to be tested and evaluated under identical meteorological conditions (Allwine et al., 2002). Since that time, its applicability to homeland security has become readily apparent. CBNP is an applied research and development program that focuses emerging science and technology on countering the challenging threat of chemical and biological weapons attacks on civilian populations (U. S. DOE, 2001). To adequately plan, train and respond to potential attacks, atmospheric models are being developed, tested, and evaluated as part of CBNP to provide users in intelligence, law enforcement, and emergency management with an integrated set of computer-based modeling tools (Allwine et al., 2002).

URBAN 2000 was conducted in Salt Lake City, Utah during October 2000. Salt Lake City has a rather complicated downtown urban building geometry (Fig. 1). The downtown area has buildings ranging in height from a few stories to 40 stories (Fig. 2 and Fig. 3) with numerous parking lots, parking structures, and open areas (Allwine et al., 2002). A set of atmospheric tracer experiments were conducted to investigate transport and dispersion around a single downtown building, through the downtown area and into the suburban area to the northwest of



Figure 1. Oblique aerial photograph of downtown Salt Lake City looking towards the northeast with the Wasatch Mountains in the background. Photograph from Don Green Photography, Salt Lake City, Utah.

downtown. Spatially dense meteorological measurements were made in support of URBAN 2000, both in the downtown area and in the suburban area. In addition, the study area was extended beyond the suburban scale by embedding URBAN 2000 in DOE's concurrent region-wide Vertical Transport and Mixing (VTMX) tracer and meteorological study (Doran et al., 2002).

Both the URBAN 2000 and VTMX studies were designed to investigate the nocturnal boundary layer in stable to neutral atmospheric conditions and both experiments were cooperative multi-agency efforts. URBAN 2000 focused on the urban nocturnal boundary layer, while VTMX focused on the valley-wide nocturnal boundary layer.

Under the URBAN 2000 funding umbrella, NOAA's Air Resources Laboratory (ARL) Field Research Division (FRD) deployed a complete sulfur hexafluoride (SF<sub>6</sub>) atmospheric tracer release and sampling facility together with several meteorological instruments. The deployed tracer facility consisted of mobile SF<sub>6</sub> line and point source release mechanisms, six mobile real-time SF<sub>6</sub> analyzers mounted in vans, and 100 stationary bag samplers together with an appropriate number of control, duplicate, and blank samplers. The tracer analysis facility (TAF), used to analyze bag samples, was not deployed to the field; instead, the samples were transported back to the FRD home office in Idaho Falls, ID for analysis. Perfluorocarbon tracers (PFTs) were also used in URBAN 2000 and VTMX,

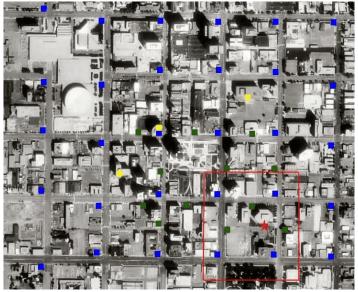


Figure 2. Map of Salt Lake City downtown building domain showing location of release site (red star), street corner samplers (blue squares), mid-block samplers (green squares), and rooftop samplers (yellow squares). Map background courtesy of USGS.

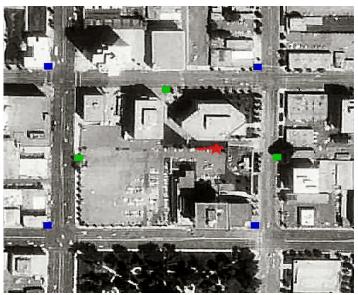


Figure 3. Map of the block and building domain surrounding the release site (red star) during Urban 2000. Also pictured is the line source (red line), the downtown street-corner samplers (blue square), and the downtown mid-block samplers (green square). Map background courtesy of USGS.

however these were under the control of other experiment participants. At the time of printing, these specific PFT reports are unknown; therefore they are not reported here. This report describes the entire SF<sub>6</sub> portion of the URBAN 2000 study. A separate report contains a summary of the meteorological data acquired by FRD as a separate part of VTMX/URBAN 2000 (Clawson and Crescenti, 2002).

The URBAN 2000 and VTMX programs worked in harmony with each other through the planning stages and into field deployment. All of the Intensive Observation Periods (IOPs) of URBAN 2000 were conducted simultaneously with VTMX IOPs and followed the VTMX IOP numbering system. However, URBAN 2000 was not operational during VTMX IOPs 3, 6, and 8. A summary of IOPs is given in Table 1. Doran et al. (2002) defined two major meteorological categories of IOPs. Their analysis is quoted here in full for the benefit of the reader for easier understanding of the results that follow in this publication.

"IOPs with well-developed drainage circulations. IOPs 5 (14–15 October), 6 (16–17 October), and 8 (19–20 October) can be characterized by clear skies, weak winds aloft at crest level, strong nocturnal radiation inversions, limited moisture in the boundary layer, and pronounced drainage flow into the Salt Lake Valley from the west, south, and east. The surface-based inversions and drainage circulations developed after sunset and persisted without significant interruption until sunrise. While the synoptic and mesoscale conditions present during these periods helped to develop these stable boundary layers, the large-scale conditions were for the most part irrelevant to IOP operations.

"IOPs modulated by synoptic and mesoscale weather systems. IOP 1 (2–3 October) was intended to test operational procedures for the field program. Operations during the evening were conducted under clear skies with drainage flows developing as the evening progressed. However, a synoptic-scale northerly pressure gradient developed overnight to such an extent that northerly winds began to penetrate into the northern end of the Salt Lake Valley before midnight and eventually reversed the downvalley (southerly) flow through the center of the valley. Drainage circulations down into the valley from the Oquirrh and Wasatch Mountains were largely unaffected, however.

"IOPs 4 (8–9 October) and 7 (17–18 October) exhibited similar boundary layer structure to those in the first category until 0500 LST. Prior to that time, clear skies, weak winds aloft, and strong surface-based radiation inversions prevailed. As a result of approaching upper-level troughs from the west, however, the nocturnal inversions were then eroded in these two instances both by surface heating and by mixing due to the downward penetration of southerly winds from aloft.

"During IOPs 2 (6–7 October) and 3 (7–8 October), split flow aloft was present with weak upper-level short waves to the southwest and northeast of Utah. A strong outbreak of cold air to the east of the Continental Divide progressed westward on 6 October and overnight. By 0000 LST, easterly flow developed through gaps in the Wasatch Mountains and spilled through Parley's Canyon into the Salt Lake Valley. At 0300 LST,

the depth of the cold air to the east of the Wasatch Mountains built to sufficient height to spill over the lower terrain from Mill Creek Canyon to the area near the University of Utah in the northeast corner of the Salt Lake Valley and led to gusts in excess of 20 m s<sup>-1</sup> that penetrated 1–2 km into the valley at the surface. These downslope wind conditions occur frequently along the Wasatch Mountains and the data collected during VTMX 2000 will provide considerable insight into their formation. The third IOP began at 1500 LST on 7 October and was terminated before midnight. Strong downslope winds persisted into the evening in the northeastern corner of the Salt Lake Valley and winds in the western part of the valley were too turbulent to permit tethersondes operations.

"Conditions during the last two IOPs (IOP 9: 20–21 October and IOP 10: 25–26 October) were affected significantly by approaching upper-level troughs. Both began in the afternoon with weak short-wave ridges overhead. Skies were broken to overcast and the strength of the nocturnal surface inversion and drainage circulations were weaker than those present during the other IOPs. A cold front entered the Salt Lake Valley at 0500 LST 21 October, ending operations during IOP 9. Southerly surface winds were enhanced during IOP 10 and provided favorable conditions for the final tracer release for the downtown region."

Table 1. Summary of URBAN 2000/VTMX IOPs.

|     | IOP Start |               | IOP End   |               |  |
|-----|-----------|---------------|-----------|---------------|--|
| IOP | Date      | Time<br>(MDT) | Date      | Time<br>(MDT) | Meteorological Summary   |
| 1   | 02 OCT 00 | 1600          | 03 OCT 00 | 0500          | Clear skies, weak winds, well-developed drainage                                   |
| 2   | 06 OCT 00 | 1600          | 07 OCT 00 | 1300          | Strong easterly downslope winds after 0000-0300 MDT penetrating 1-2 km into valley |
| 4   | 08 OCT 00 | 1600          | 09 OCT 00 | 1300          | Clear skies, weak winds, well-developed drainage, approaching trough               |
| 5   | 14 OCT 00 | 1600          | 15 OCT 00 | 1300          | Clear skies, weak winds, well-developed drainage                                   |
| 7   | 17 OCT 00 | 1600          | 18 OCT 00 | 1300          | Clear skies, weak winds, well-developed drainage, approaching trough               |
| 9   | 20 OCT 00 | 2200          | 21 OCT 00 | 0400          | Cloudy skies, weak to moderate winds, weak drainage, approaching trough            |
| 10  | 25 OCT 00 | 1600          | 26 OCT 00 | 1300          | Cloudy skies, moderate winds, weak drainage, approaching trough                    |

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#### EXPERIMENTAL DESIGN

The placement of  $SF_6$  release and sampling equipment was designed around the nested urban-suburban sampling concept. Samplers were placed on both arcs and grids in an effort to quantify transport and dispersion characteristics in both areas. Arcs were used in the suburban domain, while a grid sampling array was used in the urban or downtown area. Figure 4 shows the schematic representation of the entire experiment domain overlaid on a base map of the city. The  $SF_6$  release location is indicated by a red star in the middle of the figure. The site of the radar profiler and Doppler sodar described in Clawson and Crescenti (2002) is indicated near the bottom center of the map by a red plus sign. The two major experiment domains are represented by 1) red arcs and circles and 2) by the blue square in the center of the map. The red arcs and

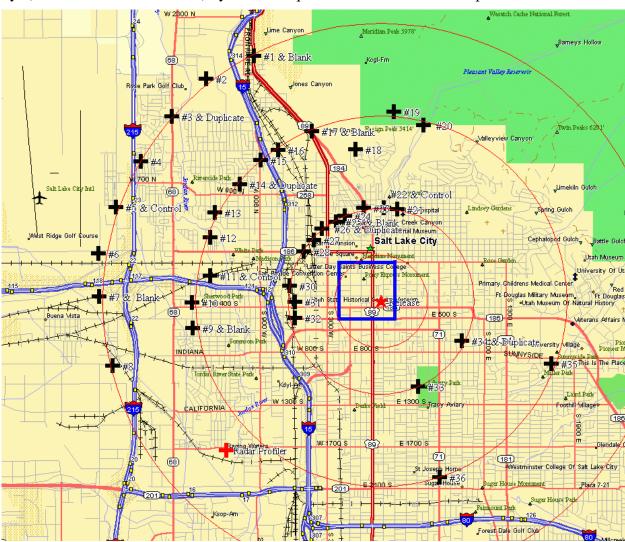


Figure 4. Map of URBAN 2000 experimental domain in Salt Lake City, UT, showing the  $SF_6$  release site (red star), suburban sampling arcs (thin red circles or arcs) and sampling sites (black plus), and the urban sampling grid array denoted by the blue box.

circles represent the approximate boundary of the suburban domain, while the blue box represents the urban boundary. The innermost circle is 1 km from the release site, while the more distant circles and arcs are 2, 4, and 6 km from the release site. Most stationary time-integrated samplers were placed to the northwest of the release site, in the prevailing downwind direction. A discussion of the locations of these samplers is given in the following sections. Details of the equipment used during the experiment are given in succeeding chapters.

The experiment domains bordered and even encroached on complex terrain. Figure 5 shows the experimental domain overlaid on a 3-dimensional map of Salt Lake City. The 6 km or outermost arc had to be truncated on its eastern boundary because of very steep mountain slopes and inaccessible terrain. The 4 km arc, although completely expanded to its desired eastern boundary, was adjusted along the northern portion of the arc at sampler locations 18, 19, and 20 because of rugged terrain. Sampler location 20 was in the bottom of City Creek Canyon. Sampler locations 21-24, on the 2 km arc were on the hill on which the state capitol building stands. Sampler location 35, on the 4 km Southeastern arc, was on a plateau also above what could be considered the main Salt Lake Valley floor. The terrain features were assumed to have a mild to strong influence on the atmospheric tracer trajectory.

Nearly all samplers were hung from hooks attached to light poles or power poles conveniently sited near the designated location. The hooks were 3.05 m AGL, which placed the samplers out of the reach of the public and prevented tampering and theft. Following this procedure sometimes resulted in placing the sampling location not precisely where it was originally specified. In addition, some samplers were specified to be placed in rugged terrain



Figure 5. Experimental domain overlaid on a 3-dimensional map. Vertical relief is enhanced 4 times the horizontal. Interstate 80 is the blue and red road at the bottom of the figure, while Interstate 15 is the north-south blue and red road to the left of center.

where no poles existed. These samplers were placed on the ground and hidden from the general public. The locations where samplers were placed on the ground were: 18, 19, and 20. Samplers at locations 71, 77, 78, and 84 were placed on building tops, as discussed below.

#### **Suburban Sampling Arcs**

A total of 36 stationary time-integrated bag samplers were placed on five suburban sampling arcs with a spacing of about 10 degrees. Sampler locations 1-32 were to the northwest of the release site in prevailing downwind directions. Sampler locations 1-8 were on the 6 km arc with numbers increasing from north to south. Sampler locations 9-20 were on the 4 km arc, with numbers increasing from south to north. Sampler locations 21-32 were on the 2 km arc, with numbers increasing from north to south. Sampler locations 33-36 were to the southeast of the release site in prevailing upwind directions. Sampler locations 33 and 34 were on the 2 km southeast arc, while sampler locations 35 and 36 were on the 4 km southeast arc. Samplers on the 1 km arc were actually arranged in the urban grid, which is discussed below.

Nearly all the suburban samplers were programmed to begin sampling when the  $SF_6$  releases began and to continue sampling for 6 hours. With 12 bags per sampler to fill, each bag was usually filled using a ½ hour time duration. However, some of the samplers were programmed to sample for 12 hours or one hour per bag. This was done to determine if a recirculation pattern developed after sunrise whereby the diluted tracer would be advected back over the sampling array. The samplers programmed to sample for one hour on the suburban arcs were at locations 2, 5, 12, 16, 25, 29, and 33-36. A summary listing of sampling times is given in Table 2, together with the general categorical arc and grid groupings.

### **Urban Street-corner Sampling Grid and Building-top Samplers**

In order to quantify transport and dispersion in the urban or downtown area, SF<sub>6</sub> samplers were placed in a grid array on every street corner in a 5-block area of downtown Salt Lake City (Fig. 6). The release mechanism was placed near the south-east corner of the array, as represented by the red star. With the release mechanism in this location, most of the samplers were climatologically downwind. A total of 36 samplers were placed in the strict street-corner grid array. Sampler location numbers in this grid array ranged from 61 to 100 and increased in number from north to south and from west to east. Four of the samplers in this number range were placed on building rooftops. Sampler location number 71 was on the top of the Hilton Hotel (56 m AGL) at 255 South West Temple. Sampler locations 77 and 78 were on top of the Wells Fargo Bank building (64 m AGL) on the northeast corner of Main and 200 South. Sampler location 84 was on top of the Federal Building (36 m AGL) on the south east corner of State Street and 100 South.

Table 2. Stationary time-integrated bag sampler categorical groupings, sampler start times, and sampling durations.

| Sampling Grid,                                    |  | Sample                           | Sample    |
|---|--|----------------------------------|-----------|
| Arc, or   |  | Start                            | Duration  |
| Grouping  | Sampler Location Number  | Time                             | (minutes) |
| 6 km Arc  | 1, 3-4, 6-8  | Beginning of Tracer IOP          | 30        |
|   | 2, 5   | Beginning of Tracer IOP          | 60        |
| 4 km Arc  | 9-11, 13-15, 17-20   | Beginning of Tracer IOP          | 30        |
| 4 KIII AIC  | 12, 16   | Beginning of Tracer IOP          | 60        |
| 2 km Arc  | 21-24, 26-28, 30-32  | Beginning of Tracer IOP          | 30        |
| 2 KIII AIC  | 25, 29   | Beginning of Tracer IOP          | 60        |
| 2 km Southeast<br>Arc                             | 33-34  | Beginning of Tracer IOP          | 60        |
| 4 km Southeast<br>Arc                             | 35-36  | Beginning of Tracer IOP          | 60        |
| Downtown<br>Street-corner                         | 61, 63, 66, 74, 81, 95, 97, 100                                | Beginning of Tracer IOP          | 60        |
| Grid  | 62, 64-65, 67-70, 72-73, 75-76, 79-80, 82-83, 85-94, 96, 98-99 | ), 72-73, 75-76, Beginning of    |           |
| Duilding Ton                                      | 71, 77, 84   | Beginning of Tracer IOP          | 30        |
| Building Top                                      | 78   | 6 hrs. After Start of Tracer IOP | 30        |
| Downtown  | 37, 39, 41, 43, 45, 47,  | Beginning of                     |           |
| Mid-block Grid                                    | 49, 51, 53, 55, 57, 59   | Tracer IOP                       | 15        |
| 38, 40, 42, 44, 46, 48,<br>50, 52, 54, 56, 58, 60 |  | 3 hrs. After Start of Tracer IOP | 15        |

Building-top sampler locations had to be moved when access to building tops was rendered impossible. This occurred twice during sampler servicing on weekends when no security personnel were available to permit entry to the top of the Wells Fargo Bank Building. During IOPs 5 and 10, samplers at locations 77 and 78 were moved to the top of the 200 South Street Parking structure located midway between State Street and 200 East on the north side of 200 South. The multi-level parking garage was 14 m AGL.

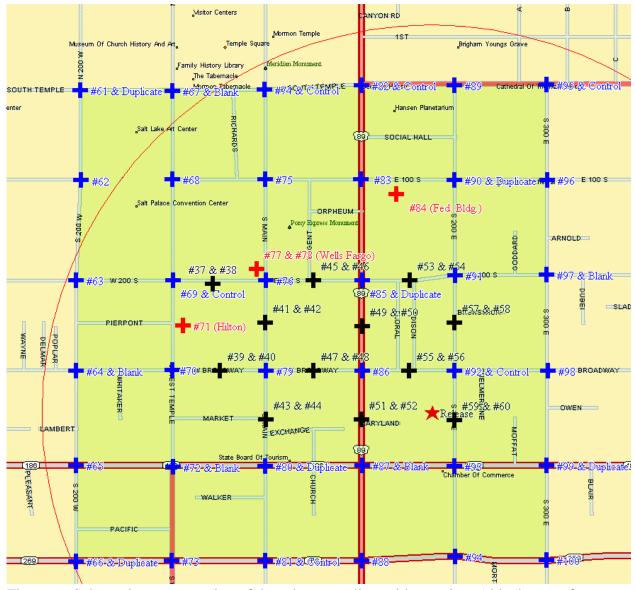


Figure 6. Schematic representation of the urban sampling grid array in a 5-block area of downtown Salt Lake City (yellow box) showing the location of the SF<sub>6</sub> release site (red star), the downtown street-corner grid array (blue plus), the downtown mid-block grid array (black plus), and the rooftop samplers (red plus).

Sample durations for samplers in the urban street-corner grid array were similar to those on the suburban arcs (Table 2). All samplers were programmed to start with the beginning of the initial  $SF_6$  release and most were programmed to sample for ½ hour per bag for a total time of 6 hours. Eight samplers were programmed to sample for one hour per bag. Those locations were 61, 63, 66, 74, 81, 95, 97, and 100. Of the samplers placed on the building tops, samplers at three locations (71, 77, and 84) were all programmed to begin sampling at the beginning of the initial  $SF_6$  release and to continue for 6 hours, with each bag containing a ½ hour sample. The sampler at location 78 was programmed to begin sampling 6 hours after the initial  $SF_6$  release,

and to continue for 6 hours, with each bag containing a ½ hour sample. Thus the two samplers placed on the Wells Fargo (77 & 78) building complemented each other with both samplers collecting a combined total of 24 sequential ½ hour samples over 12 hours.

All urban downtown street-corner grid samplers (except for duplicate, blank, and control samplers) and all roof-top samplers were fitted with capillary adsorption tube samplers (CATS). The SF<sub>6</sub> samplers so modified were placed at sampling locations 61-100. The purpose of the CATS was to sample four perfluorocarbon tracers (PFT) released in support of the concurrent VTMX study. The results of that study are not included here because the SF<sub>6</sub> tracer experiment is the focus of this document. The PFT data are to be reported by Brookhaven National Laboratory who analyzed the PFT samples.

#### **Urban Mid-block Sampling Grid**

Twenty-four additional samplers were placed at 12 mid-block sites within the urban street-corner sampling array. The samplers were placed approximately ½ way between intersections to enhance the urban array both spatially and temporally. The locations of these samplers are illustrated in Fig. 6 The sampler locations were numbered sequentially beginning with 37, and increased in number from north to south and from east to west. Two different sampler location numbers were required at each site because two samplers were placed at each site.

Sample durations for the mid-block urban samplers are given in Table 2. All samplers were programmed to provide 15-minute samples for a total sampling time of 3 hours per sampler. All samplers placed at odd-numbered locations were programmed to begin sampling at the beginning of the tracer IOP. All samplers placed at even-numbered locations were programmed to begin sampling three hours after the beginning of the tracer IOP, i.e., immediately after the sampling period of their odd-numbered counterparts ended. Hence, the total sampling time at each site was 6 consecutive hours.

### **Quality Assurance Samplers**

Quality assurance procedures were strictly followed, including collection of duplicate, blank, and control samples. The procedures are outlined in a later chapter but the locations of the samples are described here. Duplicate samples were simply samplers placed at the same location as the primary sampler and programmed with the identical start and stop times. Blank samplers were special samplers programmed and placed in like manner as the duplicate samplers along with primary samplers. These samplers sequentially pumped a nitrogen sample from a series of 12 supply bags into 12 sample bags. Control samplers were similar to blank samplers except that the supply bags contained various known concentrations of SF<sub>6</sub>. Ten duplicate samplers, 10 blank samplers, and 10 control samplers were randomly placed on the sampling arcs and in the downtown street-corner grid array to comply with the procedure to have 10% duplicate, blank, and control samples. The location of these samplers is given in Table 3. No quality control samplers were placed on building tops nor in the downtown mid-block grid array. It was too

cumbersome to take additional samplers to the tops of the buildings. The downtown midblock grid array sampling sites already had two samplers at each location, making it impossible to crowd in a third sampler.

#### **Mobile Real-time Analyzers**

Four real-time mobile SF<sub>6</sub> analyzers were deployed on the 1, 2, 4, and 6 km arcs to determine the maximum concentration, location of the maximum concentration, and extent of the SF<sub>6</sub> plume. Each analyzer was installed in a minivan, which also served as servicing vans for the stationary samplers. The mobile sampling protocol called for the van to traverse the plume perpendicular to the flow along the designated arc. This practice was followed to the extent possible. However, actual locations of freeway and railway overpasses and lack of streets or roads forced modification to the intended sampling routes. Sampling along the 4 and 6 km arcs was most greatly affected by these physical constraints. Typical sampling routes are shown in Fig. 7. The sampling routes were also altered with changing meteorological conditions. On various occasions the mobile analyzers on the outer

Table 3. Location of the quality control samplers (duplicate, blank, control).

| Sampling Grid,          |           |                        |  |  |
|-------------------------|-----------|------------------------|--|--|
| Arc, or                 | Type of   |                        |  |  |
| Grouping                | Sampler   | Location Number        |  |  |
|                         | Blank     | 1, 7                   |  |  |
| 6 km Arc                | Control   | 5                      |  |  |
|                         | Duplicate | 3                      |  |  |
|                         | Blank     | 9, 17                  |  |  |
| 4 km Arc                | Control   | 11                     |  |  |
|                         | Duplicate | 14                     |  |  |
|                         | Blank     | 25                     |  |  |
| 2 km Arc                | Control   | 22, 29                 |  |  |
|                         | Duplicate | 26                     |  |  |
| 21 0 1                  | Blank     | none                   |  |  |
| 2 km Southeast<br>Arc   | Control   | none                   |  |  |
| Aic                     | Duplicate | 34                     |  |  |
| 4.1 G .1                | Blank     | none                   |  |  |
| 4 km Southeast<br>Arc   | Control   | none                   |  |  |
| Aic                     | Duplicate | none                   |  |  |
| Downtown                | Blank     | 64, 67, 72, 87, 97     |  |  |
| Street-corner           | Control   | 69, 74, 81, 82, 92, 95 |  |  |
| Grid                    | Duplicate | 61, 66, 80, 85, 90, 99 |  |  |
|                         | Blank     | none                   |  |  |
| <b>Building Top</b>     | Control   | none                   |  |  |
|                         | Duplicate | none                   |  |  |
| Б                       | Blank     | none                   |  |  |
| Downtown Mid-block Grid | Control   | none                   |  |  |
| IVIIU-DIOCK GIIU        | Duplicate | none                   |  |  |

arcs were unable to measure  $SF_6$  due to stagnant conditions near the release site. These mobile analyzers were redeployed near the downtown area to determine the movement of the  $SF_6$  to the north, south, and east of the release site. Sampling by the mobile analyzers continued until  $SF_6$  along the various arcs could no longer be detected or until sampling was halted by the need to calibrate the instrument in preparation for the next planned dissemination of the  $SF_6$  tracer.

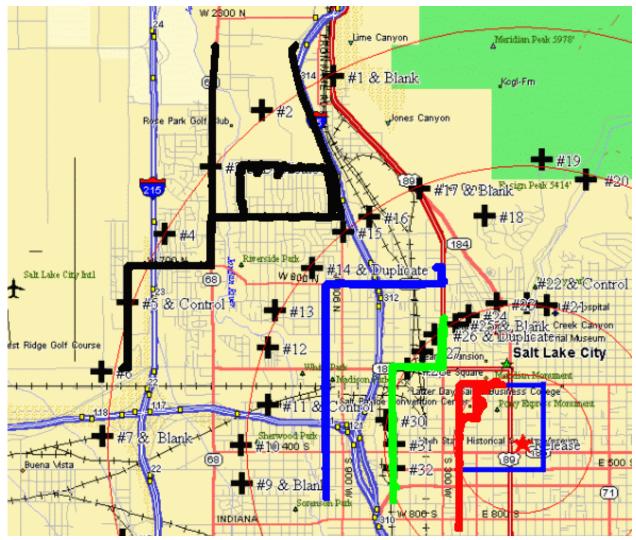


Figure 7. Typical mobile real-time  $SF_6$  analyzer sampling routes on the 1 km arc (red), 2 km arc (green), 4 km arc (blue), and 6 km arc (black).

Two additional real-time  $SF_6$  analyzers were deployed in a quasi-stationary manner approximately 1 and 2 blocks downwind from the release site. These analyzers were also installed in minivans and were deployed essentially on State and Main Streets. After the release of  $SF_6$  began, these analyzers became mobile in an attempt to determine the location of the highest  $SF_6$  concentration. Once those locations were determined, the minivans were parked and sampling of the plume continued at those sites until the plume was no longer detected. If the  $SF_6$  release had not ended before the end of the plume detection at the current site, the minivan would once more become mobile to again determine the location of the highest  $SF_6$  concentration and the process would repeat itself. Sampling by the quasi-stationary analyzers continued in this manner until  $SF_6$  could no longer be detected.

## SF<sub>6</sub> TRACER RELEASE SYSTEM

The  $SF_6$  release mechanism was custom-built for the URBAN 2000 program by NOAA at the FRD offices in Idaho Falls, ID. The system was built inside a recreational vehicle (RV) so that it could be quickly deployed to and removed from the release site with ease (Fig. 8).

Landlord restrictions placed on the release site required that the release system be setup after business hours (usually after 2200 hrs MDT) and removed by 0600 hrs MDT the following morning. The complete release system, other than the dissemination device, was entirely selfcontained in the RV and required only 115 VAC (Fig. 9). Releases of SF<sub>6</sub> were either from a point source or line source. When connected to the line source, the release mechanism was connected by means of a flexible 13 mm diameter Tygon® tube. When a release from a point source was desired, this same tube served as the dissemination device. Table 4 lists the type of dissemination, i.e., line or point source, for the various IOPs together with the beginning and ending dissemination periods.

The heart of the SF<sub>6</sub> release system was a computer-controlled mass flow controller. The system included both digital and analog output as well as computer and manual controls. Flow rate from the mass flow controller and weight change, as measured by a load cell attached to the SF<sub>6</sub> cylinder, were continuously monitored and



Figure 8. RV containing the entire SF<sub>6</sub> release system except for the dissemination device.



Figure 9. SF<sub>6</sub> release mechanism mounted inside the RV.

Table 4. Summary of SF<sub>6</sub> tracer IOPs, including release date and time, type of release (point or line), target release rate, actual average release rate from the mass flow meter, and total mass of SF<sub>6</sub> released for each release period.

|         | Tracer Start |               | Tracer End |               |                 | Target<br>Release         | Actual<br>Release                    | Total<br>Amount |
|---------|--------------|---------------|------------|---------------|-----------------|---------------------------|--------------------------------------|-----------------|
| IOP     | Date         | Time<br>(MDT) | Date       | Time<br>(MDT) | Release<br>Type | Rate (g s <sup>-1</sup> ) | Rate (g s <sup>-1</sup> )            | Released (kg)   |
| 1       | 03 OCT 00    | 0100          | 03 OCT 00  | 0200          | point           | 2                         | 2.04 <u>+</u> 0.003                  | 7.31            |
| (Trial) | 03 OCT 00    | 0300          | 03 OCT 00  | 0400          | point           | 1                         | 1.04 <u>+</u> 0.004                  | 3.77            |
|         | 07 OCT 00    | 0100          | 07 OCT 00  | 0200          | line            | 1                         | 1.03 <u>+</u> 0.002                  | 3.68            |
| 2       | 07 OCT 00    | 0300          | 07 OCT 00  | 0400          | line            | 1                         | $1.04 \pm 0.002$                     | 3.82            |
|         | 07 OCT 00    | 0500          | 07 OCT 00  | 0600          | line            | 1                         | $1.03 \pm 0.002$                     | 3.68            |
|         | 09 OCT 00    | 0100          | 09 OCT 00  | 0200          | line            | 1                         | 1.04 +0.001                          | 3.72            |
| 4       | 09 OCT 00    | 0300          | 09 OCT 00  | 0400          | line            | 1                         | 1.04 + 0.005                         | 3.82            |
|         | 09 OCT 00    | 0500          | 09 OCT 00  | 0600          | line            | 1                         | 1.03 <u>+</u> 0.003                  | 3.77            |
|         | 15 OCT 00    | 0100          | 15 OCT 00  | 0200          | line            | 1                         | 1.04 <u>+</u> 0.007                  | 3.72            |
| 5       | 15 OCT 00    | 0300          | 15 OCT 00  | 0400          | line            | 1                         | 1.04 <u>+</u> 0.003                  | 3.77            |
|         | 15 OCT 00    | 0500          | 15 OCT 00  | 0600          | line            | 1                         | 1.04 <u>+</u> 0.002                  | 3.82            |
|         | 18 OCT 00    | 0100          | 18 OCT 00  | 0200          | line            | 1                         | 1.05 <u>+</u> 0.003                  | 3.82            |
| 7       | 18 OCT 00    | 0300          | 18 OCT 00  | 0400          | line            | 1                         | 1.05 <u>+</u> 0.003                  | 3.82            |
|         | 18 OCT 00    | 0500          | 18 OCT 00  | 0600          | line            | 1                         | 1.05 <u>+</u> 0.002                  | 3.86            |
|         | 20 OCT 00    | 2200          | 20 OCT 00  | 2300          | point           | 2                         | 2.05 <u>+</u> 0.015                  | 7.26            |
| 9       | 21 OCT 00    | 0000          | 21 OCT 00  | 0100          | point           | 2                         | $2.05 \pm 0.020$                     | 7.31            |
|         | 21 OCT 00    | 0200          | 21 OCT 00  | 0300          | point           | 2                         | $2.05 \pm 0.028$                     | 7.45            |
|         | 26 OCT 00    | 0100          | 26 OCT 00  | 0200          | point           | 1                         | 1.05 +0.004                          | 3.81            |
| 10      | 26 OCT 00    | 0300          | 26 OCT 00  | 0400          | point           | 1                         | $1.05 \pm 0.004$<br>$1.05 \pm 0.006$ | 3.81            |
| 10      | 26 OCT 00    | 0500          | 26 OCT 00  | 0600          | point           | 1                         | $1.05 \pm 0.000$ $1.05 \pm 0.002$    | 3.72            |
|         | 20 OCT 00    | 0500          | 20 OCT 00  | 0000          | роші            | 1                         | 1.03 <u>+</u> 0.002                  | 3.14            |

recorded with a data logger. Total  $SF_6$  weight loss for each test was determined using the beginning and ending weight of the  $SF_6$  cylinder from an electronic scale. A schematic of the release mechanism is shown in Fig. 10. The general flow of the  $SF_6$  was from the storage bottle into the mass flow controller, through the visible flow meter, and into the Tygon tubing through which it was transported to the dissemination device. The release system was designed to release  $SF_6$  as a gas. Therefore, a heater band was placed around the  $SF_6$  cylinder to convert the liquid  $SF_6$  into gaseous  $SF_6$  before it left the cylinder and entered the control and measurement portions of the mechanism. The system was designed to release  $SF_6$  at a rate of 1-2 g s<sup>-1</sup>, but this rate could be adjusted from 0.1 to 10 g s<sup>-1</sup>.

