DEMONSTRATION OF A LONG-RANGE ATMOSPHERIC TRACER SYSTEM USING PERFLUOROCARBONS

FINAL REPORT

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DEMONSTRATION OF A LONG-RANGE ATMOSPHERIC TRACER SYSTEM USING PERFLUOROCARBONS

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Abstract. Regional-scale tracer experiments are needed to validate atmospheric dispersion aspects of air pollution models. The capability of a new system, using perfluorocarbon tracers (PFTs), for long-range dispersion experiments at reasonable cost was demonstrated in two experiments. Two PFTs (C_7F_{14} and C_8F_{16}) were released simultaneously with SF_6 and two heavy methanes.

The PFT system provides automatic sequential samplers and rapid, inexpensive analyses down to 2 parts per 10^{15} of air. PFT concentrations were measured 600 km away, up to three days after release. Performance of the PFT system was excellent and a consistent set of tracer data was obtained.

1. INTRODUCTION

Atmospheric transport and dispersion models are being used extensively to simulate the behavior of air pollutants and to estimate regional air concentrations. Increased concern over regional and international aspects of air pollution has created a need for reliable model calculations of concentrations as far as 1000 km from pollutant sources. Experimental verification of these calculations is essential to establish the credibility of the models and environmental assessments based on model simulations.

Attempts to verify model calculations with air quality data are complicated by the presence of multiple sources and imprecise knowledge of emission amounts. There is a need for nonreactive, nondepositing tracers that could be released at precisely controlled rates and measured accurately at very low concentrations. This would allow us to conduct tracer experiments which isolate atmospheric transport and dispersion from other variables and provide data for verification of this basic aspect of model calculations. Regional-scale experiments require tracers that can be unambiguously identified and measured as far as 1000 km from the release point. Sulfur hexafluoride, SF_6, has been used out to 100 km but its relatively high and variable background concentration militates against its use to much greater distances. Even at shorter distances, a tracer system is needed that would provide automatic sequential sampling and rapid, inexpensive sample analysis. A new atmospheric tracer system, using perfluorocarbons, has been developed to meet this need.

The capabilities of the perfluorocarbon tracer (PFT) system were successfully demonstrated in two long-range experiments described in this report. The experiments were designed to provide a proof-test of the perfluorocarbon tracer release, sampling, and analysis techniques and to demonstrate the feasibility of conducting long-range atmospheric dispersion experiments at reasonable cost. Each experiment involved simultaneous release of two PFT tracers along with SF_6 over a 3-hr period with concentrations measured 100 km downwind. In the primary experiment, two heavy methanes, new tracers being developed at the Los Alamos Scientific Laboratory (LASL) were also released and the perfluorocarbons and methanes were measured at a distance of 600 km as well as 100 km. Intercomparison of the PFT, SF_6, and heavy methane results has established the validity of the new tracer systems.

The perfluorocarbon tracer data on the 600 km sampling arc present an interesting case of very fast transport by a night-time low-level jet and the reappearance of tracer over the arc on the day following its first arrival. Tracer concentrations were still measurable three days after release. This experiment provides a useful case study for verification of long-range transport and dispersion models.

2. PERFLUOROCARBON TRACER SYSTEM

Investigations by Lovelock (1974) indicated that a perfluorocarbon tracer system could be developed that would be ideal for long-range dispersion studies. The NOAA Air Resources Laboratories (ARL) contracted with Lovelock to develop three different samplers as the first step in the development of the new tracer system. Prototype instruments were delivered by Lovelock in 1976. Since then ARL has been working closely with the Department of Energy's Environmental Measurements Laboratory (EML) and Brookhaven National Laboratory (BNL) in a cooperative effort to develop a practical perfluorocarbon system.

The perfluorocarbons are extremely stable non-toxic compounds, measurable at very low concentrations by gas chromatography and electron-capture detection. At present, we are working with two perfluorocarbons, perfluoromonomethylcyclohexane (PMCH; C_7F_{14}) and perfluorodimethylcyclohexane (PDCH; C_8F_{16}). Comparative data on SF_6, PMCH and PDCH are shown in Table 1. The atmospheric background concentration of PDCH is about 0.026 parts per trillion by volume (26×10^{-15}), about 1/25 of the SF_6 background. Background of PMCH is an order of magnitude lower than PDCH. The amount of tracer released in any experiment must be sufficient to distinguish the plume from background at the maximum sampling distance. The required release rate (by weight) for PDCH is about 10% that for SF_6; for PMCH it is about 1% of the SF_6 rate. Taking the higher price of the perfluorocarbons into account, the PDCH required for an experiment would cost about 20% more than SF_6; the cost of PMCH would be about 10% of the SF_6 cost.

Another factor in favor of the perfluorocarbons over SF_6 is their very uniform background concentration. SF_6 has a highly variable background because of many local sources throughout the country and the world.

Table 1. Comparative Data on SF_6 and Perfluorocarbons.

Tracer	Sulfur-Hexa-fluoride	Perfluoro-Dimethyl-cyclohexane (PDCH)	Perfluoro-Monomethyl-cyclohexane (PMCH)
Formula	SF_6	C_8F_{16}	C_7F_{14}
Mol. Wt.	146	400	350
Background (pptv)	0.6	0.026	0.0024
Cost/kg	$11	$110.	$110.
Relative Release Rate (by wt.)	100	12	1.0
Relative Cost/ Release	1.0	1.2	0.1

2.1 Tracer Release Mechanisms

The two perfluorocarbon tracers, which are liquids at ordinary temperatures, were released as aerosol sprays. Each tracer is held in a 210-liter tank on a trailer. Compressed nitrogen provides pressure to force the liquid out of the tracer tank.

The mechanics of the spray system are simple. The spray nozzle has two hoses, one from the tracer tank, and the other from a construction-type air compressor that delivers 100 psi at 100 cfm. The tracer is introduced into the fast-moving air stream, atomized through a small orifice, and released into the atmosphere. Tracer release rate is monitored with a calibrated rotometer.

A newly designed release system, which was not completed in time for these experiments, has since been tested and performed well in the DOE Atmospheric Studies in Complex Terrain (ASCOT) experiments in California in September 1980. This system, also trailer-mounted and designed to be completely self-contained (no air compressor required), vaporizes the tracer before release.

The tracer is mixed with a stream of N_2 gas to evaporate it and to carry the tracer through the system. This mixture of nitrogen and perfluorocarbon gas flows through a tube furnace. Temperature of the tube furnace is kept above the boiling point of PDCH, 105°C, to assure that the tracer is completely vaporized. From the tube furnace the mixture of N_2 and tracer gas passes through a mass flow meter where the volume is accurately metered. From there the tracer is released to the atmosphere.

The design of this system provides back-up measurements of the actual amount of released tracer. The mass flowmeter provides both instantaneous and total volumes, and also supplies a 0-5 volt dc output which is connected to a stripchart recorder. The recorded release rate shows the constancy of tracer release and provides a measurement of total output over the time of release. The system also has a large set of crane scales (0-450 kg) and a small balance (0-40 kg) to provide accurate weighings of the tracer tanks before and after release.

Both release systems were designed and built by the NOAA Air Resources Laboratories Field Research Office in Idaho Falls, Idaho.

2.2 Automatic Sequential Sampler

Based on Lovelock's prototype, R. Dietz at BNL, developed an improved sequential sampler dubbed the Brookhaven Atmospheric Tracer Sampler (BATS). The sampler consists of an Air Flow Module (lid) and a Power Control Module (base). The entire unit, shown in Figure 1, measures 36x25x20 cm and weighs 7 kg. The lid contains 23 sampling tubes filled with 150 mg of 20-50 mesh-type 347 *Ambersorb** which traps all the perfluorocarbons in the air flowing through the tube. The base contains a constant volume pump which draws air through each sampling tube in a sequence controlled by an internal digital clock. Flow rates, controlled by critical orifices, are selectable from 2 to 50 cc/min. The base also contains a digital printer that records the tube number, start time and number of pump strokes (which can be converted to air volume) for each sample. Controls in the base provide for automatic start at a preselected day and time for a preselected

*Trade name of Rohm and Hass Company.

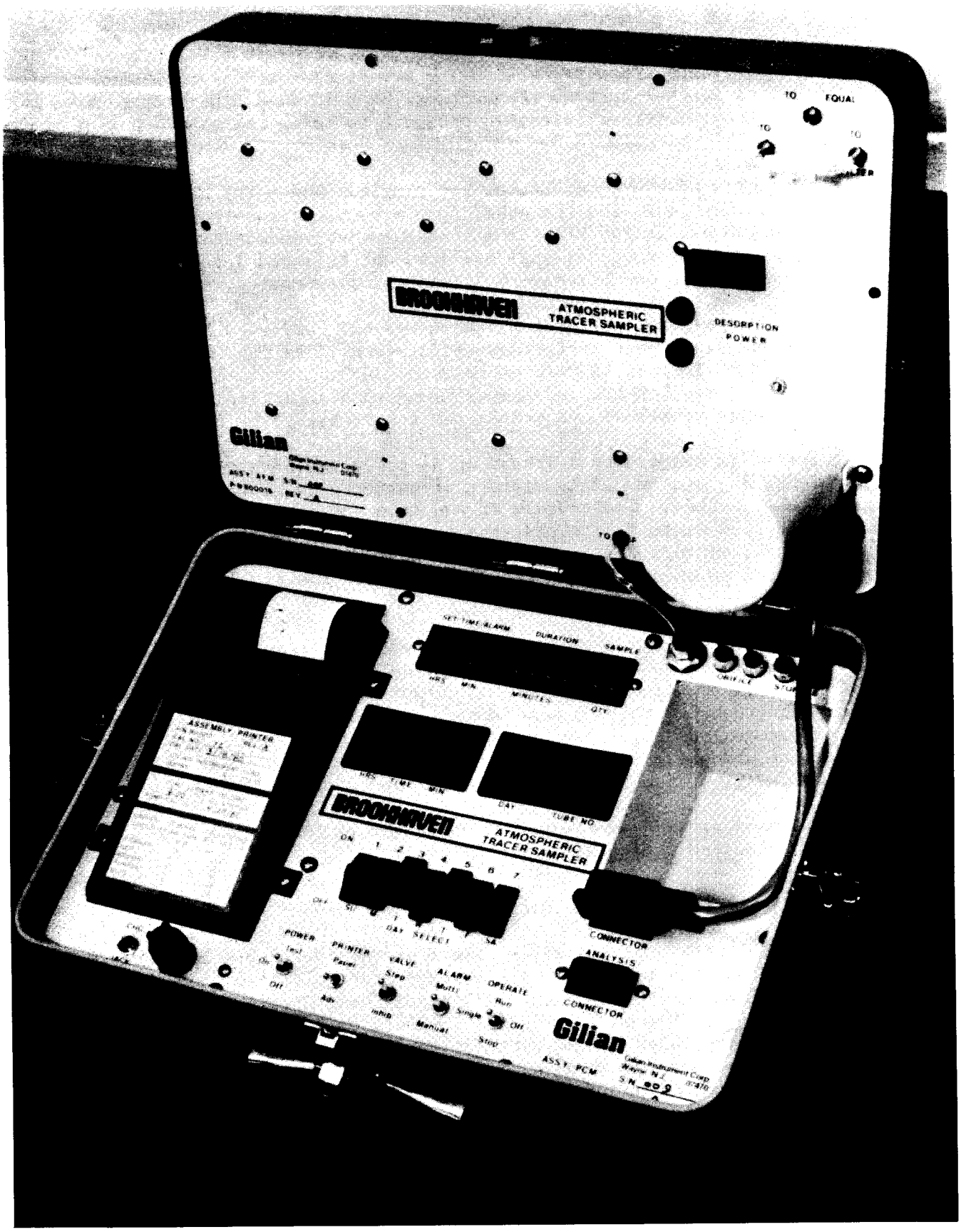

Figure 1. Automatic sequential sampler (BATS).

number of samples and duration of sampling (1 min to 1 week per tube), as well as for automatic analysis with a gas chromatograph. Internal rechargeable batteries provide sufficient power for unattended operation for up to a month. After 23 samples have been collected, the lid unit can be removed for sample analysis (in the laboratory) and a fresh lid attached in its place to continue the sampling program.

The Air Resources Laboratories contracted with Gilian Instrument Corp. for final design and production of 60 complete BATS samplers which were delivered in May 1980 for use in the July experiments. An operations manual was also prepared by Gilian (1980).

2.3 Sample Analysis System

The determination of perfluorocarbon tracer concentrations from the BATS samples is accomplished with an analysis apparatus designed, built and operated at BNL. The tracer is recovered by thermal desorption from the BATS tubes with subsequent gas chromatographic separation prior to electron capture detection. The scheme also includes chemical processing of the recovered constituents in order to destroy and remove interfering components, such as chlorofluorocarbons, which are present in the air at concentrations order of magnitude higher than that of the PFTs.

Before the sample is thermally desorbed, the BATS tube is purged with carrier gas (5% H_2 in N_2) for a short period of time to remove any traces of oxygen which otherwise would react with the PFTs during the 400°C desorption recovery. Desorption is accomplished by direct ohmic heating of the thin stainless steel wall of the BATS tube. The sample is purged from the BATS tube through a Pd catalyst bed at 260°C and then through a 120 cm Porasil F pre-cut column. The 10-cm long catalyst bed reduces any chlorofluorocarbon compounds, as well as any remaining oxygen, to their hydrogenated form, thus rendering these interfering constituents non-electron-capturing. After the surviving PFTs elute from the pre-cut column, heavier molecular weight constituents,still within the column, are purged to the atmosphere by reversing the direction of flow. Meanwhile, the eluted PFTs are reconcentrated within a 10-cm long bed of Porapak QS adsorbent. The purpose of the bed is two-fold. First, only the PFTs are retained in the Porapak QS; any lighter constituents which might ultimately interfere are flushed away. Secondly, once the Porapak QS-trapped PFTs are released into the main analytical column, the next BATS tube recovery cycle can be initiated, thus halving the overall PFT recovery and analysis time by overlapping the stages.

When the Porapak QS trap has been heated to 200°C, the PFTs are released into a second catalyst bed (2.5 cm long) for a final clean-up and flushed through a Nafion permeation dryer to remove traces of moisture before entering the main column, 6 meters of Porasil F, which is at the same temperature as the pre-cut column, 90°C. The 22 mL/min flow of carrier gas at this column temperature provides good resolution of the two PFTs. Automation is accomplished by interfacing the timing capability of the BATS with the INJECT command of a Varian CDS-111 integrator-controller, which provides the control capability for the involved valving and heating sequences within a Varian 3700 series gas chromatograph. Analyses of the 23 tubes on a BATS unit can be completed in just under 3 hours.

The present system incorporates a ^{63}Ni electron-capture detector which provides a measurement accuracy within ±10% at concentrations as low as 2 parts per

10^{15} (approximate ambient concentration of PMCH) with a sampled volume of 8 liters of air. This is the approximate volume collected in the 600 km arc samples (3-hr duration). The uncertainty in measurements near the PMCH background level is somewhat greater (about ±25%) on the 100 km arc where the volume sampled was about 2 liters (45-minute duration).

2.4 Dual-Trap Sampler

Another prototype instrument, the Dual-Trap sampler, was designed by Lovelock to combine the sampling and analysis functions into a single unit. The unit contains two sampling tubes which are automatically cycled so that one tube samples while the other is being analyzed. This instrument provided readout of PDCH tracer concentrations (no PMCH) every five minutes at the sampling site.

The original prototype has been modified at EML and BNL to provide a more rugged instrument for field use, to collect and measure PMCH and PDCH simultaneously, and to improve its detection limit by more than two orders of magnitude.

Ambient PDCH (about .03 ppt) can be measured with ±15% precision and PMCH can be measured at concentrations slightly above its ambient level of about .003 ppt. The attainment of this degree of sensitivity in a real-time field instrument is a major advance which will add significantly to long-range tracer capability.

2.5 Continuous Tracer Monitor

The third prototype sampler developed by Lovelock is a real-time continuous monitor intended primarily for use in aircraft sampling. Ambient air is drawn through a catalytic reactor that reduces the O_2 and other electron-absorbers, leaving the perfluorocarbons and nitrogen. This is passed directly to an electron-capture detector providing continuous concentration readout with only a 3-second delay.

Many problems have been encountered in the operation of this instrument, but the concept appears to be sound and work is continuing on the development of this sampler. If successful, it should be able to provide a continuous in-flight record of tracer concentrations down to 0.1 ppt or better.

3. 600-KM TRACER EXPERIMENT

A long-range tracer experiment was conducted on July 8, 1980 with the simultaneous release of two perfluorocarbons, SF_6, and to heavy methane tracers at the NOAA National Severe Storms Laboratory (NSSL) at Norman, Oklahoma. Samplers were deployed to measure tracer concentrations along arcs at 100 km and 600 km north of the release point. The objectives of the experiment were:

1) to provide a proof-test of the perfluorocarbon release, sampling and analysis techniques,

2) to test the concept of using the National Weather Service substation network for cross-country sampling,

3) to compare measurements of five different tracers to establish the validity of the new tracer techniques, and

4) to demonstrate the capability to perform long-range atmospheric transport and dispersion experiments, at reasonable cost, for verification and improvement of air pollution models.

3.1 Tracer Release

The five tracers were released simultaneously over a 3-hr period from 1900 to 2200 GMT (1400-1700 CDT) from an open field at NSSL. Release nozzles were about a meter above ground level. Flowrates were carefully monitored to assure a nearly constant release rate for each tracer. Release amounts are shown in Table 2. The amounts of perfluorocarbon and heavy methane released were calculated to produce concentrations well above the detection limit at the 600 km sampling arc. The amount of SF_6 released was sufficient to be detected at the 100 km arc for comparison with the new tracers.

Table 2. Tracer Releases on July 8, 1980

Tracer	Formula	Molecular Wt.	Release Amount (kg)
PMCH	C_7F_{14}	350	192
PDCH	C_8F_{16}	400	186
SULFUR HEXAFLUORIDE	SF_6	146	273
METHANE-20	$^{12}CD_4$	20	0.153
METHANE-21	$^{13}CD_4$	21	0.084

Tracer Release Ratios
(by Volume)

PMCH/PDCH: 1.18

SF_6/PMCH : 3.41

SF_6/PDCH : 4.02

PMCH/Me-20 : 72

PMCH/Me-21 : 137

SF_6/Me-21 : 467

It should be noted that although very small amounts of heavy methanes are required, they are relatively expensive to produce. When the costs of tracer materials and sample analysis are taken into account, the cost per experiment is comparable for perfluorocarbons and heavy methanes.

The two perfluorocarbons (PMCH and PDCH) were released as aerosol sprays from separate tanks mounted on trailers a few feet apart. The tanks were weighed immediately before and after the experiment to determine the amount released from each tank. Since the commercially available PDCH contains about 8% (by weight) PMCH and the commercial PMCH has about 2% impurities, samples of the purchased tracers were assayed at BNL prior to the experiment, and samples from the release tanks were assayed after the second experiment. The release tank weighings and the chemical assays were used to calculate the PMCH and PDCH release amounts shown in Table 2. These values are accurate within ±4%.

SF_6 was released as a gas from pressurized cylinders positioned between the perfluorocarbon trailers. The release amount was determined by weighing the cylinders before and after release and is accurate within ±2%.

The two heavy methane tracers were released as a calibrated mixture of gases from a single pressurized cylinder. The mixture was prepared at LASL and the ratio of the two methanes was determined by mass spectrometry. The total amount released was determined by weighings before and after release. Release amounts are accurate within ±1%.

The lower part of Table 2 gives the tracer release ratios, by volume, as calculated from the release amounts and molecular weights shown above. Ideally, if the tracer systems worked perfectly, these same ratios should be found in all air samples collected within the tracer plume (after ambient background concentrations are removed).

3.2 Sampling Array

Sampling arcs were established at 100 km and 600 km from the release point. Sites were selected in a sector to the north of the release site, based on a 5-year climatology of July trajectories.

3.2.1 100 km arc

Thirty sampling sites were selected at 4-5 km intervals along the roadway of HWY 51 and HWY 33 as shown in Figure 2. The latitude-longitude azimuth, and distance from the release site of each sampling site are listed in Table 3. The operational center for the 100 km arc was set up at the Agronomy Research Station, Oklahoma State University at Stillwater, OK. National Weather Service instrument shelters were set up at each location to house the BATS sequential sampler. Only seventeen samplers were available, so the sites to be instrumented had to be selected just prior to the start of the tracer release. Based on the latest trajectory forecast, two EML sampling teams deployed the BATS samplers to Sites 12-28. The tracer release began at 1900 GMT (1400 CDT) and the samplers were set to take ten 45-minute samples starting at 2130 GMT, before the tracer was expected to arrive.

A whole-air sampler (pump and plastic bag enclosed in a barrel) was co-located with each BATS sampler to collect a single sample starting when the BATS was placed at the site and ending when the BATS sampling was terminated. The purpose of the whole air samplers was to provide intercomparisons among the five tracers and aliquots were taken from each bag for perfluorocarbon, heavy methane, and SF_6 analyses.

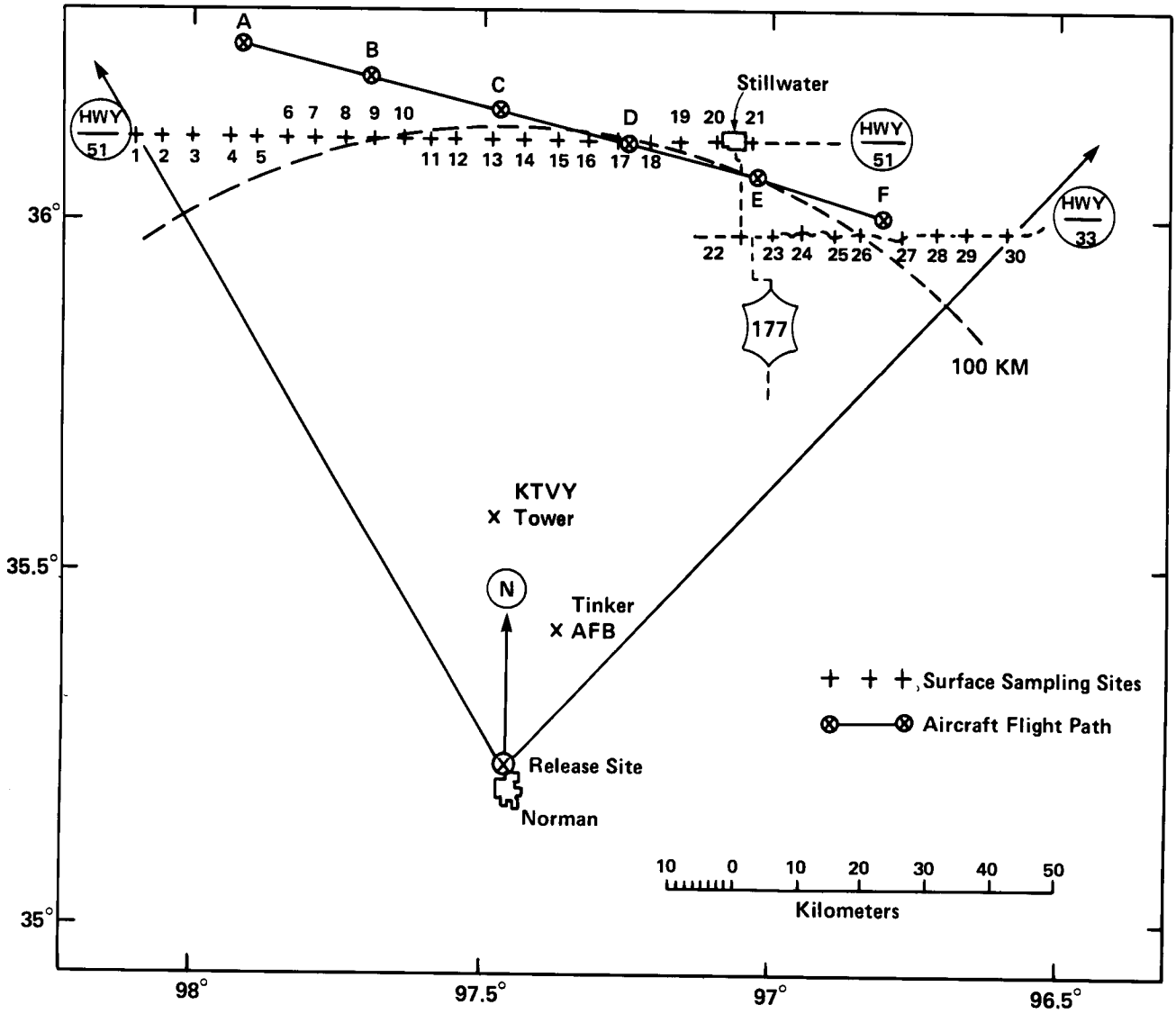

Figure 2. Location of the sequential air samplers (BATS) and aircraft sampling path at 100 km from the tracer release site.

Table 3. Location of sampling sites at the 100 Km arc.

Station No.	Latitude °N	Longitude °W	Distance[a] Km	Azimuth[a] deg
1	36.12	98.10	115	328
2	36.12	98.05	113	330
3	36.12	98.00	111	333
4	36.12	97.94	108	335
5	36.12	97.89	106	338
6	36.12	97.84	105	340
7	36.12	97.79	103	342
8	36.12	97.73	102	345
9	36.12	97.68	100	347
10	36.12	97.63	99	350
11	36.12	97.59	98	352
12	36.12	97.54	98	355
13	36.12	97.48	97	358
14	36.12	97.42	97	001
15	36.12	97.36	98	003
16	36.12	97.31	98	006
17	36.11	97.26	98	008
18	36.10	97.21	98	011
19	36.12	97.15	101	014
20	36.12	97.09	103	017
21	36.12	97.05	104	019
22	35.99	97.05	91	022
23	35.98	97.00	93	025
24	35.99	96.94	95	028
25	35.99	96.89	97	030
26	35.98	96.84	100	033
27	35.96	96.77	104	036
28	35.97	96.72	108	038
29	35.97	96.66	110	040
30	35.97	96.59	114	043
Tinker AFB	35.42	97.38		
Release Site	35.24	97.46		
KTVY Tower	35.58	97.48		

(a) Measured from Release Site.

3.2.2 600 km arc

Sampling sites on the 600 km arc, in Nebraska and Missouri are shown in Figure 3. Deployment and operation of samplers over the long distances on this arc could have presented difficult logistic problems. Fortunately, we were able to secure the cooperation of the NOAA National Weather Service (NWS) to allow us to use their substation network as a fixed sampling array. This network is comprised of over 12,000 locations in the U.S. where cooperative observers, mostly volunteers, gather weather data for the NWS.

The BATS samplers were delivered, in advance of the experiment, by NWS substation specialists to the sites shown in Figure 3. At the time of delivery, the samplers were set to take 22 three-hour samples. On the day of the experiment, after the tracer release had begun, all observers were notified by telephone to set the samplers to start automatically at 0800 GMT (0300 CDT) on July 9. The station locations and cooperative observers are listed in Table 4.

The Los Alamos Scientific Laboratory had 6 cryogenic samplers available for deployment on the 600 km arc for the collection of heavy methanes. On the evening of July 8, based on the latest wind data and forecasts, they were advised by ARL to deploy the samplers to the site indicated by double circles in Figure 3. Five sequential samples were taken at these locations at 3-hour intervals beginning at 1100 GMT (0600 CDT) on July 9.

3.3 Airborne Sampling

The Battelle Pacific Northwest Laboratory provided a DC-3 aircraft and crew for sampling missions over the 100 km and 600 km arcs. It was intended to obtain plume profiles aloft with the Lovelock real-time continuous perfluorocarbon monitor and a modified version of this instrument developed at BNL. However, neither instrument was operational on the day of the experiment. Whole-air samples were collected in plastic bags, and analyzed for all five tracers. Frequent wind measurements were also made aboard the aircraft during both sampling flights.

Three sampling passes were made at the 100 km arc along the flight path shown in Figure 2 at an altitude of 900 meters above the ground (1250 m MSL) between 2300 GMT and 0000 GMT (6-7 PM). On each pass, a plastic bag was filled with outside air along each segment of the flight path.

The aircraft returned to Wiley Post Field in Oklahoma City, refueled, and then took off for Kansas City in preparation for the 600 km sampling flight the next morning. The plume had been forecast to arrive about 1300 GMT (8 AM) but the 0600 GMT wind data indicated faster plume travel and the aircraft was rescheduled for take-off at 1230 GMT (7:30 AM) and a sampling flight path north of the 600 km arc, shown in Figure 3 was chosen to compensate for the stronger winds. Bag samples of about 12-minute duration were collected along each segment of the flight path from about 1240 to 1630 GMT at an altitude of 1200 meters above the ground (1525 meters MSL). Aliquots were transferred from each bag for later analysis by BNL and LASL.

3.4 Meteorology

On July 8-9 a broad area of high pressure dominated most of the U.S. A west-to-east oriented stationary front just north of the 600 km sampling arc was

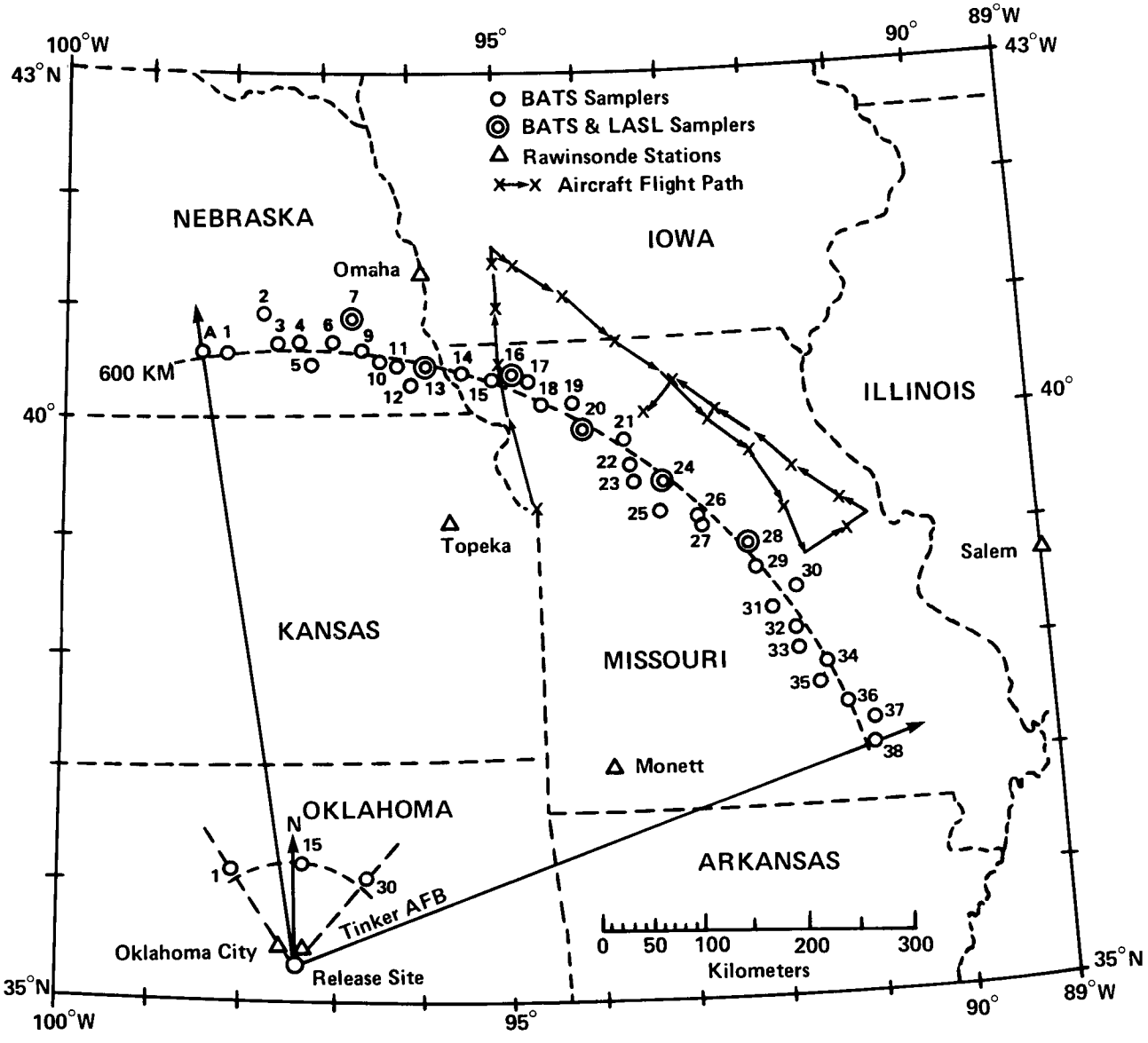

Figure 3. Location of sequential samplers (BATS), LASL samplers, and aircraft sampling flight path at 600 km from the tracer release site. The locations of rawinsonde stations are also shown.