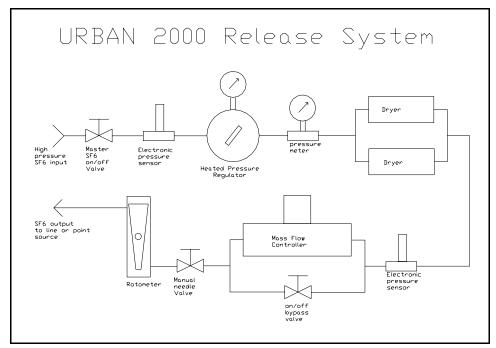


Figure 10. Schematic representation of the mobile SF<sub>6</sub> release mechanism.

### **Line Source Description**

The SF<sub>6</sub> line source was constructed of 25.4 mm inside diameter schedule 40 polyvinyl chloride (PVC) pipe. Small 0.38 mm diameter holes were drilled into the pipe at intervals of 1 m for dispensing the  $SF_6$  into the atmosphere. The pipe was glued together to form a 30 m line source. Equal pressures were measured at both ends of the pipe, therefore, it was concluded that constant pressure was maintained within the pipe throughout the tests. The pipe was attached to the chain link fence that separates the Heber Wells building on the north from the City Centre parking lot on the south. The pipe was attached at a height of about 30 cm above the Heber Wells



Figure 11. East-west fence on abrupt rise between the Heber Wells building and the City Centre parking lot. The line release pipe was attached to this fence approximately 30 cm above ground level of the upper lawn deck on the right hand side of the photo.

building ground level. The fence was on an abrupt rise of about 1.8 m above the surface of the City Centre parking lot, as shown in Fig. 11. The picture was taken before the line source was in place. Figure 12 shows a photograph of the line source inlet end taken during one of the nocturnal releases. The position of the line source in relation to the abrupt ground level change can easily be seen. The inlet end of the line source was at 40° 45.71NN, 111° 53.15NW. The terminal end of the line source was at 40° 45.71NN, 111° 53.18N W. The inflection point of where the fence bowed out between the



Figure 12. Inlet end of  $SF_6$  line source.

inlet end and the terminal end was at 40° 45.71NN, 111° 53.17NW, or approximately 27 m west of the terminal end. Both a GPS unit and Terraserver.com, which contains geo-referenced photos, verified the locations of the release.

#### **Point Source Description**

The SF<sub>6</sub> point source was simply the open end of the Tygon tubing placed in a squirrel cage fan (Fig. 13). This ensured that the SF<sub>6</sub> concentration exiting the fan was below EPA breathing standards of 1,000 ppm by volume. The location of the point source was 40° 45.71NN, 111° 53.16NW, approximately 6.7 m west of the inlet end of the line source. It was placed by the chain link fence on the raised portion of the abrupt rise described earlier.

The SF<sub>6</sub> releases were designed to provide multiple separate tests during a given IOP. For the first IOP, which was a trial test of the SF<sub>6</sub> release and real-time analyzer detection systems, two separate one-hour releases were conducted. Both of those releases were separated by one hour of no tracer release to permit transport of the material out of the



Figure 13. SF<sub>6</sub> point source terminating in a squirrel cage fan.

release area. Each succeeding tracer IOP consisted of three one-hour releases of  $SF_6$ , with each release being separated by a one-hour period of no release to permit the area to be cleansed of the tracer. Thus, a total of  $20 SF_6$  releases were conducted during 7 IOPs. A summary of the tracer releases is given in Table 4.

#### **Release Rates**

The target release rate for most IOPs was 1 g s<sup>-1</sup>, except for the first release of IOP 1 and all releases of IOP 9. Target release rates for the first release of IOP 1 were set at 2 g s<sup>-1</sup> to help the mobile real-time analyzer operators find the location of the  $SF_6$  plume and to quickly and easily determine plume concentrations. Once this purpose was achieved, the release rate for the second release of IOP 1 was decreased to the nominal rate. Wind speeds during IOP 9 were sufficiently strong to indicate a greater potential for dilution of the  $SF_6$  tracer. For this reason, the release rate was doubled to 2 g s<sup>-1</sup>.

Actual release rates from the mass flow meter were slightly higher than the target release rates. Graphs of the  $SF_6$  release rates for each IOP are shown in Figs. 14-20. The range was 2-5% greater than intended. Release rates were designed to be constant throughout each release period. This design was achieved, as can be seen in Table 4. The standard deviations of the actual flow rates from the mass flow meter indicate very constant flow rates with a maximum value of  $0.028 \, \mathrm{g \, s^{-1}}$ .

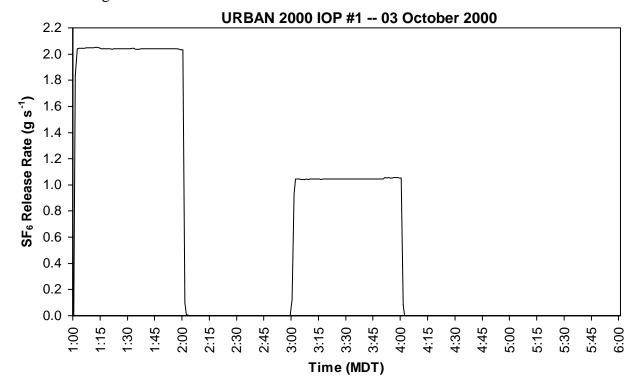


Figure 14. SF<sub>6</sub> release rates for the two release periods of IOP 1.

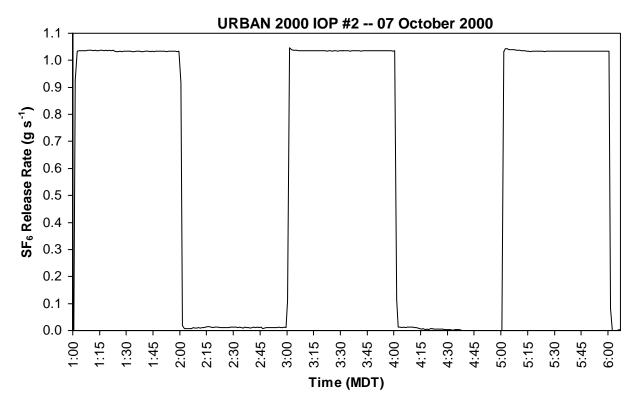


Figure 15.  $SF_6$  release rates for the three release periods of IOP 2.

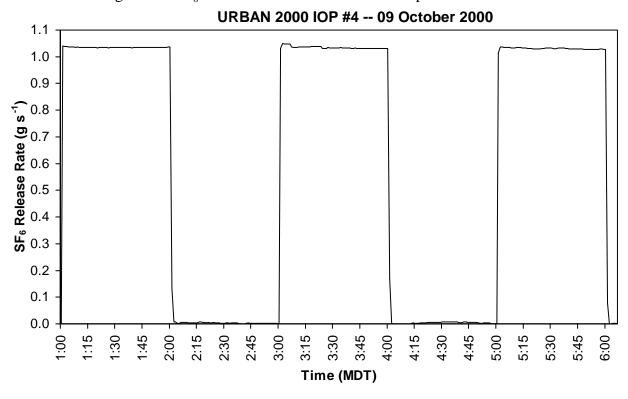


Figure 16. SF<sub>6</sub> release rates for the three release periods of IOP 4.

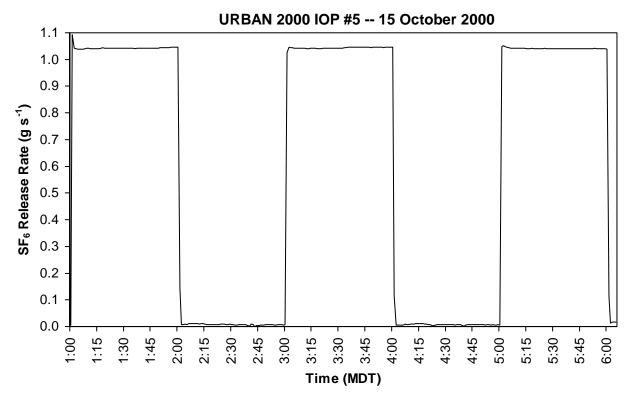


Figure 17.  $SF_6$  release rates for the three release periods of IOP 5.

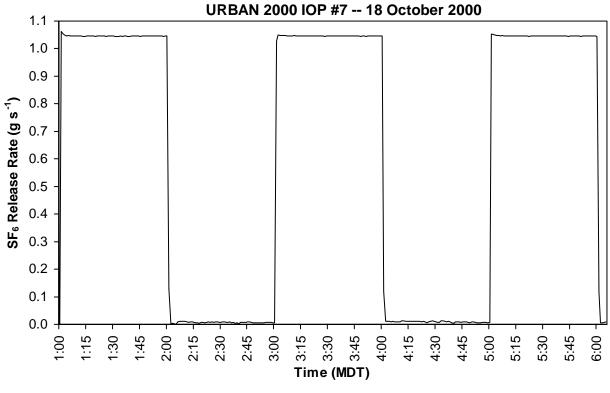


Figure 18. SF<sub>6</sub> release rates for the three release periods of IOP 7.

### URBAN 2000 IOP #9 -- 20-21 October 2000

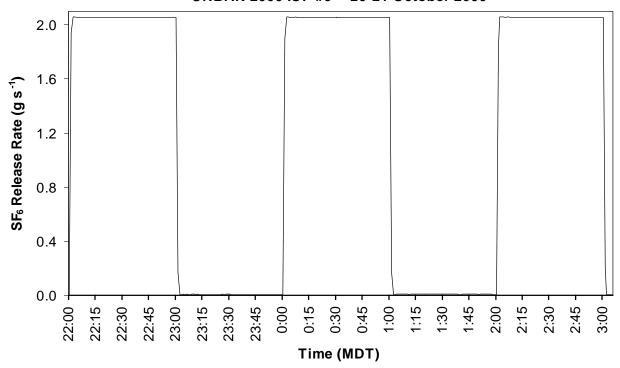


Figure 19. SF<sub>6</sub> release rates for the three release periods of IOP 9.

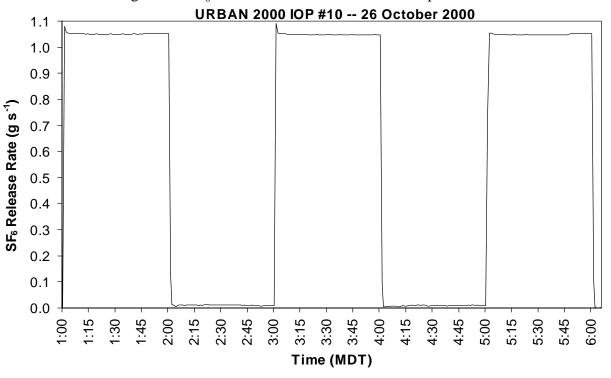


Figure 20. SF<sub>6</sub> release rates for the three release periods of IOP 10.

# TIME-INTEGRATED TRACER SAMPLE ANALYSIS

The time-integrated sampling of SF<sub>6</sub> was performed by the use of devices called PIGS (Programmable Integrating Gas Samplers). The subsequent analysis of the samples was performed by an analysis system called ATGAS (Automated Tracer Gas Analysis System). The analysis system utilized gas chromatography (GC) analysis techniques along with autosampler capabilities that together produced time integrated concentration results. The sampling and analysis systems were designed to provide average SF<sub>6</sub> concentration over specific time intervals at specific points. Typically, PIGS are placed at pre-selected sites prior to the start of an experiment and programmed to collect samples over the pre-defined period of the experiment. The PIGS collect 12 samples each by sequentially pumping air into 12 individual Tedlar® bags. After the experiment is over, the bag samples are then analyzed using the ATGAS. A new set of sample bags may be loaded into the PIGS so sampling can continue while the analysis of the previous samples takes place. By placing a relatively large number of PIGS on arcs or on a grid across the experimental area, a good footprint of the tracer plume may be determined for each sampling period. The technique allows many simultaneous measurements to be made and also offers the advantage of easy comparison to model predictions since atmospheric transport and dispersion models commonly produce time averaged concentrations at specific points.

# **Programmable Integrated Gas Samplers (PIGS)**

The PIGS were comprised of 12 microprocessor controlled air pumps contained in weatherized waxed cardboard boxes measuring 24 in x 16 in x 13 in and weighing 9 pounds as shown in Fig. 21. Inside the sampler box was a smaller cardboard box or cartridge which contained 12 Tedlar® bags as shown in Fig. 22. Each PIGS and the cartridge have unique bar code labels attached. When the PIGS were deployed for an IOP, a small handheld computer called a Timewand was used to record a unique location number at each sampling site, the PIGS number, and the cartridge number. The Timewand then downloaded the programmed start time and sample time per bag into the PIGS' memory. When all the PIGS were deployed, the Timewands were taken back to the laboratory where the Timewand data were up-loaded to the ATGAS. The PIGS collected 12 sequential air samples at the programmed start time for the programmed sample duration. After completion of each IOP, the cartridges were collected and returned to the laboratory for analysis.

### **CATS Tubes Attached to PIGS**

The urban downtown street-corner grid sampler locations, (those closest to the release site), had CATS tubes attached to the outside of the samplers (Fig 23.) The PIGS that were denoted as QC samples did not have CATS tubes attached. The CATS tubes were used to collect perfluorocarbons that were released simultaneously with the SF<sub>6</sub> tracer in support of the VTMX project.



Figure 21. Exterior of the PIGS.



Figure 22. Interior of PIGS showing the 12-bag cartridge inserted into the PIGS.

The sample CATS, the ones under the white strip shown in Fig. 23, were removed from the sampler, capped and then sent to Brookhaven National Laboratory (BNL) for analysis. The permanent CATS, the ones under the red and white stripe band, were left on the sampler and were used to protect the sample CATS from any out-gassing from the pumps, tubing, and Tedlar® bags. New sample CATS were then attached below the guard CATS for the next IOP.



Figure 23. CATS attached to PIGS.

Personnel at BNL assured us that the  $SF_6$  would flow freely through the CATS tubes into the Tedlar® bags and would not adsorb onto either of the CATS tubes in series. BNL asserted that only the perfluorocarbons would adsorb onto the sample CATS tubes. It was planned that the PIGS thus modified with CATS would be used in a dual purpose mode, i.e., sample both perfluorocarbons and  $SF_6$ .

# **Automated Tracer Gas Analysis System (ATGAS)**

The Tracer Analysis Facility (TAF) included four ATGASs. Each ATGAS is a gas chromatograph (GC) connected to an autosampler module and controlling computer as seen in Fig. 24. Each GC included an oven, maintained at 50 /C, that housed two Supelco 60/80 Molecular Sieve-5A columns (5' x 1/4" and 2' x 1/4"), a 10-port sample valve and a sample loop. Detection of SF<sub>6</sub> was accomplished using a Valco Instrument Co. Inc., Model 140BN electron capture detector (ECD) at 70 /C. The ECD's and columns were protected by a Supelco High Capacity Gas Purifier tube heated inside an oven to remove oxygen, water, carbon monoxide, and carbon dioxide as well as a Supelcarb® HC hydrocarbon trap to remove organic impurities. The carrier gas used was UHP nitrogen while the valves were actuated by clean compressed air.



Figure 24. An ATGAS showing from left to right: 1)controlling computer, 2) auto sampler (blue box behind sample cartridge), 3) ECD controller, and 4) column oven (bottom) and ECD (top).

The ATGAS computer software was developed by FRD. The calibration curve used for SF<sub>6</sub> analysis was an interpolation between calibrations that bracket the calculated area

(ARLFRD, 1997). Enhancements were made to the ATGAS software for this project to incorporate specific QC parameters and to increase efficiency. In particular, all data were automatically flagged if a bag was either outside the calibration range, below the method limit of quantitation (MLOQ), unusable due to insufficient sample volume ("flat bag") or if a low bag was analyzed more than once. The software also incorporated the flexibility to allow all quality control flags to be entered by the analyst before being uploaded to the Microsoft® Access database for later query capabilities. Any concentration data point and its corresponding QC data were fully peer reviewed before the upload to the database was performed. The software incorporates a history file system that recorded all operations done on an ATGAS. The history files were records of all events involving the PIGS and cartridges, including PIGS start record, analysis record, cartridge cleaning record, repair record, location number, cartridge check record, and cartridge pick-up record (ARLFRD, 1997). The combined history file provided an invaluable source of information in the event of a discrepancy or a question about the data. All chromatograms were also stored in the database together with the resulting calculated concentrations. This provided the capability to review the raw chromatograms at a later date if needed.

#### **Calibration**

Each ATGAS was calibrated each analysis day using six to twelve NIST ( $\underline{N}$ ational Institute of  $\underline{S}$ tandards and  $\underline{T}$ echnology) traceable SF<sub>6</sub> standards in ultra-pure air (Scott-Marin of Riverside, California). These calibration standards ranged from 1.97 pptv to 208,500 pptv. The ATGAS were calibrated for specific ranges, usually 2-5,000 pptv, 5,000-10,000 pptv, and 10,000-200,000 pptv. Since the calibration curve was based on interpolation between calibration points, this meant that if there were 12 calibration standards used, there were essentially 12 separate curves to verify. In lieu of analysis of 12 separate laboratory control standards (LCS), the calibration curves were verified by the re-analysis of these same calibration standards as if they were field samples.

One of the ways instrument performance was monitored was by the use of the instrument limit of detection (ILOD) and the instrument limit of quantitation (ILOQ). The ILOD is the lowest concentration level than can be determined to be statistically different from a blank or a 0 pptv SF $_6$  sample in the laboratory. The ILOQ is defined here to be the level at which the concentration may be determined with an accuracy of  $\pm$  30%. The recommended values are 3s for the ILOD and 10s for the ILOQ, where s is the standard deviation for measurements made on blanks or low-level standards. The ILOD and ILOQ were calculated for ATGAS #1-3 using instrument blanks of ultra high purity (UHP) nitrogen. ATGAS #1-3 were used to measure SF $_6$  levels from 0 to 10,380 pptv. ATGAS #4 was used to measure higher levels of SF $_6$  and is discussed later. The data for the detection limits are summarized in Table 5. The ILOD for all IOPs was 2 pptv and the ILOQ was 8 pptv.

An alternative method of calculating the ILOD and ILOQ is based on multiple analyses of a low concentration standard. This method is preferable over the analysis of instrument blanks since it more closely mimics the field sample analysis. The average ILOD and ILOQ for ATGAS

#1-3 using this method was 2 pptv and 8 pptv, respectively, as shown in Table 6. Both techniques of ILOD and ILOQ calculation using blanks or a low-level standard produced identical results. Therefore, for laboratory analysis purposes, all data less than 8 pptv, the ILOQ, but greater than 2 pptv, the ILOD, were flagged and considered to be estimates. All data below 2 pptv, the ILOD, were considered indistinguishable from zero.

Table 5. Instrument limit of detection (ILOD) and instrument limit of quantitation (ILOQ) values based on blank analyses.

|         | ` `           |           |        |        |           |
|---------|---------------|-----------|--------|--------|-----------|
|         | Average       |           |        |        |           |
| ATGAS   | Concentration | Standard  | ILOD   | ILOQ   | Number of |
| Number  | (pptv)        | Deviation | (pptv) | (pptv) | Samples   |
| 1       | -0.41         | 1.0       | 3      | 10     | 59        |
| 2       | 0.33          | 0.1       | 2      | 5      | 191       |
| 3       | 0.23          | 0.8       | 2      | 8      | 167       |
| Average | 0.05          | 0.8       | 2      | 8      |           |

An ILOD and ILOQ for ATGAS #4 was calculated using a low-level standard. Blanks could not be used because this ATGAS was calibrated at a much higher concentration level than the other ATGAS's in order to analyze the extremely high  $SF_6$  sample concentrations. The calibration range for this ATGAS was 10,380-208,500 pptv. The ILOD and ILOQ for ATGAS #4 was 1,117 and 3,725 pptv respectively (Table 6).

Table 6. Instrument limit of detection (ILOD) and instrument limit of quantitation (ILOQ) values based on a low-level standard.

|              |        | Percent  |           |        |        | Number  |
|--------------|--------|----------|-----------|--------|--------|---------|
| <b>ATGAS</b> | Conc.  | Recovery | Std. Dev. | ILOD   | ILOQ   | of      |
| Number       | (pptv) | (%)      | (pptv)    | (pptv) | (pptv) | Samples |
| 1            | 3.47   | 103      | 1.0       | 3      | 10     | 26      |
| 2            | 3.47   | 97       | 0.35      | 1      | 3      | 16      |
| 3            | 3.47   | 103      | 1.0       | 3      | 10     | 45      |
| Average      |        | 101      | 0.79      | 2      | 8      |         |
|              |        |          |           |        |        |         |
| 4            | 10,380 | 101      | 372       | 1,117  | 3,725  | 17      |

The number of samples for the instrument blanks method is much larger than the low-level standard method due to the fact that the lab blank cartridge consisted of 12 bags containing only UHP nitrogen. The low level standard results are taken from the calibration checks and only one bag in the cartridge contained the low-level  $SF_6$  concentration used in the calculation.

The method limit of detection (MLOD) and method limit of quantitation (MLOQ) were calculated in the same manner as the ILOD and ILOQ except that the data used to calculate these values stemmed from field analyses rather than laboratory analyses. Used in this manner, the MLOD and MLOQ include all sampling variability as well as the laboratory analysis variability.

The standard deviation of the 552 field blank analyses resulted in an average of 3.3 pptv and a standard deviation of 4.5 pptv. Therefore, the MLOD of all IOPs was 14 pptv and the MLOQ was 45 pptv. Thus all concentration data less than 45 pptv, (the MLOQ), but greater than 14 pptv, (the MLOD), were appropriately flagged and considered to be estimates. All concentration data below 14 pptv, the MLOD, were considered indistinguishable from zero and were also appropriately flagged. A summary of the MLOD and MLOQ using the field blanks for each IOP can be seen in Table 7.

Table 7. The method limit of detection (MLOD) and method limit of quantitation (MLOQ) based on field blanks.

|         |         | Standard  |        |        |           |
|---------|---------|-----------|--------|--------|-----------|
| IOP     | Average | Deviation | MLOD   | MLOQ   | Number of |
| Number  | (pptv)  | (pptv)    | (pptv) | (pptv) | Samples   |
| 2       | 2       | 3         | 9      | 30     | 115       |
| 4       | 3       | 4         | 10     | 32     | 111       |
| 5       | 7       | 7         | 22     | 74     | 90        |
| 7       | 3       | 5         | 15     | 51     | 99        |
| 9       | 1       | 3         | 8      | 26     | 27        |
| 10      | 4       | 5         | 15     | 49     | 110       |
| Average | 3.3     | 4.5       | 14     | 45     |           |

The MLOD and MLOQ were also calculated using a low-level standard of 20 pptv from the series of field deployed controls. The analysis of the 50 field samples resulted in an MLOD of 13 pptv and an MLOQ of 42 pptv (Table 8.) These values compare well with the field blank-based MLOD and MLOQ values. The MLOD and MLOQ used to compile the final data set were based on field blanks as described in the previous paragraph. The number of samples for the field blanks was much larger due to the fact that the field blank cartridge consisted of 12 bags containing only UHP nitrogen. Therefore, since 10 field blank cartridges were analyzed per IOP,

Table 8. The method limit of detection (MLOD) and method limit of quantitation (MLOQ) based on a low level standard.

|         |          | Standard  |        |        |           |
|---------|----------|-----------|--------|--------|-----------|
| IOP     | Recovery | Deviation | MLOD   | MLOQ   | Number of |
| Number  | (%)      | (pptv)    | (pptv) | (pptv) | Samples   |
| 2       | 104      | 1.5       | 5      | 16     | 8         |
| 4       | 103      | 6.5       | 14     | 48     | 9         |
| 5       | 109      | 6.3       | 15     | 50     | 9         |
| 7       | 123      | 2.1       | 27     | 90     | 10        |
| 9       | 104      | 1.3       | 4      | 13     | 4         |
| 10      | 109      | 3.9       | 10     | 34     | 10        |
| Average | 109      | 3.6       | 13     | 42     |           |

the maximum number of samples per IOP was 120. The number of samples for the low level standard was significantly less since only one bag in the cartridge contained the  $SF_6$  concentration that the results were calculated on. Therefore, since there were 10 field control cartridges with only one bag containing the required  $SF_6$  concentration, the maximum number of samples per IOP was 10.

Since the data set for the low level standard was so much smaller, the outliers in the smaller data set could greatly influence the results. Although both methods of calculating the MLOD and MLOQ by field blanks or a low level standard resulted in very close results, the number of field blanks analyzed was almost ten times greater thereby giving a much more statistically reliable result and was used in the final data set.

## **Quality Assurance**

Quality assurance and quality control procedures were followed, where applicable, as stated in protocols established in the Environmental Protection Agency's (EPA) Guidance for Data Quality Assessment (EPA, 2000), the general requirements for the competence of calibration and testing laboratories of ISO/IEC Guide 25 (ISO, 1990) and the Quality Systems established by the National Environmental Laboratory Accreditation Conference (NELAC, 2000). Although our research-based automated analysis of tracer gases has no specified method performance or regulatory criteria, we complied with the established quality control procedures stated below, where applicable, to provide high quality data that is both accurate and reliable.

Laboratory quality control procedures consisted of 16 steps listed below and described in detail in the following paragraphs:

- 1. Pre-deployment maintenance of PIGS
- 2. Pre-deployment analysis of all PIGS cartridges
- 3. Re-analysis of 10% of cartridges used in previous IOP
- 4. Sample check-in
- 5. Daily calibration of each ATGAS
- 6. Initial calibration verification (ICV)
- 7. Atmospheric background checks
- 8. Laboratory (instrument) blanks
- 9. Continuing calibration verification (CCV)
- 10. Laboratory duplicates
- 11. Laboratory controls
- 12. Field blanks
- 13. Field duplicates
- 14. Field controls
- 15. Data verification
- 16. Method verification

### **Pre-deployment maintenance of PIGS**

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

## Pre-deployment analysis of all PIGS cartridges

Prior to deployment to the field, approximately 700 cartridges were cleaned, 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 yielding concentrations greater than 10 pptv were recleaned and re-analyzed. All bags were stored in an evacuated state until their use.

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

After the completion of each IOP, all cartridges were cleaned with UHP nitrogen. Ten percent 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.

### Sample Check-in

All cartridges were checked-in prior to analysis. 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 additional QC flagging of the final data output.

# Daily calibration of each ATGAS

Each ATGAS was calibrated at the beginning of each analysis day using six to twelve NIST traceable SF<sub>6</sub> standards as described previously. The calibration standards ranged from 1.97 pptv to 208,500 pptv. ATGAS #1-3 were usually calibrated from 1.97 pptv to 10,380 pptv while ATGAS #4 was calibrated from 10,380-208,500 pptv (see Table 9). The calibration ranges of ATGAS #1-3 were modified occasionally to accommodate the concentration ranges on samples being analyzed. Concentrations of samples were calculated by interpolation between concentrations of calibration gases.

Table 9. Calibration concentration ranges for each ATGAS.

|              | Lowest Concentration     | Highest Concentration    |
|--------------|--------------------------|--------------------------|
| ATGAS Number | Calibration Point (pptv) | Calibration Point (pptv) |
| 1            | 1.97                     | 10,380                   |
| 2            | 1.97                     | 10,380                   |
| 3            | 1.97                     | 10,380                   |
| 4            | 10,380                   | 208,500                  |

### **Initial calibration verification (ICV)**

After each ATGAS calibration was completed, the curves were validated by analyzing the same calibration standards as samples. The recoveries were required to be within  $\pm 15\%$  or the standards were re-analyzed. If the recoveries still did not meet the acceptance limits, the bags were refilled and analyzed again. If they still were not acceptable, the instrument was recalibrated.

### Atmospheric background checks

A background check was analyzed on one ATGAS every analysis day to determine the SF<sub>6</sub> concentration in the laboratory atmosphere. 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. Background levels in the laboratory varied from 5 pptv to 37 pptv.

# 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 and that there was no carry-over from previously analyzed high concentration standards. The blank consisted of a cartridge of twelve bags that were each filled with UHP nitrogen. The concentration results of all bags were required to be less than the lowest calibration standard. If the concentration of one or more of the bags was not within 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 as estimates and re-analyzed. If there were still indications of contamination, the problem was identified and fixed before analysis continued. A total of 417 instrument blanks were analyzed that ranged in concentration from -2.38 to 4.04 pptv. Most results were in the range of  $\pm 1$  pptv. These figures indicate no significant evidence of contamination in the laboratory or the ATGAS, especially when compared to the measured laboratory background levels.

### **Continuing calibration verification (CCV)**

Approximately every 2 hours during the operation of the ATGAS, the validity of the instrument calibration curves were checked by analyzing all the calibration standards as samples, just as was done for the ICV. The standards were required to have a recovery of  $\pm 30\%$  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 as estimates if a re-analysis could not be completed.

# **Laboratory duplicates**

ATGAS instrument precision was checked by the use of laboratory duplicates. Each day at least one field sampler cartridge was analyzed in duplicate on each ATGAS. 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  $\pm 20$  %. Any result not within the acceptable limits was either re-analyzed or flagged as an estimate. A summary of the duplicate results can be seen in Table 10. The average RPD for all laboratory duplicates above the ILOQ of 8 pptv, was calculated to be -1.2% with an average standard deviation of 3.4 %. Table 10 also shows the RPD in different concentration ranges at the 95% confidence level. All laboratory duplicate RPD's were less than 10%, at the 95% confidence level except for those below the ILOQ indicating excellent instrument precision.

Table 10. Summary of laboratory duplicate results using relative percent difference (RPD) at different concentration ranges.

|   | Average |              |                     | Number  |
|---|---------|--------------|---------------------|---------|
| Conc. Range   | RPD     | RPD Std. Dev | 95% Confidence (2s) | of      |
| (pptv)  | (%)     | (%)          | (%)                 | Samples |
| 0-10 ( <iloq)< td=""><td>-1.1</td><td>5.4</td><td>10.8</td><td>86</td></iloq)<> | -1.1    | 5.4          | 10.8                | 86      |
| 10-50   | -2.6    | 3.9          | 7.8                 | 74      |
| 50-1000   | -1.3    | 4.6          | 9.2                 | 54      |
| 1,000-100,000   | 0.1     | 1.8          | 3.6                 | 50      |

A regression analysis was performed on the entire laboratory duplicate data set. The intercept was used as an indicator of constant bias, while the slope was used as an indicator of proportional or relative bias. The correlation coefficient was used as an indicator of precision. The regression analysis yielded an intercept of -1.11 and a slope of 0.9996 indicating essentially no constant or relative bias. The correlation coefficient was 0.9998 indicating excellent precision. A graph of the analysis is shown in Fig. 25.

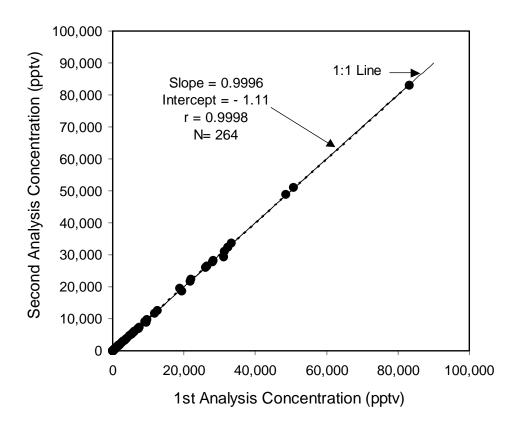


Figure 25. Linear regression of laboratory duplicates.

# **Laboratory controls**

Laboratory controls consisted of combining the data from all ICV's and CCV's. A regression analysis was performed on the combined data. Figure 26 shows the linear correlation of the true value of the standard to their analyzed concentrations. The regression analysis yielded both a slope and correlation coefficient of one and an intercept of 17.7 pptv. This indicates extremely good accuracy and precision within the ATGAS.

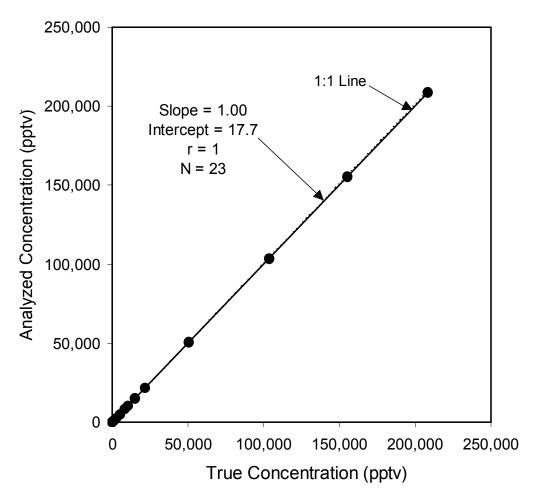


Figure 26. Linear regression of laboratory controls.

Table 11 shows the percent recovery, standard deviation, and the relative standard deviation (RSD) (the standard deviation relative to its concentration). All RSD's were less than 10% except for those control standards below the ILOQ where noise of the instrument became a much greater contributor to the overall signal. The average RSD for calibration standards above the ILOQ was 4% indicating extremely good instrument accuracy and precision.

Table 11. Summary of laboratory controls.

| Average       |  |  |  |   |
|---------------|--|--|--|---|
| Analyzed      | Percent  | Standard   | Number   |   |
| Concentration | Recovery   | Deviation  | of   | RSD   |
| (pptv)        | (%)  | (ppt)  | Points   | (%)   |
| 2.46          | 125  | 3.2  | 86   | 130   |
| 3.57          | 103  | 0.9  | 86   | 26  |
| 8.16          | 99   | 1.0  | 100  | 12  |
| 20.0          | 100  | 1.5  | 79   | 8   |
| 40.6          | 100  | 2.1  | 97   | 5   |
| 83.1          | 100  | 5.1  | 137  | 6   |
| 198           | 99   | 8.3  | 130  | 4   |
| 409           | 100  | 16.1   | 127  | 4   |
| 844           | 100  | 23.4   | 126  | 3   |
| 1,560         | 100  | 47.5   | 125  | 3   |
| 2,091         | 101  | 54.1   | 47   | 3   |
| 2,117         | 101  | 113  | 75   | 5   |
| 2,480         | 100  | 43.2   | 5  | 2   |
| 5,074         | 100  | 90.3   | 48   | 2   |
| 5,133         | 101  | 175  | 68   | 3   |
| 8,390         | 100  | 565  | 42   | 7   |
| 10,465        | 101  | 327  | 16   | 3   |
| 15,227        | 102  | 745  | 50   | 5   |
| 21,971        | 100  | 685  | 49   | 3   |
| 50,683        | 100  | 723  | 25   | 1   |
| 103,274       | 100  | 1,666  | 16   | 2   |
| 155,396       | 100  | 3,104  | 16   | 2   |
| 208,786       | 100  | 3,726  | 16   | 2   |
|               | Analyzed Concentration (pptv)  2.46 3.57 8.16 20.0 40.6 83.1 198 409 844 1,560 2,091 2,117 2,480 5,074 5,133 8,390 10,465 15,227 21,971 50,683 103,274 155,396 | Analyzed Concentration (pptv) (%)  2.46 125 3.57 103 8.16 99 20.0 100 40.6 100 83.1 100 198 99 409 100 844 100 1,560 100 2,091 101 2,117 101 2,480 100 5,074 100 5,133 101 8,390 100 10,465 101 15,227 102 21,971 100 50,683 100 103,274 100 155,396 100 | Analyzed<br>Concentration<br>(pptv)Percent<br>(%)Standard<br>Deviation<br>(ppt)2.46<br>3.57125<br>103<br>20.03.2<br>100<br>1.5<br>100<br>1.5<br>100<br>1.5<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>101<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>100 | Analyzed Concentration (pptv)         Percent Recovery (%)         Standard (ppt)         Number of Points           2.46         125         3.2         86           3.57         103         0.9         86           8.16         99         1.0         100           20.0         100         1.5         79           40.6         100         2.1         97           83.1         100         5.1         137           198         99         8.3         130           409         100         16.1         127           844         100         23.4         126           1,560         100         47.5         125           2,091         101         54.1         47           2,117         101         113         75           2,480         100         43.2         5           5,074         100         90.3         48           5,133         101         175         68           8,390         100         565         42           10,465         101         327         16           15,227         102         745         50 |

#### 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. High concentrations of SF<sub>6</sub> in the field blanks (>MLOQ) were good indicators of holes in the sampling bag, clips not properly closed or other operational problems. The field blanks were set at 10 locations and each were used to check for any source of contamination or leaks within the PIGS or in later handling of the cartridges. A total of 552 field blanks were analyzed with 77% of the results flagged as usable, i.e. no problems associated with the analysis of the samples. The other 23% of the data was unusable due to analysis, sampling or material errors. The blanks were contained in a specially built PIGS that housed two cartridges (Figs. 27 & 28). One cartridge, on the right in Fig. 28, was the source cartridge and contained prefilled bags of ultra high purity (UHP) nitrogen. The second cartridge, on the left in Fig. 28, was the blank cartridge and captured the



Figure 27. Exterior of blank and control PIGS.



Figure 28. Interior of blank and control PIGS showing the 12-bag source (right) and receiver cartridges (left).

nitrogen that was transferred from the source cartridge via the pumping mechanisms during the tests. The field blank concentrations ranged from -1.38 pptv to 43 pptv. The average was 3 pptv with a standard deviation of 4 pptv. Most results were greater than zero indicating some slight contamination during sampling and/or handling. This contamination was negligible however, since it was less than one tenth the MLOQ of 45 pptv. This slight contamination should have no effect on the sample results.

## Field duplicates

Field duplicates were placed at 10 locations in each IOP to check for imprecision and bias in the sampling, handling and storage of samples. These duplicates were placed directly across from each other 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. Usable results were reported for 83% of the field duplicates. It was unfortunately discovered during the quality assurance review after all the IOP's were completed, that some of the samples denoted as duplicates had much higher concentrations than their corresponding primary samples. The duplicates that had results outside of established acceptance limits of  $\pm 30\%$  were only from those locations that used the CATS tubes, i.e., the samplers in the downtown street-corner sampling grid. A hypothesis was developed based on these observations and a study was undertaken to determine if SF<sub>6</sub> was indeed adsorbed in the CATS tubes contrary to assurances received from BNL personnel. The study showed that the CATS tubes did indeed adsorb SF<sub>6</sub>. Therefore, the duplicate data were subsequently calculated and categorized as those with CATS tubes and those without CATS tubes. In actuality, the samplers with CATS tubes should not be considered as duplicates at all. Due to the CATS tubes attachment, both the sampler denoted as a sample and the sampler denoted as the duplicate were not collecting the same air sample. To be a true duplicate, the sample must be collected in exactly the same manner. This did not happen with the use of CATS tubes. The with CATS data is presented here only as an explanation for the differences in the field duplicate QC. The with

CATS results have no connection to the precision of the true field duplicates in this project. They were considered as a separate data set and were not used for QC purposes.

The linearity of the duplicate results with concentrations greater than the MLOQ of 45 pptv obtained from samples *without* CATS tubes can be seen in Fig. 29. In this graph, the slope of 0.983, the correlation of 0.989 and the intercept of -0.56 indicate a data set almost free of bias.

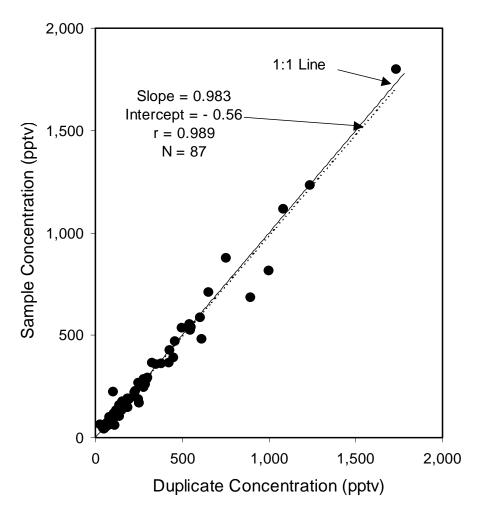


Figure 29. Linear regression of field duplicates with concentrations greater than 45 pptv (MLOQ) obtained from samples without CATS tubes.

### **Field controls**

Field controls were placed at 10 locations in each IOP to check for any bias and inaccuracy introduced during the sampling, handling, and storage of the samples. Usable results were reported for 82% of the field controls. Each control PIGS was placed alongside a sample PIGS. The controls were contained in a specially built PIGS that housed two cartridges and are identical in appearance to the blank PIGS (Figs. 27 & 28). One cartridge was the source cartridge

(on the right in Fig. 28), and contained prefilled bags of calibration gases. The second cartridge, (on the left in Fig. 28), was the control cartridge and captured the calibration gas that was transferred from the source cartridge via the pumping mechanisms during the IOP's.

The results of the field control analyses can be seen in Table 12. The accuracy of the controls above the MLOQ of 45 pptv increased greatly, as indicated by the percent recoveries. Although the recoveries above 45 pptv were very good, the standard deviations caused a large increase in the RSD's, indicating some obvious variability within the PIGS. This variability may be due to incomplete tube sealing, sample pump differences, or bags with holes. Since the PIGS were covered, any tubes or bags that might be leaking slightly could cause a concentration buildup inside the PIGS which may be drawn into other incompletely sealed bags. This behavior was most often observed in the lower concentration control samples that were more susceptible to slight concentration increases. Precision of the entire method was estimated by using the RSD's for the field controls. The RSD's ranged from 16% to 760% with the highest RSD's resulting, expectedly, from the standards below the MLOQ of 45 pptv. The average RSD's for the standards above the MLOQ was 34%. Bias of the method was indicated by comparing the known concentrations to the 95% confidence intervals of the average. Seven of the 12 known standards were not within the 95% confidence intervals of the calculated average. This indicates that there was some bias in the sampling method, especially below the MLOQ where it would be expected.

Table 12. Summary of field controls.

|        |         | 14616 12. 84 | minary of field control | <b>.</b>  |     |
|--------|---------|--------------|-------------------------|-----------|-----|
| True   | Average | Percent      | Estimated Standard      |           |     |
| Conc.  | Conc.   | Recovery     | Deviation               | Number of | RSD |
| (pptv) | (pptv)  | (%)          | (%)                     | Points    | (%) |
| 1.97   | 10.2    | 518          | 15                      | 49        | 760 |
| 3.47   | 11.0    | 317          | 14                      | 49        | 130 |
| 8.28   | 12.8    | 155          | 9.4                     | 49        | 70  |
| 20     | 22.7    | 114          | 5.6                     | 50        | 25  |
| 40.6   | 43.7    | 108          | 21                      | 51        | 48  |
| 83.5   | 80.6    | 97           | 24                      | 20        | 30  |
| 200    | 191     | 96           | 132                     | 50        | 69  |
| 410    | 374     | 91           | 87                      | 52        | 23  |
| 844    | 774     | 92           | 155                     | 52        | 20  |
| 1,560  | 1,466   | 94           | 739                     | 52        | 50  |
| 2,087  | 2,079   | 100          | 334                     | 46        | 16  |
| 5,080  | 4,411   | 87           | 1,586                   | 46        | 30  |

A linear regression of the "true" control concentration to the average analyzed concentration of the controls above the MLOQ of 45 pptv can be seen in Fig. 30. The slope was 0.883 with an intercept of 30.3 and a correlation coefficient of 0.998. The slope of less than 1 indicates a relative bias and the positive intercept indicates a constant positive bias. However, these biases were small enough that they should not significantly affect the data results.

The highest concentration data point at approximately 5,000 pptv offsets the slope of the line a great deal. This was due to the fact that there were several outliers within the data set from which this average was calculated. These data points were investigated thoroughly and no valid reason was found for their removal. Data points are only removed if a valid reason could be found, i.e., a sampling or analysis error. Random error data points are not removed so as not to subjectively bias the data.

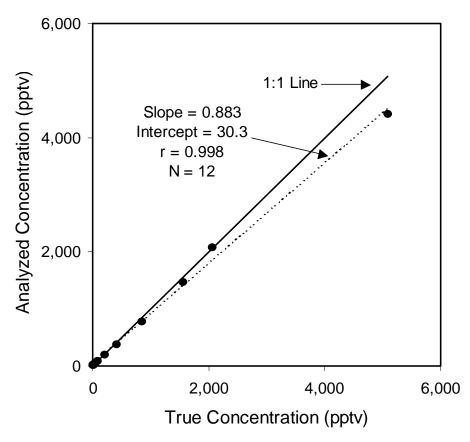


Figure 30. Linear regression of field controls.

### **Data verification**

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, automatic electronic transfer of data from the ATGAS's into a Microsoft® Access database and generation of time history plots. The analyst and at least one other person familiar with the data analysis process reviewed all data. 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 (Fig. 31) which summarized the results of all QC data generated for that batch, and a data verification sheet (Fig. 32) to ensure the verifier had checked all QC parameters.

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

| Analyst        | Debbie Lacro              | oix             |            |           | Verified By           | 1. <u>Brad</u><br>1/12/01 |             |          |                  |
|----------------|---------------------------|-----------------|------------|-----------|-----------------------|---------------------------|-------------|----------|------------------|
| Date:          | 10/25/2000<br>VTMX Test 3 | and 1           |            |           | Deter                 | 1/12/01                   |             |          |                  |
| Project<br>GC# | V I WIX Test 3            | and 4           |            |           | Date:                 | 1/1901                    |             |          |                  |
| Parameter      |                           |                 |            |           |                       |                           |             |          |                  |
|                | G2001025.R                | 07              |            |           |                       |                           |             |          |                  |
| Print File:    |                           |                 |            |           |                       |                           |             |          |                  |
|                |                           |                 |            |           |                       |                           |             |          |                  |
|                | n Verification            |                 |            | Lab Blank |                       | Calibration               | Check (±20% | 6)       | Background Level |
|                |                           |                 |            |           | Cal.Std)              |                           |             |          |                  |
| Bag #          | True Value                | Result          | % Recovery | Bag #     | Result                | True Value                | Result %    | Recovery | Bag # Result     |
|                |                           |                 |            |           |                       |                           |             |          | #1 4.32          |
| #1             | 1.97                      | 1.95            | 99         | #1        | 0.00                  | 844                       | 820.73      | 97       | #2 4.75          |
| #2             | 3.47                      | 3.35            | 97         | #2        | 0.38                  | 20                        | 19.16       | 96       | #3 5.18          |
| #3             | 8.28                      | 7.48            | 90         | #3        | 0.40                  |                           |             |          | Average 4.75     |
| #4<br>#5       | 20<br>40.6                | 19.9            | 100<br>97  | #4<br>#5  | 0.65                  |                           |             |          |                  |
| #6             | 83.5                      | 39.47<br>82.04  | 98         | #6        | 0.79<br>0.00          |                           |             |          |                  |
| #7             | 200                       | 196.4           | 98         | #7        | 0.45                  |                           |             |          |                  |
| #8             | 410                       | 403.31          | 98         | #8        | 0.50                  |                           |             |          |                  |
| #9             | 844                       | 834.06          | 99         | #9        | 0.57                  |                           |             |          |                  |
| #10            | 1560                      |                 | 99         | #10       | 0.80                  |                           |             |          |                  |
| #11            | 2087                      | 2057.84         |            | #11       | 0.53                  |                           |             |          |                  |
| #12            | 5080                      |                 | 99         | #12       | 1.16                  |                           |             |          |                  |
|                |                           |                 |            |           |                       |                           |             |          |                  |
| Final Cali     | oration Verifi            | cation (±20%    | ó)         | Comments  | s/Corrective Actions: |                           |             |          |                  |
| minimum        |                           |                 |            |           |                       |                           |             |          |                  |
| Bag #          | True Value                | Result          | % Recovery |           |                       |                           |             |          |                  |
|                |                           |                 |            |           |                       |                           |             |          |                  |
| #1             | 1.97                      | 1.85            | 94         |           |                       |                           |             |          |                  |
| #2<br>#3       | 3.47                      | 3.23            | 93         |           |                       |                           |             |          |                  |
| #4             | 8.28                      | 7.60            | 92         |           |                       |                           |             |          |                  |
| #4<br>#5       | 20.00<br>40.60            | 19.35<br>38.84  | 97<br>96   |           |                       |                           |             |          |                  |
|                |                           |                 |            | -         |                       |                           |             |          |                  |
| #6<br>#7       | 83.50<br>200              | 80.53<br>192.26 | 96<br>96   |           |                       |                           |             |          |                  |
| #8             | 410                       | 396.52          | 97         |           |                       |                           |             |          |                  |
| #9             | 844                       | 820.59          | 97         |           |                       |                           |             |          |                  |
| #10            | 1560                      | 1519.36         | 97         |           |                       |                           |             |          |                  |
| #11            | 2087                      | 2019.48         | 97         |           |                       |                           |             |          |                  |
|                |                           | 7000            |            |           |                       |                           |             |          |                  |
| #12            | 5080                      | 4924.36         | 97         |           |                       |                           |             |          |                  |

Figure 31. Example laboratory quality control sheet.

| Quality Control Verification Sheet  | Date:           | 10/01/1 |                          | 7 |
|---|-----------------|---------|--------------------------|---|
|   | Verifier Brad   | Brap    |                          |   |
|   | Data File (     | 9 100/0 | Data File & 100/013, 201 |   |
|   | Project VYTAX-1 | STAK-   |                          |   |
|   | YES             | ON      | NA                       |   |
| Data package contains complete and legible:   | Þ               | - 1     |                          |   |
| Raw data<br>Logbookcopy<br>Octobookcopy   |                 |         |                          |   |
| The same print file and data file are on the raw data sheet, logbook copy and QC sheet  | Э               |         |                          |   |
| Dates match on the raw data sheet, logbook copy and QC sheet  | Þ               |         |                          |   |
| The same project and test number are on the QC sheet and raw data   | Д               |         |                          |   |
| The same GC number is on the QC sheet and raw data  | Þ               |         |                          |   |
| All pressures are ok (>300). Any that are lower have been crossed out as unusable.  | Þ               |         |                          |   |
| All data has been crossed out that has "bad analysis flags" and has been noted as needing to be re-run (RR).  | Þ               |         |                          |   |
| All data has been crossed out that has "don't use" flags.   | P               | 0       |                          |   |
| All data has been crossed out that has any "F" check -in flags. Noted as flat bags.   | þ               |         |                          |   |
| All "L" check-in flags have been circled.   | 8               |         |                          |   |
| The background level was reported. The background level is greater than the lab blank indicating there is no leakage within the system.                           | · 🗆             | ) Sel   |                          |   |
| All data is crossed out if greater than 10% <u>higher</u> than the highest calibration standard and is flagged as needing to be re-run(RR).                       | Ъ               |         |                          |   |
| All data is crossed out if less than 10% tower than the lowest calibration standard and is flagged as needing to be re-tun(RR) (except if lowest sid is 1.97ppt). | ۵               |         |                          |   |
| All anomalies reported on the logbook copies are reported on the QC sheet.  | Д               |         |                          |   |
| All the data has been transferred correctly from the raw data to the QC sheet.  | Ы               |         |                          |   |
| Calibration curve verification was within 10% of the true value. Any anomalies are noted.   | ß               |         |                          |   |
| Lab blanks were analyzed and were less than the lowest calibration standard.  |                 | 9       |                          |   |
| Recoveries for the calibration checks were within $\pm$ 20% or the instrument was recalibrated.   | Þ               |         |                          |   |
| Duplicates were analyzed and were within ±20 RPD.   |                 | Þ       |                          |   |
| Data is usable as noted.  | Ŋ               |         |                          |   |
| Verifer Comments:   |                 |         |                          |   |
|   |                 |         |                          |   |
|   |                 |         |                          | 1 |
|   |                 |         |                          |   |

Figure 32. Example quality control verification sheet.

Once all raw laboratory data verification had taken place, the final data set was checked for usable results for each bag. Time plots as seen in Fig. 33 for each location were also reviewed to ensure there were no missing data points. If for any reason there was no usable data for a bag and there was no specified reason for the missing data such as a flat or damaged bag, the sample was re-analyzed.

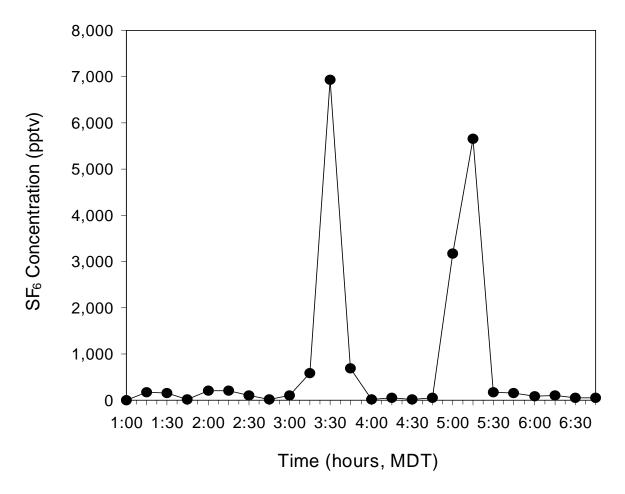


Figure 33. Example time plot for sampler location 53 for IOP 10.

### **Method verification**

All field data were verified to make sure there was a result for every location, cartridge, and sample bag. Mapped plots were created and reviewed to ensure all data were reasonable with respect to each release. The sampler servicing record (Fig. 34), 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 were also reviewed as well as chromatograms to determine any suspicious data points. All suspicious data were appropriately flagged.

#### NOAA SAMPLER SERVICING RECORD SHEET VTMX Route: CATS# 1 Project: Test(s): TimeWand: Mark one: Deployment Retrieval Sampler Cartridge CATS Time Location Number Number Number (local) Comments or Problems GFDD10 GFODD4 GF0081 GF 0088 (DUP) SN DUOS GF ODS& SN 1098 LC0062 GF OD72 GF DOG 3 GF 0041 SN 299 GF0021 SN GF 0079 SNDDA SN (44) GFOD9 D GFDD96 SN 0483 SN 1229 GF 002 GF DD7 8 GF 0314 SN SN () 391 TC 1081 GF DDD9 LC GF SN GF SN LC GF SN

Figure 34. Example field sample servicing record.

LC

LC

GF

GF

SN

SN

### **Quality Assurance Summary**

A summary of the instrument (laboratory) and method (field) blank analyses is shown in Table 13. The average concentration of method blanks was 3 pptv, much higher than that of the laboratory blanks of 0.05 pptv. The standard deviation, ILOD, and ILOQ were all approximately five times higher for the method blanks. The method blank average of three indicates a slight bias while the standard deviation of four indicates an increase in imprecision. These higher results would all be expected due to the increased sources of error in field sampling, handling, and storage of the samples. Since the instrument blank average was much lower than the ILOQ of 8 pptv and the method blank average was much lower than the MLOQ of 45, there was no indication of any significant blank contamination within the analysis instrumentation or the total method.

Table 13. Comparison of instrument and method blanks.

| Blank Type        | Number of Samples | Range (pptv)  | Average (pptv) | Standard<br>Deviation<br>(pptv) | LOD<br>(pptv) | LOQ (pptv) |
|-------------------|-------------------|---------------|----------------|---------------------------------|---------------|------------|
| Instrument        | 417               | -2.38 to 4.04 | 0.05           | 0.8                             | 2             | 8          |
| (Laboratory)      | 550               | 1 20 4 - 42   | 2              | 4                               | 1.4           | 45         |
| Method<br>(Field) | 552               | -1.38 to 43   | 3              | 4                               | 14            | 45         |

A summary of the laboratory and field control analyses can be seen in Table 14. The average recoveries of both the laboratory and field controls were excellent as seen by the 100% and 96% recoveries respectively. There was, however, an increase in the relative standard deviation (RSD) from 4% to 36% for the field controls. This indicates some expected imprecision in the total method due to sampling and handling. The overall accuracy of the method however, was not significantly affected by these variabilities.

Table 14. Comparison of laboratory and field controls.

|                         |                   | Average Recovery | Average RSD |
|-------------------------|-------------------|------------------|-------------|
| Control Type            | Number of Samples | (%)              | (%)         |
| Instrument (Laboratory) | 12                | 100              | 4.0         |
| Method (Field)          | 23                | 96               | 36          |

A summary of the instrument and field duplicate analyses can be seen in Table 15. The average RPD of both the laboratory and field duplicates *without* CATS duplicates were very close at -1.3% and 0.9% respectively indicating good accuracy resulting from sampling and handling methods. The standard deviation of 26% was higher for the field duplicates indicating some imprecision resulting from the sampling and handling methods.

Table 15. Summary of laboratory and field without CATS duplicates.

|                |             | Std. Deviation of the |                   |
|----------------|-------------|-----------------------|-------------------|
|                | Average RPD | RPD                   |                   |
| Duplicate Type | (%)         | (%)                   | Number of Samples |
| Instrument     | -1.3        | 4.4                   | 264               |
| (Laboratory)   |             |                       |                   |
| Method (Field) | 0.9         | 26                    | 88                |
| without CATS   |             |                       |                   |

The quality assurance system was designed around the stated 16 quality control steps to provide evidence that the reported data met defined standards of quality. The pre-deployment PIGS maintenance ensured that all the electronics for each PIGS were working as needed for the project. The pre-deployment cartridge cleaning ensured that all bags were clean prior to their use and the cleaning and analysis of 10% of the cartridges following an IOP ensured that there would be no contamination or carryover that could be detrimental to the results of the next IOP. The use of the sample check-in procedures ensured proper flagging and later sorting of samples. The calibration, ICV's, and CCV's provided evidence of instrument stability and accuracy. The instrument duplicates and controls indicated excellent instrument precision and accuracy while the lab blanks and background blanks indicated a total lack of contamination within the analysis system. The field duplicates and controls indicated an expected increase in imprecision due to the sampling and handling methods that did not significantly effect the data results. The field blanks indicated a slight, also expected, contamination. The accuracy of the data was not affected by these slight method variations. Data and method verification were used as a source of peer review to identify a reasonable result for each sample bag.

# **Sample Analysis Summary**

A total of 600 sample cartridges (100 per IOP), were analyzed for this study for a total of 7200 field samples. The percentage of usable results was 92%. The percentage of samples within specified concentration ranges can be seen in Fig. 35. A majority of the field samples (51.3%) were below the MLOQ of 45 pptv which was not unexpected. This left only 48.7% of the samples above the MLOQ. Sample concentrations ranged from below the MLOQ of 45 pptv to 245,000 pptv. The majority of the sample concentrations above the MLOQ were in the range of 1,000 to 10,000 pptv. Only 4% of all sample concentrations were greater than 10,000 pptv.

Four ATGAS' were utilized to provide high throughput and to cover the extensive range of sample concentrations. The ATGAS calibrations were altered throughout the study to adjust to changing sample concentrations. Due to the extreme variability in concentration ranges for the samples, many cartridges required multiple analyses on other ATGAS' calibrated in higher concentration ranges in order to fall within the needed calibration range for the samples.

## Concentration Range of Samples

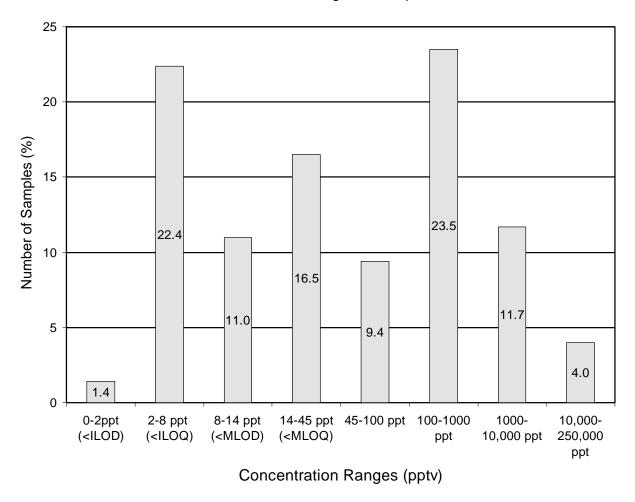


Figure 35. Concentration range of samples for all IOP's.

Of the 7200 field samples analyzed, 172 or 2.4% were checked in as "low bags". These were bags that had air in them, but the bag was not sufficiently full to permit multiple analyses on the ATGAS. Low bag samples that were analyzed a second time on the ATGAS were qualified as estimates since there may not have been a sufficient volume of air for a proper analysis. Samples checked in as "damaged" accounted for 12 or 0.2% of the total analyzed. These samples were contained in a PIGS that was destroyed by the Salt Lake City Police bomb squad. Concerned citizens reported finding the box in a wooded area and the police, worried about a possible bomb, proceeded to shoot and destroy the lower portion of the PIGS where the Tedlar® bags were housed as seen in Figure 36. All samples for this cartridge were lost.

Samples checked in as "flat" accounted for 428 or 5.9% of the total analyzed. Of these, 248 or 60% of the flat bags were from IOP number nine. During deployment of PIGS for this IOP, some were inadvertently programmed with the wrong start date. The result of this mistake

was that the PIGS failed to begin sampling at the designated start time. The mistake was discovered during the routine check of the PIGS during the course of the IOP and immediately corrected. However, the mistake resulted in 248 flat bags before the problem was corrected. One sample was checked in as "incomplete hookup" due to a missing Tedlar® bag. In all, 613 samples or 8.5% of the 7200 total were attributed to field errors, which included low or flat bags due to improper PIGS programming, clips being opened or closed improperly, and damaged or missing Tedlar® bags. There were usable results for 92% of all bags.



Figure 36. Sample cartridge destroyed by police bomb squad.

## **CATS Tubes Adsorption of SF**<sub>6</sub>

As discussed in previous sections, some of the PIGS were fitted with CATS tubes to permit simultaneous sampling of  $SF_6$  and PFTs. Personnel from BNL assured us that CATS tubes would not adsorb  $SF_6$ . Subsequent analysis of the field duplicate  $SF_6$  sampler concentration data indicated that the BNL assertion was in error. Additional follow-on laboratory studies were conducted to determine how much  $SF_6$  was most likely adsorbed onto the CATS tubes. The studies, using known  $SF_6$  concentrations ranging from 83.5 pptv to 103,600 pptv, indicated that the CATS tubes adsorbed approximately 40% of the  $SF_6$  concentration. This correlates to the duplicate sampler data presented in Table 16 where the average recovery for the *with* CATS duplicates was 63%, (an adsorption of approximately 40%). The recovery of the duplicates *without* CATS tubes (6 km, 4 km, 2 km, and SE locations) had an average recovery of 104%. The laboratory studies also suggested that  $SF_6$  adsorption was slightly dependent upon the air temperature at the time of sampling with less adsorption at higher temperatures. Not enough studies were performed to fully characterize this, but the effect appears to be small. Therefore, air temperature was probably not a factor. In addition, the average air temperatures during the IOP's were within a few degrees of each other. (Clawson and Crescenti, 2002).

It was also discovered that the CATS tubes in the presence of clean air, desorbed about 50% of the residual SF<sub>6</sub> that was adsorbed during the previous collection cycle. Since the guard

or permanent CATS were retained for each IOP, another study was conducted to determine how much SF<sub>6</sub> was adsorbed on the guard CATS that remained on each sampler. Pumping UHP nitrogen through only the guard CATS yielded an SF<sub>6</sub> concentration of approximately 10% of that previously sampled through the guard CATS. Therefore, during field sampling a small amount of SF<sub>6</sub> was probably desorbed as more SF<sub>6</sub> was adsorbed onto the CATS tubes with each succeeding IOP. This adsorption/desorption process was probably one of the causes for the higher standard deviation in the *with* CATS data. Other causes could have been the differing rates of SF<sub>6</sub> adsorption per CATS tube and temperature fluctuations.

Table 16. Recoveries and standard deviations of field duplicates with and without CATS tubes.

| Average Recovery          |     |                        |  |  |  |
|---------------------------|-----|------------------------|--|--|--|
| Compared to the Duplicate |     |                        |  |  |  |
| Sampler Location          | (%) | Standard Deviation (%) |  |  |  |
| Without CATS              |     |                        |  |  |  |
| 3                         | 107 | 19                     |  |  |  |
| 14                        | 97  | 21                     |  |  |  |
| 26                        | 99  | 17                     |  |  |  |
| 1034                      | 113 | 19                     |  |  |  |
| Average                   | 104 | 19                     |  |  |  |
| With CATS                 | _   |                        |  |  |  |
| 85                        | 65  | 32                     |  |  |  |
| 90                        | 55  | 16                     |  |  |  |
| 99                        | 53  | 19                     |  |  |  |
| 80                        | 68  | 30                     |  |  |  |
| 1061                      | 72  | 30                     |  |  |  |
| 1066                      | 66  | 25                     |  |  |  |
| Average                   | 63  | 25                     |  |  |  |

The linearity of the results of the samples *with* CATS tubes can be seen in Fig. 37. In this graph, the slope of 0.726, the correlation of 0.943 and the intercept of -162 indicate a very biased data set.

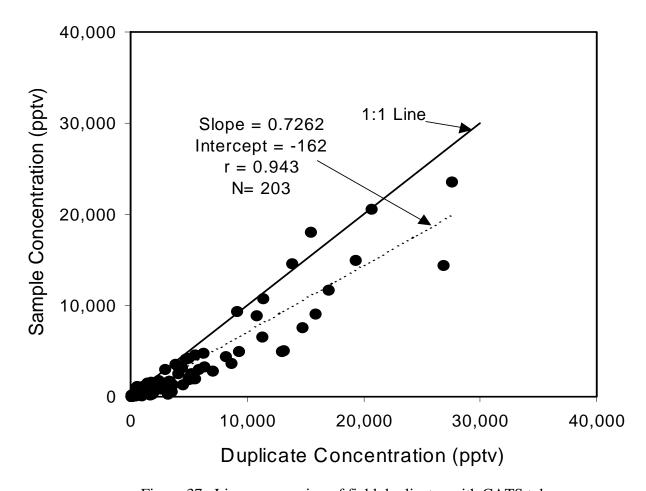


Figure 37. Linear regression of field duplicates with CATS tubes.

The average RPD and standard deviation of the *with* and *without* CATS data can be seen in Table 17. The average RPD of the field duplicates *with* CATS tubes was much higher than that of the field duplicates *without* CATS tubes indicating a highly inaccurate method. The standard deviation was 1.5 times higher than the field duplicates *without* CATS, indicating that the CATS tubes caused more imprecision in the sampling and handling method.

Table 17. Summary of duplicates with and without CATS tubes.

|                    | Std. Deviation of the |     |                   |
|--------------------|-----------------------|-----|-------------------|
|                    | Average RPD           | RPD |                   |
| Duplicate Type     | (%)                   | (%) | Number of Samples |
| Field with CATS    | 50.4                  | 39  | 203               |
| Field without CATS | 0.9                   | 26  | 88                |

### **CATS Tubes SF<sub>6</sub> Correction Factor**

Six sampling locations (61, 66, 80, 85, 90, and 99) had a whole air sampler with CATS tubes collocated with a sampler without CATS tubes. By comparing the data collected by these samplers over the entire study, approximate correction factors for the CATS tubes adsorption were determined. Jerry Allwine of the Pacific Northwest National Laboratory (2002, personal communication), suggested the following equation be used:

Correction = 
$$2.193 \text{ x (original result)}^{0.9583}$$
 (1)

IOP 9 was not corrected because no CATS tubes were used during IOP 9. In the case of duplicate or collocated samplers where neither sampler had CATS tubes attached, data from the sampler designated as "duplicate" were NOT used in the final data set. Data from the duplicate sampler were used for QC purposes only.