Table 4. Sampling sites at the 600 Km arc

Station No.	Location	Observer	Latitude °N	Longitude °W	Azimuth[a] deg.
NEBRASKA					
A	Hastings	Ralph A. Powell	40.60	98.35	352
1	Clay Center 5W	Jim Chapman	40.53	98.15	354
2	Bradshaw	Jack Pugh	40.88	97.75	358
3	Fairmont	Andrew Anderson	40.63	97.58	000
4	Friend	Jim Hannon	40.65	97.28	001
5	Western	Kenneth Roesler	40.40	97.20	002
6	Crete	Dr. Delbert King	40.62	96.95	004
7	Lincoln (WSO)	Orval Jurgena	40.85	97.75	005
9	Firth	Roland Beach	40.53	96.60	007
10	Sterling	Raymond Zink	40.47	96.38	008
11	Tecumseh	Arthur Lempke	40.37	96.18	010
12	Table Rock 4N	Betty Vrtiska	40.23	96.08	011
13	Auburn 5NNE	Daryl Obermeyer	40.45	95.80	012
MISSOURI					
14	Fairfax	Dillard Price	40.33	95.40	015
15	Skidmore	Donald Brown	40.28	95.08	018
16	Maryville 2E	George Wolfe	40.35	94.83	020
17	Conception	Br. Damian Larson	40.25	94.68	022
18	King City	John Martin	40.05	94.52	023
19	Pattonsburg	Mrs. Kenneth Mason	40.05	94.13	026
20	Hamilton 2 W	William Kuhnert	39.75	94.03	028
21	Chillicothe	Sam Bowling	39.77	93.55	031
22	Coloma	Mrs. Freda Trussel	39.53	93.53	033
23	Carrollton	Harold Finley	30.37	93.50	034
24	Brunswick	John M. Smith	39.42	93.12	036
25	Marshall	Steve Hilton	39.12	93.18	038
26	New Franklin	Mrs. Ronda Thiessen	39.00	92.77	040
27	Boonville	Rolland Goode	38.97	92.75	041
28	Columbia (WSO)	Dave Horner	38.65	92.22	046
29	Jefferson City	Robert Block	38.58	92.15	048
30	Freedom	Mrs. Velma Niewald	38.47	91.70	052
31	Vienna	Henry Kaiser	38.20	91.98	053
32	Vichy (FAA)	Newton Lipplitt	38.12	91.77	055
33	Rolla	Dr. Al Spreng	37.95	91.77	057
34	Cook Station	Mrs. Ozella Brand	37.82	91.43	060
35	Salem	Warren Sellers	37.63	91.53	061
36	Bunker	Mrs. Grace Shaffer	37.45	91.22	064
37	Ellington	Billy Swyres	37.20	90.93	066
38	Van Buren	Gerry Whittle	36.98	91.02	068

(a) Measured from Release Site.

associated with a weak low pressure center moving slowly eastward (see Figures 4 and 5). The wind flow in the boundary layer (surface to about 2500 m) over the central U.S. was predominantly from the south-southwest around a strongly persistent high pressure system centered in the southeastern U.S. This weather pattern was associated with the severe "heat wave" in the central U.S. during July 1980. Afternoon surface temperatures in the experimental area generally rose above 38°C (100°F) during the entire period of the experiment.

3.4.1 Forecast tracer trajectories

In order to alert the sites in advance to prepare for sampling, forecast trajectories were prepared on a daily basis. Trajectories starting at 6-hour intervals were determined from a computer program using the NOAA National Meteorological Center forecast gridded wind fields. The forecast obtained the morning of July 8, based on 0000 GMT data, was for trajectories starting 18 to 24 hours later (for a planned tracer release time of 1900 GMT). The plume centerline was forecast to move to the northeast across the eastern part of the 100 km arc and then continue northeast-to-north crossing near the center of the 600 km arc. Based on the forecast, preparations continued for a 1900 GMT release. The last forecast before release was obtained at noon (based on 1200 GMT data) for a trajectory starting at 1800 GMT. The plume centerline was forecast to be in about the same position as before with a slight northeast shift at the 600 km arc. The tracer was released with the knowledge that backing (counter-clockwise shifting) of the local winds was forecast during the afternoon turbulent mixing. This insured that the plume would cross the 100 km arc shifting from east to west as time progressed.

3.4.2 Special rawinsonde observations

Special rawinsonde observations up to 500 mb were taken at Tinker AFB, about 20 km north-northeast of the release site, starting the morning of July 8. Data are given in Table 5 for observations from July 8, 1700 GMT to July 9, 0300 GMT. The data include height, wind direction, wind speed, and temperature. In addition, a transport layer height was computed from each temperature sounding (Heffter, 1980). The transport layer height, TLH, and average wind speed and direction in the layer,are given at the bottom of the table for each sounding.

Special upper-air observations were also requested from several stations in the regular National Weather Service rawinsonde network. Extra soundings were taken at Omaha, NE; Topeka, KS; and Monett, MO, on July 8, 1800 GMT, July 9, 0600 GMT and 1800 GMT. All special rawinsonde data collected for this experiment, including the Tinker AFB soundings, have been included in the NAMER-WINDTEMP data tapes available at the National Climatic Center, Asheville, NC (see Appendix C, Heffter, 1980).

3.4.3 Aircraft winds

The PNL sampling aircraft took wind observations at the 100 km arc along the flight path shown in the lower part of Figure 6. The upper figure shows a plot of the winds by longitude (along the flight path) versus time. To locate the geographic position of any wind, read directly down (along a constant longitude) from the plotted wind position of the upper figure to the intersection along the flight path in the lower figure. The winds are tabulated in Table 6.

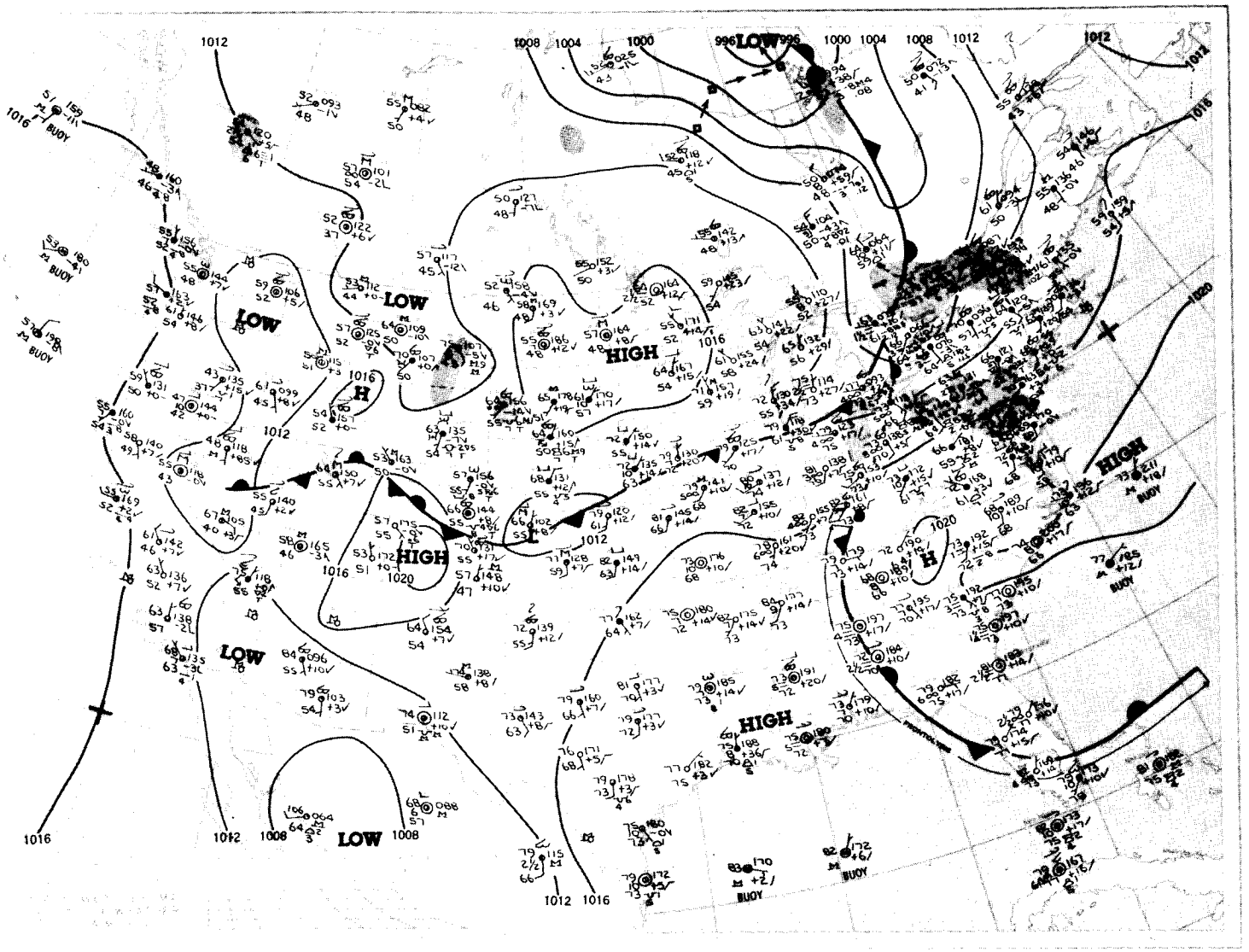

Figure 4. Surface weather map for 1200 GMT, Tuesday, July 8, 1980.

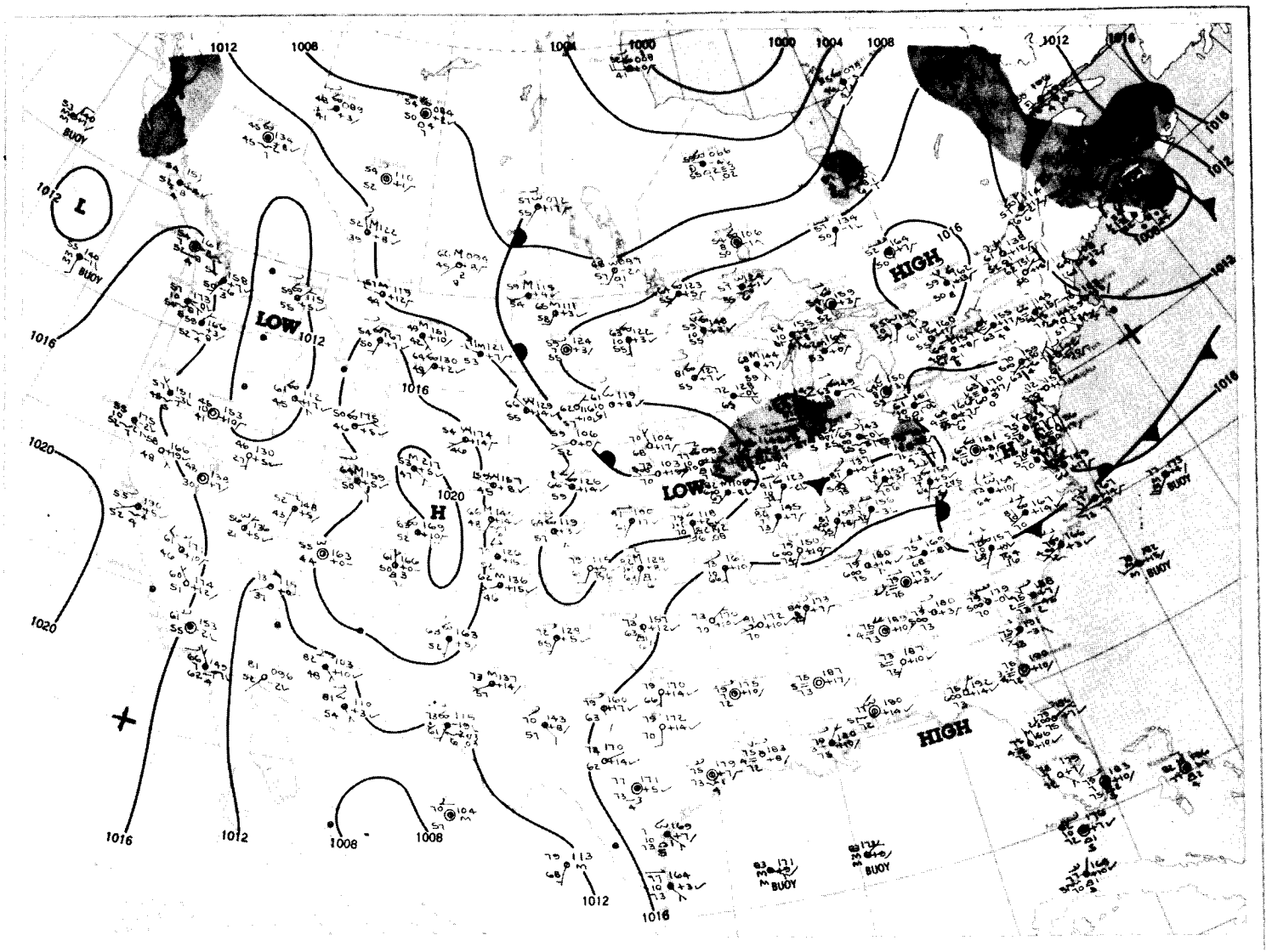

Figure 5. Surface weather map for 1200 GMT, Wednesday, July 9, 1980.

TABLE 5. TINKER AFB RAWINSONDE DATA FOR THE JULY 8 EXPERIMENT.

08 JUL 80 17GMT

HT M,MSL	DIR DEG	SPD M/SEC
387	190	2.0
610	210	7.7
915	205	7.2
1220	210	6.6
1551	210	6.6
1830	210	6.6
2135	215	7.7
2440	205	9.7
2745	195	11.2
3050	185	12.8
3215	185	14.4
3660	185	15.4
4270	185	9.2
4880	195	5.6
5490	190	8.2

HT M,MSL	PRES MB	TEMP DEG K
387	969	305
1551	850	295
3215	700	287
4351	609	278
5212	548	274
5960	500	271

TLH M,MSL	DIR DEG	SPD M/SEC
2270	209	7

08 JUL 80 19GMT

HT M,MSL	DIR DEG	SPD M/SEC
387	170	3.0
610	170	5.1
915	185	6.1
1220	200	5.6
1550	205	6.1
1830	210	6.1
2135	215	8.2
2440	210	9.7
2745	200	11.3
3211	195	15.4
3660	195	16.9
4270	210	10.2
4880	235	5.6
5795	210	6.1

HT M,MSL	PRES MB	TEMP DEG K
387	969	307
1550	850	295
1888	817	291
2004	806	292
2329	776	291
3211	700	286
4470	600	277
5960	500	271

TLH M,MSL	DIR DEG	SPD M/SEC
1990	196	5

08 JUL 80 21GMT

HT M,MSL	DIR DEG	SPD M/SEC
387	170	4.1
610	170	10.8
915	180	10.3
1220	190	9.8
1623	190	9.3
1830	195	8.8
2135	205	9.3
2440	200	12.9
2745	195	12.9
3288	205	16.0
3355	205	17.0
3660	215	13.9
3965	225	9.3
4270	220	7.2
4880	240	3.6
5795	235	4.6

HT M,MSL	PRES MB	TEMP DEG K
387	976	309
1623	850	296
2089	805	292
2294	786	292
3288	700	286
5297	547	273
6030	500	271

TLH M,MSL	DIR DEG	SPD M/SEC
2280	188	9

09 JUL 80 00GMT

HT M,MSL	DIR DEG	SPD M/SEC
387	180	5.1
610	175	9.2
915	175	9.7
1220	170	9.7
1525	175	10.2
1531	175	10.2
1830	180	10.8
2135	185	10.2
2440	195	11.3
2745	210	12.3
3194	220	13.3
3355	220	13.3
3660	230	9.2
4270	205	2.0
4880	260	3.6
5490	280	5.1

HT M,MSL	PRES MB	TEMP DEG K
387	966	309
516	952	307
1531	850	297
2256	781	290
2683	743	288
3194	700	286
5940	500	270

TLH M,MSL	DIR DEG	SPD M/SEC
2630	180	10

09 JUL 80 03GMT

HT M,MSL	DIR DEG	SPD M/SEC
387	170	2.6
610	170	16.0
915	175	15.4
1220	180	13.9
1526	190	12.4
1830	200	11.3
2135	205	11.3
2440	210	10.8
2745	220	9.8
3192	250	4.6
3660	210	2.6
4270	205	4.6
4880	285	1.5
5490	315	2.1

HT M,MSL	PRES MB	TEMP DEG K
387	966	304
500	952	304
550	945	306
1526	850	298
2530	755	288
2830	728	289
3192	700	287
3460	673	286
3960	628	281
5594	500	271

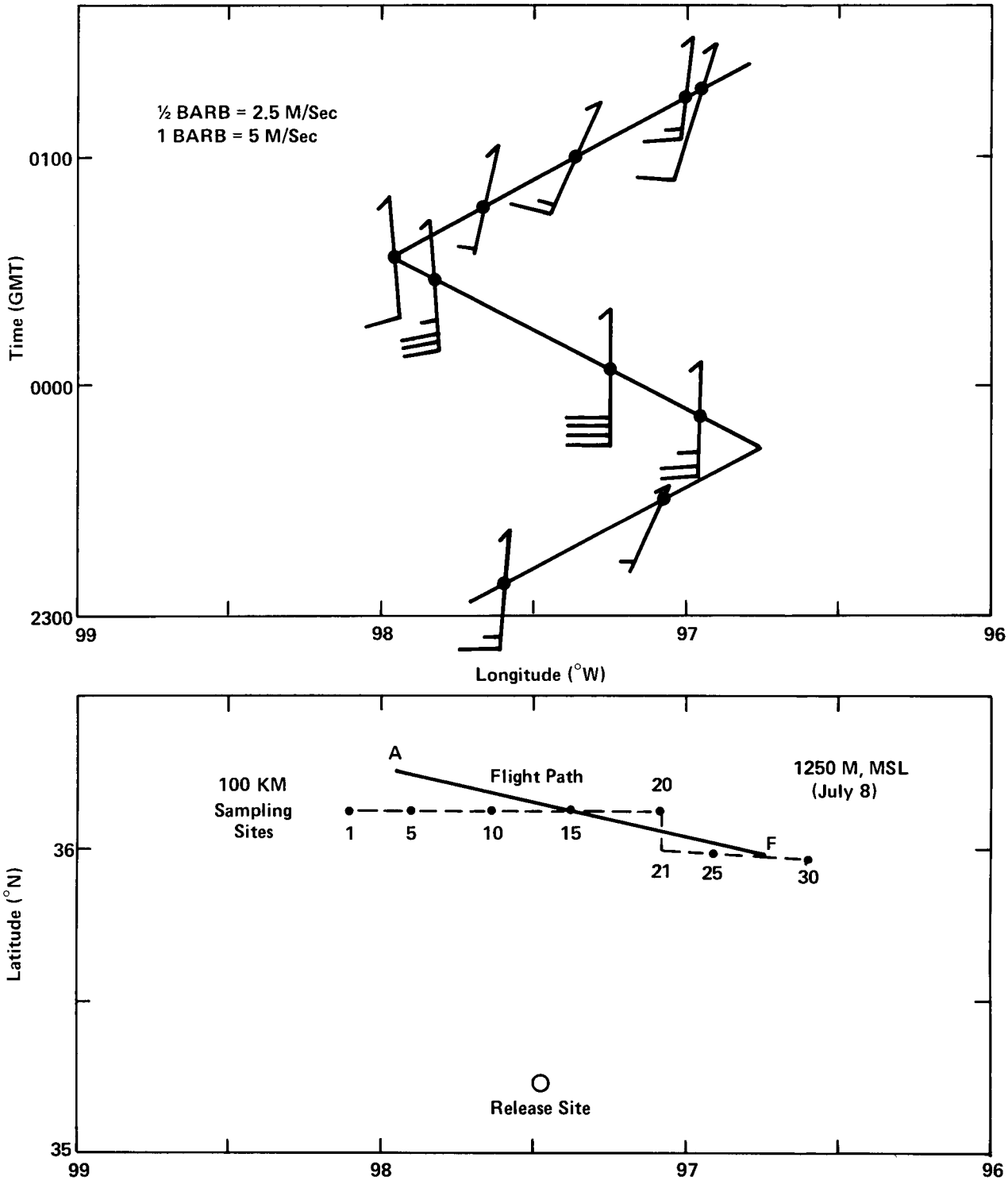

Figure 6. Wind observations at 1250 meters (MSL) along the 100 km arc aircraft sampling path.

Table 6. Aircraft wind observations at 1250 meters (MSL) along the 100 km arc.

Time (GMT)	Direction (deg.)	Speed (m/sec)
2304	186	6.7
2315	205	2.6
2326	182	13.9
2332	181	19.6
2344	178	17.5
2347	176	6.2
2353	194	3.1
0000	205	7.2
0008	188	6.7
0009	198	5.7

The sampling aircraft also took wind observations at the 600 km arc along the flight path shown in Figure 7 (plotted similar to Figure 6). These winds are also tabulated in Table 7.

Table 7. Aircraft wind observations at 1525 meters (MSL) along the 600 km arc.

Time (GMT)	Direction (deg.)	Speed (m/sec)	Time (GMT)	Direction (deg.)	Speed (m/sec)
1304	267	20.1	1504	265	13.9
1313	271	19.0	1511	263	16.0
1316	271	19.0	1516	262	17.0
1327	272	19.0	1526	265	14.4
1328	272	19.0	1528	269	13.4
1340	327	10.3	1533	265	12.9
1346	332	13.4	1540	259	10.3
1352	318	12.9	1544	261	8.8
1358	312	12.4	1550	256	12.4
1404	309	15.4	1554	262	14.4
1416	279	11.8	1556	263	15.4
1427	254	18.0	1604	255	18.5
1440	277	12.4	1607	258	16.0
1449	267	13.4	1617	260	8.8
1452	255	17.0	1622	244	8.8

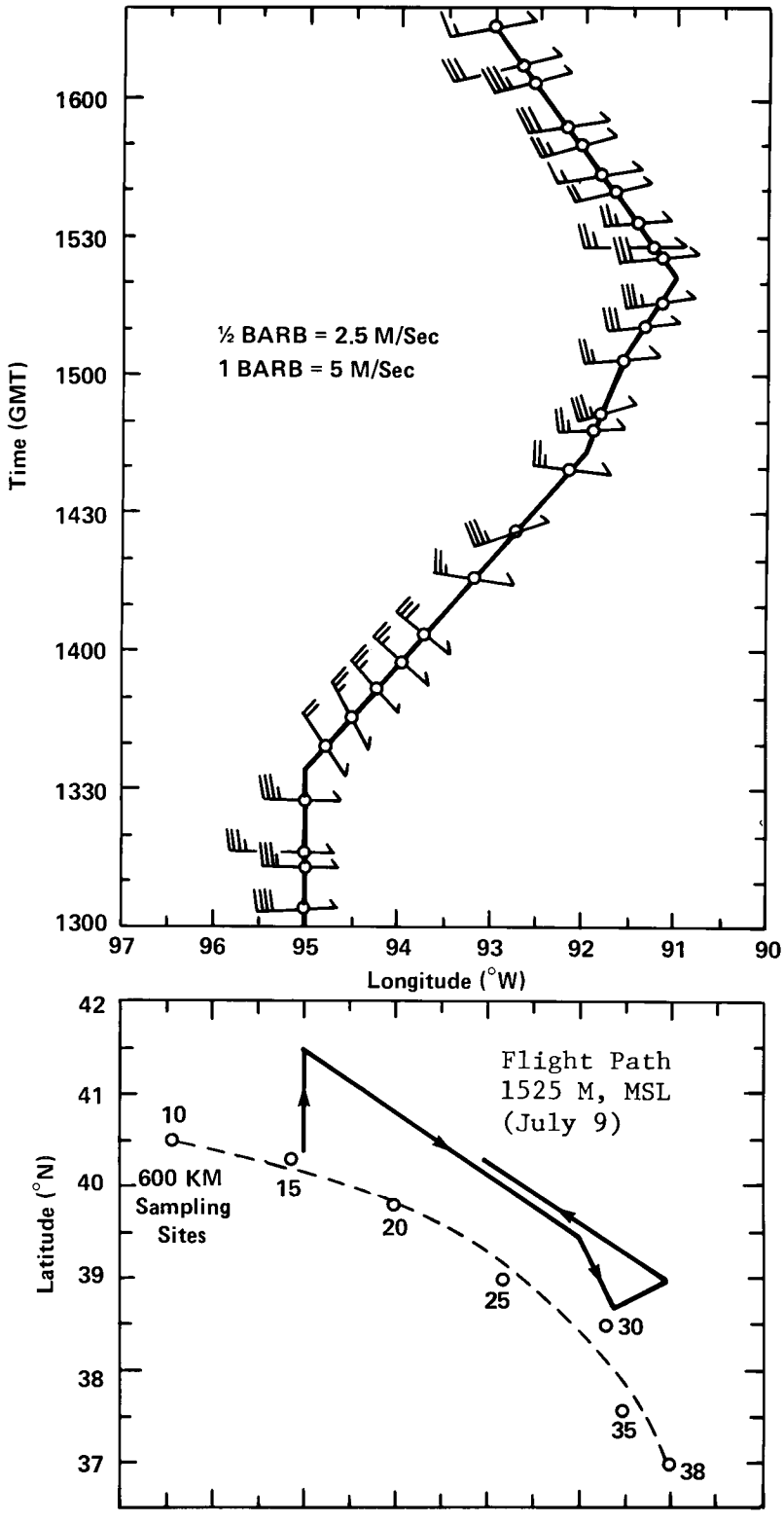

Figure 7. Wind observations at 1525 meters (MSL) along the 600 km aircraft sampling path.

3.4.3 Post-facto tracer trajectories

Tracer trajectories to the 100 km arc were hand-calculated using average winds in the computed transport layer as determined from the Tinker AFB soundings. Trajectories for the start and end of the tracer release are shown in Figure 8 with times (GMT) indicated along each trajectory. Also shown is the expected plume width. The calculated plume position and arrival time at the 100 km arc agreed well with the tracer data although the actual plume extended further to the west (see Section 3.5.1).

Tracer trajectories to the 600 km arc were computed using the ARL-ATAD model (Heffter, 1980). Meteorological input data were obtained from the NAMER-WINDTEMP data base. The computed trajectories are shown in Figure 9. The solid trajectory is determined from winds averaged in a computed variable transport layer; the dashed trajectory is from winds averaged in a constant layer 150 to 600 m above terrain. The calculated plume centerline at the 600 km arc using the variable transport layer was about 200 km east of the measured peak concentration; the calculated position using the 150-600 m layer was in better agreement, about 100 km east of the actual position.

3.5 Sampling Results

3.5.1 100 km sampling results

The BATS sequential samplers and whole air samplers were installed at Sites 12 through 28. The 45-minute sequential sample concentrations are given in Table 8. Due to analysis problems, no data are available for Site 17.

The PMCH sampling results on the 100 km arc are shown graphically in Figure 10. The sampling sites are plotted as a function of the azimuth from the release site. The scale gives the distance in kilometers between sampling sites projected onto the 100 km arc.

During the initial sampling period (2100-2145 GMT), the PMCH concentrations at all sampling sites are at or slightly above the background concentration of about 2.4 parts per 10^{15}. During the second sampling period (2145 to 2230 GMT), approximately 3 hours after the start of tracer release, concentrations had increased by three orders of magnitude with the plume centered between Sites 12 and 16. The backing of the winds with time carried the tracer plume further west than expected and the portion of the plume west of Site 12 was not sampled.

The next samples (2230 to 2315 GMT) show the peak PMCH concentrations. Later samples show decreasing concentration with the plume centerline shifting toward the west. As will be seen later, aircraft sampling data indicated that plume concentrations west of Site 12 probably decreased very rapidly.

During the sampling period 0130-0215 GMT (July 9), about 4 hours after the end of the release, concentrations along the 100 km arc had returned to near-background levels. Sites 23 through 28 had background concentrations during the entire sampling period.

The Dual-Trap sampler, described in Section 2.4, was operated along the 100 km arc but the only non-background data obtained was at Site 20 from 2227 to 2314 GMT as shown in Table 9. The average PDCH concentration for this period was 228 parts

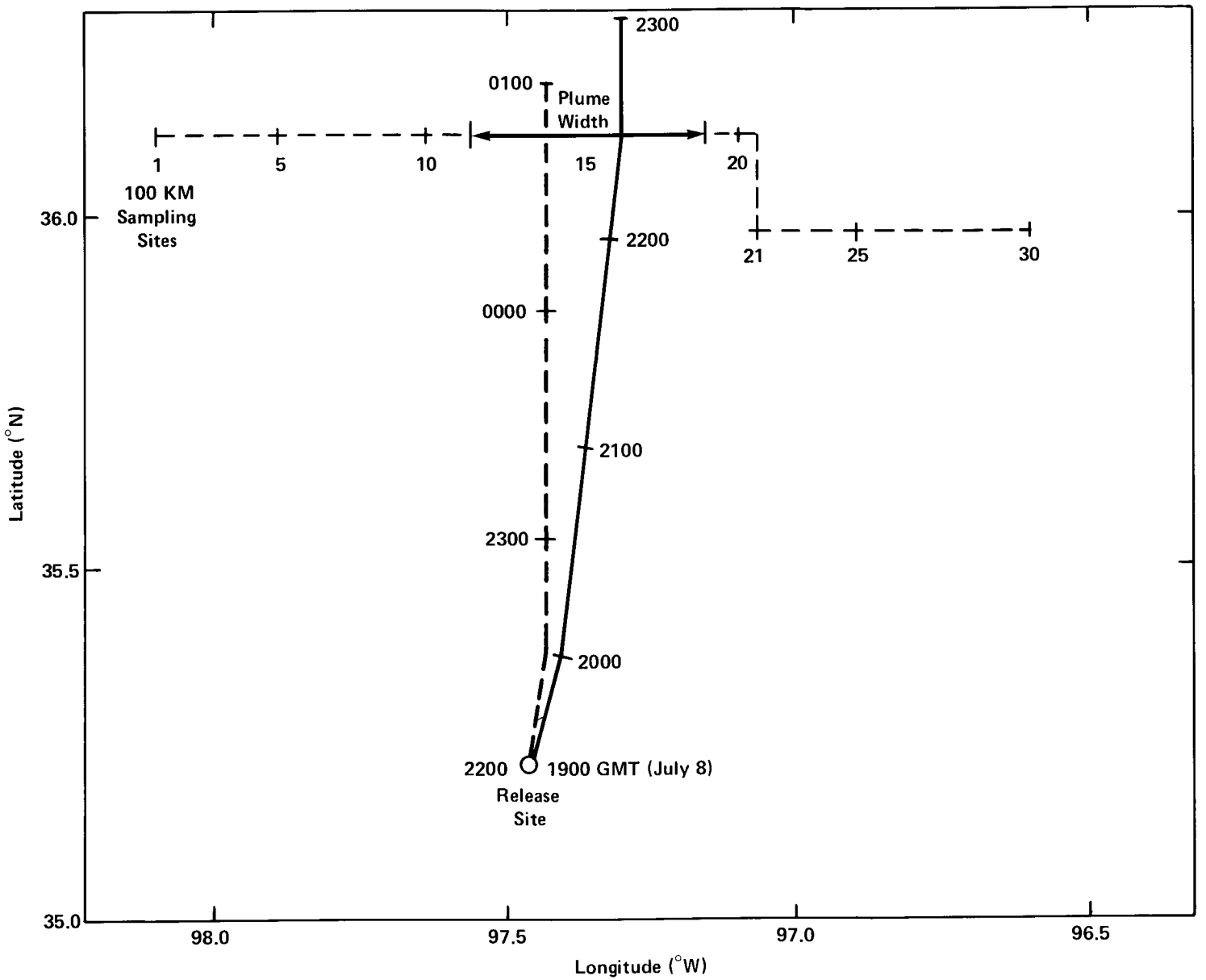

Figure 8. Calculated transport layer trajectories to the 100 km arc for the 3-hour tracer release on July 8.