The specific steps followed in the data correction procedure were:

- 1. For the six locations with a collocated duplicate sampler (61, 66, 80, 85, 90, 99), the datum from the duplicate sampler were substituted for the original data where it was available. If the duplicate sampler datum was missing or unusable, the original datum was corrected and flagged as such.
- 2. All values that were below the MLOD (flag 6) were left uncorrected. These values should be viewed as 0. It would be erroneous to correct a 0 into a value that may appear to be a significant non-null measurement.
- 3. All unusable values were left unchanged (flags 4 and 5).
- 4. All other values were corrected by using the correction equation given above and the data flag was changed accordingly. (i.e. flag 1 became 7; 2 became 8; 3 became 9)

# **Data Flags**

Table 18 displays the data flags attached to the final data. These flags are used as an aid in tracking the quality of the data. Data with associated flag values of 4, 5, and 6 were not used in presenting the data in the Results Section.

Table 18. Description of quality control flags stored with the data.

| Flag | Description  |
|------|--|
| 1    | good data  |
| 2    | below the method limit of quantitation (MLOQ=45 pptv), so view as an estimate  |
| 3    | view as an estimate because of problems in analysis  |
| 4    | unusable data because of problems in the field (e.g missing sample, improper hookup, bag was flat, shot with gun, etc.) Concentrations are set to -999.0.  |
| 5    | unusable because of bad analysis in laboratory. Concentrations are set to -999.0.  |
| 6    | below the method limit of detection (MLOD=14 pptv). These values are not statistically distinguishable from 0 and should be treated as 0 or null values.   |
| 7    | good data corrected for CATS tube adsorption   |
| 8    | originally below the method limit of quantitation (MLOQ=45 pptv), but corrected for CATS tube adsorption. View as an estimate. Note that this flag is set based on the initial or analyzed data value being less than 45 pptv. The correction will yield values up to 84.2 pptv that have this flag. |
| 9    | estimates because of problems in analysis that have been corrected for CATS tube adsorption  |

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# REAL-TIME TRACER SAMPLE ANALYSIS

Continuous  $SF_6$  concentration measurements were made using an FRD-built mobile analysis system shown in Fig. 38. The real-time  $SF_6$  analyzers are vehicle mounted systems that make measurements of atmospheric  $SF_6$  concentrations with a response time of just under one second (Benner and Lamb, 1985). Six units were deployed for the URBAN 2000 experiment (Fig. 39). The rapid response time and mobile nature of the analyzers make them ideally suited for measurements of plume widths and structure. The attempt is made to sample the  $SF_6$  plume by driving across the plume perpendicular to the plume centerline, as much as road conditions will permit. They have been utilized in experiments measuring both across wind and along wind diffusion parameters commonly used in transport and dispersion models and Gaussian plume models (Watson et al., 1998, Watson et al., 2000, Clawson et al., 2001). The heart of the system is the TGA–4000 (Tracer Gas Analyzer) manufactured by Scientech, Inc. of Pullman, WA. It also includes a computer-controlled calibration system and an integrated global positioning system (GPS). Each data point is tagged with sampling time and location from the GPS system. The TGA instrument is described in detail elsewhere (Watson et al., 1998), but has since been modified for greater mobility. A schematic representation of the system is shown in Fig. 40.

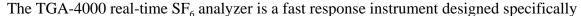




Figure 38. NOAA continuous mobile SF<sub>6</sub> tracer gas analysis system installed in the rear seat of an SUV, showing computer controlled TGA-4000 (bottom) and calibration gas container (lower right).



Figure 39. Mobile real-time SF<sub>6</sub> analyzer sampling fleet.

to measure the concentration of  $SF_6$  in ambient air. The TGA–4000 uses a tritium based electron capture detector (ECD) to detect  $SF_6$ . The ECD is very sensitive to halogenated compounds such as chloro-fluorocarbons and  $SF_6$  as well as oxygen. Oxygen interferes with the ECD operation and is, therefore, removed from the sample prior to introducing it into the ECD. This is done by reacting the oxygen in the air stream with hydrogen in a catalytic reactor and removing the resultant water with a semi-permeable membrane. The detection limit of the ECD is about 10 parts per trillion volume (pptv) under ideal laboratory conditions. The maximum concentration limit is about 10,000 pptv, but can be doubled with the aid of a dilution system.

The TGA-4000 signal along with real-time GPS position, instrument temperatures, and

ambient pressure are collected by a laptop computer at the rate of 2 Hz. The computer stores the data for later post-processing and also simultaneously displays the TGA-4000 signal for operator interpretation and control. Using this display, the operator determines the plume concentration and position by using software controls to

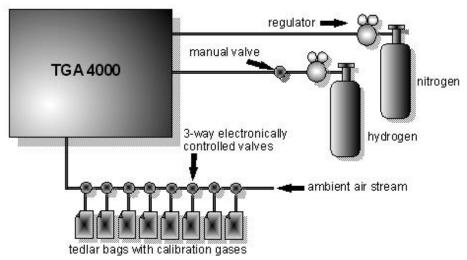


Figure 40. Schematic representation of the NOAA continuous  $SF_6$  tracer gas analyzer.

"mark" the beginning and ending of the plume trace. The operator can then communicate this information via wireless means to personnel directing the test.

## **Calibration**

The mobile  $SF_6$  analysis system incorporates a calibration system for real-time mobile calibration of the TGA-4000. Calibration of the instrument was accomplished by allowing it to sample calibration mixtures of known concentrations of  $SF_6$  and recording the output corresponding to each concentration.  $SF_6$  concentrations of sample air are then determined by linearly interpolating between the calibration concentrations whose output values bracket the TGA-4000 output. The calibration functions are all controlled by the laptop computer when initiated by the operator.

The  $SF_6$  calibration standards were stored in Tedlar bags identical to those used in the PIGS, which were described in the previous chapter. The bags were connected to the TGA-4000 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 10,380 pptv  $SF_6$ . 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.

Reported  $SF_6$  concentrations above that of the highest calibration (10,380 pptv) must be regarded as having a much higher degree of uncertainty. Not only is extrapolation much more uncertain than interpolating between calibrations, but the TGA-4000 detectors become saturated at approximately 10,000 ppt. Above this level, large changes in  $SF_6$  concentration result in little or no change in the TGA-4000 output. Extrapolations in this range could easily result in very large errors and must be viewed as very uncertain. The exception to this rule was when the dilution system was in use. Two of the TGA-4000's were fitted with a system to dilute the incoming sample with an equal amount of ultra-pure air. This reduced the  $SF_6$  concentration to  $\frac{1}{2}$ 0 of the sample concentration. The sample concentration measured in this mode was multiplied by 2 to yield the true sample concentration. In this way, concentrations up to 20,760 pptv (twice the highest calibration) could be effectively measured with acceptable accuracy. Laboratory tests indicated that the relative error of the measurements did not increase significantly when the dilution system was used. The dilution system could be turned on or off by the operator as needed. Table 19 lists the times the dilution system was in use. For these cases, concentrations up to 20,760 pptv may be regarded as reasonably certain.

Two quantities that are useful for evaluating instrument performance are the limit of detection (LOD) and the limit of quantitation (LOQ). The LOD 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 LOQ is typically defined to be the level at which the concentration may be determined with an accuracy of ±30%. The recommended values for these are 3**F** for LOD and 10**F** for LOQ, where **F** is the standard deviation for measurements made on blanks or low standards (Keith et. al., 1983). Since the TGA-4000 is measuring continuously, every point may be viewed as a measurement of a blank so long as the TGA-4000 is sampling clean air. **F** then becomes the standard deviation of the TGA-4000 baseline signal. As part of the start-up procedure, the operators calculated this value before every test. The results are summarized in Table 20. Typically, peaks with maximum concentrations below the LOD are not reported. Concentrations below the LOQ should be viewed as less certain.

Table 19. Plume crossings when the dilution system was in use. For these cases, values above 20,760 pptv must be regarded as very uncertain. In all other cases, values above 10,380 pptv must be viewed as very uncertain.

| IOP | Unit | Plume crossings |
|-----|------|-----------------|
| 1   | 7    | 11-17           |
| 2   | 2    | all             |
| 4   | 2    | 1-8             |
| 5   | 2    | 1-7             |
| 7   | 2    | 1-14            |
| 9   | 2    | all             |
| 10  | 2    | 2-11            |

Table 20. Limit of detection (LOD)/limit of quantitation (LOQ) values in pptv for the real-time  $SF_6$  analyzers calculated from baseline variations.

|         | Mobile Real-time SF <sub>6</sub> Sampling Unit |         |        |        |        |         |
|---------|--|---------|--------|--------|--------|---------|
| IOP     | Unit 1   | Unit 2  | Unit 3 | Unit 5 | Unit 6 | Unit 7  |
| 1       | n/a  | n/a     | n/a    | n/a    | 30/100 | 12/40   |
| 2       | 30/100   | 14/47   | 23/77  | 30/100 | 33/110 | 13/43   |
| 4       | 41/137   | 14/47   | 35/117 | 31/103 | 28/93  | 17/57   |
| 5       | 19/63  | missing | 19/63  | 30/100 | 20/67  | 29/97   |
| 7       | 18/60  | 24/80   | 23/77  | 34/113 | 26/87  | missing |
| 9       | 20/67  | 20/67   | 20/67  | 24/80  | 32/107 | 25/83   |
| 10      | 18/60  | 13/43   | 25/83  | 22/73  | 34/113 | 20/67   |
| Average | 24/80  | 17/57   | 24/80  | 29/97  | 29/97  | 19/63   |

To determine the overall accuracy and precision of the real-time analyzer measurements, calibrated analyzers were allowed to sample gas mixtures of known SF<sub>6</sub> concentrations. The percent recovery (i.e., 100% multiplied by the measured concentration divided by the actual concentration) for each test was recorded. Ninetyseven tests were made and are summarized in Table 21. These tests were made over a period of two months on multiple

Table 21. Percent recovery of SF<sub>6</sub> concentrations by real-time analyzers sampling known mixtures as unknowns.

| SF <sub>6</sub> concentration (pptv) | average<br>recovery<br>(%) | standard<br>deviation<br>(%) | number<br>of trials |
|--------------------------------------|----------------------------|------------------------------|---------------------|
| 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                  |
| all samples                          | 103                        | 8.7                          | 97                  |

analyzers. Most 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 did 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.

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 were within this range. The standard deviations for all of the groups reported were less than 8.7%, which should be a reasonable estimate of precision for this study. From this, we conclude that the 95% confidence intervals for the analyzer measurements are  $\pm 17\%$ .

One additional characteristic of the TGA-4000 operation should be noted. When exposed to very abrupt changes in SF<sub>6</sub> concentration (e.g. several hundred pptv change over a period of about one second), the TGA-4000 tends to overshoot and then gradually recover. On increasing concentrations, it will shoot above the correct level; on decreasing concentrations, it will drop below the correct level. This effect seems to be tied to the cleanliness of the detector and has not been successfully quantified. It is not evident on gradual concentration changes and typically does not show up in field operations. However, in this study, TGA-4000s in vans driving out of well defined plumes sometimes exhibited some of this behavior. Some of the reported plume concentrations show a drop below zero concentration followed by a gradual recovery. For example, see IOP 1, unit 7, plume crossing 5 (Figure 41). When using data exhibiting this characteristic, it is probably best to set the negative concentrations to zero.

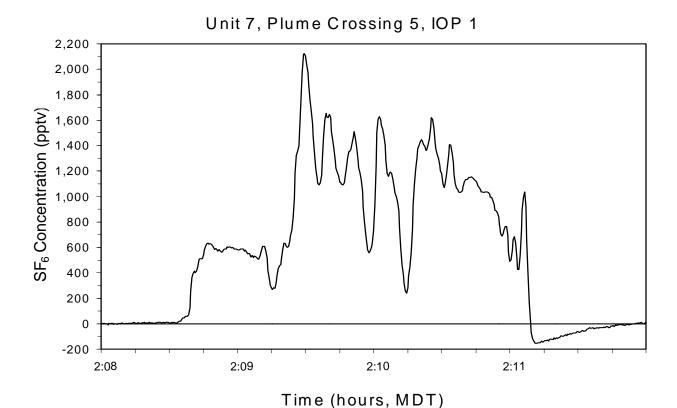


Figure 41. Example of TGA-4000 overshoot. The negative values on the trailing (right) edge of the concentration profile are caused by the detector overshooting after the abrupt drop in concentration.

# **Quality Control**

The quality control (QC) procedures for the real-time analyzers consisted of three steps that are described in detail below:

- 1. Monitoring of key operational parameters of each analyzer.
- 2. Post processing review of all calibrations.
- 3. Review of all operator-marked plume crossings by two people.

## Monitoring of key operational parameters

Analyzer operators completed a Settings Record data sheet as they ran the real-time analyzers. 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 (Fig. 42). These sheets were reviewed for any large changes in the parameters that could indicate a problem with the analyzer. Any changes were investigated and required maintenance was performed.

|       |             |                           |                            |              |                     | TG                        | A-400(                     | Setting                                | TGA-4000 Settings Record     | 7    |      |              |       |                |                 |                        |
|-------|-------------|---------------------------|----------------------------|--------------|---------------------|---------------------------|----------------------------|--|------------------------------|------|------|--------------|-------|----------------|-----------------|------------------------|
| TGA n | TGA number: | 3                         |                            |              |                     |                           |                            |  |                              |      |      |              |       |                |                 |                        |
| date  | time        | N <sub>2</sub><br>primary | N <sub>2</sub><br>delivery | EX.1<br>flow | EX.2<br>flow        | H <sub>2</sub><br>primary | H <sub>2</sub><br>delivery | sample<br>controller                   | H <sub>2</sub><br>controller | zero | gain | cal<br>slope | гор   | Air<br>primary | Air<br>delivery | dilution<br>controller |
| 11/91 | 8020        | 00H                       | 1 1                        | 150          | $\bar{\mathcal{U}}$ | 906                       | 30                         | 181                                    | 96.5                         | 193  | ٦    |              | 5     |                | :               |                        |
|       | 1900        | 1320                      |                            |              |                     | 928                       | 38                         |  |                              |      |      |              |       |                |                 |                        |
| T A   | <u> </u>    |                           | 10.5                       | 148          | 81                  | 800                       | 30                         | 181                                    | 96.5                         | 184  | 7    | 932 1627     | 627   |                |                 |                        |
| 10/15 | 5/10/15     |                           |                            |              |                     |                           |                            |  |                              |      |      | 955 33.92    | 33.92 |                |                 |                        |
|       | 5773        | 79D                       |                            |              |                     | ()99)                     | 29                         | n was                                  |                              |      |      | 967 18.24    | 18.24 |                |                 | -                      |
| 1/01  | 10/16/2210  | 1770                      | 7                          | 150          | 17                  | 019                       | 30                         | 181                                    | 95,5                         |      |      |              |       |                |                 |                        |
|       | 3330        | 710                       | 10,5                       |              |                     |                           | 30                         | Spike to Tan                           |                              |      |      |              |       |                |                 |                        |
| 10/17 | 7 2340      | 969)                      | 11                         | 150          | 15                  |                           | 30                         | 181                                    | 97.2                         | 188  | 7    | 1029 29.76   | 39.76 |                |                 |                        |
| 10/18 | 0530 81     |                           |                            |              |                     | <b>45</b> 144             |                            | a : a : 1                              |                              |      |      | 1077 20,46   | 30,46 |                |                 |                        |
| ,     | 0753        |                           |                            |              | •                   |                           |                            | and any of the defence of              |                              |      |      | 5801         | 17.99 |                |                 |                        |
|       | 10807       | 310                       | 1                          |              |                     | QQh                       | 36                         |  |                              |      |      |              |       |                |                 |                        |
| 02/01 |             | 1830                      | 10                         | 150          | 23 406              |                           | 36                         | h/L)                                   | 96                           | 161  | 7    |              |       |                |                 |                        |
| د     | 1346        | 1796                      | 16,5                       |              |                     | 360                       | 30                         |  |                              |      |      |              | 2     |                |                 |                        |
|       | 2045        | 1730                      | 10                         | 150          | 23                  | 350                       | 30                         | 77                                     | 9                            | 461  | 7    | 966 2493     | 24.93 |                |                 |                        |
| 10/01 | Place       | )                         |                            |              |                     |                           | ,                          |  |                              |      |      | 994 16.93    | 16.93 |                |                 |                        |
|       | 8180        |                           |                            |              |                     |                           | ¥* .                       |  |                              |      |      | 1205/15.99   | 5.8   |                |                 |                        |
|       | OHBY        | 1380                      | 0                          |              |                     | 260                       | 36                         | e<br>e<br>v                            |                              |      |      | 1004 20022   | 20,22 |                |                 |                        |
|       |             |                           |                            |              |                     |                           |                            | e.,                                    |                              | ,    |      |              |       |                |                 |                        |
|       |             |                           |                            |              |                     |                           |                            |  |                              |      |      |              |       |                |                 |                        |
|       |             |                           |                            |              |                     |                           |                            | ************************************** |                              |      |      |              |       |                |                 |                        |
|       |             |                           |                            |              |                     |                           |                            |  |                              |      |      |              |       |                |                 |                        |

Figure 42. Example Settings Record for TGA 3.

### **Post-processing review of calibrations**

After an IOP was completed, the calibrations from each analyzer were carefully reviewed. Any calibration points with problems such as significant baseline drift, contamination, accidental instrument adjustments, etc., were identified and eliminated. If the calibrations showed evidence of significant sensitivity drift during the test, the calibrations were divided into two groups, typically an "early" group and a "late" group. Each group was used to calculate concentrations for plume crossings within the time frame they encompassed. If no significant sensitivity drift was observed, all calibrations were averaged together and used for concentration calculations.

#### Review of operator-marked plume crossings

Analyzer operators identified  $SF_6$  plume crossings and marked them on the computer screen using computer function keys. They also recorded details of each plume crossing, e.g., time, concentration, latitude and longitude, together with other pertinent observations in a notebook. After a test, the marked plumes were compared with the notebook to ensure that marked plumes were above the LOD and that they were not false peaks caused by extraneous factors such as altitude changes, bumps, interfering chemicals in the air, etc. The plume crossings were checked for correct identification of instrument baseline on leading and trailing sides of each peak. The entire data set was examined for possible plume crossings that may have been missed. Once necessary corrections were made, the plume crossings were converted to concentrations and placed in separate files. The entire set of plume crossings were then reviewed for errors by a second person.

#### **Comments on released data**

The final processed data from the real-time SF<sub>6</sub> tracer analyzers includes a file for each non-null plume crossing, a track file containing the analyzer's route for the entire IOP, and a READ.ME file that describes file format and possible problems in the data. Null traverses are easily determined by plotting the track file as a range and bearing from the release point. The plume crossing files are then easily matched with the track and null traverses subsequently become readily apparent. Because of the high frequency nature of the data, flags were not included with each data point. Please consider the LOD and LOQ reported in this section when using the data for calculations. Also refer to the READ.ME file for additional considerations.

The position (longitude and latitude) of the analyzer was measured with a GPS (Global Positioning System) receiver. Close proximity of tall buildings in downtown Salt Lake City sometimes caused errors in the positions. These errors are still present in the files. The READ.ME file contains more details and a list of identified problems.

## TRACER ANALYSIS RESULTS

This section presents a summary of the  $SF_6$  time-integrated tracer sampler (PIGS) and quasi-stationary real-time tracer analyzers' sampling results for each IOP that included an  $SF_6$  release. The results are presented in summary form. No attempt has been made to show all the details of the sampling. Rather, the intent is to provide a cursory overview of the results as a guide to those who may want to use these results for more detailed studies. Tracer transport and concentration characteristics for each IOP are summarized in separate sections that follow this introductory section. The figures in each separate IOP section can be grouped into five different categories which are discussed in the following paragraphs.

Figures 44, 49, 54, 59, 64, and 69 show both temporal and spatial PIGS tracer concentration results from the downtown urban sampling grid array. The colored circles represent a certain range of concentration: 14 to 100 pptv (blue), 100 to 1,000 pptv (green), 1,000 to 10,000 pptv (brown) and > 10,000 pptv (red). The unfilled squares indicate locations of the hour-long samplers. An 'x' indicates bad data. The gray unfilled circles indicate that the concentration measured was below the MLOD limit.

Figures 45, 50, 55, 60, 65, and 70 show PIGS SF<sub>6</sub> tracer concentration time history results from the downtown rooftop samplers.

Figures 46, 51, 56, 61, 66, and 71 are graphs of the data from the suburban sampling arcs. Each figure is the data from one IOP. The top plot presents data from the 6 km arc, the middle plot presents data from the 4 km arc, and the bottom plot represents data from the 2 km arc. Following one color of triangles horizontally across a plot presents the concentration time series evolution for one sampler. The sampler number, denoted by Sxx, is given at the end of each horizontal line where xx is the sampler number. Following a set of triangles vertically represents the concentration distribution along an arc for a given time. It must be noted that the ranges used for each plot are different as seen in the legends.

If all data from the samplers was good, i.e. always detectable concentration levels with no sampler or laboratory analysis problems, each graph in Figures 46, 51, 56, 61, 66, and 71 would look similar to a filled-in grid. However, because there were some sampler issues and other problems the figures appear to be missing quite a lot of data. However most of what appears to be missing data is due to values below the MLOD meaning the values were statistically indistinguishable from zero. These were not plotted so that the lowest ranges of each graph would not have to be extended to zero. IOP 9 (Figure 66) suffered from a PIGS programming error that was not detected and corrected until later in the experiment. This caused the loss of data near the beginning of the IOP.

Figures 47, 52, 57, 62, 67, and 72 are plots of the PIGS SF<sub>6</sub> concentration time series from the four samplers located to the southeast of the release point, i.e., the southeast 2 and 4 km arcs. As can be seen the highest concentration at these locations occurred during IOP 7.

Tables 22-28 and Figures 43, 48, 53, 58, 63, 68, and 73 summarize the results from the mobile tracer analyzers. The tables give the general route each van traveled, the total number of traverses over the route, and how many traverses yielded a plume detection or not, what the maximum tracer concentration from all traverses was, and the bearing and range from the release point to the maximum concentration location. Null passes were determined by plotting the analyzer bearing from the release point for the entire period of its operation. The times when the analyzer measured SF<sub>6</sub> were superimposed on this plot, leaving the null passes through the plume unmatched and easily identified. The mobile analyzers did not sample continuously during the IOPs as periodic calibrations of the instruments were required between tracer releases.

The map displays (Figures 43, 48, 53, 58, 63, 68, and 73) show a dot on a base map of the experiment region indicating the location where the peak tracer concentration value of each non-null plume traverse was recorded. The dot size and hue vary with concentration and time respectively to provide a visual summary of the measurements made by the analyzers. The GPS readings for these peak values were reviewed for errors and corrected prior to plotting.

All of the IOPs associated with URBAN 2000 were conducted under weak wind conditions except IOP's 9 and 10 where winds were more moderate. In the downtown area, the average wind speed was approximately 0.62 m s<sup>-1</sup> averaged over all IOPs (Clawson and Crescenti, 2002.)

IOP 1 was a pretrial test case that was coincident with the first VTMX IOP. It was designed to test the tracer release rates and mobile analyzer tracer detection capabilities both in close proximity to the release site and as far away as 6 km. Thus, only two mobile analyzers and no PIGS samplers were deployed for this IOP. There were no established mobile analyzer sampling routes.

Two releases were used. The rate for the first release was twice that of the second release. Table 22 presents a summary of the results from the two mobile analyzers. The results, shown in Figure 43, indicate the plume moved to the NNW. Although this was not a complete test, the data from the real-time analyzers appear to be of similar quality and exhibits similar tracer transport patterns as was observed in the subsequent IOPs. An extensive analysis was not performed on this IOP, but the data are commended to the reader for further investigation.

Table 22. Summary of IOP 1 SF<sub>6</sub> real-time analyzer sampling unit (TGA) activity.

| Sam-<br>pling<br>Unit<br>(TGA#) | General<br>Sampling<br>Route | Total<br>Number<br>of<br>Traverses | Number<br>of<br>Null<br>Traverses | Number<br>of<br>Non-null<br>Traverses | Maximum<br>Concentration<br>(pptv) | Bearing from Release Site (deg.) | Range<br>from<br>Release<br>Site<br>(km) |
|---------------------------------|------------------------------|------------------------------------|-----------------------------------|---------------------------------------|------------------------------------|----------------------------------|--|
| 1km<br>(#6)                     | 300 W                        | 11                                 | 3                                 | 8                                     | 8,540                              | 286                              | 1.27                                     |
| 4km<br>(#7)                     | 300 S,<br>200 W              | 26                                 | 4                                 | 22                                    | 33,500 <sup>1</sup>                | 277                              | 0.21                                     |

<sup>&</sup>lt;sup>1</sup>Dilution system was turned on during peak causing a spike.

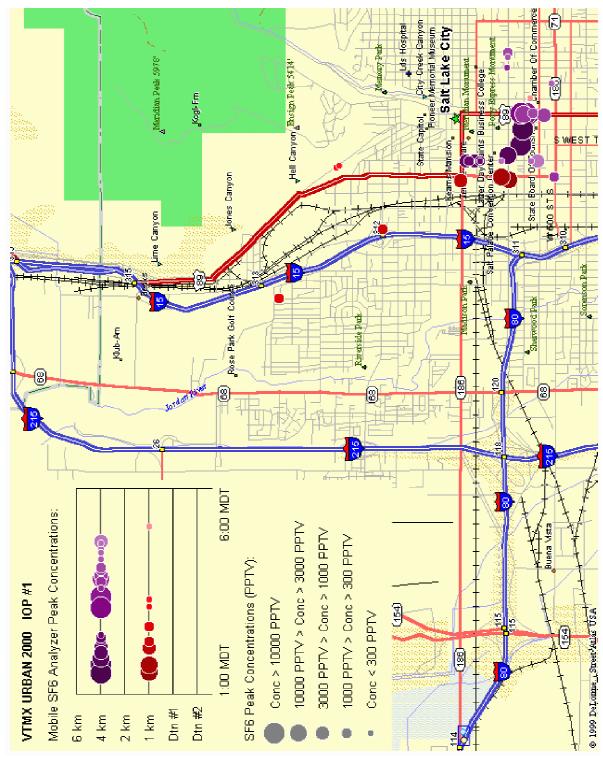


Figure 43. IOP 1 maximum  $SF_6$  concentration of each plume crossing all Sampling Units and time of measurement (upper left). Size of dot increases with increasing concentration. Dots on map indicate the geographical location of each maximum concentration. Color hue changes with increasing time.

### **Downtown Grid Samplers**

Figure 44a and b presents the measured tracer concentrations from the downtown urban grid for IOP 2. During the initial release of  $SF_6$  (0100-0200 MDT), the largest concentrations were measured to the north and west particularly at the mid-block locations. With additional tracer releases, more  $SF_6$  was detected to the south and east of the release point. As the IOP progressed the winds became more variable. At the end of the experiment, winds were light and variable causing a significant concentration buildup in the downtown area. In other words, the  $SF_6$  tracer did not fully disperse between tracer release periods; instead residual  $SF_6$  concentration levels continued to rise between releases.

#### **Rooftop Samplers**

The maximum rooftop concentration of approximately 3,600 pptv (Fig. 45) was measured atop the Federal Building (north of the release point) at the end of the first release period (0200 MDT). This concentration was nearly four times the concentration that was measured by the neighboring PIGS sampler located at the surface street corner immediately to the northwest of the building. It was also an order of magnitude larger than the sampler located at the surface street corner immediately to the northeast of the building. The concentration was nearly twice the next highest rooftop concentration which was measured atop the Hilton Hotel. Immediately after the peak occurred the integrated value dropped to less than 200 pptv until 0630 MDT when the concentration rose to almost 1,000 pptv. The first peak measured atop the Hilton was at 0230 hours and the second at 0630 hours. These two peaks were the half-hour integrated values measured subsequent to the end of the first and third release periods respectively. These two peak concentration measurements were of the same order of magnitude as the stationary downtown samplers' peak values.

Another feature evident in the rooftop samplers was the concentration response to the three  $SF_6$  tracer release periods. The three main peaks in time correspond to those release periods.

There were three peak values measured atop the Wells Fargo building that were approximately of the same magnitude. These values were cyclic (the peaks had about the same value each time) but not periodic (there was not a constant time between peaks). The first and third peaks corresponded to the same time that the Hilton Hotel peaks were measured, i.e. the half-hour integrated values measured subsequent to the end of the release periods. The Wells Fargo peak values occurred at the same time except the second peak was the measured value at the end of the second release period.

The Federal Building concentration measurements were fairly flat during the middle part of the experiment from 0230 to 0600 MDT. The concentrations measured at the Wells Fargo building and Hilton Hotel displayed similar trends which may be expected since these two

locations were fairly close together. By 0730 MDT, concentration levels had dropped below detection limits at the top of the Wells Fargo building.

### **Suburban Arc Samplers**

Figure 46 shows the results from IOP 2 for the northwest suburban sampling arcs. At 0230 MDT, large concentrations of  $SF_6$  were detected by samplers 26, 27, and 28 which were located northwest of the release point on the 2 km arc. (These 'large' concentration values were three to ten times smaller than the rooftop values discussed earlier.) At 0300 MDT, the large concentrations were detected on the 4 km arc by samplers 14, 15, and 16 which were northwest of the release point. These concentrations were about half as large as those detected on the 2 km arc. A large concentration reading was also seen on the 6 km arc at 0300 MDT. No clear trajectory or concentration patterns were observed for the last two tracer releases of IOP 2. Small concentration values were observed up to 4 hours after the release ended on all three northwest sampling arcs.

Figure 47 shows the concentrations measured by the southeast grid samplers during this IOP. Small concentrations were detected on the 2 km circle by samplers 33 and 34 indicating that some tracer diffused, against the prevailing wind. Concentrations on the southeast 4 km circle (35 and 36) were zero.

#### **Mobile Analyzers**

Table 23 presents a summary of the mobile analyzers' activities for IOP 2. Both units #1 and #2 measured very high concentrations very near the release point. The mobile analyzers had a number of null traverses possibly indicating the variable nature of the wind and the meandering nature of the plume. The bearings indicate that the maximum concentrations were observed to the west and northwest of the release point, in the main, as was also observed by the downtown PIGS. However, unit #6 measured a peak concentration to the southeast of the release site towards the end of the experiment.

The mobile analyzers did not measure significant tracer concentration levels in regions near the suburban arcs until about 0230 to 0300 MDT (Fig. 48) which was the result of advection of the tracer material from the first release. The highest concentration measurements were located near the downtown area. Only this IOP saw significant concentration levels detected to the southeast and southwest of the release point. The winds during the second and third release periods did not advect the tracer out to the arcs in sufficient quantities to permit easy detection by the real time analyzers. These instruments were subsequently redeployed into the areas north, east and south of the release site. These redeployed mobile analyzers measured significant quantities of the tracer in all directions from the release site.

# **Summary**

The tracer plume trajectory was primarily to the west and northwest but with significant excursions in all directions from the release site. Some tracer was detected 2 km from the release point to the southeast. Earlier in the experiment wind speeds were slightly greater which caused the  $SF_6$  tracer to be advected to greater distances. In the IOP, higher tracer concentrations were detected by real-time analyzer unit #3 traversing the 6 km route. At later times, the  $SF_6$  plume could not be found at this distance.

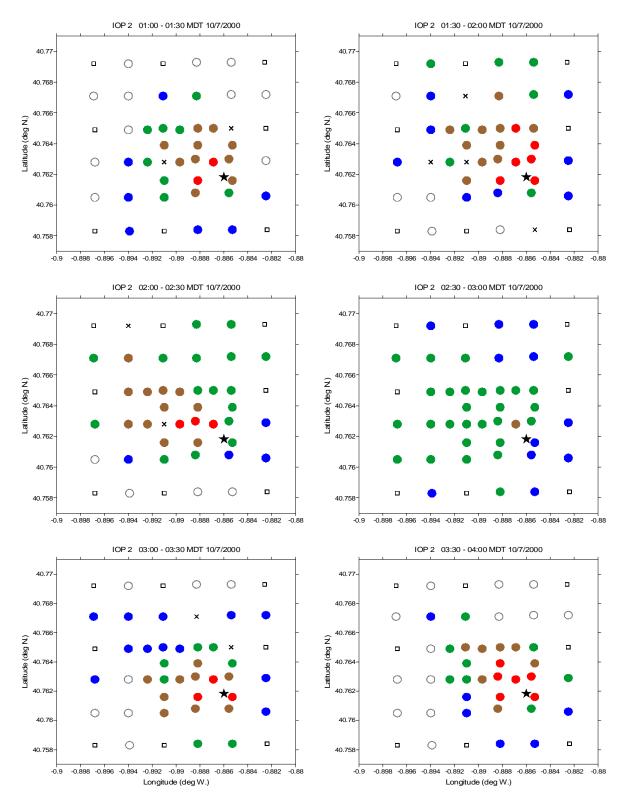


Figure 44a. Downtown urban PIGS  ${\rm SF_6}$  tracer concentration footprints during IOP 2 from 0100-0400 MDT.

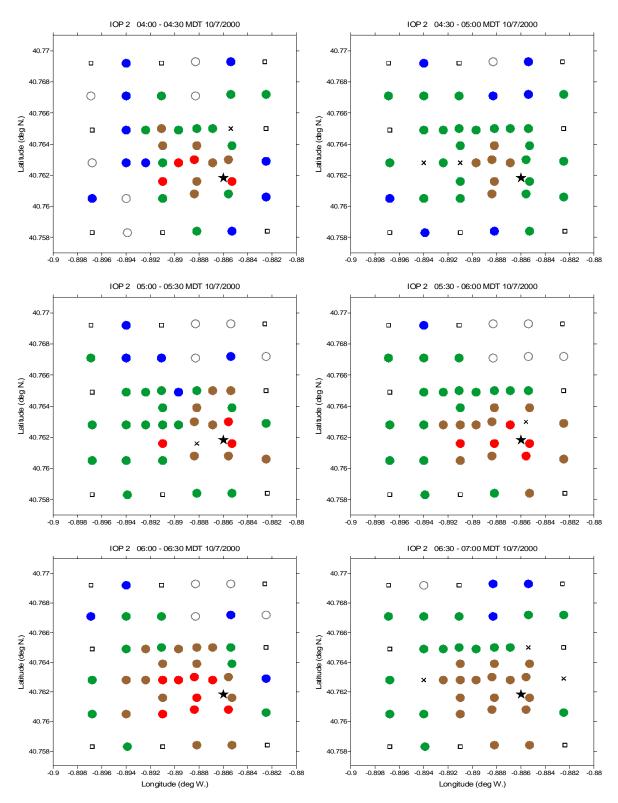


Figure 44b. Downtown urban PIGS  ${\rm SF_6}$  concentration footprints during IOP 2 from 0400-0700  $\,$  MDT.

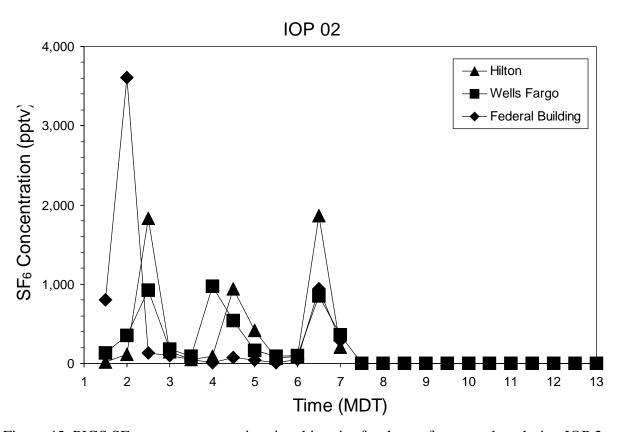


Figure 45. PIGS  $SF_6$  tracer concentration time histories for the rooftop samplers during IOP 2.

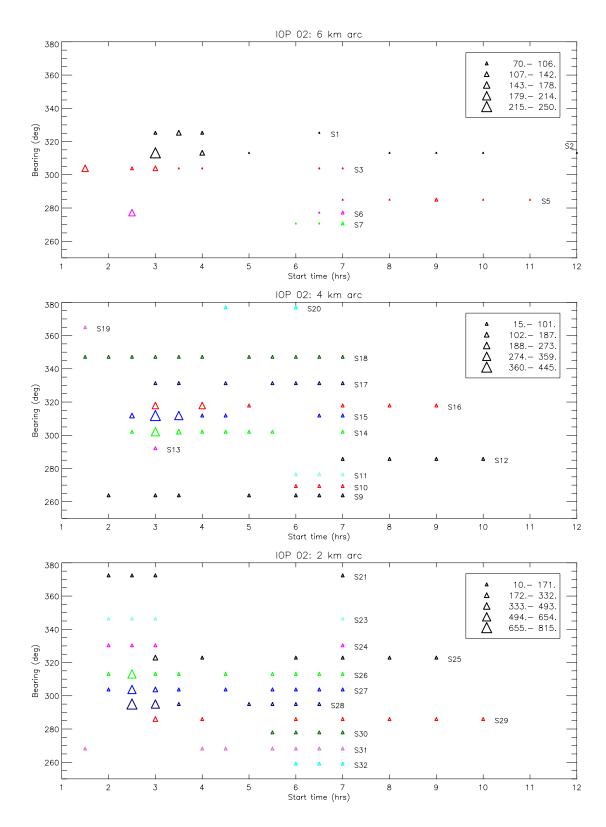


Figure 46. PIGS  $SF_6$  tracer concentration time histories for the 2, 4, and 6 km arcs during IOP 2.

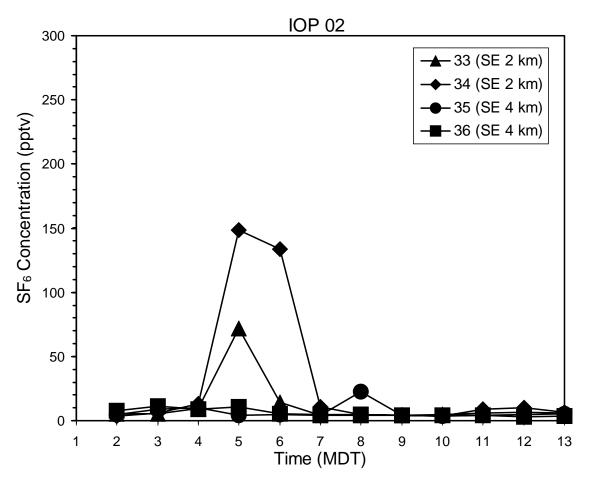


Figure 47. PIGS  $SF_6$  concentration time histories for the southeast 2 and 4 km sampling arcs during IOP 2.

Table 23. Summary of IOP 2  $SF_6$  real-time analyzer sampling unit (TGA) activity.

| -                       |                                | 0                                  |                                   | , ,                                   | , ,                                | •  |  |
|-------------------------|--------------------------------|------------------------------------|-----------------------------------|---------------------------------------|------------------------------------|--|--|
| Sam- pling Unit (TGA #) | General<br>Sampling<br>Route   | Total<br>Number<br>of<br>Traverses | Number<br>of<br>Null<br>Traverses | Number<br>of<br>Non-null<br>Traverses | Maximum<br>Concentration<br>(pptv) | Bearing<br>from<br>Release<br>Site<br>(deg.) | Range<br>from<br>Release<br>Site<br>(km) |
| Dtn#1<br>(#1)           | Main St,<br>State St,<br>200 E | 8                                  | 0                                 | 8                                     | 17,500                             | 316  | 0.36                                     |
| Dtn#2<br>(#2)           | State St.                      | 15                                 | 0                                 | 15                                    | $23,900^{1}$                       | 338  | 0.59                                     |
| 1km<br>(#6)             | S. Temple,<br>500 E            | 26                                 | 4                                 | 22                                    | 7,650                              | 111  | 0.81                                     |
| 2km<br>(#5)             | S. Temple,<br>300 W            | 25                                 | 6                                 | 19                                    | 3,550                              | 256  | 0.81                                     |
| 4km<br>(#7)             | 600 N,<br>600 S                | 30                                 | 5                                 | 25                                    | $15,100^2$                         | 233  | 1.18                                     |
| 6km<br>(#3)             | 2300 N,<br>Dupont              | 32                                 | 12                                | 20                                    | 734                                | 322  | 7.23                                     |

<sup>&</sup>lt;sup>1</sup>Dilution system was turned on during peak causing a spike. <sup>2</sup>Van was closer than 4 km to the source.

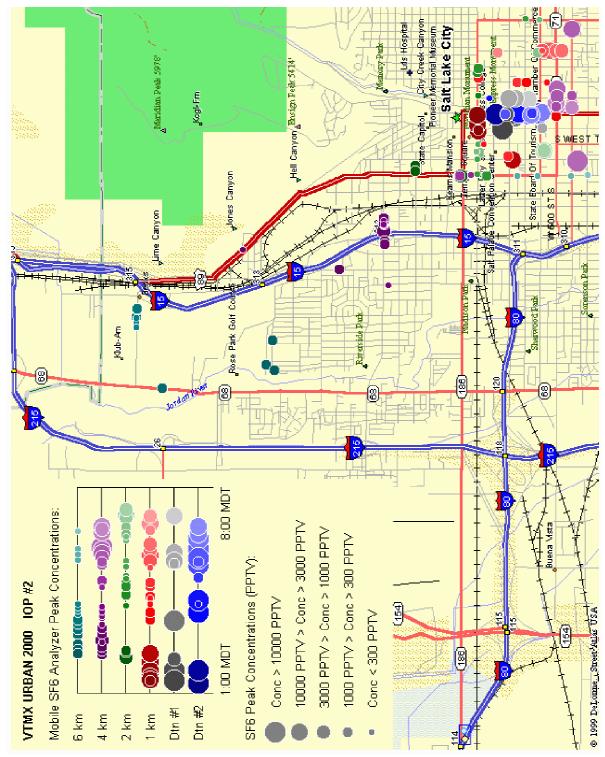


Figure 48. Maximum  $SF_6$  concentration of each plume crossing for all real-time analyzers as a function of time of measurement during IOP 2 (upper left). Size of dot increases with increasing concentration. Dots on map indicate the geographical location of each maximum concentration. Color hue changes with increasing time.

### **Downtown Grid Samplers**

IOP 4 (Fig. 49 a, b) saw a greater dispersion of SF<sub>6</sub> and larger regions of higher concentrations in the downtown area than was seen in IOP 2. However, concentrations to the southeast were not as large. Nevertheless, a large amount of tracer was observed to the south of the release site, indicating some transport of tracer material away from the prevailing downwind northwest suburban arcs. During all release periods the plume followed State Street as large concentrations were measured along this street. During the non-release periods, the peak concentrations shifted to the west along Broadway and southwest along Main Street. During the third release period, the block bounded by State Street, 2<sup>nd</sup> South, Main Street, and Broadway was saturated with a high concentration of SF<sub>6</sub>.

### **Rooftop Samplers**

Figure 50 shows the time histories of the measured rooftop concentrations. The three release periods were distinctly observed at almost every sampler location. Again the sampler atop the Federal Building measured the largest concentrations as occurred in IOP 2. At 0200 MDT a concentration of 5,825 pptv was measured and at 0400 MDT a concentration of 10,272 pptv was measured. The third release resulted in a maximum concentration measurement of only 240 pptv on top of the Federal Building. The measurements atop the Wells Fargo building were similar for all release periods. A concentration of just under 1,000 pptv was measured at 0800 MDT and detectable tracer levels were measured until 1300 MDT. The large concentrations observed by the street-level samplers surrounding the Wells Fargo Building were not seen atop the building at 64 meters AGL. Measurements atop the Hilton Hotel followed a similar trend as the Wells Fargo Building though the first peak did not occur at the same time. The Hilton Hotel peak concentrations were slightly less than those measured at the Wells Fargo Building.

#### **Suburban Arc Samplers**

Results for the northwest suburban arc samplers are shown in Figure 51. For the first tracer release period, a significant concentration was measured at sampler #15 on the 4 km arc at 0230 MDT. This sampler is located to the NNW of the downtown area indicating the plume centerline turned slightly to the west from the northerly direction seen downtown. However, the plume was fairly spread out by the time it reached the 2 km arc as concentrations were measured almost the full length of the instrumented arc. The northwest movement of the core of the plume is also supported by the higher concentration measurement of sampler #1 on the 6 km arc. The concentrations measured by samplers #11, #12, and #13 on the 4 km arc and samplers #5, #6, and #7 on the 6 km arc were essentially zero also supporting the NNW movement of the plume.

However at later times, quite high concentrations were detected by samplers 27 through 30 located on the 2 km arc indicating the plume from the third release shifted more to the west. This is consistent with the observations from the downtown grid and rooftop measurements.

Also the plume may have stayed nearer the ground since the concentrations were higher for these 2 km samplers than the concentrations measured by 2 km samplers at earlier times. The plume of the third release spread rather quickly to the 4 and 6 km arcs as significant concentrations were measured at these ranges just shortly after the 2 km samplers detected significant concentrations.

Figure 52 shows the concentrations measured by the southeast grid samplers for this IOP. Samplers #33 and #34 on the southeast 2 km arc measured small concentrations at 0600 and 0700 MDT after the third release period. Sampler location #35 on the southeast 4 km arc also showed an elevated concentration at 0600 MDT.

#### **Mobile Analyzers**

Table 24 presents a summary of the mobile analyzers' activities for IOP 4. The peak concentrations measured by vans #1 and #2 along Main and State streets correspond well to the high average concentrations measured by the downtown grid samplers.

At early times the mobile analyzers detected significant tracer concentrations in the downtown area out to the 2 km arc in the north, northwest, and west directions.

Figure 53 indicates that the plumes headed generally NW but at later times also spread to the west where significant concentrations were measured on Highway 68 and I-215. This confirms the same results as observed by the urban and suburban samplers. Concentrations measured by unit #6 on the 1 km route appeared to be cyclic possibly corresponding to the three release periods. At later times, unit #6 also measured a significant peak (> 10,000 pptv) to the south of the release point. At about the same time, sampler #88 in the downtown grid reported a similar integrated value. Evidence of the cyclic nature of the plume is also seen on the 2 km arc route (Fig. 53).

#### **Summary**

Large tracer concentrations were seen to the north at the street-level downtown grid samplers and on the top of the Federal Building after the first two release periods, similar to what was seen in IOP 2. After the third release period, all the rooftop concentration measurements were about 2,000 pptv or less though the nearby grid samplers were much higher. This would indicate that the plume stayed nearer to the ground and shifted more to the northwest.

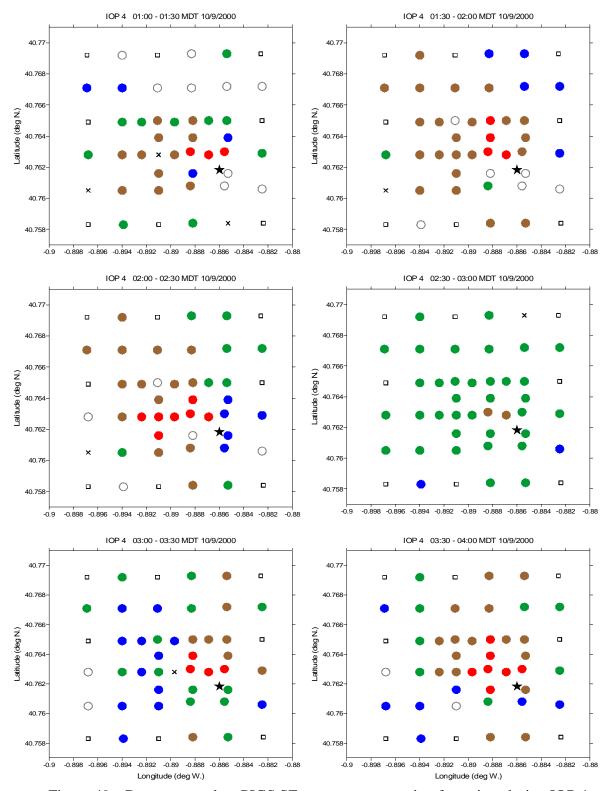


Figure 49a. Downtown urban PIGS  ${\rm SF_6}$  tracer concentration footprints during IOP 4 from 0100-0400 MDT.

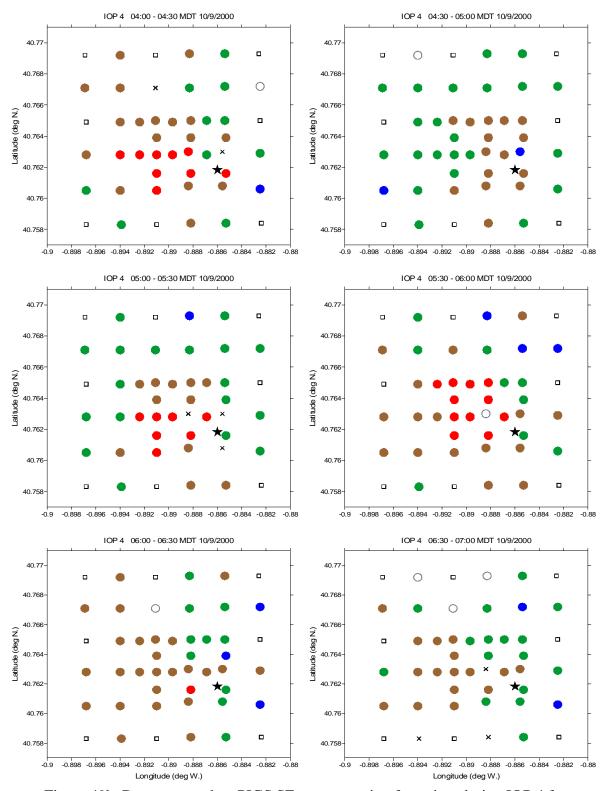


Figure 49b. Downtown urban PIGS  ${\rm SF_6}$  concentration footprints during IOP 4 from 0400-0700 MDT.

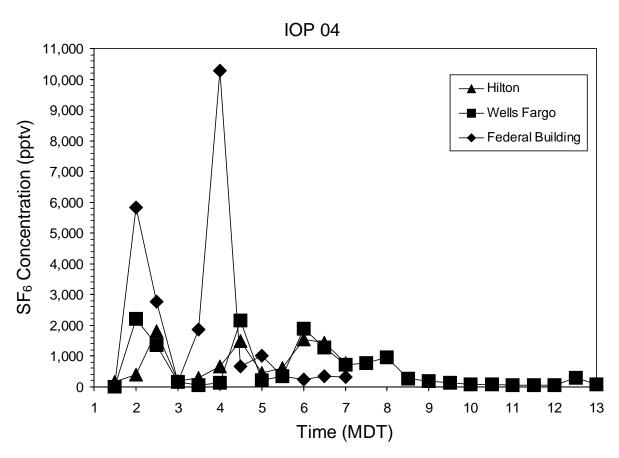


Figure 50. PIGS  $SF_6$  tracer concentration time histories for the rooftop samplers during IOP 4.

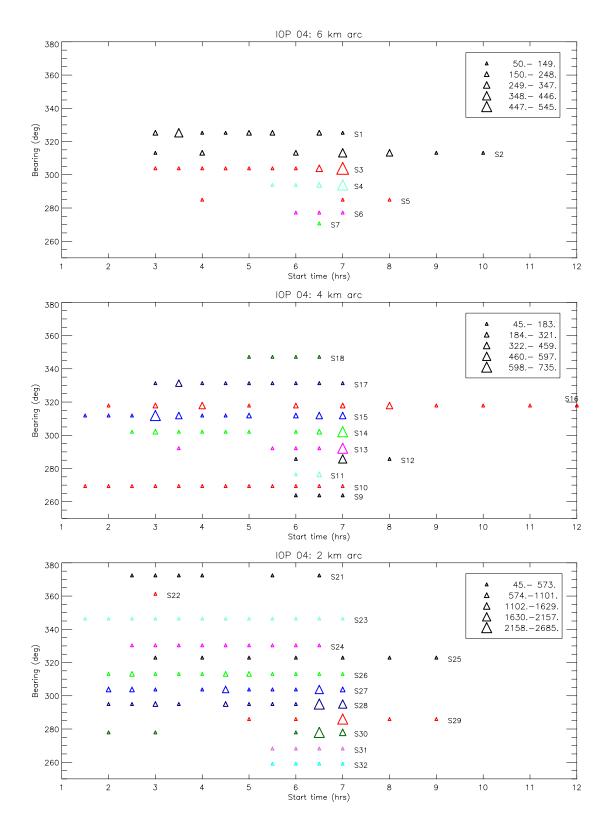


Figure 51. PIGS  $SF_6$  tracer concentration time histories for the 2, 4, and 6 km arcs during IOP 4.

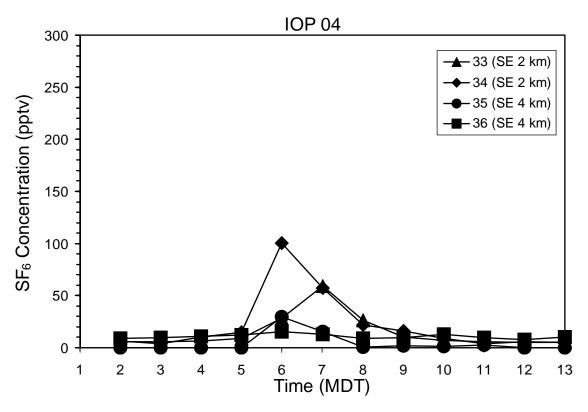


Figure 52. PIGS  $SF_6$  concentration time histories for the southeast 2 and 4 km sampling arcs during IOP 4.

Table 24. Summary of IOP 4  $SF_6$  real-time analyzer sampling unit (TGA) activity.

| Sampling Unit (TGA #) | General<br>Sampling<br>Route | Total<br>Number<br>of<br>Traverses | Number<br>of<br>Null<br>Traverses | Number<br>of<br>Non-null<br>Traverses | Maximum<br>Concentration<br>(pptv) | Bearing<br>from<br>Release<br>Site<br>(deg.) | Range<br>from<br>Release<br>Site<br>(km) |
|-----------------------|------------------------------|------------------------------------|-----------------------------------|---------------------------------------|------------------------------------|--|--|
| Dtn#1 (#1)            | Main St.                     | 9                                  | 0                                 | 9                                     | 16,800                             | 297  | 0.50                                     |
| Dtn#2<br>(#2)         | State St.                    | 12                                 | 0                                 | 12                                    | 31,200*                            | 306  | 0.18                                     |
| 1km<br>(#6)           | 600 N,<br>200 W              | 26                                 | 1                                 | 25                                    | 16,400                             | 211  | 0.44                                     |
| 2km<br>(#5)           | N. Temple,<br>300 W          | 30                                 | 5                                 | 25                                    | 13,400                             | 315  | 1.65                                     |
| 4km<br>(#7)           | 600 N,<br>Redwood<br>Rd.     | 44                                 | 10                                | 34                                    | 15,700*                            | 314  | 6.31                                     |
| 6km<br>(#3)           | 2300 N                       | 42                                 | 9                                 | 33                                    | 1,810                              | 297  | 1.32                                     |

<sup>\*</sup> Analyzer over-ranged giving an inaccurately low reading.

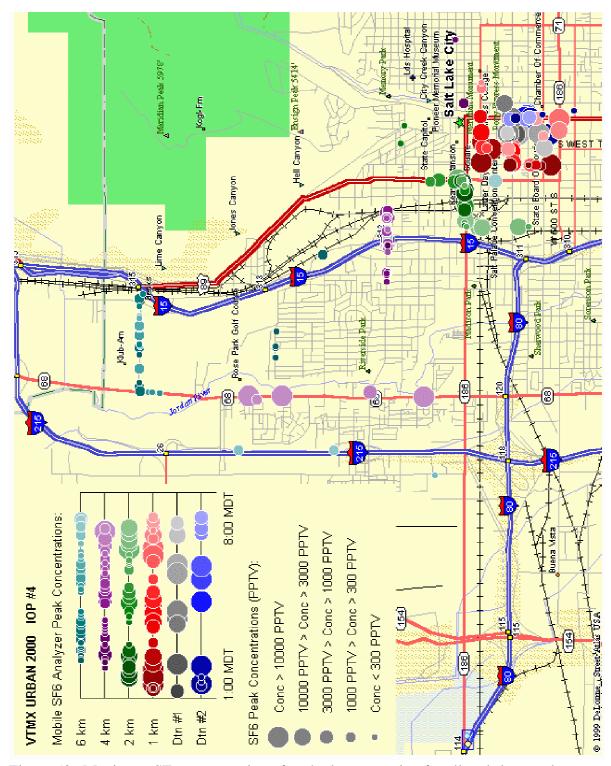


Figure 53. Maximum  $SF_6$  concentration of each plume crossing for all real-time analyzers as a function of time of measurement during IOP 4 (upper left). Size of dot increases with increasing concentration. Dots on map indicate the geographical location of each maximum concentration. Color hue changes with increasing time.

### **Downtown Grid Samplers**

Figure 54 a, b shows the results obtained from the downtown urban grid for IOP 5. During the first release period (0100 - 0200 MDT), the tracer mainly moved west along 400 S and along Broadway though small concentration levels were detected to the north and east of the downtown grid. After the first release period (0200-0230 MDT), there was a little movement of the plume north along Main street. The tracer continued to dilute during the second half of the first non-release period (0230 - 0300 MDT) such that measured SF<sub>6</sub> levels were less than 1,000 pptv in most locations towards the center of downtown and less than 100 pptv near the edges of the grid. But small concentration levels were evident at almost all downtown locations and the tracer did not completely leave the area before the second release began. During the second release period (0300 - 0400 MDT), the tracer moved more northerly along 200 E, State, and Main streets though significant concentrations were still detected directly west of the release site. After the second release period (0400 - 0430 MDT), the significant tracer concentrations shifted more to the west and northwest. Just before the beginning of the third release, almost all stations reported concentrations of 1,000 pptv or less than was observed at the end of the first non-release period. During the third release period (0500 - 0600 MDT), the tracer moved north along 200 E and State Street and west along Broadway, 200 S and 100 S. After the third release ended (0600 - 0700 MDT), concentration levels decreased to the west and increased to the north during the first half of the third non-release period, but then this was reversed during the second half of this the third non-release period. This might point to the meandering of the plume from north to west.

IOP 5 saw little transport of the tracer to the southeast. By the end of the experiment, small levels (< 100 pptv) of SF<sub>6</sub> were detected in the southeast corner of the urban grid.

### **Rooftop Samplers**

The three tracer release periods were again easily observed in the rooftop sampler concentration time history plots (Fig. 55). During the first release period, small concentrations were detected atop the three instrumented buildings. However, after the first release ended (0200-0230 MDT), a concentration of just over 3,000 pptv was measured atop the Hilton Hotel. This corresponds to the magnitude of the concentration measurements from the street-level grid samplers near the Hilton and is consistent with the westward movement observed generally by all ground-level samplers. During the first non-release period, the measurements atop the other two buildings were small. During the second release period as the plume shifted to the northwest, the concentration level atop the Wells Fargo building increased sharply ( $\sim$ 10,000 pptv at 0400 MDT) and the Federal Building' sampler showed a modest increase ( $\sim$  1,400 pptv at 0400 MDT). After the second release period, average concentration levels atop all three buildings were in the 1,000 to 1,200 pptv range which eventually decreased to several hundred at the end of the non-release period. During the third release period, concentration levels atop the Wells Fargo building again increased significantly to a peak average value of 11,768 pptv at 0630 MDT. At the same time the Federal Building sampler measured the SF<sub>6</sub> concentration level

at 4,060 pptv. After 0700 MDT tracer concentration levels continued to be measured atop the Wells Fargo building and alternated between about 200 pptv and 50 pptv for the next four hours.

The largest tracer concentrations measured from rooftop samplers during IOP 5 came from the Wells Fargo building at the end of the second and third release periods (0400 and 0630 MDT respectively). These were very large concentrations (about 10,000 pptv and 11,800 pptv).

## **Suburban Arc Samplers**

Figure 56 shows the time histories of the ground samplers located on the northwest suburban arcs. At 0200 MDT sampler #30, which is primarily west of the release point, detected a concentration around 1,000 pptv strengthening the argument the plume initially moved west. By 0230 MDT, tracer was detected all along the 2 km arc. After 0300 MDT, concentration levels to the west of the release point on the 2 km arc went to zero. In fact, after this time no significant tracer concentration levels were detected south and west of the approximate line formed from sampler #27 to sampler #14 to sampler #3.

After the plume shifted more to the north, IOP 5 results seem to indicate that the plume tended to follow along the foothills crossing over sampler #17 and across and to the east of sampler #1. At the end of the third release period, the tracer was detected at samplers #21, #22, and #23 which were directly north and slightly east of the release point. The plume did not continue due north into the mountains (as evidenced by the zero concentration measurements of samplers #19 and #20) but shifted towards the west as evidenced by the measurements of samplers #18 and #17.

At 1100 MDT, a small amount of  $SF_6$  was detected at sampler #33 on the southeast 2 km arc located to the southeast of the downtown grid (Fig. 57). This feature possibly indicates some recirculation of the tracer material back to the southeast with the reversal of the wind direction during the day.

#### **Mobile Analyzers**

Table 25 shows a summary of the mobile analyzers sampling activity for IOP 5. It is interesting to note that with only 1 city block separating the routes of van #1 and van #2 and van #1 doing more passes, van #1 had 3 null traverses. The route of van #1 is one block west of the route of van #2. The plume misses by van #1 might be due to the meandering of the plume as noted by the PIGS samplers discussed above.

Figure 58 presents the results of the mobile analyzers for IOP 5. Van #6 had the route at approximately 1 km distance from the release point. Its route along 200 W and South Temple coincided with the west and north sides of the downtown grid. (However, this route was not strictly adhered to.) Of 25 passes, only two were null traverses. The first null traverse was within the first 12 minutes after the release. The second null traverse occurred after 0700 MDT and after the tracer material had been advected out of the area. Otherwise, as long as the van sampled

to the north or west of the release point, peak concentration levels typically were in the thousands of pptv.

As noted earlier the northwest suburban arc PIGS samplers did not detect appreciable values of  $SF_6$  south of the line formed by samplers #27, #14, and #3. However, the mobile analyzers continued to detect  $SF_6$  plumes, but the peak concentrations became smaller and smaller with time. Van #5 on the 2 km arc measured peak  $SF_6$  concentrations no higher than 300 pptv during the second release period. But between the second and third release periods (0400-0500 MDT) short-time duration peak values of up to 10,000 pptv were detected to the NNW of the release point.

Van #7 traveled the 4 km route. Towards the end of the first release period, significant concentration levels were detected west of the release point along this route. After the first release period ended, concentrations were about 700 pptv or less as measured by this TGA. During the second release period, measured concentration levels were about 300 pptv or lower. Towards the end of the second release period and approximately 20 minutes after the release ended (about 0354 to 0419 MDT), several null passes were completed, i.e. no tracer was detected during these passes. Around 0435 MDT during a non-release period, a peak of about 1,600 pptv was measured to the northwest by this van. About 0445 MDT a second peak of about 2,200 pptv was measured in the same area. During the third release period (0500 to 0600 MDT), peak concentration levels were small (< 600 pptv) until about 0548 MDT when a peak of about 2,200 pptv was detected to the NNW. However, by 0600 MDT the concentration levels were reduced to about 600 pptv in the same area where the 2,200 pptv peak was measured. After the end of the third release period (0600 to 0700 MDT), a peak of about 3,500 pptv was detected around 0627 MDT to the NNW and at 0631 MDT a peak of almost 3,000 pptv was measured. Concentration levels gradually decreased after this time in the same area along the main railroad route.

Van #3 handled the 6 km route. On this route no  $SF_6$  tracer was detected until after the first release period ended because the operator had difficulty locating the plume. Tracer material was then detected along most of the western part of this route and did not exceed 250 pptv. During the second release period (0300-0400 MDT), a peak of almost 900 pptv was measured to the NNW from the release point near I-15 at about 0311 MDT. Between the second and third release periods (0400-0500 MDT), concentration levels did not exceed 80 pptv in the northwest 'box' part of the route until about 0455 MDT when levels near 300 pptv were detected. During the third release period, peak concentration levels remained around 300 pptv until about 0535 MDT when the concentration levels started to decrease. A peak of about 700 pptv was detected just before 0700 MDT to the NNW along I-15. The farthest northern extent of  $SF_6$  concentration was detected during this IOP just north of the I-15 and Highway 89 interchange by van #3.

#### **Summary**

During the first release period the SF<sub>6</sub> tracer plume moved mainly to the west. During the second release period, the plume moved in a more northerly direction. The third release period saw significant concentration levels to the north and west, but particularly to the north. This was

corroborated by the rooftop measurements and by the mobile analyzers. They initially saw some concentration levels to the west but later in the IOP the highest concentration levels were found to the northwest. The second and third release tracer plumes tended to hug the base of the mountains along the US-89 and I-15 corridors on the 4 and 6 km arcs.

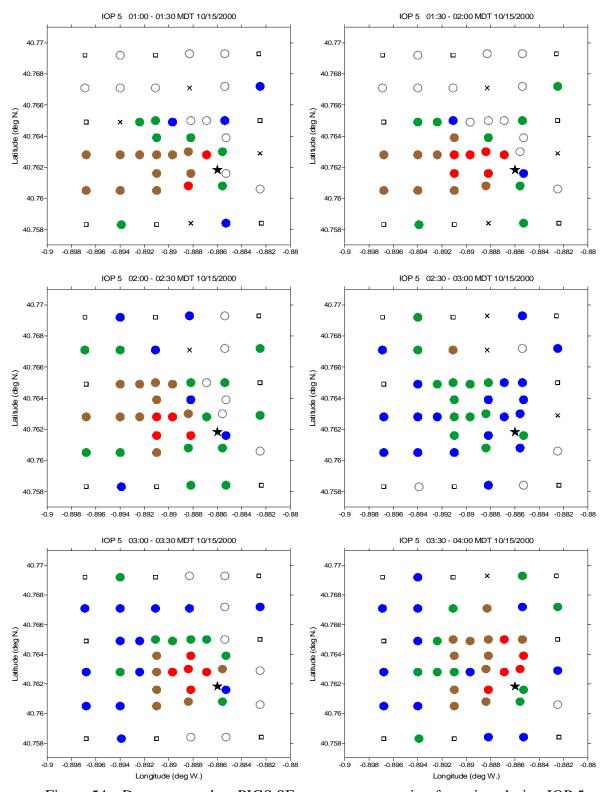


Figure 54a. Downtown urban PIGS  ${\rm SF_6}$  tracer concentration footprints during IOP 5 from 0100-0400 MDT.