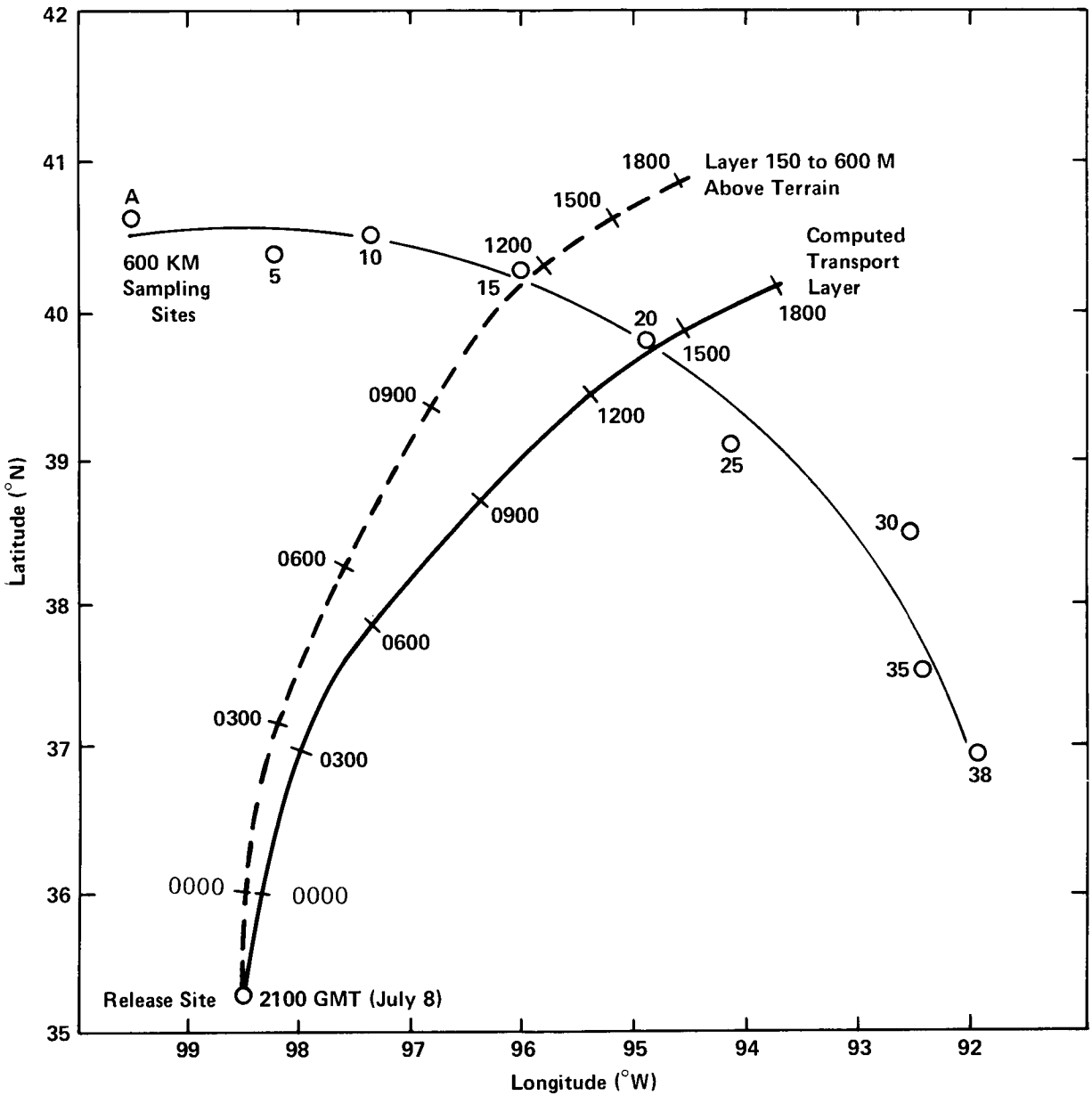

Figure 9. Comparison of the transport layer trajectory with the trajectory in a layer 150 to 600 meters above terrain.

TABLE 8

100 KM ARC

TRACER CONCENTRATIONS (PARTS PER 10^{15})

STATION	12		13		14		15	
START TIME(GMT)	PMCH	PDCH	PMCH**	PDCH**	PMCH	PDCH	PMCH	PDCH
JULY 08								
2100	3.1	25	4.	28	4.7	26	4.9	25
2145	650.	580	1300.	890	1010.	920	860.	760
2230	4000.	2980	5900.	3900	4670.	3500	2730.	2380
2315	2840.	2160	2700.	2000	1650.	1370	1260.	1110
JULY 09								
0000	2170.	1700	500.	390	182.	182	88.	96
0045	43.	67	4.	32	4.5	28	4.0	25
0130	4.6	32	-	32	5.0	28	4.8	23
0215	4.1	30	4.	31	4.4	27	5.*	28
0300	3.6	26	4.	31	4.6	27	5.*	28
0345	3.1	26	4.	26	4.4	28	10.*	25

STATION	16		18		19		20	
START TIME(GMT)	PMCH	PDCH	PMCH	PDCH	PMCH	PDCH	PMCH	PDCH
JULY 08								
2100	3.0	26	3.0	31	3.0	27	3.7	28
2145	1110.	980	290.	270	130.	150	16.	40
2230	2810.	2440	2100.	1780	560.	480	215.	238
2315	1000.	920	340.	310	50.	66	14.	41
JULY 09								
0000	90.	101	3.*	23	3.*	25	3.8	30
0045	9.*	28	3.*	23	1.*	26	4.5	29
0130	3.*	27	3.*	24	3.*	26	4.1	31
0215	4.*	27	4.*	26	3.*	26	4.2	31
0300	6.*	27	3.*	24	2.*	27	4.2	31
0345	10.*	28	-	-	1.*	26	4.1	31

STATION	21			22		23-28	
START TIME(GMT)	PMCH	PDCH	START TIME(GMT)	PMCH	PDCH	PMCH	PDCH
JULY 08			JULY 08				SEE FOOT NOTE A
2205	27.1	44	2130	5.7	37		
2250	3.6	24	2215	4.1	24		
2335	2.8	23	2300	3.4	25		
JULY 09			2345	3.8	27		
0020	2.7	25	JULY 09				
0105	3.1	25	0030	3.7	26		
0150	2.9	24	0115	5.5	27		
0235	2.8	25	0200	3.5	25		
0320	3.4	25	0245	4.2	29		
0405	2.8	25	0330	4.3	26		
0450	2.5	25	0315	3.9	27		

- \- NO DATA

- * VALUE UNCERTAIN DUE PRIMARILY TO CONTAMINATION IN LAB ANALYZER.

- ** POOR DESORPTION POWER, CORRECTION ESTIMATED.

- A SAMPLING SITES 23-28 HAD BACKGROUND PMCH AND PDCH CONCENTRATIONS IN ALL SAMPLES.

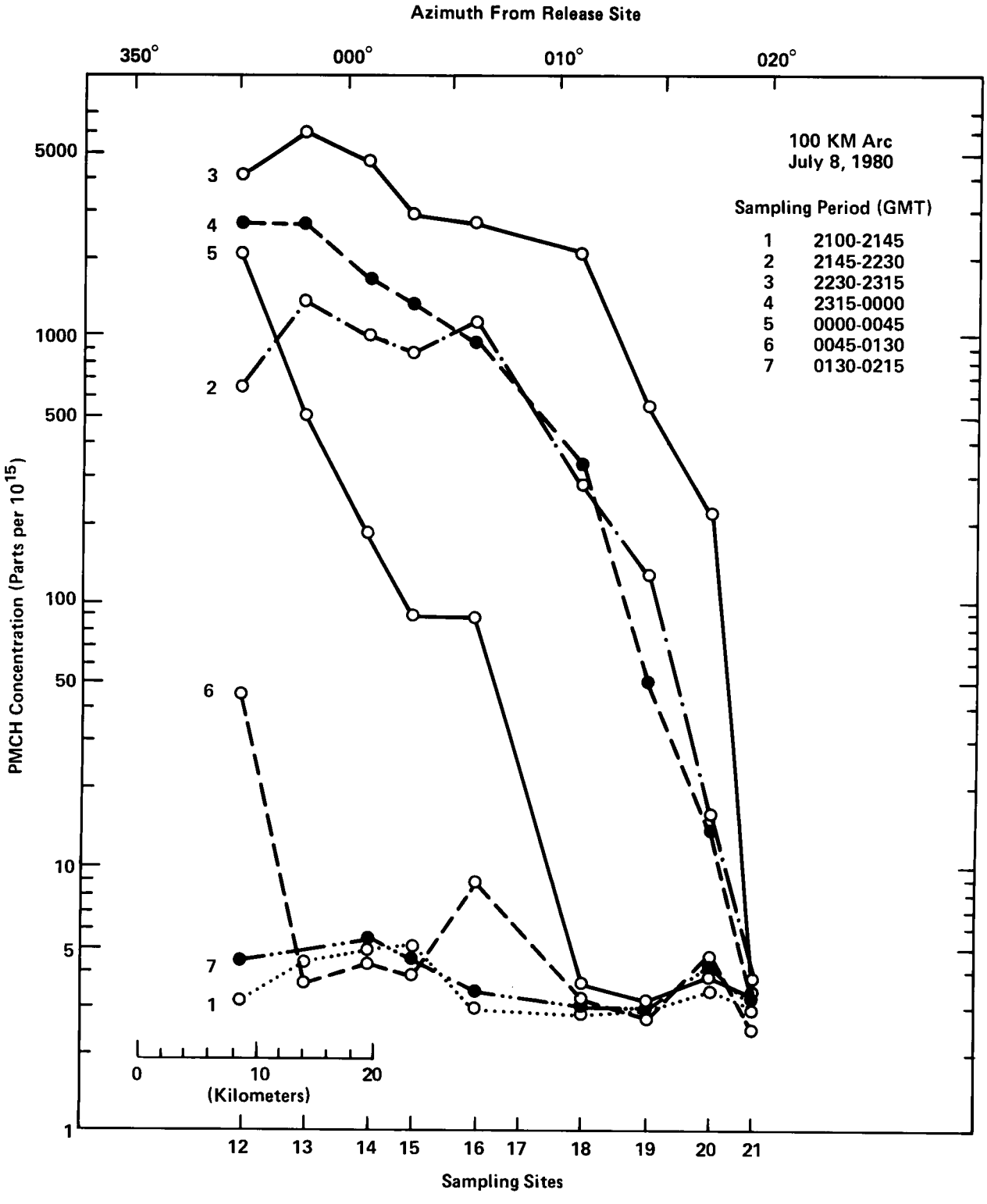

Figure 10. Average 45-min PMCH concentrations along the 100 km arc from the July 8 experiment.

per 10^{15}. The PDCH results from the BATS sequential sampler at Site 20 for the 2230 to 2315 GMT sampling period (see Table 8) show an average PDCH concentration of 238 parts per 10^{15}, in very good agreement with the Dual-Trap sampler.

Table 9. Dual-Trap Sampler Results at Site 20 (100 km Arc), July 8, 1980.

Sample Mid-Time (GMT)	PDCH Parts per 10^{15}
2227	60
2231	--
2236	180
2241	250
2246	660
2251	320
2255	400
2300	280
2304	160
2309	45
2314	35

A single whole air bag sample for the entire sampling period was collected at each BATS sampling site. Laboratory analysis of aliquots from these samples, performed at BNL, indicated nearly all were severely contaminated and could not be used. It appears that the contamination (concentrations of SF_6, PMCH, and PDCH all were too high) most likely occurred while the aliquots (in small plastic bags) were stored at the BNL laboratory. Pin-hole leaks in the bags could have allowed a slow penetration of laboratory air which often has very high concentrations of all three tracers. Fortunately, aliquots from some of the same whole air samples, taken by LASL for analysis, showed no evidence of contamination. Comparison of their results with the BATS data at the same sites is shown in Section 5.5.

3.5.2 100 km aircraft samples

Tracer concentrations measured on three passes over the flight path shown in Figure 2 are given in Table 10. Figure 11 shows the average PMCH concentrations on each segment of the flight path (solid bars) along with the average PMCH measurements obtained at the ground with the BATS samplers at about the same time (2230-0000 GMT). Concentrations aloft are quite comparable to those at the ground.

Since good PMCH data were not obtained at either end of the flight path, estimated PMCH concentrations (dashed bars) were calculated from the measured SF_6. First, the general SF_6 background of 600×10^{-15} was subtracted from the measured SF_6. Then the SF_6 concentration was divided by the SF_6/PMCH release ratio of 3.41. For the three passes along flight segment B to E, the PMCH estimated from the SF_6 value is very close to the measured PMCH. The estimated PMCH along segments A-B and E-F indicate a sharp drop in concentration. In fact, these concentrations were probably very close to background, since other analyses done at LASL suggest that

Table 10. Airborne Whole-Air Sample Concentrations (parts per 10^{15}).

Sampling Time (GMT) (July 8, 1980)	PMCH[1]	PDCH[1]	SF_6[2]	Me-21[2]
		Path A to B		
2342-2346	?	?	1200	--
2348-2353	?	?	1300	--
		Path B to C		
2302-2305	990	835	3600	8.87
2337-2342	930	985	3100	6.21
2353-2357	880	810	3900	6.87
		Path C to D		
2306-2311	3200	3300	12700	36.6
2332-2337	2800	2400	8500	21.8
2357-0002	5400	4600	14500	29.6
		Path D to E		
2311-2316	1300	1400	4300	9.92
2327-2332	?	?	2100	--
0002-0007	?	?	1600	--
		Path E to F		
2316-2321	?	?	1200	--
2324-2327	?	?	1300	--
0007-0012	?	?	1300	--

(1) BNL analysis.

(2) LASL analysis.

? Bad data (contamination).

-- No analysis performed.

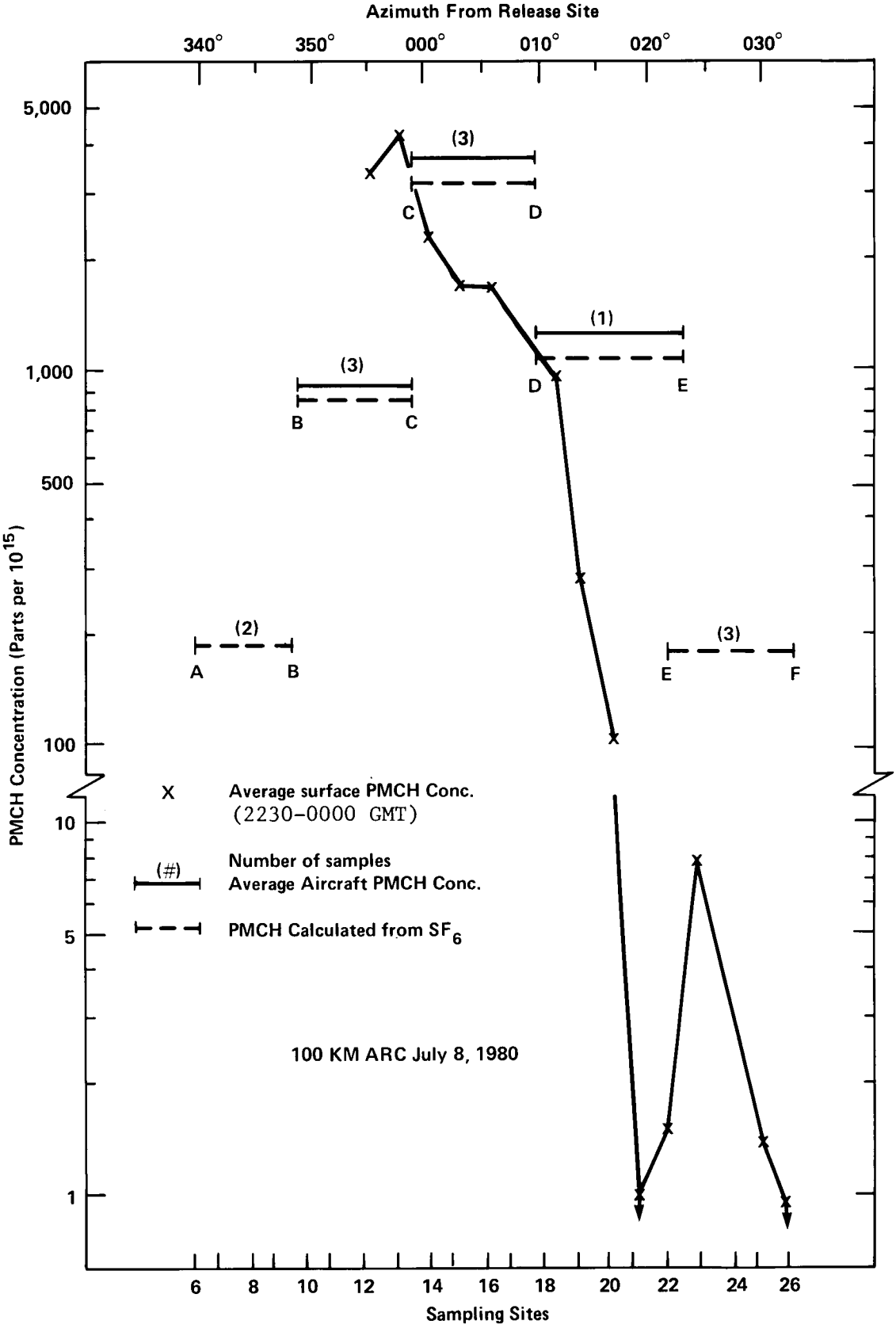

Figure 11. Comparison of PMCH concentrations aloft with surface concentrations.

SF_6 values on the order of $1100x10^{-15}$, obtained with their analyzer, are actually background values. Thus, the aircraft samples suggest that only a small portion of the plume extended west of Site 12, where no surface samplers were deployed.

The whole-air samples obtained in this flight also provided critical data for intercomparison of PFT's, heavy methanes and SF_6 measurements (see Section 5.4).

3.5.3 600 km surface samples

Forecast trajectories based on 1200 GMT (July 8) wind data indicated that a tracer release starting at 1900 GMT would arrive at the 600 km arc at about 1300 GMT (July 9) with the center line of the plume crossing over Site 20 (Hamilton, MO). All sampling sites (note that Site 8 had been eliminated) along the 600 km arc (Figure 3) were alerted to start sampling at 0800 GMT (July 9), five hours before the expected arrival time. A low level wind jet developed during the night transporting the tracer material faster than expected and further to the west.

The 3-hour sample concentrations along the 600 km arc are given in Table 11. Sites that are not listed (14, 21, 22) failed to obtain samples.

The PMCH concentrations for the first 6 sampling periods are shown in Figure 12. The peak plume concentrations arrived at about the time sampling commenced. The plume centered between Site 9 (Firth, NE) and Site 15 (Skidmore, MO). By 2300 GMT (sampling period 6) the PMCH at all sites was near the background level of about 2 parts per 10^{15}. Sampling sites east of Site 19 are not included in this figure since all samples at those sites showed background levels during the first 6 sampling periods.

The entire record of PMCH concentrations at all sites between July 9 (0800 GMT) and July 11 (2000 GMT) along the 600 km arc is shown in Figure 13. The ordinate shows the sampling sites plotted as a function of azimuth from the release site.

Solid dots indicate a measured PMCH concentration less than 3 parts per 10^{15} (for all practical purposes they can be assumed to be background concentrations) while crosses indicate concentrations at or above 3 parts per 10^{15}.

The initial plume probably arrived at the 600 km arc just before sampling began at 0800 GMT on July 9 with a duration of about 15 hours (2300 GMT, July 9) before background levels are seen at all locations. Background concentrations are seen for the next 15 hours, whereupon the July 11, 1400 to 1700 GMT samples (about 40 hours after release) show a secondary plume arriving at the 600 km arc.

The maximum concentrations of this secondary plume are about two orders of magnitude lower than the initial plume but they cover a much larger area. Although PDCH concentrations are close to background ($26x10^{-15}$) they confirm the presence of the secondary plume. The duration of this plume on the arc was about 30 hours. At present we are not sure whether this is a return of the initial plume or, possibly, tracer material that lagged behind the main plume. These data provide an interesting meteorological case study and will be investigated further.

4. 100-KM EXPERIMENT

A second, more limited, tracer experiment was conducted on July 11, 1980 to provide another test of the perfluorocarbon system.

TABLE 11

600 KM ARC

TRACER CONCENTRATIONS (PARTS PER 10^{15})

STATION	A		01		02		03	
	PMCH	PDCH	PMCH*	PDCH*	PMCH	PDCH	PMCH	PDCH
START TIME(GMT)								
JULY 09								
0800	2.8	29	2.0	21	3.6	28	3.7	26
1100	2.7	27	2.0	19	3.5	29	2.3	25
1400	2.7	27	1.7	18	3.1	27	2.3	26
1700	2.4	26	1.7	17	2.8	22	2.2	24
2000	2.5	23	1.7	17	2.4	21	3.1	28
2300	-	-	1.5	15	2.4	21	-	-
JULY 10								
0200	-	-	1.7	16	2.3	22	-	-
0500	-	-	1.7	16	2.3	24	2.8	29
0800	-	-	1.6	17	2.3	20	-	-
1100	-	-	1.5	16	2.6	24	-	-
1400	-	-	1.6	14	2.4	23	-	-
1700	-	-	1.8	15	2.1	21	-	-
2000	-	-	1.4	15	2.5	23	-	-
2300	-	-	1.6	16	2.3	19	-	-
JULY 11								
0200	-	-	2.2	16	5.0	23	-	-
0500	-	-	2.6	13	5.4	22	-	-
0800	-	-	2.0	17	3.2	25	-	-
1100	-	-	1.8	15	2.6	24	-	-
1400	-	-	1.8	17	2.2	20	-	-
1700	-	-	1.6	16	2.2	21	-	-

STATION	04		05		06		07	
	PMCH	PDCH	PMCH	PDCH	PMCH	PDCH	PMCH	PDCH
START TIME(GMT)								
JULY 09								
0800	2.6	30	-	-	17.2	37	3.2	30
1100	2.6	30	-	-	10.5	70**	2.8	32
1400	2.7	30	-	-	2.6	28	-	-
1700	2.6	28	2.3	22	2.6	27	2.8	27
2000	2.5	27	2.9	29	2.9	26	2.4	28
2300	2.3	28	2.9	29	3.0	26	3.2	27
JULY 10								
0200	2.5	28	2.8	31	2.4	27	2.3	27
0500	2.5	29	2.7	32	2.6	27	2.4	28
0800	2.5	28	2.8	33	-	-	2.3	28
1100	2.4	28	2.7	31	3.1	28	2.5	28
1400	2.4	28	2.7	32	2.6	27	3.3	29
1700	-	-	2.4	31	3.5	27	8.2	31
2000	2.4	27	2.9	30	3.8	27	10.1	34
2300	3.4	29	3.4	30	6.0	29	9.8	34
JULY 11								
0200	8.6	33	6.4	34	9.0	32	4.0	29
0500	5.0	31	3.9	32	6.6	30	5.6	30
0800	3.2	30	2.5	30	4.0	29	4.8	30
1100	2.5	29	2.9	30	3.2	28	2.7	28
1400	2.4	30	2.4	30	2.7	28	2.4	26
1700	2.5	30	2.4	30	2.5	27	2.3	26

- NO DATA

* CONCENTRATIONS TOO LOW (DESORPTION PROBLEM).

** CONCENTRATION TOO HIGH.

TABLE 11 (CON'T)

600 KM ARC

TRACER CONCENTRATIONS (PARTS PER 10^{15})

STATION	09		10		11		12	
START TIME(GMT)	PMCH	PDCH	PMCH	PDCH	PMCH	PDCH	PMCH	PDCH
JULY 09								
0800	627.	598	1280.	970	1010.	710	900.	700
1100	63.	82	820.	600	530.	340	186.	182
1400	3.9	26	26.	44	164.	106	99.	108
1700	3.2	24	2.7	25	28.	34	32.	54
2000	2.6	22	3.6	25	5.3	18*	4.1	29
2300	2.7	25	2.8	24	2.4	13*	2.6	27
JULY 10								
0200	2.2	25	2.8	25	2.5	19*	2.6	28
0500	2.3	25	2.8	25	2.4	11*	2.6	28
0800	2.3	25	2.8	26	2.2	9*	2.6	28
1100	2.4	25	2.7	27	2.2	9*	2.6	28
1400	2.6	25	2.6	26	2.4	12*	-	-
1700	3.2	26	4.3	26	3.8	9*	3.3	28
2000	-	-	4.5	26	3.0	6*	2.8	27
2300	4.1	25	5.1	28	3.4	9*	2.9	27
JULY 11								
0200	6.2	27	5.7	29	-	-	-	-
0500	5.0	26	5.3	29	-	-	6.5	31
0800	-	-	4.2	29	-	-	3.4	29
1100	2.3	25	2.5	26	-	-	2.7	29
1400	2.2	24	2.3	26	-	-	2.6	28
1700	2.1	23	2.4	25	-	-	2.4	27

STATION	13		15		16		17	
START TIME(GMT)	PMCH	PDCH	PMCH	PDCH	PMCH	PDCH	PMCH	PDCH
JULY 09								
0800	980.	790	16.	37	4.8	29	2.5	25
1100	500.	420	2.6	26	2.5	26	2.4	25
1400	350.	310	4.5	26	4.3	27	2.9	25
1700	66.	83	11.	31	6.4	29	3.0	25
2000	-	-	6.4	27	5.7	28	3.2	24
2300	-	-	2.5	24	2.7	24	2.5	24
JULY 10								
0200	-	-	2.5	25	2.6	24	2.4	25
0500	2.9	28	-	-	2.3	24	2.4	24
0800	2.2	27	2.4	25	2.3	24	2.5	25
1100	2.4	28	-	-	2.2	24	2.5	27
1400	7.9	32	5.5	27	13.	33	10.	34
1700	16.	39	11.	31	10.	32	12.	35
2000	6.8	31	7.2	28	8.1	30	9.3	33
2300	7.0	31	7.2	28	7.0	21*	7.5	31
JULY 11								
0200	7.9	33	7.5	29	7.3	29	8.8	33
0500	10.	35	8.1	29	7.6	29	9.1	33
0800	8.4	35	7.9	30	8.1	29	8.5	33
1100	7.3	34	5.9	28	7.6	29	8.2	33
1400	6.3	33	2.8	24	3.4	25	3.3	27
1700	-	-	2.4	23	6.2	28	-	-

- NO DATA

* VALUES UNCERTAIN DUE TO LAB ANALYZER PROBLEMS.

TABLE 11 (CON'T)

600 KM ARC

TRACER CONCENTRATIONS (PARTS PER 10^{15})

STATION	18		19		20		23	
	PMCH	PDCH	PMCH	PDCH	PMCH*	PDCH*	PMCH	PDCH
START TIME(GMT)								
JULY 09								
0500	2.4	27	2.6	28	1.8	18	2.6	28
1100	2.3	26	2.6	28	1.7	18	2.5	23
1400	2.5	27	2.5	27	2.4	22	2.4	27
1700	-	-	2.5	27	2.9	24	2.5	26
2000	-	-	2.4	26	2.4	23	2.3	26
2300	-	-	2.4	27	2.3	22	2.3	25
JULY 10								
0200	-	-	2.4	27	2.2	22	2.4	26
0500	-	-	2.4	28	2.0	20	2.4	27
0800	-	-	2.4	28	2.1	22	2.4	27
1100	-	-	2.5	28	2.1	22	2.4	27
1400	-	-	5.1	29	2.3	21	2.4	27
1700	-	-	10.	33	2.4	22	2.3	26
2000	-	-	6.7	30	1.6	14	2.3	26
2300	-	-	7.4	31	2.4	23	2.3	26
JULY 11								
0200	-	-	10.	35	8.7	29	2.5	27
0500	-	-	9.2	35	9.3	31	5.4	30
0800	-	-	9.7	34	7.6	27	5.7	30
1100	-	-	8.7	33	5.3	26	2.9	27
1400	-	-	3.1	27	3.1	22	2.4	26
1700	-	-	2.6	27	2.4	20	2.4	26

STATION	24		25		26		27	
	PMCH	PDCH	PMCH	PDCH	PMCH	PDCH	PMCH	PDCH
START TIME(GMT)								
JULY 09								
0800	2.0	27	2.5	27	2.2	-	-	-
1100	2.0	27	2.7	28	2.2	-	2.6	26
1400	2.0	28	2.6	28	2.2	-	2.6	27
1700	2.0	28	2.5	25	-	-	2.4	26
2000	2.1	28	2.4	25	2.1	-	2.4	27
2300	2.1	27	2.4	26	-	-	2.4	26
JULY 10								
0200	2.0	26	2.5	27	1.9	-	2.5	27
0500	2.0	25	2.5	28	2.1	-	2.5	27
0800	2.1	26	2.6	28	2.1	-	2.5	27
1100	2.1	27	2.6	29	2.2	-	-	-
1400	2.1	27	2.4	28	2.0	-	-	-
1700	2.1	27	2.5	27	1.9	-	-	-
2000	2.1	27	2.4	27	1.9	-	-	-
2300	1.9	26	2.4	28	1.9	-	-	-
JULY 11								
0200	1.8	24	2.7	29	3.0	-	-	-
0500	2.0	25	4.1	30	5.7	-	-	-
0800	2.1	26	2.6	29	-	-	-	-
1100	4.4	29	2.5	29	-	-	-	-
1400	7.9	33	2.4	28	2.4	-	-	-
1700	9.3	34	2.4	28	2.2	-	-	-

- NO DATA

* VALUES UNCERTAIN, SAMPLE VOLUMES HAD TO BE ESTIMATED.

TABLE 11 (CON'T)

600 KM ARC

TRACER CONCENTRATIONS (PARTS PER 10^{15})

STATION	28		29		30		31	
START TIME(GMT)	PMCH	PDCH	PMCH	PDCH	PMCH	PDCH	PMCH	PDCH
JULY 09								
0800	2.3	27	2.5	28	2.0	27	2.9	25
1100	2.7	29	2.5	29	2.4	29	3.3	26
1400	2.0	25	2.4	29	-	-	2.8	26
1700	2.2	25	2.3	28	1.9	26	2.9	22
2000	2.1	25	2.5	28	1.9	25	3.1	25
2300	2.1	25	2.5	29	1.9	26	2.8	27
JULY 10								
0200	2.3	28	2.5	29	2.0	27	2.5	28
0500	2.3	28	2.4	29	-	-	2.7	28
0800	2.3	28	2.5	30	2.0	27	2.6	27
1100	2.2	26	2.5	30	2.1	27	3.3	27
1400	2.2	26	2.6	29	2.0	27	2.6	27
1700	2.0	25	2.8	29	2.0	26	2.6	27
2000	2.0	23	2.4	29	2.0	26	2.6	27
2300	1.9	22	2.5	28	2.0	26	2.6	27
JULY 11								
0200	3.1	24	2.6	29	2.0	26	2.7	28
0500	4.6	24	2.7	30	2.2	27	2.8	28
0800	3.3	22	3.0	31	2.3	28	2.8	29
1100	1.9	23	2.8	30	2.2	27	2.8	29
1400	1.7	21	2.5	29	2.1	27	2.7	27
1700	1.7	21	2.7	30	2.1	26	2.7	27

STATION	32		33		34		35	
START TIME(GMT)	PMCH	PDCH	PMCH	PDCH	PMCH	PDCH	PMCH	PDCH
JULY 09								
0800	2.8	30	2.6	27	3.4	27	2.3	30
1100	2.8	30	2.6	28	2.9	27	2.4	30
1400	2.7	30	2.6	26	2.6	26	2.5	29
1700	2.3	29	2.4	26	2.6	25	-	-
2000	2.6	29	2.5	26	2.5	25	2.3	29
2300	2.6	29	2.5	26	2.6	25	2.3	30
JULY 10								
0200	2.9	29	2.4	25	2.7	27	2.4	30
0500	2.7	30	2.6	27	2.7	26	2.4	30
0800	2.7	30	2.5	28	2.9	26	2.3	30
1100	2.8	31	2.6	28	2.8	27	2.5	30
1400	2.7	30	2.7	28	2.7	26	2.5	30
1700	2.7	30	3.3	33	2.6	26	-	-
2000	2.6	29	2.6	27	2.3	23	-	-
2300	2.6	29	2.5	27	2.6	25	-	-
JULY 11								
0200	2.7	30	2.5	28	2.6	25	-	-
0500	2.8	30	2.6	28	2.7	26	-	-
0800	2.6	30	2.6	29	2.6	24	-	-
1100	2.7	30	2.7	29	-	-	-	-
1400	2.7	30	3.1	29	2.7	26	-	-
1700	2.6	29	2.5	28	2.5	24	-	-

- NO DATA

TABLE 11 (CON'T)

600 KM ARC

TRACER CONCENTRATIONS (PARTS PER 10^{15})

STATION	36		37		38	
	PMCH	PDCH	PMCH	PDCH	PMCH	PDCH
START TIME(GMT)						
JULY 09						
0800	2.1	26	2.6	27	-	-
1100	2.0	26	2.3	27	2.1	27
1400	2.0	25	2.3	26	2.0	26
1700	2.0	26	2.5	27	1.8	26
2000	2.0	26	2.1	28	1.7	24
2300	2.0	26	2.6	27	1.8	24
JULY 10						
0200	2.2	25	2.0	26	1.9	25
0500	2.1	26	2.3	26	2.0	25
0800	2.1	26	2.0	28	2.4	31
1100	2.2	26	2.6	26	2.0	25
1400	2.2	26	2.8	26	2.0	24
1700	2.0	26	2.5	26	1.9	24
2000	1.9	26	2.7	28	1.8	25
2300	1.8	23	2.7	27	1.9	25
JULY 11						
0200	2.1	24	2.6	30	2.0	26
0500	2.0	24	2.2	27	2.0	26
0800	1.9	23	2.6	34	2.2	27
1100	2.0	25	2.8	30	2.1	26
1400	2.0	24	-	-	2.0	25
1700	1.9	24	-	-	1.9	25