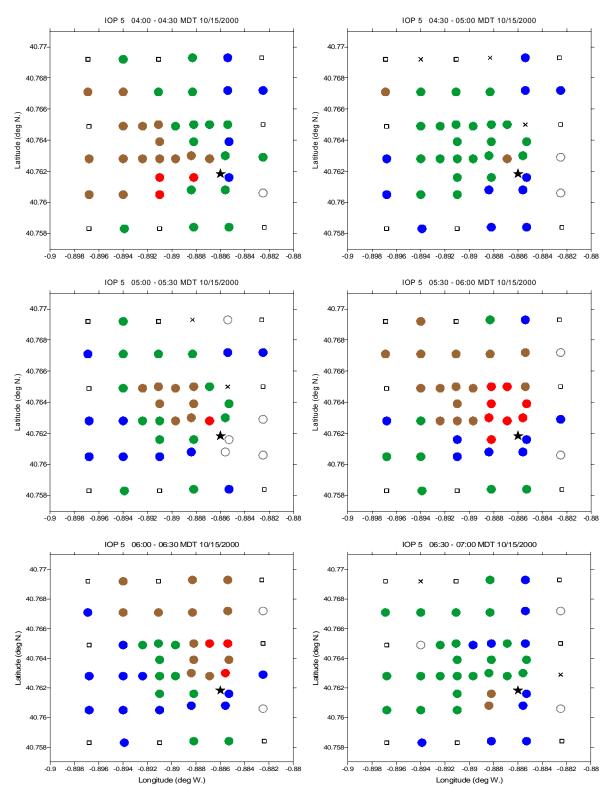


Figure 54b. Downtown urban PIGS  ${\rm SF_6}$  concentration footprints during IOP 5 from 0400-0700 MDT.

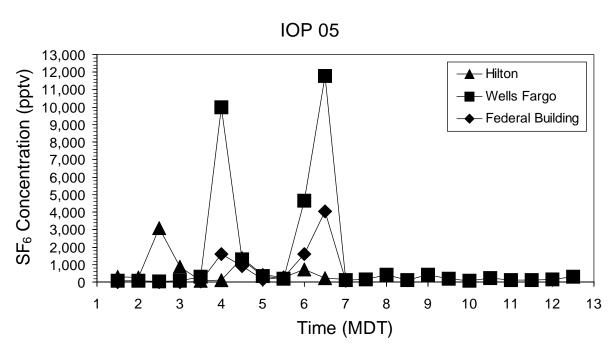


Figure 55. PIGS SF<sub>6</sub> tracer concentration time histories for the rooftop samplers during IOP 5.

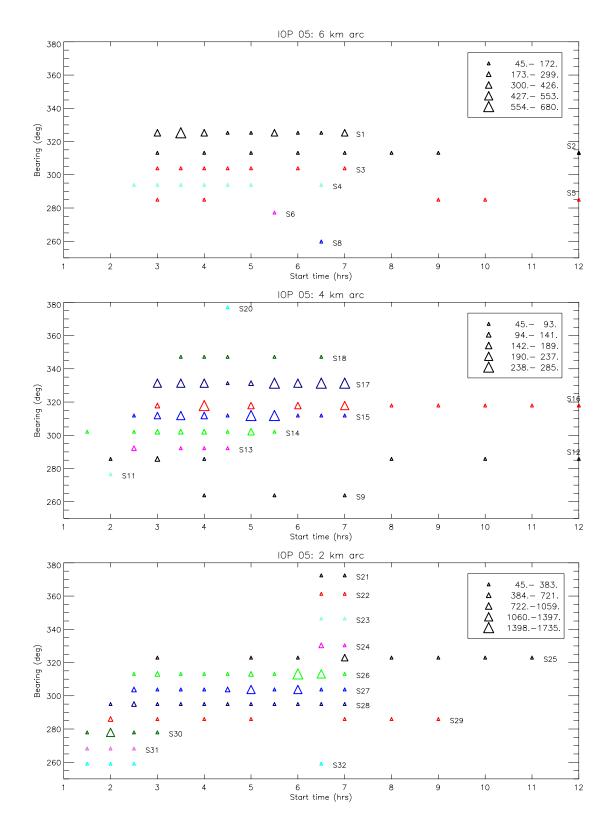


Figure 56. PIGS  $SF_6$  tracer concentration time histories for the 2, 4, and 6 km arcs during IOP 5.

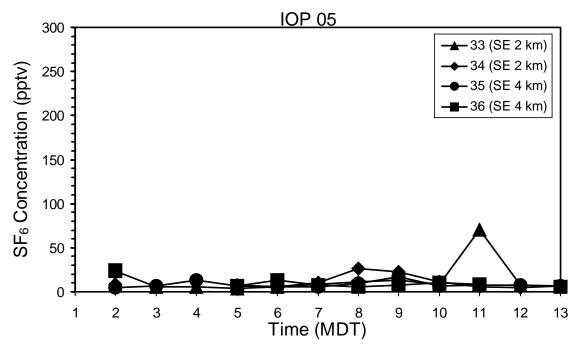


Figure 57. PIGS  $SF_6$  concentration time histories for the southeast 2 and 4 km sampling arcs during IOP 5.

Table 25. Summary of IOP 5 SF<sub>6</sub> real-time analyzer sampling unit (TGA) activity.

| Sam- pling Unit (TGA #) | General<br>Sampling<br>Route  | Total<br>Number<br>of<br>Traverses | Number<br>of<br>Null<br>Traverses | Number<br>of<br>Non-null<br>Traverses | Maximum<br>Concentration<br>(pptv) | Bearing<br>from<br>Release<br>Site<br>(deg.) | Range<br>from<br>Release<br>Site<br>(km) |
|-------------------------|-------------------------------|------------------------------------|-----------------------------------|---------------------------------------|------------------------------------|--|--|
| Dtn#1 (#1)              | Main St.                      | 18                                 | 3                                 | 15                                    | 15,900                             | 297  | 0.49                                     |
| Dtn#2<br>(#2)           | State St.                     | 10                                 | 0                                 | 10                                    | 25,100*                            | 230  | 0.28                                     |
| 1km<br>(#6)             | S. Temple,<br>200 W           | 25                                 | 2                                 | 23                                    | 14,900                             | 262  | 0.94                                     |
| 2km<br>(#5)             | N. Temple,<br>300 W,<br>600 W | 40                                 | 1                                 | 39                                    | 9,930                              | 304  | 1.90                                     |
| 4km<br>(#7)             | 600 N, 900<br>W, 1000W        | 39                                 | 5                                 | 34                                    | 3,570                              | 324  | 2.82                                     |
| 6km<br>(#3)             | 2300 N,<br>Victoria<br>Way    | 34                                 | 5                                 | 29                                    | 873                                | 334  | 6.73                                     |

<sup>\*</sup> Analyzer over-ranged giving an inaccurately low reading.

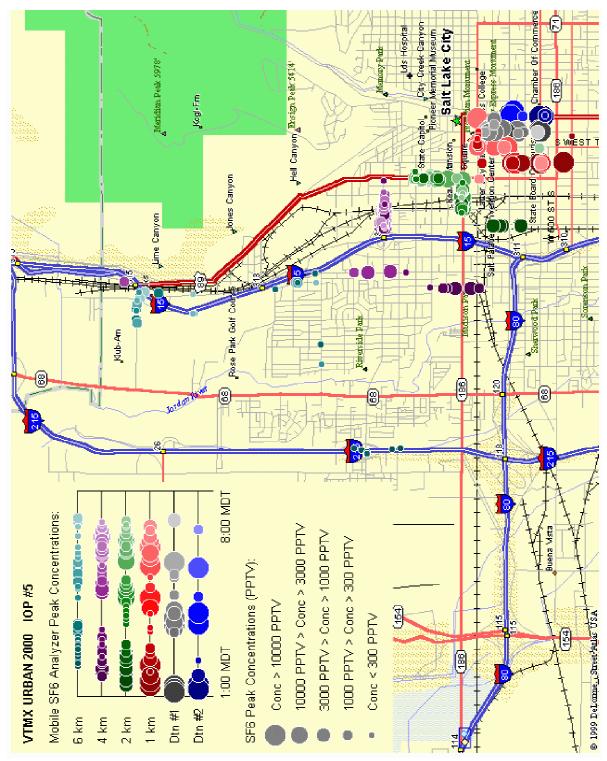


Figure 58. Maximum  $SF_6$  concentration of each plume crossing for all real-time analyzers as a function of time of measurement during IOP 5 (upper left). Size of dot increases with increasing concentration. Dots on map indicate the geographical location of each maximum concentration. Color hue changes with increasing time.

## IOP 7

# **Downtown Grid Samplers**

Concentrations were not high immediately around the release point for the first 30 minutes of the first tracer release period of IOP 7 (Fig. 59 a, b). The SF<sub>6</sub> tracer initially headed west along and between Broadway and 400 S. At the end of the first half hour of releasing SF<sub>6</sub>, sampler #67 (located in the northwest corner of the urban grid) and sampler #98 (located to the east of the release point) detected the tracer. Other samplers between #67 and the release point did not detect any significant levels of SF<sub>6</sub> indicating some lofting might have been present. It also seems unusual that sampler #98 detected significant levels of SF<sub>6</sub> while sampler #92 that was just one block west and closer to the release point did not measure any SF<sub>6</sub>. From aerial photographs of building obstructions it appears there could have been a fairly direct path between sampler #98 and the release point allowing SF<sub>6</sub> to reach this sampler while other nearby samplers did not detect any tracer. During the last 30 minutes of the first tracer release period, the tracer was detected at all locations in the center of the grid and at some locations on the west and north boundaries. Sampler #96 on the eastern boundary also detected the tracer. Between the first and second tracer release periods (0200 - 0300 MDT), concentrations of  $SF_6$  were detected at the north end of the grid on State Street and 200 E. Some tracer also migrated more to the south and east of the release point. Concentration levels gradually decreased but were still elevated significantly at many sampling locations at the start of the second tracer release period.

During the second release period, concentration levels immediately to the southwest of the release point increased, but the concentration levels for the rest of the grid did not significantly change from the previous non-release sampling period. After the second tracer release period ended, tracer concentration levels to the northwest increased during the first 30 minutes of sampling (0400 - 0430 MDT) indicating significant meandering of the wind. Concentration levels then decreased in the next 30 minutes of sampling (0430 - 0500 MDT) to a fairly uniform value over much of the grid.

During the third release period, the concentrations again increased to the west and to the north from the release site during the first 30 minutes of release. The second 30 minutes of the release period (0530 - 0600 MDT) saw greater concentration increases to the west and southwest. After all releases had ended, concentrations in the northern half of the grid decreased significantly during the 0600 - 0630 MDT sampling period but stayed about the same in the southern half as was seen at the end of the previous release period. During the final 30-minute sampling period, the higher concentration levels shifted to the northwest corner while the center of the grid again had a fairly uniform distribution.

#### **Rooftop Samplers**

Three distinct concentration peaks were again observed in the rooftop concentration time history plots (Fig. 60). Concentrations of less than a few hundred pptv were measured by the building-top samplers during the first release period. There was a sudden spike in the

concentration level (~3,100 pptv) atop the Federal building located to the north of the release point after the first release period ended between 0200 and 0230 MDT. But the concentration level quickly decreased during the next sampling period (0230 - 0300 MDT) at this station. After the second release period ended, all three building top samplers recorded concentration increases. The largest concentration level (~1,900 pptv) was measured on top of the Hilton Hotel, the next largest at the Wells Fargo building, and then the Federal building. Thus, concentrations decreased from west to north. During the third release period, the Federal building sampler recorded an increase in concentration a little over ~1,900 pptv while the other two buildings' samplers saw decreases at the same time. This change in phase indicates some change in wind speed and direction during the six hours of the three release and sampling periods.

The extended time period samplers on the Wells Fargo building recorded a sudden increase in  $SF_6$  concentration at 1200 MDT to about 2,000 pptv from about 100 pptv. Prior to this the concentration levels were generally less than 200 pptv. The concentration level was still elevated at 1230 MDT but completely dispersed by 1300 MDT. This sudden increase many hours after the last release period might be due to some mesoscale recirculation effects.

#### **Suburban Arc Samplers**

Results from the northwest suburban arcs for IOP 7 are shown in Figure 61. The lowest concentration range of up to 660 pptv for the 2 km arc covered approximately the entire range for the other two arcs.

The lofting effect noted earlier is also seen in the suburban sampling data. Higher concentrations were recorded at 0130 MDT by samplers #27 and #28 which were located approximately along the line northwest of the release point through sampler #67's location.

The highest concentration on the 2 km arc occurred at 0400 MDT (end of the second release period) and was recorded at sampler #31. This sampler was directly west of the release point. Significant spread of the tracer plume was evident as all samplers on the 2 km arc showed measurable levels of the tracer material at 0230 - 0300 MDT. This phenomena continued to be observed for the remainder of the test.

The  $SF_6$  measured along the 4 km arc also showed significant spread in the tracer plume. It is particularly noticeable at 0430 - 0500 MDT. The  $SF_6$  plume exhibits a distinct turn to the north. The plume centerline appears to pass over the northern end of the 6 km arc next to the eastern mountains as the highest concentrations were measured there.

Figure 62 shows the concentrations measured by the suburban samplers located in the southeast quadrant. These samplers during this IOP measured the highest levels of  $SF_6$  of any of the IOPs. A significant portion of the  $SF_6$  plume from the first release period (0100 - 0200 MDT) initially affected sampler #34 on the southeast 2 km arc at 0200 - 0300 MDT. Sampler #34 to the ESE of the release point recorded concentration levels averaged over a hour period of 250 pptv.

The affect was also observed in the other sampler on the southeast 2 km arc and also the two samplers on the southeast 4 km arc to lesser degrees. The affect lasted until 1 to 2 hours after all releases had ended. Thus, a significant meander of the wind direction could be assumed to be present during this IOP.

# **Mobile Analyzers**

Table 26 summarizes the results from the mobile sampling units for IOP 7. Figure 63 shows the peak SF<sub>6</sub> concentrations for each plume crossing for all mobile sampling units. It is interesting to note how far the tracer traveled in an east-west direction. It was detected by all the mobile analyzers at the extremes of their routes. The tracer filled mainly the northwest quadrant from the release point but significant concentration levels were also measured in all directions although not at great distances.

The two null passes of van #6 on the '1 km' route were conducted within the first 17 minutes of the beginning of the first release. At about 0120 MDT the tracer was first detected by this TGA at the southern end of the route. The route of this van was modified from that depicted in Figure 7. The new route included streets to the east and south of the release point so that the van essentially circled the release point. It detected instantaneous high concentrations on all sides of the downtown grid box show in Figure 7. At 0143 a concentration near 16,000 pptv was detected to the WNW. The tracer in this area slowly decreased after the first release period ended (0200-0300 MDT). Part way through this non-release period the van moved to the east side of the downtown grid box and detected a peak concentration level of about 12,000 pptv at 0224 MDT. After this peak reading the concentration decreased to the east also. Late in the second release period, the concentration to the south and west increased again to almost 16,000 pptv. After the end of the second release period, a short duration spike of 6,000 pptv occurred to the north. During the third release period, about 0545 MDT, a peak concentration of about 12,000 pptv was measured, and shortly thereafter at 0553 MDT a peak near 16,000 pptv was detected in the same area. These high concentrations continued to be observed for a short time after the end of the third release period. By 0628 MDT, a peak concentration to the west was near 8,000 pptv. After that, the concentration levels on the western boundary of the downtown grid continued to drop as measured by TGA #6.

The two null crossings of van #5 also occurred during the first release period. It took a period of time for the tracer to travel out to the 2 km range. The first peak of SF<sub>6</sub> was detected about 0130 MDT to the northwest. This quickly increased to 13,000 pptv over about the next 20 minutes. Between the first and second release periods, the concentration levels dropped considerably. The highest peak recorded during this time was about 900 pptv. The largest peak measured during the second release period was near 9,000 pptv around 0334 MDT. Smaller concentration levels were detected to the southwest during the rest of this period. After the second release period ended, peak concentrations remained around 2,000 pptv for up to half an hour. The SF<sub>6</sub> slowly decreased after this to concentration levels of 600-800 pptv. These measurements were made to the west and northwest. During the third release period,

concentration levels did not start to rise into the thousands until 0551 MDT to the northwest on the 2 km route.

Van #7 on the 4 km route measured the first traces of SF<sub>6</sub> at 0150 MDT to the northwest. The concentration was small - about 120 pptv. Since small amounts of tracer were detected on the 4 km route, the van was pulled in closer to the downtown area during the second release period and traveled a square route around the release point. The TGA detected concentrations of approximately 1,100 pptv to the southeast and 2,200 pptv to the west early during the second release period. From about 0338 to 0344 MDT, concentration levels of nearly 11,000 - 12,000 pptv were measured to the southwest. Concentration levels to the west decreased during this time. After the end of the second release period, the van moved back out to resume traversing the 4 km route. Early during this period, peak concentration levels of around 1,600 pptv were detected to the west and north (Fig. 63). At 0425 MDT the concentration level reached 2,200 pptv to the northwest. Concentration levels dropped during the remainder of this non-release period. During the third release period, the van focused on the northwest corner of the route. Concentration levels remained low in this area until close to 0600 MDT when the SF<sub>6</sub> concentration increased to nearly 3,500 pptv. After the final release period ended, the van traversed the whole 4 km route. Concentration levels to the west reached 1,600 pptv and to the north reached 2,100 pptv. Concentration levels to the northwest decreased after 0650 MDT.

Van #3 on the 6 km route did not detect any significant levels of SF<sub>6</sub> during much of the first release period. Part way through the first release period, the van moved in closer to an area between the 1 and 2 km routes. Here the TGA detected concentration levels of about 4,000 pptv. The van then started to move back out toward the 6 km route around 0140 MDT. Near the location of the NNW corner of the 2 km route, this TGA measured SF<sub>6</sub> levels of 11,000 pptv. Between the first and second release periods, the van traveled near the east-west leg of its route and did not detect concentration levels above 70 pptv except for one reading at 0220 MDT of a concentration level near 600 ppty. During the first half of the second release period, the van traveled north following the foothills. The concentration levels along this path did not exceed 70 ppty. Then during the second half of the second release event, the van moved to the western side of the study area and traveled a north-south path on 2200 W paralleling I-215. The peak concentration detected along this route was just over 300 ppty. The van then moved to the east and traveled a north-south route along highway 68. Here the van measured concentration levels around 1,200 pptv and was made towards the end of the second release period. Concentration levels slowly decreased after the end of the second release period in the area between the 4 and 6 km arcs. During the third release period (0500 to 0600 MDT), the TGA detected only one plume crossing with a peak of about 180 pptv at 0545 MDT near Interstate 15. After the end of the final release period, the major peaks in concentration were detected to the west and WNW with maximum values of nearly 800 pptv. Concentrations to the north were very low (<100 pptv).

About 0330-0400 hours the mobile analyzer traversing the plume near the 6 km arc measured tracer concentration levels between 300-3,000 pptv. The highest concentration measured by the nearest 6 km PIGS samplers (#6 and #7) in the same area was less than 250 pptv. This might indicate a rather large spike detected by the mobile analyzer but which was

'integrated' out by the stationary samplers. This IOP also saw the highest concentration levels directly east of downtown. (See also Figure 62, IOP7, sampler #34 where the highest concentration levels were detected of any of the southeast samplers.)

# **Summary**

The concentration footprints from IOP 7 indicate an extensive east-west transport of the tracer material as well as along the well-established path to the northwest along the edges of the mountains. Further study combined with valley wind measurements is needed to fully describe the fate of the tracer material during this IOP.

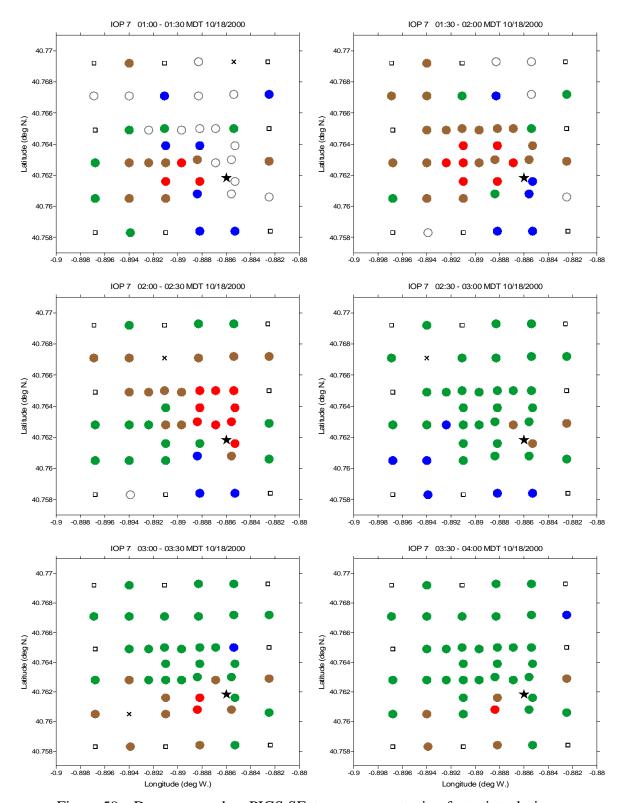


Figure 59a. Downtown urban PIGS  ${\rm SF_6}$  tracer concentration footprints during IOP 7 from 0100-0400 MDT.

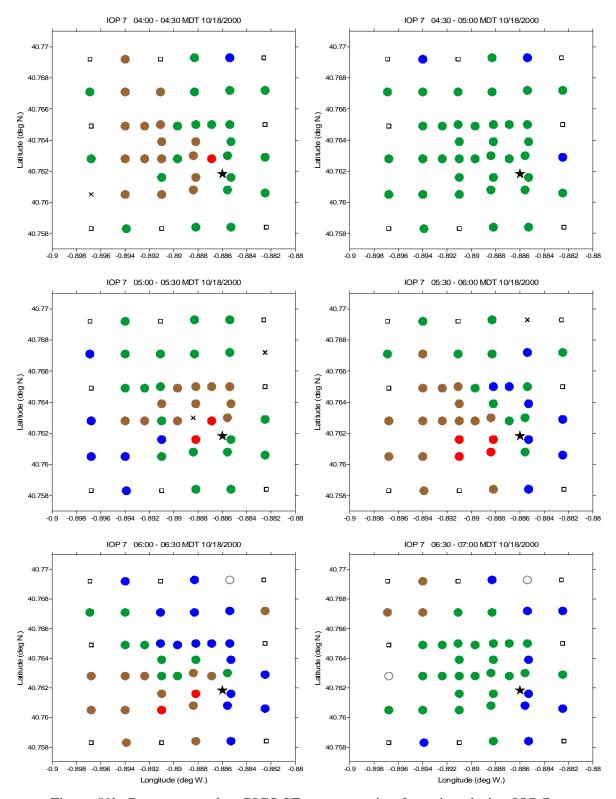


Figure 59b. Downtown urban PIGS  ${\rm SF_6}$  concentration footprints during IOP 7 from 0400-0700 MDT.

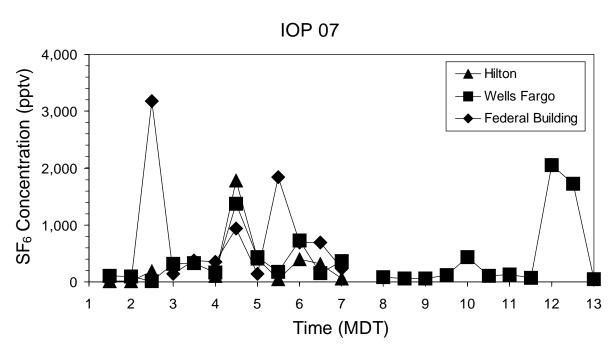


Figure 60. PIGS  $SF_6$  tracer concentration time histories for the rooftop samplers during IOP 7.

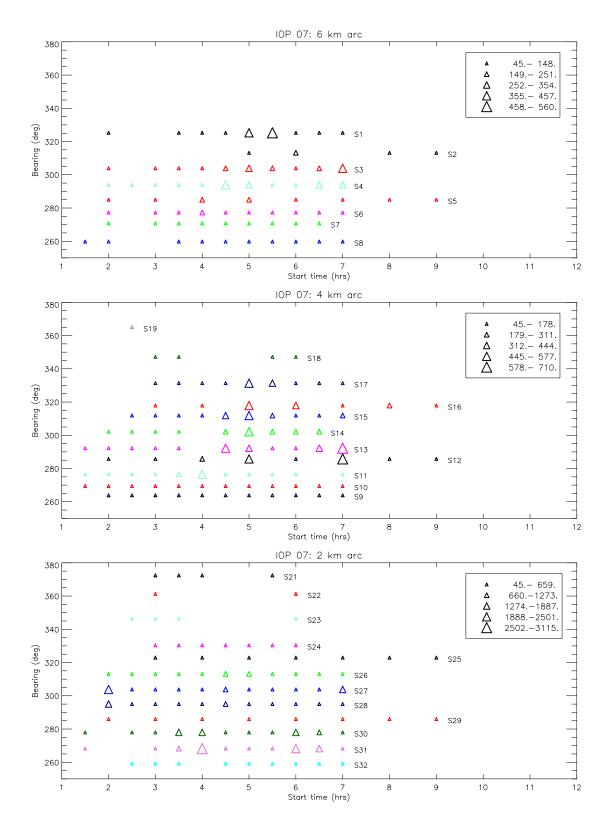


Figure 61. PIGS  $SF_6$  tracer concentration time histories for the 2, 4, and 6 km arcs during IOP 7.

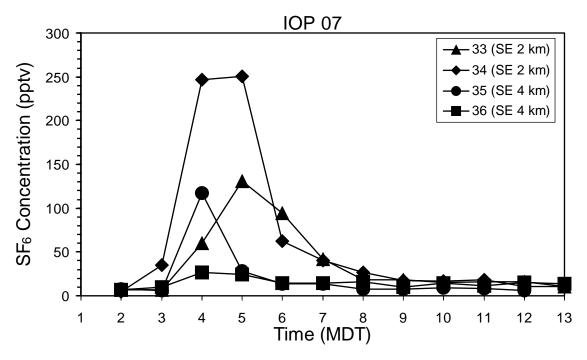


Figure 62. PIGS  $SF_6$  concentration time histories for the southeast 2 and 4 km sampling arcs during IOP 7.

Table 26. Summary of IOP 7 SF<sub>6</sub> real-time analyzer sampling unit (TGA) activity.

| Sampling Unit (TGA #) | General<br>Sampling<br>Route         | Total<br>Number<br>of<br>Traverses | Number<br>of<br>Null<br>Traverses | Number<br>of<br>Non-null<br>Traverses | Maximum<br>Concentration<br>(pptv) | Bearing<br>from<br>Release<br>Site<br>(deg.) | Range<br>from<br>Release<br>Site<br>(km) |
|-----------------------|--------------------------------------|------------------------------------|-----------------------------------|---------------------------------------|------------------------------------|--|--|
| Dtn#1<br>(#1)         | Main St.                             | 16                                 | 2                                 | 14                                    | 16,700                             | 265  | 0.46                                     |
| Dtn#2<br>(#2)         | State St.                            | 16                                 | 0                                 | 16                                    | 30,000*                            | 240  | 0.25                                     |
| 1km<br>(#6)           | S. Temple,<br>200 W,<br>500 S        | 22                                 | 2                                 | 20                                    | 17,800                             | 291  | 0.95                                     |
| 2km<br>(#5)           | N. Temple,<br>300 W, 600<br>W        | 48                                 | 2                                 | 46                                    | 13,100                             | 315  | 1.69                                     |
| 4km<br>(#7)           | 1000 W,<br>600 N                     | 31                                 | 5                                 | 26                                    | 11,700*                            | 239  | 0.75                                     |
| 6km<br>(#3)           | 2300 W,<br>700 N,<br>Victoria<br>Way | 23                                 | 3                                 | 20                                    | 10,900                             | 300  | 1.57                                     |

<sup>\*</sup> Analyzer was over-ranged giving an inaccurately low reading.

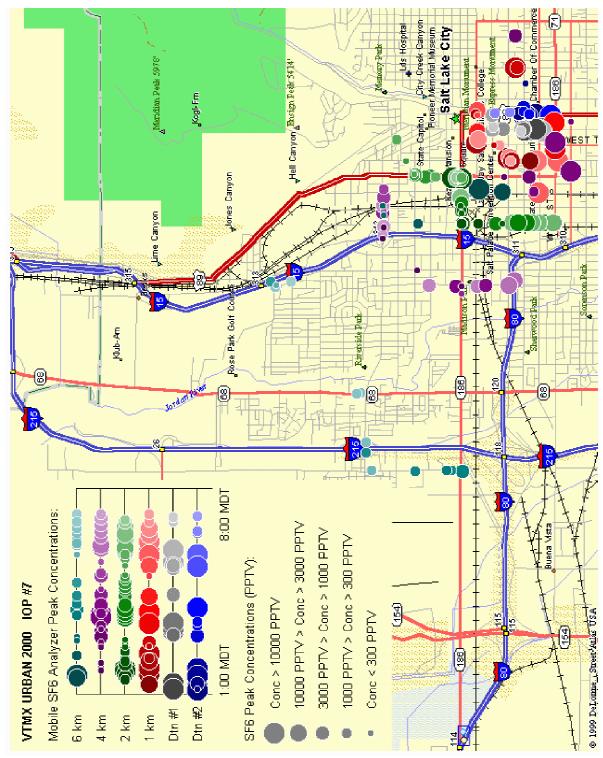


Figure 63. Maximum  $SF_6$  concentration of each plume crossing for all real-time analyzers as a function of time of measurement during IOP 7 (upper left). Size of dot increases with increasing concentration. Dots on map indicate the geographical location of each maximum concentration. Color hue changes with increasing time.

## IOP9

The start time for this IOP was three hours earlier and the release rate was twice the rate of the other IOPs (2, 4, 5, 7, and 10). The mid-block grid samplers and all of the samplers on the 2 km arc were initially programmed with the wrong start time. Thus substantial data is missing for the first 3 hours of the IOP. Also IOP 9 and IOP 10 were characterized by higher wind speeds and more consistent wind directions than the other IOPs.

# **Downtown Grid Samplers**

Figure 64a and b shows the results from the downtown grid samplers for IOP 9. During the first release period the tracer moved primarily west along 400 S. Some of the tracer also moved toward the northwest corner of the grid. After the first release period ended, the tracer was transported off the grid so that all samplers detected levels below the MLOQ limit (45 pptv) except in the immediate vicinity of the release point. During the second release period, the SF<sub>6</sub> moved primarily to the southwest corner of the grid with small concentrations directly south of the release point and some small concentrations detected on the northwestern boundary of the grid. After the end of the second release period, the tracer was again transported off the grid with the only significant levels measured by the samplers near the release point in the southwest direction. By the second half of this non-release period, the incorrectly programmed mid-block samplers became active. During the third release period, the tracer moved to the west along 400 S and Broadway and north along Main Street similar to the first release and additionally west on 200 S. At the end of the third release period, the highest concentrations were again to the west and southwest with significant SF<sub>6</sub> concentrations detected along the western border of the grid. After the last release period ended, the tracer was again transported off the grid so that only low levels of SF<sub>6</sub> were detected near the release point.

#### **Rooftop Samplers**

The concentration time histories of the rooftop samplers again showed the cyclical pattern of the three release periods (Fig. 65). The highest concentrations measured on the building rooftops occurred atop the Hilton Hotel for all three release periods and is northwest of the release point. The highest concentration of approximately 1,600 pptv was measured at the end of the third release period. Concentration levels measured atop the Federal building never exceeded 300 pptv and the majority of the time were much less than that. The concentrations measured on top of the Wells Fargo building tended to follow the trends measured at the Hilton. The largest concentration measured at the Wells Fargo building was about 900 pptv.

# **Suburban Arc Samplers**

Figure 66 shows the results from the northwest suburban arcs for IOP 9. The data from the 2 km arc for times between 2200 and 0100 MDT is missing due to improper programming of the samplers. After the samplers began working at 0100 MDT, the highest concentrations were detected to the west of downtown (samplers #30 and #31). This is consistent with the

predominantly westward movement of the plume observed from the urban grid samplers. The plume centerline appeared to shift to the north because the highest concentrations measured on the 4 km and 6 km arcs were more to the northwest of downtown.

The samplers in the southeast quadrant measured only insignificant levels of  $SF_6$  (Fig. 67). All values were less than 10 pptv.

## **Mobile Analyzers**

Table 27 presents a summary of the mobile analyzers sampling activity for IOP 9.

Van #6 working the 1 km route had three null traverses. The first occurred at the beginning of the IOP. The first large concentration peak was detected around 2222 MDT during the first release period directly west of the release point (Fig. 68). This peak approached 16,000 pptv. The peak concentration levels to the west remained high during the first release period from 7,000 pptv to 16,000 pptv. After the first tracer release period ended, the SF<sub>6</sub> was quickly transported out of the area and the peak concentration declined to 1,700 pptv. During the second release period, the peak concentration was again near 16,000 pptv, However, the location of this reading was very near the release point when the van took a detour. The highest concentration level measured on the 1 km route was near 13,000 pptv to the WSW. After the second release period ended, concentration levels quickly dropped to about 3,500 pptv within seven minutes. Near the start of the third release period (0212 MDT) peak concentrations were measured near 2,500 pptv to the west and northwest. When the release began, this quickly climbed to over 9,000 pptv where the concentration level remained for most of the rest of the third release period. Near the end of the third release period, concentration levels dropped to around 5,500 pptv. But at the end of the third release period, concentration levels to the northwest shot up to near 11,500 pptv. The concentration quickly dropped within 10 minutes to just over 200 pptv. Except for one small detour this van stayed to the west and northwest of the release point. The high concentrations it measured indicate that the plume moved west from the release site.

Van #5 was assigned the 2 km route and maintained its assigned route. Therefore, all of the observations were made to the west or northwest. Four traverses detected no tracer. The first null traverse was at the beginning of the first release period before the tracer had an opportunity to spread very far. The second null traverse occurred at the beginning of the second release period. The third was near the beginning of the third release period. The fourth occurred 24 minutes after the final release period ended. The first detection of SF<sub>6</sub> on the 2 km arc made by TGA #5 came about 20 minutes after the start of the release with a peak concentration near 7,000 pptv, NNW of the release point. The maximum peak measured by this van occurred about 25 minutes after the beginning of the first release period almost due west of the release site and approached 12,000 pptv (Table 27). High concentration levels were also detected to the northwest (about 4,200 pptv) during the first release period. The highest concentration detected after the end of the first release period was about 1,200 pptv measured right after the end of the period to the northwest. The maximum concentration measured during the second release period was about 4,500 pptv to the northwest. This occurred near the end of the release period (2449

MDT). The concentration level increased initially after the end of the second release period to near 6,000 pptv. By 0142 MDT the concentration had dropped to less than 140 pptv. The peak of the third release period was not detected until about 0237 MDT to the northwest and approached 3,900 pptv. The concentration dropped to just over 1,500 pptv by the end of this release period. The concentration level in this area quickly dropped to less than 160 pptv after the end of the final release period.

Van #7 was assigned the 4 km route. The van maintained its route for the most part. A few detours were made in searching for the plume. The peak concentration during the first release period was about 4,100 pptv measured in the northwest direction from the release point at about 2237 MDT. Therefore it only took about 37 minutes for the tracer to reach the 4 km arc in substantial quantity. The peak during the second release period was about 2,100 pptv to the WNW. During the third release period, a peak of about 1,400 pptv was detected about 0238 MDT. All of these peak concentrations were detected to the northwest of the release site.

Van #3 covered the 6 km route. The route was followed for the most part. The van did not reach the southern part of the 6 km route until after 2235 MDT where it started to sample along the 6 km route. While traversing the route during the first release period, the highest peak measured was a little over 1,000 pptv along 700 N around 2239 MDT. The van traveled 400 S or state route 186 west to get to the 6 km route. Along this highway, a peak concentration of around 2,500 pptv was measured at 2233 MDT and is reported in Table 27. After the first release period ended, the van traveled a zigzag course along Dupont to the north, down Garnette south, west along 1000 N, then south along Redwood road to 700 N. During this time the peak concentration approached 400 pptv and then finally dropped to zero when a null traversal was reported. During the second release period, two traversals were reported along the same route as just mentioned but also including 2200 W. The peak concentration was about 700 pptv which was detected right at the end of this period close to sampler #5 on the 6 km arc. During the third release period, the peaks were measured along 1000 N - the highest peak being about 700 pptv at 0249 MDT.

#### **Summary**

The stronger and more consistent winds might explain why during the non-release periods of IOP 9 (Fig. 64 a, b) the concentration of  $SF_6$  decreased significantly in the downtown grid area. By the end of the IOP, little tracer was detected there. During the release periods the highest concentrations were measured WSW for IOP 9. The mobile analyzers also support the idea of the plume moving initially west from the release site and then veering to the north. With the higher wind speeds, concentration levels were detected by the mobile analyzers near the 4 and 6 km arcs at earlier times than for the IOPs previously reported (Table 27 and Figure 68).

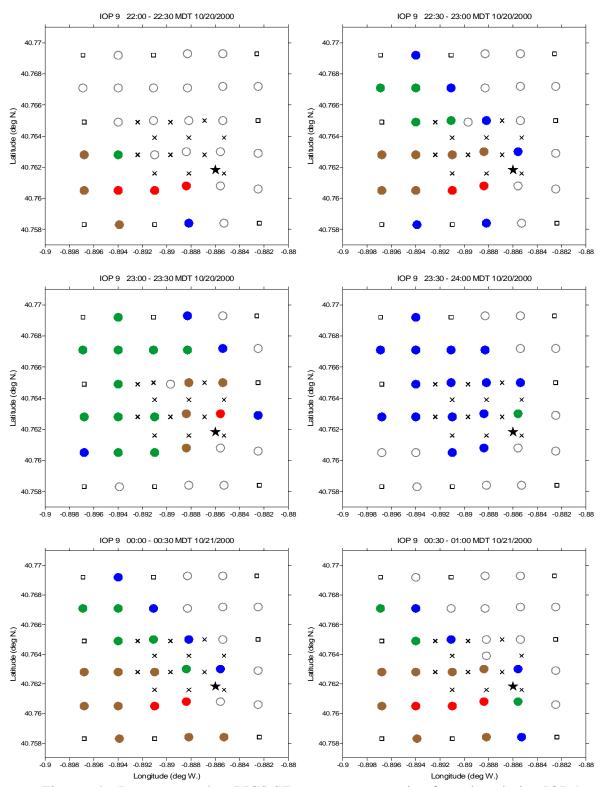


Figure 64a. Downtown urban PIGS  $SF_6$  tracer concentration footprints during IOP 9 from 0100-0400 MDT.

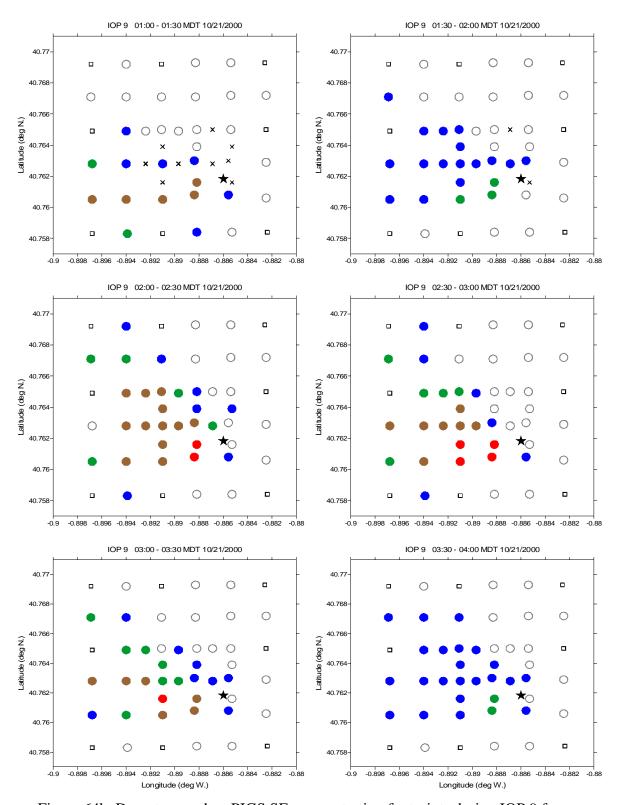


Figure 64b. Downtown urban PIGS  $SF_6$  concentration footprints during IOP 9 from 0400-0700 MDT.

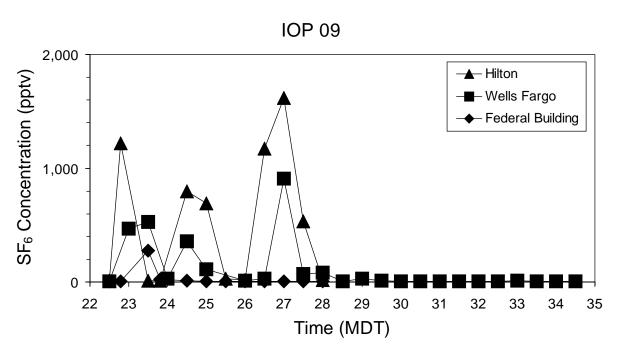


Figure 65. PIGS SF<sub>6</sub> tracer concentration time histories for the rooftop samplers during IOP 9.

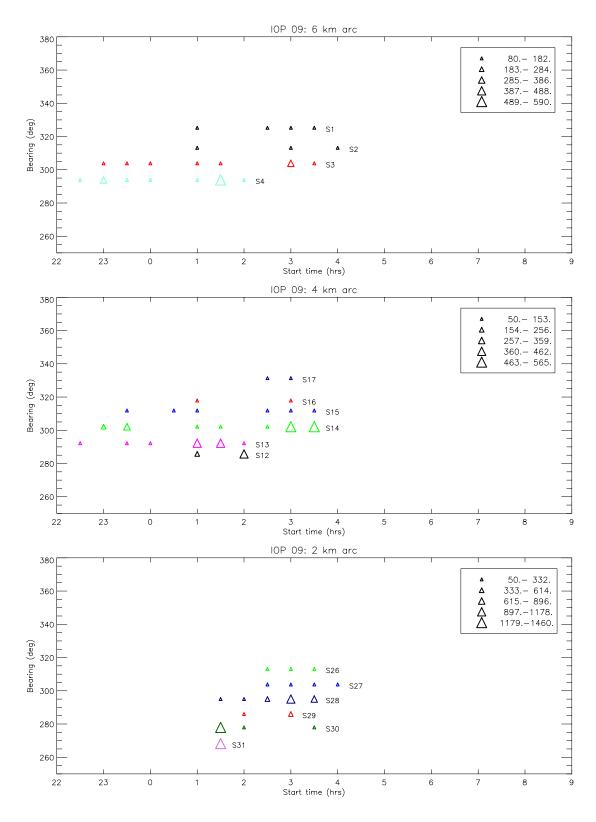


Figure 66. PIGS  $SF_6$  tracer concentration time histories for the 2, 4, and 6 km arcs during IOP 9.

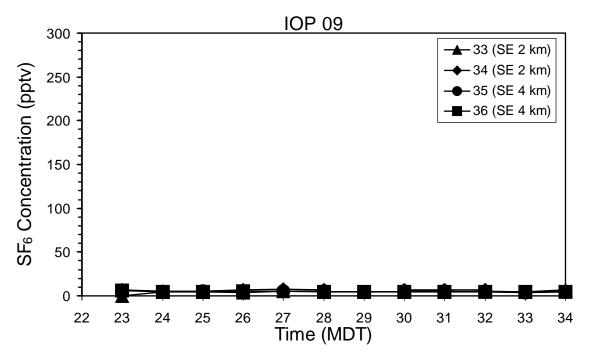


Figure 67. PIGS  $SF_6$  concentration time histories for the southeast 2 and 4 km sampling arcs during IOP 9.

Table 27. Summary of IOP 9 SF<sub>6</sub> real-time analyzer sampling unit (TGA) activity.

| Sam- pling Unit (TGA #) | General<br>Sampling<br>Route | Total<br>Number<br>of<br>Traverses | Number<br>of<br>Null<br>Traverses | Number<br>of<br>Non-null<br>Traverses | Maximum<br>Concentration<br>(pptv) | Bearing<br>from<br>Release<br>Site<br>(deg.) | Range<br>from<br>Release<br>Site<br>(km) |
|-------------------------|------------------------------|------------------------------------|-----------------------------------|---------------------------------------|------------------------------------|--|--|
| Dtn#1 (#1)              | Main St.                     | 9                                  | 0                                 | 9                                     | 16,500                             | 249  | 0.48                                     |
| Dtn#2<br>(#2)           | State St.                    | 4                                  | 0                                 | 4                                     | 25,000*                            | 265  | 0.19                                     |
| 1km<br>(#6)             | 400 S, 200<br>W              | 23                                 | 3                                 | 20                                    | 16,000                             | 264  | 0.94                                     |
| 2km<br>(#5)             | N. Temple,<br>600 W          | 41                                 | 4                                 | 37                                    | 11,800                             | 273  | 1.89                                     |
| 4km<br>(#7)             | 1000 W,<br>900 W             | 28                                 | 9                                 | 19                                    | 3,480                              | 283  | 2.95                                     |
| 6km<br>(#3)             | 1500 W,<br>Redwood<br>Rd     | 31                                 | 6                                 | 25                                    | 2,550                              | 287  | 3.63                                     |

<sup>\*</sup> Analyzer was over-ranged giving an inaccurately low reading.

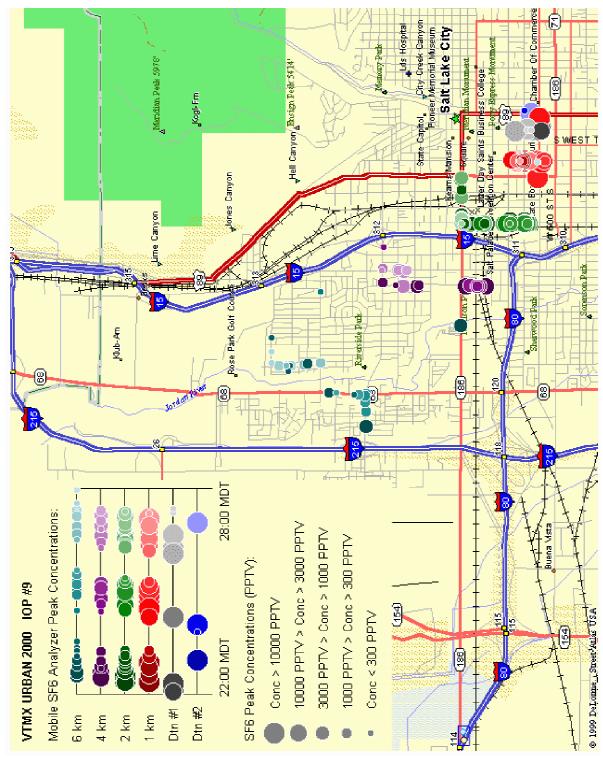


Figure 68. Maximum  $SF_6$  concentration of each plume crossing for all real-time analyzers as a function of time of measurement during IOP 9 (upper left). Size of dot increases with increasing concentration. Dots on map indicate the geographical location of each maximum concentration. Color hue changes with increasing time.

#### **IOP 10**

# **Downtown Grid Samplers**

Figure 69a and b shows the results from the downtown grid samplers for IOP 10. During the first release period the tracer initially moved west along Broadway, 400 S and 200 S. During the second half hour of the first release period, the tracer moved more to the north than the west with increasing concentrations on State Street at the northern end of the grid. During the second release period the tracer again initially moved west along Broadway and 200 S. By the end of the second release period significant concentrations were also observed at the north end of the downtown grid. The second and third non-release periods were similar to the first, i.e. tracer was detected almost every where but the levels decreased significantly. The third release period saw the tracer initially spread to the north then during the second half of the period once more move to the west. After the end of each release period, the tracer advected out of the grid so that only a few locations northwest of the release site exhibited elevated concentrations.

## **Rooftop Samplers**

Figure 70 shows the tracer concentrations from the three buildings with samplers on their roofs. As with all previous IOPs, the concentration time histories exhibited cyclical patterns that followed the cyclical tracer release patterns. The highest concentrations (about 3,050 to 3,200 pptv) were measured atop the Wells Fargo building at the end of the second release period and at the middle of the third release period. At the end of the first release period, the highest concentration (about 800 pptv) was on top of the Federal building to the north of the release point. The concentrations measured atop the Hilton never exceeded 600 pptv.

#### **Suburban Arc Samplers**

Figure 71 presents the results from the suburban arc samplers. The peak concentrations on the 2 km arc were measured by samplers #27 and #28 located to the northwest of the release point consistent with the tracer movement seen in the downtown area. At later times the plume centerline moved farther north as evidenced by the concentrations detected by the samplers along the northern part of the arc. Samplers #14 and #15 on the 4 km arc and samplers #2 and #3 on the 6 km measured the highest concentrations on their respective arcs again indicating that the plume moved to the northwest. With the distinct northwest movement of the plume, the samplers to the southeast did not measure any appreciable SF<sub>6</sub> concentrations as seen in Figure 72.

#### **Mobile Analyzers**

Table 28 and Figure 73 summarize the results from the mobile analyzers of IOP 10.

Van #6 on the 1 km route had only 1 null traversal and this occurred during the first 10 minutes of the first release. The concentration peaks during the first release were recorded north of the release point (about 3,600 pptv at 0142 MDT) and west (about 7,000 pptv at 0152 MDT).

The peak concentration measured after the first release period ended was nearly 10,000 pptv at 0205 MDT. During the second release period, the measured peak was about 2,600 pptv to the west at 0338 MDT. Peaks of about the same magnitude were also measured to the northwest. After the second release period a peak of about 11,000 pptv at 0407 MDT was recorded to the west. The peak concentrations recorded during the third release period were all to the north consistent with the readings from the downtown grid samplers. The peak concentration was near 5,000 pptv at 0527 MDT. The peak recorded in Table 28 (about 13,600 pptv) was measured after the end of the third release period at 0647 MDT when the van drove directly west of the release site.

Van #5 traveled the 2 km route. During the first release period, the van deviated somewhat from its route at the northern end in search of the plume. The peak concentration of over 1,400 pptv was recorded about 0156 MDT to the northwest from the release site along Highway 186. The concentration level continued to increase in this area as a peak of about 2,250 pptv was detected at 0203MDT, just after the end of the first release period. Then the concentration decreased in the northwest sector until it started to increase again during the second release period. The largest peak for the second release period approached 4,500 pptv and was detected to the WNW around 0340 MDT. Between the second and third release periods, the peak concentration of about 2,750 pptv was measured at 0410 MDT near the intersection of 1000 W and Highway 186. The third release period highest concentration peak (over 1,400 pptv) was detected in the same northwest area at almost 0600 MDT. For the period following the third release, a peak of almost 1,200 pptv was quickly detected at about 0602 MDT still to the northwest. The concentration levels rapidly decreased from this time.

Van #7 on the 4 km arc did not detect the tracer until after 0130 MDT. The peak concentration for the first release period was just over 400 pptv at 0132 MDT at approximately the intersection of 600 N and 900 W. Between the first and second release periods, the peak concentration was detected in the same area at about 0217 MDT with a value of about 600 pptv. The concentrations decreased until the second release period. During the second release period, a peak concentration of about 1,000 pptv was recorded at 0352 MDT near the above mentioned intersection. Following the second release period, the peak concentration location did not move. The peak concentration was about 900 pptv at 0403 MDT and for the rest of the period the concentrations declined until the third release period. The peak for the third release period was similar to that previously observed (~1,000 pptv) and was detected around 0538 MDT NNW of the release site.

The 6 km route was covered by van #3 but the route was modified somewhat to concentrate on areas where peak plume concentrations were located. The van traveled farther north of Dupont between Redwood Road and I-15. The first plume detection during the first release period was to the NNW along Dupont street. The peak concentration value was about 180 pptv measured at 0141 MDT. Between the first and second release periods, the peak concentration that approached 400 pptv was detected along Redwood Road around 0240 MDT. Not until about 0356 MDT was a peak concentration (about 350 pptv) detected during the second release period. It was measured in about the same location (along Redwood Road) as for

the previous period. Between the second and third release periods, three peak concentrations of approximately 500 pptv were detected to the northwest and NNW, two along Redwood Road and one north of Dupont Street at 0406 MDT, 0414 MDT, and 0418 MDT, respectively possibly indicating some meander of the plume but nothing of the magnitude of the meander observed in IOPs 2, 4, 5, and 7. Again during the third release period, three peak concentrations were detected during traverses of Redwood Road and between Redwood Road and I-15. The concentrations were between about 250 to 275 pptv and detected at times 0538 MDT, 0546 MDT, 0553 MDT. Following this last release period, the tracer concentration levels stayed close to the peak values of the last period and in the same area until about 0619 MDT when the concentration levels started to drop. By 0630 MDT, concentration levels were less than 40 pptv.

## **Summary**

Higher wind speeds and consistent wind directions resulted in the tracer being transported primarily northwest and NNW. It seems unusual that the concentration levels measured on top the Hilton were smaller than the other two buildings because it is located more to the WNW of the release point which is the direction the ground samplers indicated the tracer moved. However, the highest concentrations were measured at the Wells Fargo building - the tallest building with samplers - which is northwest of the release point. The PIGS suburban samplers and mobile analyzers further suggest that the plume moved in the northwest direction. No material advected to the southeast.

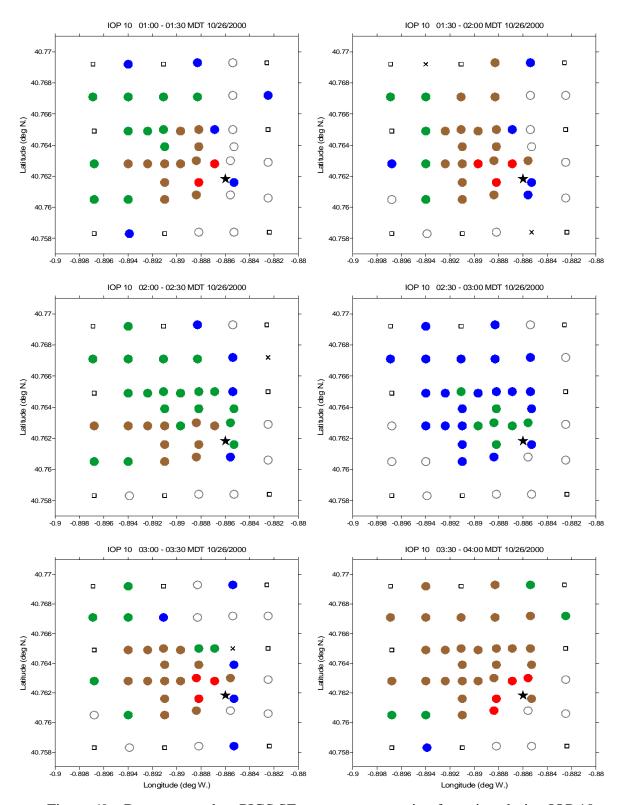


Figure 69a. Downtown urban PIGS  ${\rm SF_6}$  tracer concentration footprints during IOP 10 from 0100-0400 MDT.

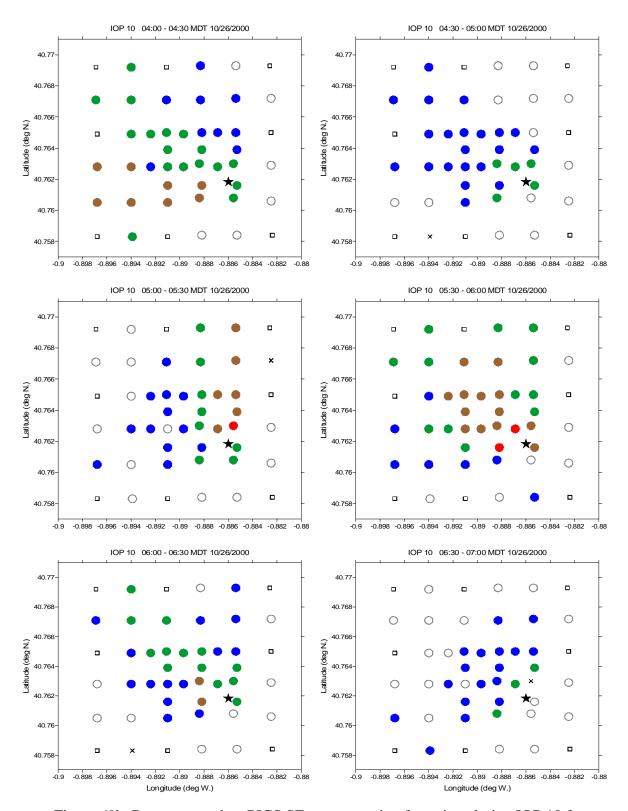


Figure 69b. Downtown urban PIGS  ${\rm SF_6}$  concentration footprints during IOP 10 from 0400-0700 MDT.

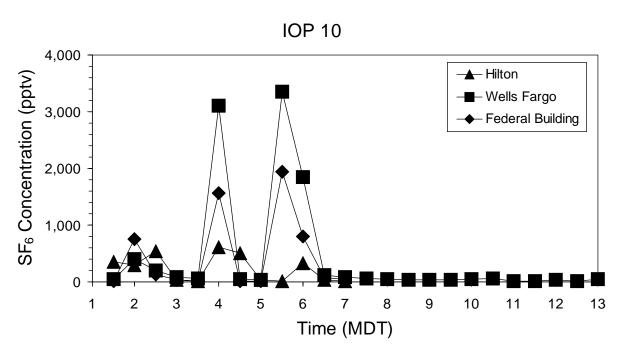


Figure 70. PIGS  $SF_6$  tracer concentration time histories for the rooftop samplers during IOP 10.

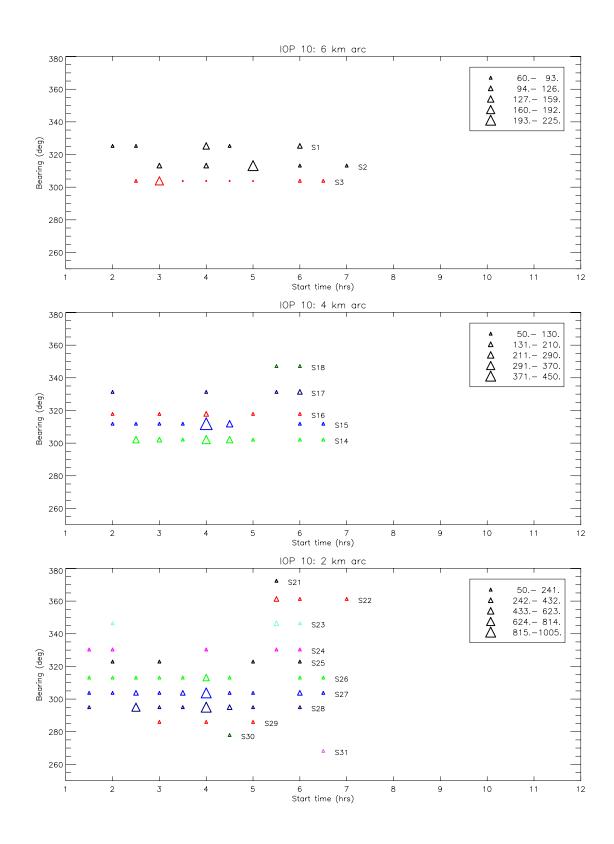


Figure 71. PIGS  $SF_6$  tracer concentration time histories for the 2, 4, and 6 km arcs during IOP 10.

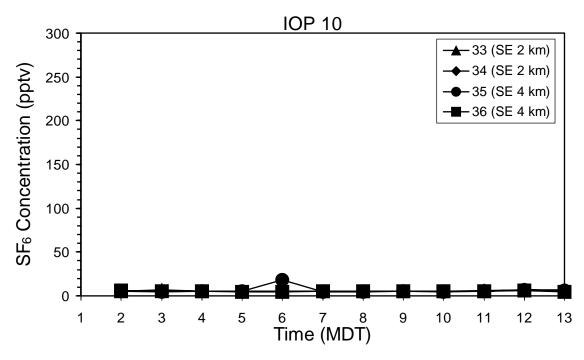


Figure 72. PIGS  $SF_6$  concentration of time histories for the southeast 2 and 4 km sampling arcs during IOP 10.

Table 28. Summary of IOP 10  $SF_6$  real-time analyzer sampling unit (TGA) activity.

| Sam- pling Unit (TGA #) | General<br>Sampling<br>Route  | Total<br>Number<br>of<br>Traverses | Number<br>of<br>Null<br>Traverses | Number<br>of<br>Non-null<br>Traverses | Maximum<br>Concentration<br>(pptv) | Bearing<br>from<br>Release<br>Site<br>(deg.) | Range<br>from<br>Release<br>Site<br>(km) |
|-------------------------|-------------------------------|------------------------------------|-----------------------------------|---------------------------------------|------------------------------------|--|--|
| Dtn#1 (#1)              | Main St.                      | 16                                 | 5                                 | 11                                    | 15,800                             | 253  | 0.48                                     |
| Dtn#2<br>(#2)           | State St.                     | 14                                 | 1                                 | 13                                    | 27,200*                            | 299  | 0.25                                     |
| 1km<br>(#6)             | S. Temple,<br>200 W           | 28                                 | 1                                 | 27                                    | 13,600                             | 47   | 0.03                                     |
| 2km<br>(#5)             | N. Temple,<br>600 W,<br>300 W | 46                                 | 5                                 | 41                                    | 4,310                              | 294  | 2.08                                     |
| 4km<br>(#7)             | 600 N                         | 30                                 | 6                                 | 24                                    | 1,040                              | 311  | 3.46                                     |
| 6km<br>(#3)             | 2300 N,<br>Redwood<br>Rd.     | 32                                 | 3                                 | 29                                    | 524                                | 324  | 7.49                                     |

<sup>\*</sup> Analyzer was over-ranged giving an inaccurately low reading.

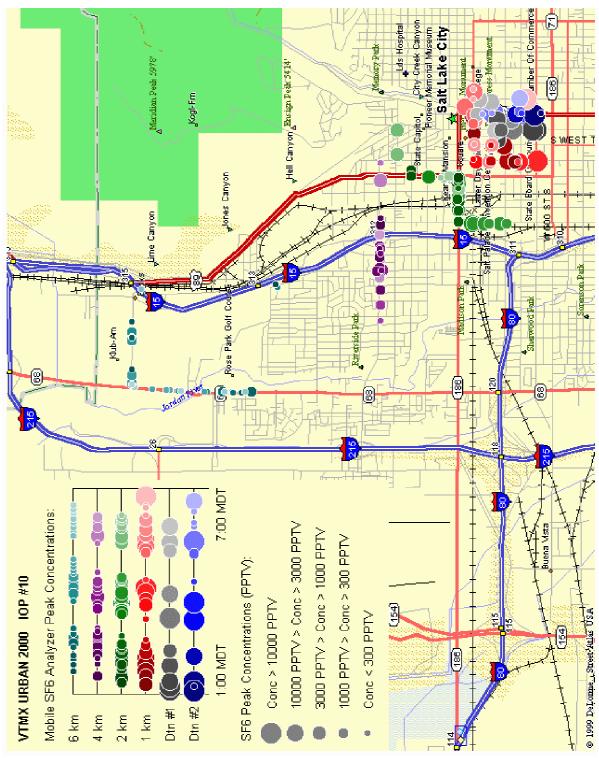


Figure 73. Maximum  $SF_6$  concentration of each plume crossing for all real-time analyzers as a function of time of measurement during IOP 10 (upper left). Size of dot increases with increasing concentration. Dots on map indicate the geographical location of each maximum concentration. Color hue changes with increasing time.

#### Summary

Generally the plumes from the various IOPs tended toward the NW or NNW moving along the base of the mountains. No significant concentrations were observed by samplers south of 270° except for IOP 4 for which case it is suspected that the plume might have wandered farther south.

IOP 1 was a test case to determine how well the mobile analyzers would detect the tracer concentrations for different release rates. No PIGS samplers and only two mobile analyzers were deployed, but some useable data was obtained.

During IOP 2 and particularly near the beginning of the IOP, the  $SF_6$  tracer was detected in all directions around the release site, i.e. the tracer was detected to the southeast on the 2 km arc. Later, the winds died down and the tracer was no longer detected at the farthest distances where it had been detected earlier.

The SF<sub>6</sub> tracer covered the northwest quadrant during IOP 4 though significant concentration levels were detected to the south by the mobile analyzers towards the end of the IOP.

During IOP 5 the tracer plume hugged the base of the mountains as it traveled to the north and west. Early in the IOP, some elevated concentration levels were detected to the southwest. And some small levels were detected to the WNW along I-215 in the middle of the IOP. But predominantly the tracer was transported to the NNW.

The transport of the tracer was more east and west during IOP 7 along with the more common transport to the northwest. The strong east-west transport was different from the other IOPs.

IOPs 9 and 10 had stronger winds and more consistent wind directions which resulted in the downtown area essentially being 'cleaned out' during the periods between releases. The plumes moved northwest and NNW respectively for these two IOPs.

# **ACKNOWLEDGMENTS**

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# Appendix A Duplicate Sampler Studies

#### **DUPLICATE SAMPLER STUDIES**

#### **INTRODUCTION**

While analyzing the  $SF_6$  concentration data from the programmable integrating gas samplers (PIGS) used in the URBAN-2000 study, it became apparent that the differences between some duplicate samplers (i.e. two samplers placed at the same location) were larger than would be expected from random variations. It was also noted that variations were much larger in duplicate samplers placed closer to the release location and consequently having greater concentrations of  $SF_6$ .

To investigate the cause of the variations, a series of experiments were conducted. The experiments, conducted between August and December 2001 are described below and were designed to answer three questions:

- 1. <u>Pulsed Sampling</u>. Does the "pulsed sampling" of the PIGS give accurate results when the tracer gas (i.e.  $SF_6$ ) may not be well, i.e., in locations close to the release?
- 2. <u>Diffusion Before Retrieval</u>. Do the sample cartridges lose significant concentration by diffusion through the diaphragm sampling pumps when the bags are unsealed and kept in the samplers until they are retrieved?
- 3. <u>Aging/Holding Times</u>. How does diffusion over time affect the concentration in the sample bags? Could higher diffusion rates at higher concentrations account for the observed variations?

These tests were not designed to be exhaustive characterizations of these potential problem areas. Rather, they were designed to indicate if there were any large problems that could account for the URBAN 2000 differences. The duplicates from the URBAN 2000 study commonly showed concentration differences of over 40%. Any problem that could regularly cause differences of that size should be readily apparent during simple tests such as these.

#### **BACKGROUND**

For many years, the Air Resources Laboratory Field Research Division (ARLFRD) has sampled atmospheric tracer by using bag samplers like those shown in Figs. A-1 and A-2. These consist of 12 miniature diaphragm pumps and controlling electronics attached inside a waxed cardboard box and are referred to as programmable integrating gas samplers (PIGS), or simply "samplers".