- NO DATA

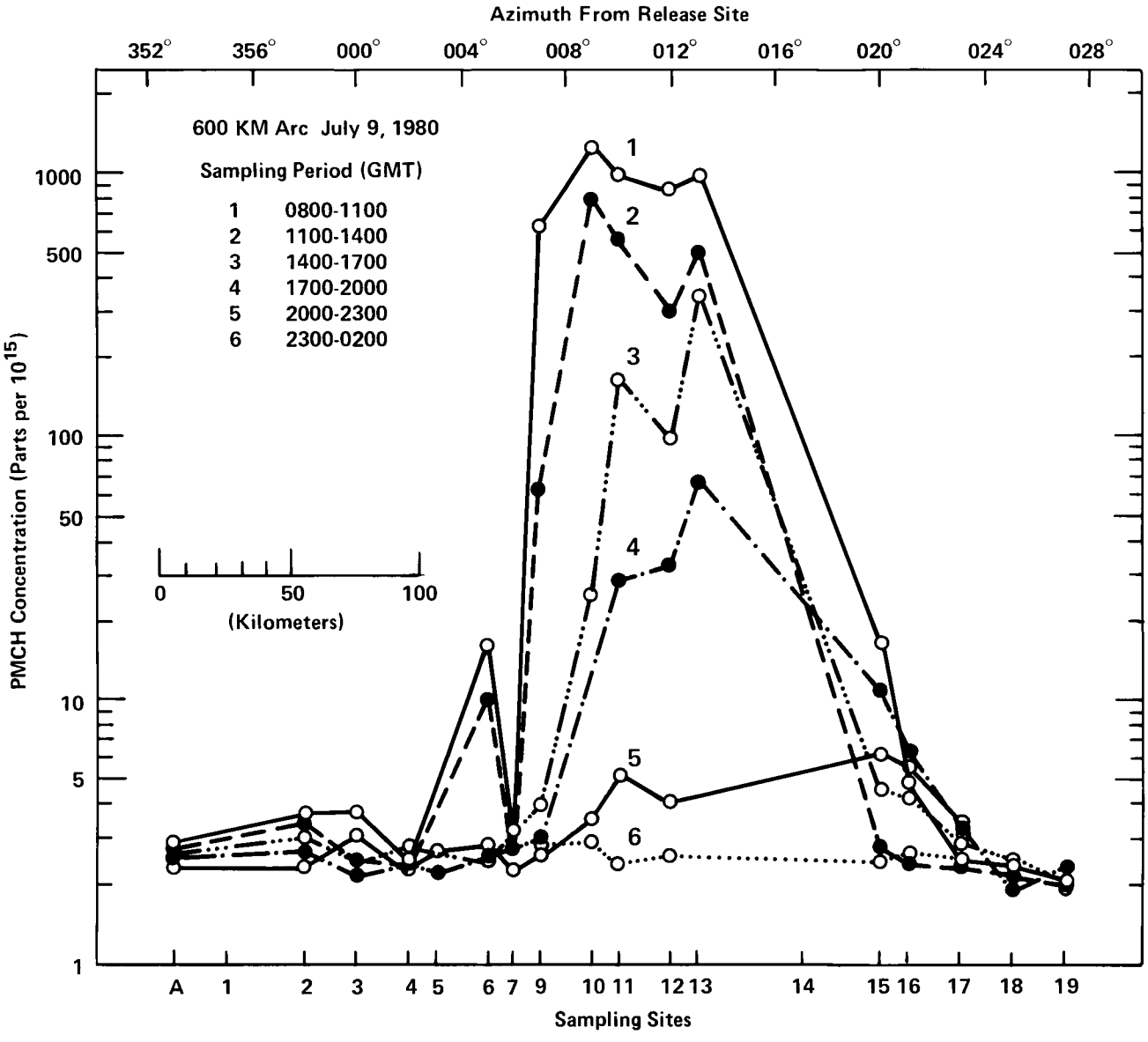

Figure 12. Average 3-hour PMCH concentrations along the 600 km arc.

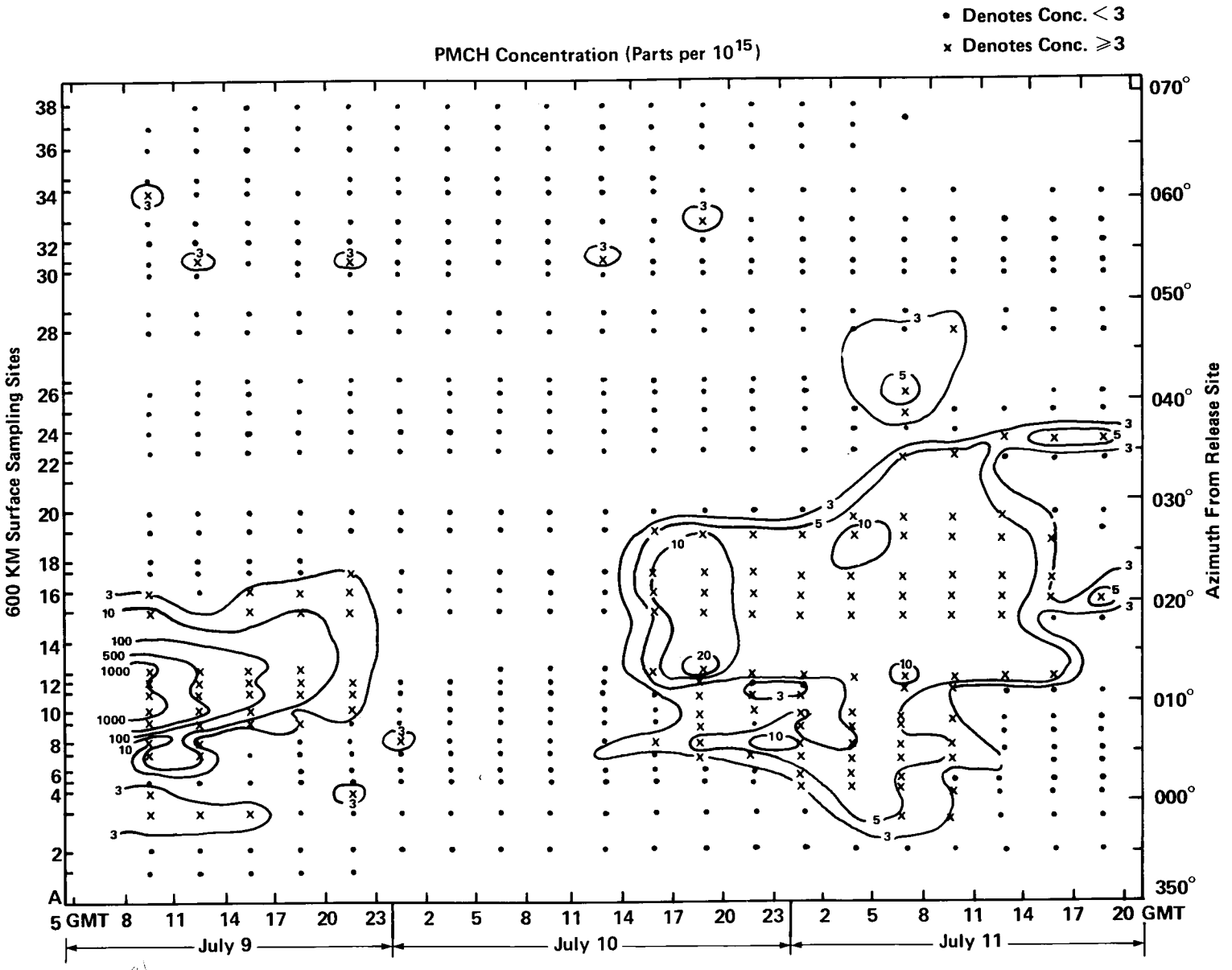

Figure 13. Average 3-hour PMCH concentrations along the 600 km arc for the period July 9, 0800 GMT to July 11, 2000 GMT.

4.1 Tracer Release

The two perfluorocarbons and SF_6 were released over a 3-hour period (1900-2200 GMT) using the same release systems at the same site as in the first experiment. Release amounts, shown in Table 12, were calculated to produce concentrations well above the detection limits at the 100 km arc. Also shown are the tracer release ratios (by volume).

Table 12. Tracer Releases on July 11, 1980.

Tracer	Release Amount (kg)
PMCH	21
PDCH	26
SULFUR HEXAFLUORIDE	283

Tracer Release Ratios (by Volume)

PMCH/PDCH:	0.91
SF_6/PMCH:	33
SF_6/PDCH:	30

4.2 Sampling Array

In this experiment, sampling was done only at 100 km downwind of the release site, using the same array as in the first experiment. Based on the latest trajectory forecast, three EML sampling teams deployed the BATS sequential samplers to Sites 13-30. The tracer release began at 1900 GMT (2 PM) and the samplers were set to start at 2200 GMT (5 PM) and take nine 45-minute samples. The same samplers were used in both experiments with sampling tubes 1-10 being exposed in the July 8 experiment and tubes 12-13 exposed on July 11. As in the first experiment, a whole-air sampler was co-located with each sequential sampler to collect a single sample over the entire period for comparison of SF_6 and perfluorocarbon concentrations.

4.3 Meteorology

As shown in Figure 14, on July 11 the broad area of high pressure continued to dominate most of the U.S. The wind flow in the boundary layer over the 100 km experimental area remained from the south-southwest.

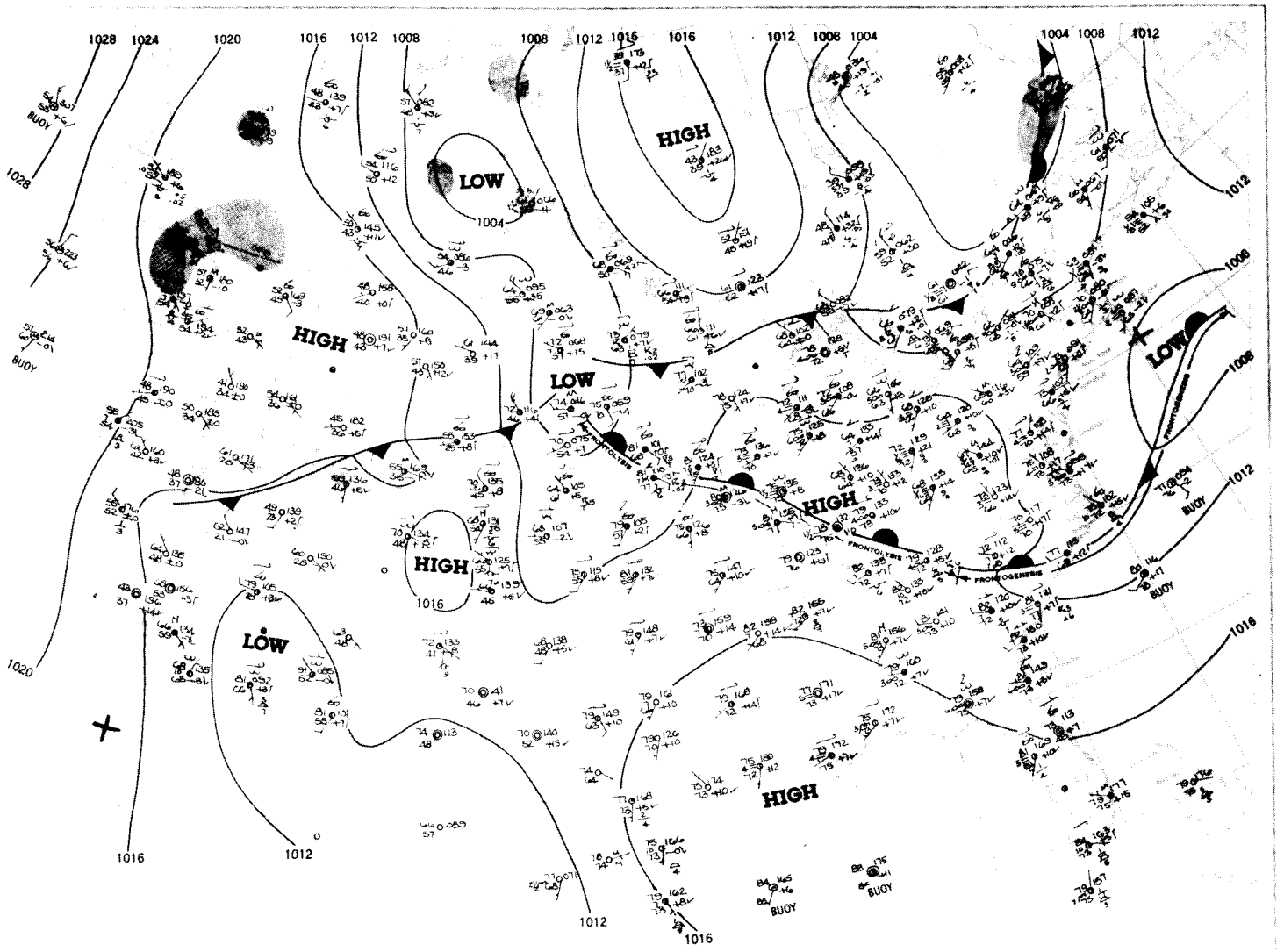

Figure 14. Surface weather map for 1200 GMT, Friday, July 11, 1980.

4.3.1 Special rawinsonde observations

Special rawinsonde observations up to 500 mb were again taken at Tinker AFB starting on the morning of July 11. Data are given in Table 13 for observations from July 11, 1800 GMT to July 12, 0000 GMT. The calculated transport layer height (TLH) and average wind speed and direction in the layer are given for each sounding.

4.3.2 Post-facto tracer trajectories

Tracer trajectories shown in Figure 15 were calculated for the start and end of the release period using the Tinker AFB soundings. Since the plume was still passing over the 100 km arc at the time of the last Tinker sounding, an average wind of 180 deg and 6 m/sec was estimated to complete the 2200 GMT trajectory. The estimated plume width is shown in the figure. The calculated plume position and arrival time at the 100 km arc agree well with the measured tracer data (see Figure 16).

4.4 Sampling Results

The BATS sequential samplers were installed at Sites 13 through 30. The 45-minute tracer concentrations are given in Table 14. Data for sites not listed were lost due to sampler malfunction (Site 13) or analysis problems (Site 25).

The PMCH results are plotted in Figure 16. The initial sampling period (2200-2245 GMT) showed concentrations near background at all sampling locations. The next sampling period (2245-2330 GMT) shows concentrations at Sites 14 through 24 at about 50 times background levels. During the third sampling period (2330-0015 GMT) peak plume concentrations are reached at Sites 14 through 21 with decreasing concentrations to the east.

During subsequent sampling periods, an orderly decrease in the PMCH concentration occurs at all sampling sites and by the eighth sampling period (0315-0400 GMT) the concentration are approaching background levels again.

Since there was not sampling west of Site 14, the plume width could not be determined but the trajectories (Figure 15) suggest that the plume did not extend much beyond Site 14.

Whole-air samples again were unusable due to contamination which apparently occurred in the BNL Laboratory.

5. EVALUATION OF PERFLUOROCARBON TRACER SYSTEM

These experiments were designed primarily as a proof-test of the perfluorocarbon tracer system. Our evaluation will focus on the performance of the release, sampling, and analysis systems, and the reliability of the tracer concentration measurements.

5.1 Tracer Release

The two perfluorocarbons were released via separate, but identical, aerosol spray mechanisms. In both experiments, 3-hour releases were accomplished without any problem and the actual release amounts were within 10% of the intended amounts.

TABLE 13. TINKER AFB RAWINSONDE DATA FOR THE JULY 11 EXPERIMENT.