Figure A-1. PIGS sampler.



Figure A-2. PIGS sampler with cartridge.



Figure A-3. PIGS cartridge.



Figure A-4. PIGS sampler with lid on.

A smaller box containing 12 Tedlar bags is referred to as a "cartridge" as in Fig. A-3. This cartridge is placed inside of the sampler and each bag is attached to a rubber tube which both supports the bag and provides an entrance and exit for the sampled air as in Fig. A-4. A plastic clip located on the tube provides a means to seal the bag when sampling or analysis is not in progress.

Use of these samplers follows this basic procedure:

- 1. A cartridge is "cleaned" by flushing the bags several times with UHP nitrogen.

  At the end of the cleaning, the bags are evacuated and then sealed by closing the clips.
- 2. The cartridges are transported to the sampling locations where one cartridge is placed in each sampler. The bag entrance tubes are connected to the pumps, one bag for each pump. The clips on the entrance tubes are then opened.
- 3. The controlling electronics are then programmed for a sampling start time and sampling duration for each bag.
- 4. Beginning at the programmed start time, the controlling electronics sequentially fill the

12 bags with each bag being filled for the programmed sampling duration. In order to prevent the bags from being overfilled, the pumps are not run continuously, but are "pulsed" for short bursts or "strokes" that last less than a second. The time between these strokes is calculated to provide a full, but not over inflated, bag at the end of the sampling duration.

5. After the sampling is complete, an operator returns to the sampling site, closes the clips to seal the bags and removes the cartridge from the sampler. Depending on the logistics of the experiment, a number of hours (but typically not more than a day) may elapse between completion of the sampling and removal of the cartridge. The cartridges are then transported to the laboratory for analysis. Several days or weeks may elapse between the arrival of the cartridge at the laboratory and its final analysis.

The three questions listed in the introduction were based on three possible weaknesses in this sampling methodology: (1) the pulsed sampling method, (2) the time the cartridges spend sitting in the samplers before they are returned, and (3) the time the cartridges spend waiting in the laboratory for analysis.

#### EXPERIMENTAL PROCEDURE

The experimental setup is shown in Fig. A-5. A six-foot long, 2-inch diameter PVC pipe was suspended horizontally. SF<sub>6</sub> calibration gas and ultra pure air were injected in one end of the pipe. The flows of the gases were set with the mass flow controllers as seen in the bottom of Fig. A-5. The other end of the pipe was vented to the outside of the building by means of a vinyl hose. Halfway down the pipe (3 feet from the injection end), nine tubing ports were installed. These were equally spaced around the circumference of the pipe (Fig. A-6). The samplers and, in some tests, continuous analyzers were attached to these sampling ports. For Test #7, three additional ports were added 6.5 inches further down the tube, (i.e. 42.5 inches from the injection end of the pipe). Ports that were not being used during a given test were closed off by attaching a short piece of tubing and closing it with it clip.



Figure A-5. Experimental setup.



Figure A-6. Tubing ports with 3 ports downstream.

Seven tests were designed to answer questions 1 and 2, the effect of the pulsed sampling method and the effect of cartridges sitting in the samplers. All of the samples were then reanalyzed periodically over the next five months to determine the effect of diffusion on the samples as they waited for analysis in the laboratory in answer to question 3.

#### **SUMMARY OF TESTS**

Tests #1 and #2 were designed to check the effect of diffusion while the cartridges were left in the samplers at a moderate concentration. The  $SF_6$  concentration in the pipe was adjusted to approximately 1,000 pptv. The sampling parameters for each test were identical as was the concentration in the pipe. Test #1 used six samplers and two continuous analyzers. Test #2 used seven samplers and two continuous analyzers and was conducted one day after Test #1. The only difference between the tests was that the cartridges filled in Test #2 were allowed to sit in the samplers for 5 days with the clips open before they were retrieved and analyzed. The Test #1 cartridges were retrieved and analyzed immediately.

Tests #3 and #4 were designed to test the effect of the pulsed sampling method when sampling a poorly mixed atmosphere. Mass flow controllers were used to pulse the  $SF_6$  calibration gas flowing into the pipe on and off with a period of 30 seconds. Test #3 attempted to generate a "worst case scenario" where the concentration of  $SF_6$  and the "pulsing" of the pumps were at exactly the same frequency. In this case, samplers that happened to be "in phase" with the concentration would measure a higher than average concentration while those that happened to be "out of phase" would measure a much lower concentration. Test #4 attempted to generate the "best case scenario" where the  $SF_6$  was sampled continuously. The concentration was pulsed exactly as it was in Test #3 but the sampler pumps ran continuously. Thus by comparing the results of Tests #3 and #4, a "worst case" effect of the pulsed sampling could be seen. See Test #7 for a measurement of more randomly pulsed concentrations.

Tests #5 and #6 are repeats of Tests #1 and #2, with the only difference being that the average concentration was adjusted to be approximately 50,000 pptv. The intent of these tests was to see if the increased concentration gradients between the samples in the bags and the outside atmosphere increased the effects of diffusion while the cartridges were waiting in the samplers.

Test #7 was a continuation of the pulsed sampling tests begun in Tests #3 and #4. In Test #7, an attempt was made to set up a sampling scenario that more closely matched the sampling that was performed by the close-in samplers of the URBAN-2000 experiment. The mass flow controllers were programmed to provide 1 second pulses of about 8,000 pptv. The samplers and the concentration were set up to pulse at the same average period of 5 seconds but a computer was used to randomize the concentration pulses around this average to better approximate the more random processes of atmospheric mixing. Three of the samplers were moved to new ports about 6.5 inches down the tube. The distance of this move was calculated to provide approximately the same "flow time" difference as would have occurred between duplicate samplers during average conditions observed in URBAN-2000. The goal was to see if any

statistically significant concentration differences could be observed between samplers in a situation that approximated the URBAN-2000 sampling, but with an atmosphere that was known to be poorly mixed (i.e. tracer passing the samplers in high concentration puffs).

#### **Pulsed Sampling**

The first question posed in the introduction of this report asks:

1. Does the "pulsed sampling" of the whole air samplers give accurate results when the tracer gas (i.e.  $SF_6$ ) may not be well mixed, i.e., in locations close to the release?

Results from Tests #3, #4, and #7 were designed to address this question. Test #3 was set up to be a worst-case scenario where the sampler's pulses were synchronized with the concentration puffs in the sampling pipe. Both were set up to run with a period of 30 seconds. Two continuous analyzers sampled the gas in the sampling pipe to verify that the concentration puffs were not mixing into a uniform concentration. Figure A-7 shows an example output from one of these analyzers. If a sampler happened to be in phase with the puffs, it would always sample the maximum concentration and show a higher than average concentration. If it happened to be in phase with the gaps between puffs, it should show a lower than average concentration.

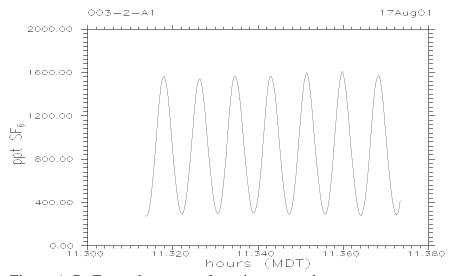


Figure A-7. Example output of continuous analyzer.

#### Test #3

Test #3 was conducted on August 16, 2001. An 18.6 ppb  $SF_6$  standard was diluted to provide a pulsed flow with an average concentration of approximately 1,000 pptv and allowed to flow through the sampling pipe. The samplers ran for a total of 50 minutes per bag, pulsing on 30 second intervals for a total of 100 pumping bursts. Table A-1 shows the average

concentrations, standard deviations and percent relative standard deviation (RSD) of all the bags. The average concentration was 971 pptv with an average standard deviation of 164 and an average RSD of 17%. Each cartridge appeared to be scattered over approximately the same range. There was no indication of some higher cartridges and others that tended to be lower, creating a bias in the data, as was anticipated from the synchronized sampling. It doesn't appear that the worst case for pulsed sampling was able to generate a statistically significant difference in the average concentration of all the bags in each cartridge. The only observable effect was an increase in variation in each bag causing a large amount of imprecision in this sampling method. However, even this "worst case scenario" resulted in a representative portion of the atmosphere being sampled over time.

**Test #4**Table A-1. Results of analysis of cartridges for Test #3.

| Cartridge ID | Average Cartridge Concentration (pptv) | Standard Deviation (pptv) | RSD (%) |
|--------------|--|---------------------------|---------|
| 265          | 960                                    | 155                       | 16      |
| 466          | 1010                                   | 175                       | 17      |
| 158          | 984                                    | 145                       | 15      |
| 1251         | 923                                    | 246                       | 27      |
| 321          | 953                                    | 132                       | 14      |
| 1047         | 986                                    | 147                       | 15      |
| 191          | 982                                    | 147                       | 15      |

Test #4 was conducted on August 23, 2001. An 18.6 ppb  $SF_6$  standard was diluted to provide a pulsed flow with an average concentration of approximately 1,000 pptv and allowed to flow through a 2 inch diameter PVC pipe in which nine holes were drilled evenly space around its diameter. Samplers were attached to these holes via rubber tubing and the  $SF_6$  was pulsed as in Test #3, except the samplers were programmed to sample almost continuously generating a "best case scenario". Table A-2 shows the average cartridge concentrations, standard deviations and percent RSD of all the bags. The average concentration was 1,035 pptv with an average standard deviation of 41 pptv and an average RSD of 4%. The difference between Test #3 and Test #4 should be representative of the worst-case effect of the pulsed sampling.

Table A-2. Results of analysis of cartridges for Test #4.

| Cartridge ID | Average Cartridge<br>Concentration (pptv) | Standard Deviation (pptv) | RSD (%) |
|--------------|---|---------------------------|---------|
| 361          | 1056                                      | 16                        | 2       |
| 532          | 1037                                      | 58                        | 6       |
| 1201         | 1046                                      | 56                        | 5       |
| 163          | 1016                                      | 32                        | 3       |
| 1266         | 962                                       | 76                        | 8       |
| 169          | 1078                                      | 29                        | 3       |
| 1278         | 1048                                      | 19                        | 2       |

#### Comparison of Test #3 and #4

Table A-3 shows a summary of the results from Tests #3 and #4. As can be seen, the variation in Test #3 was much larger than that for Test #4 with the spread of the data approximately 4 times that of Test #4. The relative percent difference (RPD) of the average concentrations for Test #3 and Test #4 was 6.4%, within the 95% confidence intervals. These results indicate that there is no significant difference between the average cartridge concentrations when the atmosphere is not well mixed, however, there is a significant difference in the variability between bags in these two tests as seen by the variance.

Table A-3. Summary results of Test 3 and 4.

| Test Number | Average Cartridge<br>Concentration (pptv) | Standard Deviation (pptv) | RSD (%) |
|-------------|---|---------------------------|---------|
| Test 3      | 971                                       | 164                       | 17      |
| Test 4      | 1035                                      | 41                        | 4       |

#### **Test #7**

Test #7 was conducted on September 12, 2001. An 18.6 ppb SF<sub>6</sub> standard was diluted to provide a random pulsed flow with a pulse concentration of approximately 8,000 pptv and attached to flow through the sampling pipe. Three extra ports were added downstream from the existing ports and will be discussed in a separate section later. SF<sub>6</sub> was pulsed varying randomly from 0 to 10 seconds. Table A-4 shows the average concentrations, standard deviations and RSD of all the bags in Test #7. The average concentration of all the upstream ports was 1,390 pptv with an average standard deviation of 98 pptv and an average RSD of 7%. The RSD was much

closer to that of Test #4 (RSD = 4%) where samplers ran continuously than to that of Test #3 (RSD = 17%).

Table A-4. Results of analysis of cartridges for Test #7.

| Cartridge ID | Average Cartridge Concentration (pptv) | Standard Deviation (pptv) | RSD (%) |
|--------------|--|---------------------------|---------|
| 1115         | 1385                                   | 85                        | 6       |
| 1094         | 1470                                   | 31                        | 2       |
| 173          | 1451                                   | 72                        | 5       |
| 248          | 1338                                   | 80                        | 6       |
| 188          | 1397                                   | 137                       | 10      |
| 243          | 1249                                   | 171                       | 14      |
| 190          | 1437                                   | 111                       | 8       |

#### Comparison between all three tests

The RSD's for Tests #3, #4 and #7 are shown in Table A-5. Test #3 resulted in the highest RSD with Tests #4 and #7 being fairly equivalent. This shows that the "worst case scenario" of sampling a poorly mixed atmosphere where the pumps pulse at the same frequency as the  $SF_6$  puffs did in fact produce greater imprecision in the data. The precision was much better when the tracer pulses were more random as in Test #7. Since real-world sampling should involve noticeable randomness, results from actual sampling should more closely approximate Test #7.

The RPD's of the average concentrations for tests 3 and 4 and the RSD differences are shown in Table A-6. The RPD of the average concentration could only be calculated for Test #3 and #4 since Test #7 was run at a slightly higher concentration. Therefore, since Test #7 was run at a slightly higher concentration, the average concentration, and standard deviation are expectedly slightly higher. The average RSD is used for comparison rather than the RPD. The difference in the RSD between Tests #4 and #7 was 3%, much better than that between Tests #3 and #4 at 13% and Tests #3 and #7 at 10%. Test #3, although extremely variable, still resulted in sampling a representative portion of the atmosphere. These results indicate that the pulsed sampling method does an adequate job of sampling the tracer over time even when the tracer is not well mixed in the atmosphere.

Table A-5. Average concentration, standard deviation and RSD for Tests 3, 4 and 7.

| Test Number | Average<br>Concentration (pptv) | Average Standard<br>Deviation (pptv) | Average RSD (%) |
|-------------|---------------------------------|--------------------------------------|-----------------|
| 3           | 971                             | 164                                  | 17              |
| 4           | 1035                            | 41                                   | 4               |
| 7*          | 1390                            | 98                                   | 7               |

<sup>\*</sup> Run at a slightly higher concentration.

Table A-6. RPD of the average concentration and RPD of the average RSD between tests 3, 4 and 7.

| Test Number | RPD of the Average<br>Concentration (%) | RSD Difference (pptv) |
|-------------|---|-----------------------|
| 3 and 4     | 6.4                                     | 13                    |
| 3 and 7*    |   | 10                    |
| 4 and 7*    |   | 3                     |

<sup>\*</sup>Run at a slightly higher concentration.

#### **Differences Between Upstream and Downstream Ports**

Three extra ports were added downstream during Test #7 to mimic the placement of the duplicate cartridges during the URBAN-2000 study. This test was done to see if placement of the cartridges had an effect on the data when the atmosphere is not well mixed as seen in Table A-7. The average concentration for the upstream ports was 1390 pptv with an average standard deviation of 98 pptv and an average RSD of 7%. The downstream ports had an average concentration of 1369 pptv, an average standard deviation of 101 pptv and an average RSD of 7%. There were no significant concentration differences between the upstream and downstream ports. The RPD between the upstream and downstream port average concentrations was 2%, well within the quality control acceptance limit criteria of  $\pm$  20% for field duplicates. These results indicate that the placement of the duplicate cartridges for the URBAN-2000 study should not have had a significant effect on the results even though the sampled atmosphere was not well mixed.

Table A-7. Average concentration, standard deviation and RSD for the upstream and downstream locations.

| Port Location | Average<br>Concentration<br>(pptv) | Average Standard<br>Deviation (pptv) | Average RSD (%) |
|---------------|------------------------------------|--------------------------------------|-----------------|
| Upstream      | 1390                               | 98                                   | 7               |
| Downstream    | 1369                               | 101                                  | 7               |

#### Timewand Variability in Test #3, #4 and #7

The variability of using different Timewands to download the sampling information was also checked in Test #3, #4 and #7. When the samplers are programmed, the start time and sampling duration for each bag are downloaded to the sample for a combination handheld computer and bar code reader called a Timewand. In each of these tests, two different Timewands were used to download the sampling data. Half of the samplers were programmed with each Timewand. Table A-8 shows the average concentrations for both timewands and their RPD and RSD's. The results of -1.8%, 1.4% and 5.7% for the RPD's indicate that there is no significant difference in concentrations when different timewands are used to download sampling data. The RSD's indicate that there is no significant difference in the variability of the data.

Table A-8. Average concentrations, RSD and RPD of Tests #3, #4 and #7.

| Test<br>Number | Average<br>Concentration<br>Using 1st<br>Timewand<br>(pptv) | Average<br>RSD Using<br>1st<br>Timewand<br>(%) | Average<br>Concentration<br>Using 2nd<br>Timewand<br>(pptv) | Average<br>RSD Using<br>2nd<br>Timewand<br>(%) | RPD of Average Concentration (%) |
|----------------|---|--|---|--|----------------------------------|
| 3              | 955   | 2.1  | 972   | 4.9  | -1.8                             |
| 4              | 1060  | 3.2  | 1045  | 2.1  | 1.4                              |
| 7*             | 1362  | 4.6  | 1287  | 5.4  | 5.7                              |

<sup>\*</sup>Run at a slightly higher concentration.

#### **Diffusion Before Retrieval**

The second question posed in the introduction of this report asks:

2. Do the sample cartridges lose significant concentration by diffusion through the diaphragm sampling pumps when the bags are unsealed and kept in the samplers until they are retrieved?

A comparison was made of cartridges analyzed immediately to those left with the clips open and the cartridges not removed from the samplers for five days before analysis. Averages were calculated based upon the first day's analysis. Tests #1 and #2 were done using a concentration of approximately 1,000 pptv. Test #5 and #6 were done using a much greater concentration, approximately 50,000 pptv.

#### **Tests #1 and #2**

Test #1 was conducted on August 14, 2001. An 18.6 ppb  $SF_6$  standard was diluted to a concentration of approximately 1000 pptv and attached to flow through the sampling pipe. After sampling, the cartridges were immediately removed from the samplers and analyzed. Test #2 was conducted on 8-15-01. An 18.6 ppb  $SF_6$  standard was again diluted to a concentration of approximately 1000 pptv and attached to flow through the sampling pipe. This time however, after sampling, the clips were left open and the cartridges were not removed from the samplers for five days. The average concentration results as well as the average standard deviation and average RSD can be seen in Table A-9. The RPD between the average concentrations of Test #1 and #2 was 2.6%. Test #2's result is 97% of Test #1, well within the 95% confidence interval of Test #1.

Table A-9. Results of analysis of cartridges for Tests 1 and 2.

| Test Number | Average<br>Concentration<br>(pptv) | Average<br>Standard Deviation<br>(pptv) | Average RSD (%) |
|-------------|------------------------------------|---|-----------------|
| 1           | 1226                               | 52                                      | 4.2             |
| 2           | 1194                               | 56                                      | 4.7             |

#### **Tests #5 and #6**

Test #5 was conducted on 8-24-01. A 20 ppm SF<sub>6</sub> standard was diluted to a concentration of approximately 50,000 pptv and attached to flow through the sampling pipe. After sampling, the cartridges were immediately removed from the samplers and analyzed. Test #6 was conducted on August 27, 2001. A 20 ppm SF<sub>6</sub> standard was again diluted to a concentration of approximately 50,000 pptv and attached to flow through the sampling pipe. After sampling, the clips were left open and the cartridges were not removed from the samplers for five days. The cartridges were analyzed immediately after removal from the samplers. The average concentration results as well as the average standard deviation and average RSD can be seen in Table A-10. The RPD between the concentrations was 2.7%. Test #6's results were 97% of Test #5, well within the 95% confidence interval of Test #5.

Table A-10. Results of analysis of cartridges for Tests 5 and 6.

| Test Number | Average<br>Concentration (pptv) | Average Standard<br>Deviation (pptv) | Average RSD (%) |
|-------------|---------------------------------|--------------------------------------|-----------------|
| 5           | 65,990                          | 5030                                 | 7.6             |
| 6           | 64,244                          | 5371                                 | 8.4             |

Both test set results had slightly lower concentration levels in the bags that were held for five days while the standard deviation increased slightly. However, these differences are not statistically significant. The RSD for Tests #1 and #2 were almost identical as were the RSD results for Tests #5 and #6. The RPD's for both sets of tests were about 8%. These results show no significant reduction in  $SF_6$  concentration if the bags are left in the samplers with their clips open for up to 5 days, regardless of the concentration. The valves in the diaphragm pumps appear to be sufficient to ensure that there is no change in the concentration of  $SF_6$  in the Tedlar bags over at least a 5-day period.

#### **Aging/Holding Times**

The last question posed in the introduction of this report asks:

3. How does diffusion over time affect the concentration in the sample bags? Could higher diffusion rates at higher concentrations account for the observed variations?

All cartridges that were used for the seven tests were held for a period of up to 147 days to address these questions. The total number of bags analyzed for all tests was 544.

#### Test #1

The bags for Test #1 were analyzed 8 times from the sampling date at 0 days, 7 days, 14 days, 21 days, 28 days, 62 days, 93 days and 121 days. The number of bags dropping below 80% of the initial concentration (i.e. going "bad") is shown for each date in Table A-11. During the entirety of the test, 8.3 % of the 72 bags were determined to be "bad" bags.

Table A-11. Number of "bad" bags and when they occurred for Test #1.

| Days After Sampling Period | Number of Bags Becoming "Bad" |
|----------------------------|-------------------------------|
| 0                          | 0                             |
| 7                          | 3                             |
| 14                         | 1                             |
| 21                         | 0                             |
| 28                         | 0                             |
| 62                         | 1                             |
| 93                         | 1                             |
| 121                        | 0                             |

Test #2

These samples had already been held for 5 days in the samplers with the clips open. These bags were analyzed 7 times from the sampling date at 5 days, 13 days, 20 days, 27 days, 65 days, 97 days and 134 days as seen in Table A-12. During the entirety of the test, 12% of the 83 bags were determined to be "bad" bags.

Table A-12. Number of "bad" bags and when they occured for Test #2.

| Days After Sampling Period | Number of Bags Becoming "Bad" |
|----------------------------|-------------------------------|
| 5                          | 0                             |
| 13                         | 3                             |
| 20                         | 4                             |
| 27                         | 1                             |
| 65                         | 0                             |
| 97                         | 2                             |
| 134                        | 0                             |

#### Test #3

After sampling, these bags were analyzed 5 times from the sampling date at one month intervals at 0 days, 31 days, 63 days, 91 days and 128 days as seen in Table A-13. During the entirety of the test, 18% of the 56 bags were determined to be "bad" bags.

Table A-13. Number of "bad" bags and when they occurred for Test #3.

| Days After Sampling Period | Number of Bags Becoming "Bad" |
|----------------------------|-------------------------------|
| 0                          | 1                             |
| 31                         | 2                             |
| 63                         | 1                             |
| 91                         | 1                             |
| 128                        | 5                             |

#### Test #4

After sampling, these bags were analyzed 8 times from the sampling date at 0 days, 7 days, 14 days, 21 days, 28 days, 63 days, 94 days, and 129 days as seen in Table A-14. During the entirety of the test, 19 % of the 84 bags were determined to be "bad" bags.

Table A-14. Number of "bad" bags and when they occurred for Test #4.

| Days After Sampling Period | Number of Bags Becoming "Bad" |
|----------------------------|-------------------------------|
| 0                          | 0                             |
| 7                          | 7                             |
| 14                         | 2                             |
| 21                         | 2                             |
| 28                         | 2                             |
| 63                         | 1                             |
| 94                         | 2                             |
| 129                        | 0                             |

#### Test #5

These bags were analyzed 8 times from the sampling date at 0 days, 7 days, 14 days, 21 days, 28 days, 61 days, 94 days, and 147 days as seen in Table A-15. During the entirety of the test, 21 % of the 81 bags were determined to be "bad" bags.

Table A-16. Number of "bad" bags and when they occurred for Test #6.

| Days After Sampling Period | Number of Bags Becoming "Bad" |
|----------------------------|-------------------------------|
| 5                          | 0                             |
| 7                          | 4                             |
| 14                         | 1                             |
| 21                         | 5                             |
| 55                         | 2                             |
| 87                         | 2                             |

#### Test #6

These bags were analyzed 6 times from the sampling date at 5 days, 12 days, 19 days, 26 days, 60 days and 92 days as seen in Table A-16. During the entirety of the test, 17 % of the 84 bags were determined to be "bad" bags.

Table A-15. Number of "bad" bags and when they occurred for Test #5.

| Days After Sampling Period | Number of Bags Becoming "Bad" |
|----------------------------|-------------------------------|
| 0                          | 0                             |
| 7                          | 4                             |
| 14                         | 1                             |
| 21                         | 0                             |
| 28                         | 0                             |
| 61                         | 3                             |
| 94                         | 3                             |
| 147                        | 6                             |

#### **Test #7**

After sampling, these bags were analyzed 6 times from the sampling date at 0 days, 7 days, 14 days, 21 days, 53 days and 99 days as seen in Table A-17. During the entirety of the test, 23 % of the 84 bags were determined to be "bad" bags.

Table A-17. Number of "bad" bags and when they occurred for Test #7.

| Days After Sampling Period | Number of Bags Becoming "Bad" |
|----------------------------|-------------------------------|
| 0                          | 0                             |
| 7                          | 5                             |
| 14                         | 0                             |
| 21                         | 3                             |
| 53                         | 9                             |
| 99                         | 2                             |

#### **Holding Time Summary**

Those that had a concentration of less than 80% of the first day's analysis were labeled as "bad" bags. Of the 544 bags analyzed, 17% were considered "bad" up to an analysis period of 147 days. Most "bad" bags were apparent by the second week where 34% of "bad" bags occurred. Therefore, 6% of the total number of bags analyzed were "bad" within the second week. Since 544 bags were analyzed, approximately 1 bag per every 2 cartridges was considered "bad" within the first week. The following weeks, 2 through 14, revealed only small numbers of bags going "bad", about 2% per week or 1 bag per every 4 cartridges per week. No bags went "bad" after about week 17. Ninety percent all the bags remained a constant concentration over significant periods of time, but a few lost concentration very rapidly.

To determine why the bags were going "bad", all of the bags that went "bad" in the first few analyses were manually removed from their cartridge and examined. The reasons for their drastic reductions in concentration can be seen in Figure A-8. The significant drop in concentration is attributed to catastrophic damage such as holes in the bag, leaking o-rings and leaking valve threads on the inlet fittings with the largest contributor being badly sealed seams. These seams may not have been properly sealed when the bag was made, or could have become damaged during usage over time, including over inflation during the cleaning procedure. It is evident that the bags must be meticulously sealed when being made and overinflation should be avoided.

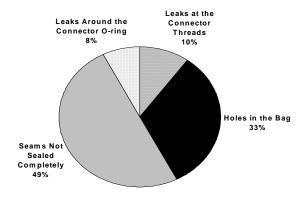


Figure A-8. Reasons for "bad" bags.

Different reasons for leaking bags are shown in Figs. A-9 through A-13. The bag in Fig. A-9 was leaking at the corner seams. It was probably not sealed well when it was made. Fig. A-10 shows a bag that was leaking near the connector threads and Figure A-11 shows the leakage at the connector O-ring. Fig. A-12 is a picture of a leaking seam at the top of the bag, probably caused by use over time and possible overinflation. Figure A-13 shows a pinhole in the bag.



Figure A-9. Leakage at corner seams.

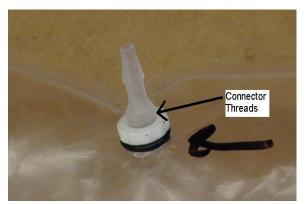


Figure A-10. Leakage at connector threads.

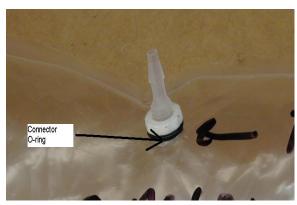


Figure A-11. Leakage at connector O-ring.



Figure A-12. Leakage at the top seam.



Figure A-13. Pinhole leak.

As can be seen by Table A-18, even after 4 weeks, 90% of the bags are still estimated to be "good" (within 80% of the original concentration), and after 10 weeks, 80% are estimated to still be "good". Diffusion over time does not significantly effect the concentrations. Extreme changes in concentration were due to catastrophic occurrences rather than diffusion.

Table A-18. Estimated Good bags over time.

| Week Number | Good Bags (%) |
|-------------|---------------|
| 1           | 98            |
| 2           | 93            |
| 3           | 91            |
| 4           | 89            |
| 5           | 88            |
| 6           | 86            |
| 7           | 85            |
| 8           | 83            |
| 9           | 81            |
| 10          | 80            |
| 11          | 78            |
| 12          | 76            |
| 13          | 75            |
| 14          | 73            |
| 15          | 71            |
| 16          | 70            |
| 17          | 69            |
| 18          | 69            |
| 19          | 69            |
| 20          | 69            |
| 21          | 69            |

## GC and TGA Comparison

Two TGA's were used for Tests #1, #2, #3 and #4 to estimate sample concentration in the sampling tube. The TGA results are shown in Table A-19. The RPD results show extremely good agreement between the two TGA's.

Table A-19. RPD comparison for TGA#2 and #6.

| Test Number | TGA #2 | TGA #6 | RPD (%) |
|-------------|--------|--------|---------|
| 1           | 1040   | 1046   | 0.6     |
| 2           | 1029   | 1038   | 0.9     |
| 3           | 890    | 892    | 0.2     |
| 4           | 761    | 748    | 1.7     |

A comparison of the TGA results and the GC results are seen in Table A-20. The RPD's increased although three of the four are still within  $\pm$  20%.

Table A-20. Comparison of TGA and Analysis Results.

| Test Number | Average<br>Concentration for<br>TGA#2 and #6 (pptv) | Average<br>Concentration from<br>Analysis (pptv) | RPD (%) |
|-------------|---|--|---------|
| 1           | 1043  | 1226   | 16      |
| 2           | 1034  | 1194   | 14      |
| 3           | 891   | 965  | 8       |
| 4           | 755   | 1051   | 33      |

#### **SUMMARY**

#### **Pulsed Sampling**

Tests #3, #4 and #7 were designed to check the adequacy and accuracy of the pulsed sampling method in an atmosphere that is not well mixed. Test #3, was designed to generate "worst case scenario" data while Test #4 was designed to generate "best case scenario" data. Test #7 was designed to generate similar "real-world" data that resulted in URBAN-2000. Test #3 resulted in much more variable data, but an RPD of the average concentration result was within 6.4% of Test #4. Test #4 and Test #7 resulted in similar data with an average RSD difference of

only 3%. These tests show that the pulsed sampling method does an adequate job for sampling  $SF_6$  over time even when the atmosphere is not well mixed.

The variability of Timewand download sequence was investigated to determine if the use of different Timewands would effect the concentration results. The RPD's for three tests using two different Timewands were -1.8%, 1.4% and 5.7%. There was no significant difference in concentrations when using different Timewands to download the sampling information. These results indicate that using different Timewands to download the sampling information does not affect the concentration results. There were no indications of data variability resulting from the use of different Timewands.

The addition of three extra ports were used to provide approximately the same "flow time" difference that would have occurred between duplicate samplers during average conditions during URBAN-2000. There was no significant difference between the concentration of the upstream and the downstream ports. The RPD between these two sets of ports was 2%, well within acceptance limit criteria of  $\pm$  20% for field duplicates. These results indicate that the placement of the duplicate cartridges for the URBAN-2000 study should not have had a significant effect on the results even in an atmosphere that is not well mixed.

#### **Diffusion Before Retrieval**

Tests #1, #2, #5 and #6 were designed to check diffusion through the pumps when cartridges are left in the samplers with clips open for a period of time. The RPD of both the high concentration and low concentration average results was 3%. There was no significant difference in concentration between those cartridges analyzed immediately and those that were analyzed 5 days later regardless of concentration. These tests indicate that the sample cartridges do not lose significant concentration by diffusion through the diaphragm sampling pumps when the bags are unsealed and kept in the samplers for up to 5 days.

#### **Aging/Holding Times**

All seven tests were used to check diffusion and changes in  $SF_6$  concentration over time for high and low concentrations. During the entire 5-month study, 17% of the bags were considered "bad", while 6% of the 544 went "bad" by the second week. After 4 weeks, 90% of the bags are estimated to still be within 80% of their original concentration. After 10 weeks, 80% of the bags are estimated to still be 80% of their original concentration.

Large changes in concentration were due to four major occurrences. These occurrences were holes in the bags, leaks in the connector threads, leaks around the connector o-rings and incomplete seals of the seams. Diffusion did not prove to be an issue even up to 5 months. Since the bad seams were so prevalent, extreme care must be taken in the construction of the bags as well as their inflation.

## TGA/GC Comparison

Two TGA's were used during 4 of the tests to immediately determine the approximate concentration that was being sampled. The TGA's agreed extremely well with each other, with the highest RPD of less than 2%. The RPD's between the TGA's and the GC's were much higher (8%-33%), still well within acceptable limits especially considering the comparison of two different methods. These results indicate very good agreement between these two methods.

#### RECOMMENDATIONS

All cartridges should be retrieved from the sample cartridges within at least 5 days of sampling. These tests have shown that SF<sub>6</sub> concentration is not affected up to the 5-day period.

Extreme care should be taken when Tedlar sample bags are made and when filled with any gas. The seams must be inspected carefully after manufacture and the bags must not be overinflated due to the excessive stress on the seam seals.

Samples should be analyzed as soon after sampling as possible due to the possibility of leaking bags. However, samples can be stored up to 5 months without significant sample concentration changes.

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## Appendix B Individual SF<sub>6</sub> Plume Traverses

(Contents of Appendix B is in attached CD)