11 JUL 80 18GMT

HT M,MSL	DIR DEG	SPD M/SEC
387	200	2.0
610	200	4.1
915	200	6.6
1220	205	7.7
1542	215	6.6
1830	225	6.1
2135	225	5.1
2440	215	4.6
2745	210	5.1
3203	185	6.1
3355	180	6.6
3660	190	5.6
4270	205	3.6

HT PRES M,MSL	MB	TEMP DEG K
387	967	309
1322	871	299
1524	850	296
2343	774	288
2454	764	290
3203	700	286
3848	647	284
5960	500	270

TLH M,MSL	DIR DEG	SPD M/SEC
2410	211	5

11 JUL 80 20GMT

HT M,MSL	DIR DEG	SPD M/SEC
387	240	4.1
610	190	6.1
915	195	6.6
1220	200	6.1
1531	195	6.1
1830	200	7.2
2135	195	5.6
2440	200	5.6
2745	210	5.6
3050	215	5.1
3193	200	5.6
3355	200	5.6
3660	210	5.1

HT PRES M,MSL	MB	TEMP DEG K
387	966	310
1531	850	297
2534	756	288
2648	746	288
3193	700	286
3323	689	286
3553	670	286
5960	500	271

TLH M,MSL	DIR DEG	SPD M/SEC
2770	197	6

11 JUL 80 22GMT

HT M,MSL	DIR DEG	SPD M/SEC
387	240	3.0
610	205	6.1
915	205	7.2
1220	210	7.7
1524	215	6.1
1830	210	6.1
2135	205	6.1
2440	210	7.2
2745	215	6.6
3186	215	6.6
3355	210	5.6
3660	220	4.4
4270	220	5.1
4880	235	3.6
5795	285	5.6

HT PRES M,MSL	MB	TEMP DEG K
387	965	311
524	950	308
1524	850	298
2664	744	287
2944	720	287
3186	700	286
3719	656	286
5950	500	270

TLH M,MSL	DIR DEG	SPD M/SEC
2850	209	6

12 JUL 80 00GMT

HT M,MSL	DIR DEG	SPD M/SEC
387	210	3.0
610	190	5.6
915	180	6.6
1220	180	6.6
1518	190	6.6
1830	195	6.6
2135	200	6.6
2440	210	7.2
2745	225	7.6
3050	235	6.6
3185	245	5.6
3660	290	4.1
4270	270	3.0
4880	240	3.6
5185	265	3.0

HT PRES M,MSL	MB	TEMP DEG K
387	964	310
1518	850	299
2581	751	288
3002	715	287
3185	700	287
3532	671	287
5950	500	271

TLH M,MSL	DIR DEG	SPD M/SEC
2830	196	6

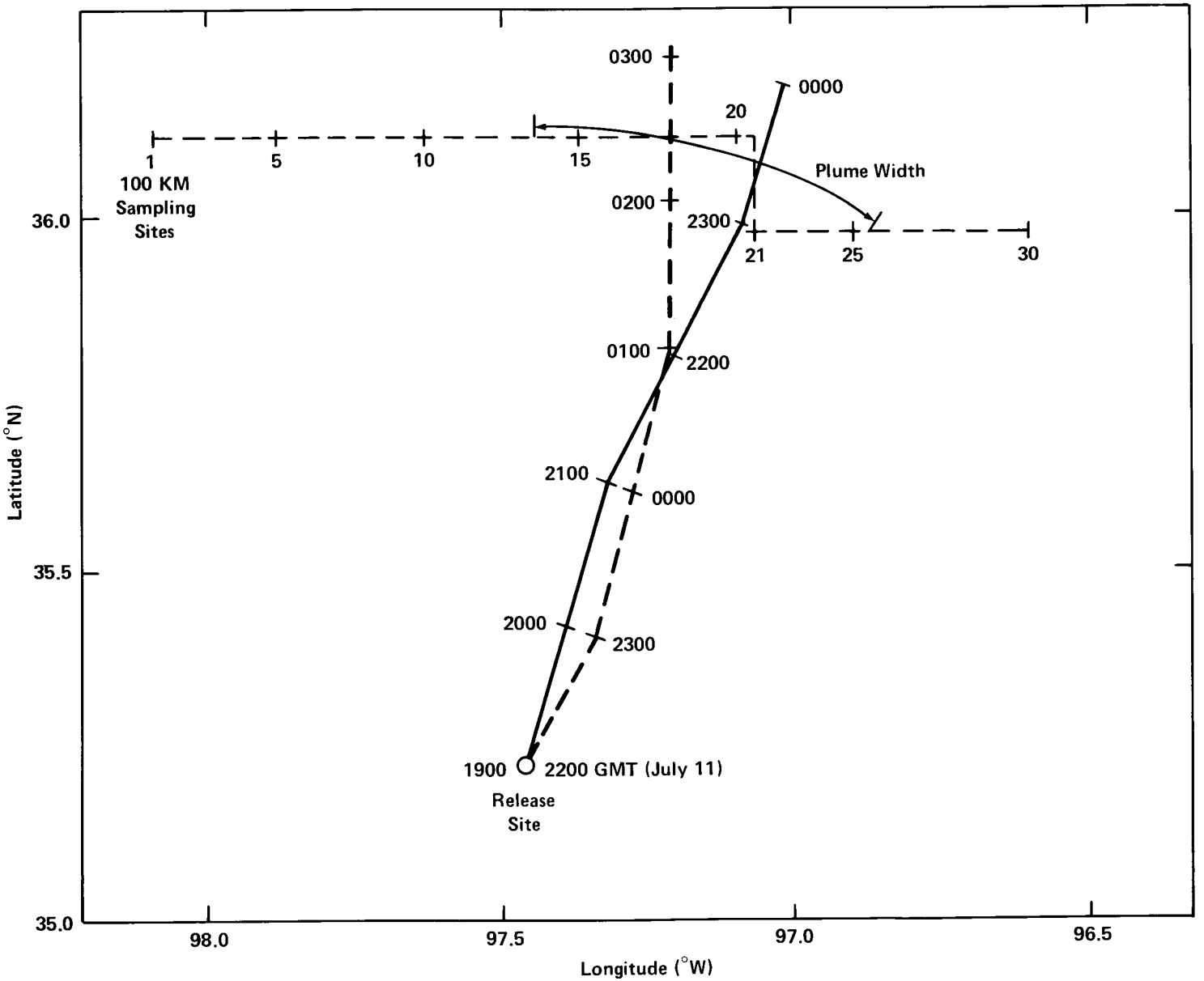

Figure 15. Calculated transport layer trajectories to the 100 km arc for the 3-hour tracer release on July 11.

TABLE 14

100 KM ARC

TRACER CONCENTRATIONS (PARTS PER 10^{15})

STATION	14		15		16		17	
	PMCH	PDCH	PMCH	PDCH	PMCH	PDCH	PMCH**	PDCH**
START TIME(GMT)								
JULY 11								
2200	3.6	27	3.*	26	3.8	26	2.	23
2245	38.	61	50.*	87	110.	157	12.	9
2330	270.	337	280.	337	241.	323	180.	150
JULY 12								
0015	178.	221	190.	255	142.	207	90.	70
0100	65.	97	-	-	68.	117	50.	50
0145	37.	70	1.*	70	25.	54	28.	24
0230	13.	44	2.*	38	9.5	35	12.	13
0315	5.4	34	2.*	26	5.3	30	-	-
0400	-	-	3.*	25	4.7	30	-	-

STATION	18		19		20		21	
	PMCH	PDCH	PMCH	PDCH	PMCH	PDCH	PMCH	PDCH
START TIME(GMT)								
JULY 11								
2200	4.5	33	2.*	36	4.2	27	3.5	28
2245	75.	111	40.*	74	38.	60	127.	186
2330	259.	349	330.	400	302.	357	360.	430
0015	216.	299	-	-	236.	288	126.	164
JULY 12								
0100	99.	149	-	-	66.	95	42.	71
0145	49.	87	-	-	30.	55	21.	45
0230	24.	57	-	-	23.	47	11.*	33
0315	10.	40	-	-	7.7	30	1.*	27
0400	7.1	36	-	-	-	-	11.*	25

STATION	22		23		24		26	
	PMCH*	PDCH	PMCH	PDCH	PMCH	PDCH	PMCH	PDCH
START TIME(GMT)								
JULY 11								
2200	10.	34	4.0	28	8.2	28	3.5	25
2245	300.	400	219.	263	56.	84	3.9	26
2330	200.	240	145.	175	76.	109	14.	37
JULY 12								
0015	100.	84	46.	67	33.	60	7.9	31
0100	40.	65	20.	40	25.	51	3.5	25
0145	20.	39	-	-	9.3	31	3.1	25
0230	-	30	6.*	25	5.5	30	3.1	24
0315	5.	30	3.*	22	5.4	28	3.3	24
0400	2.	28	9.*	24	5.2	28	3.1	24

SEE FOOT NOTE A

- NO DATA

* VALUE UNCERTAIN DUE TO CONTAMINATION IN LAB ANALYZER.

** POOR DESORPTION. CORRECTION ESTIMATED.

A SAMPLING SITES 27-30 HAD BACKGROUND PMCH AND PDCH CONCENTRATIONS IN ALL SAMPLES.

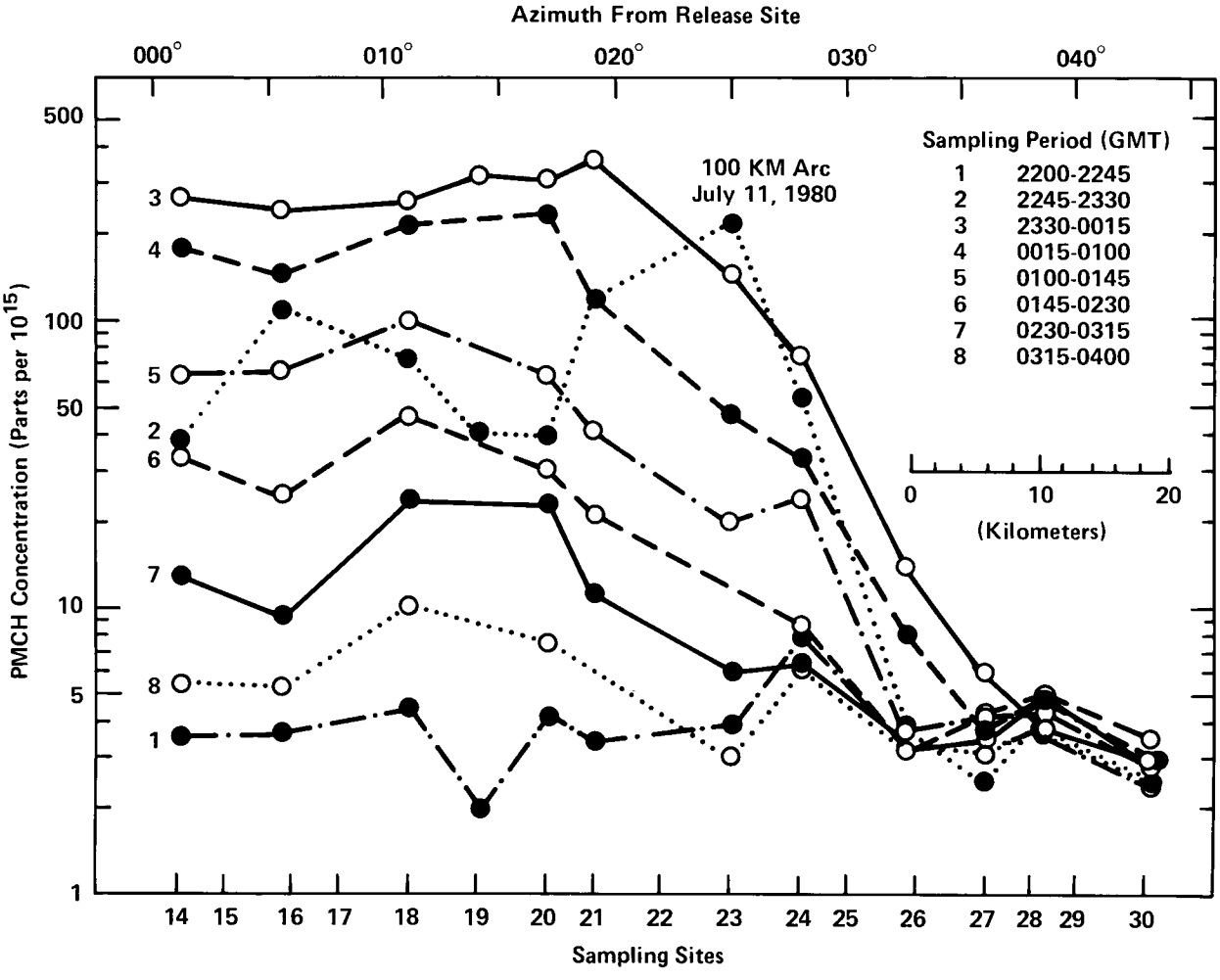

Figure 16. Average 45-min PMCH concentrations along the 100 km arc from the July 11 experiment.

A newly designed release mechanism, in which the tracers are vaporized, was not ready in time for these experiments but it was tested and used successfully in September, 1980. The new system provides more precise control and continuous recording of release rates.

5.2 BATS Sampling and Analysis System

The heart of the perfluorocarbon tracer system is the BATS automatic sequential sampler and the associated analysis apparatus.

The over-all performance of the BATS system was excellent in this first field trial. As shown in Table 15, 72% of the 1121 scheduled samples provided good tracer concentration data. Of the 28% lost, or poor data, 5% was due to human error (e.g., failure to turn on the sampler) and the remainder was about equally divided between sampler malfunctions and sample analysis problems. Sampler malfunctions were due most often to pump failures. Some units developed problems in the electronic control circuitry. Modifications to the design of the BATS sampler are under consideration to alleviate these problems.

Table 15. Performance of BATS Sampling-Analysis System.

	Number	Percent
Scheduled Samples	1121	100
Good Data	810	72
Sampling Failures	134	12
Analysis Failures	123	11
Human Error	54	5
Total Lost or Poor Data	311	28

Several problems in the analysis apparatus and procedures became evident during analysis of the large number of samples. The most troublesome was the presence of a contaminant that interferred with the PMCH chromatograph peak in many analyses. Eventually, it was discovered that the contamination was coming from a screen used in the Porapak QS trap in the analysis apparatus. The resolution of this, and other minor problems, should reduce the amount of data lost in analysis to well below the 10% level experienced in this experiment.

Another problem that complicates the determination of tracer concentrations is the non-linear response of the present electron-capture detector. Various attempts to reduce this non-linearity, which shows a change in response factor as much as 2-fold, depending on the size of the sample being analyzed, have not succeeded. Evidence in the literature suggests that the strength of the 8 mCi ^{63}Ni foil in the electron capture detector is about an order of magnitude too intense for the strongly electronegative PFTs. Lower activity foils will be substituted in an attempt to correct this problem.

5.3 Reliability of BATS Concentration Measurements

The reliability of tracer concentrations obtained with the BATS sequential samplers can be checked by comparing the PMCH and PDCH measurements. If the tracers behave identically in the atmosphere and the tracer release, sampling, and analysis systems function perfectly, the measured PMCH/PDCH concentration ratio in every sample (after backgrounds are subtracted) would be the same as the ratio of the release amounts of the two tracers. Comparison of the measured tracer ratios with the release ratio therefore provides a good test of the entire tracer system.

Figure 17 shows a plot of PMCH versus PDCH concentrations measured with the sequential samplers on the 100 km arc in the July 8 experiment. Background concentrations (2.4 parts per 10^{15} for PMCH and 26 parts per 10^{15} for PDCH) have been subtracted out. Only those 22 samples where both tracers had concentrations at least twice background were used for this comparison. When the concentrations are near background, uncertainties in the background value can have a large effect on the tracer ratio. The straight line in Figure 17 represents the tracer release ratio of 1.18. The measured mean ratio in the 22 samples is exactly what it should be and there is remarkably little scatter about the true ratio.

Very similar results were obtained at the 600 km arc (Figure 18). There are 13 samples with concentrations at least twice background and the mean measured PMCH/PDCH ratio is 1.19, again with very little deviation from the release ratio of 1.18. The inset shows a plot of PMCH versus PDCH for the highest concentrations observed during the second appearance of tracer on the 600 km arc on July 10. The PDCH concentrations were less than twice background in all of these samples. It is, therefore, not surprising that the data show more scatter. The mean ratio of 1.09 is still quite close to the 1.18 release ratio.

Many samples obtained at the 600 km arc over the 3-day period showed background concentrations. The background to be subtracted from each concentration was estimated separately from each sampler. Estimated background values varied from 2.2 to 2.5×10^{-15} for PMCH and from 24 to 28×10^{-15} for PDCH. The consistency of the background measurements attests to the good precision of tracer measurements at these levels.

Figure 19 shows a plot of PMCH against PDCH concentrations on the 100 km arc for the July 11 experiment. In this experiment there were 31 samples with concentrations at least twice background. The mean measured PMCH/PDCH ratio was 0.88, with very little scatter about the release ratio of 0.91.

In the two experiments there were a total of 66 BATS sequential samples with concentrations at least twice background. Most of the measured PMCH/PDCH ratios are within ±5% of the release ratio, all are within ±20%, over a concentration range from 20 to 5000 parts per 10^{15}. These results are excellent but they do not constitute a complete test of the BATS samplers. Any inaccuracies in sample volume or mechanical problems (e.g., timing errors) would have the same effect on both tracers. Therefore, as a further test, duplicate BATS samplers were set up at three of the sampling sites. As luck would have it, data from one sampler in each pair, were lost due to failure of the sampler or analysis problems. Some degree of independent verification of the BATS result was achieved by comparison with whole-air samples (Section 5.5).

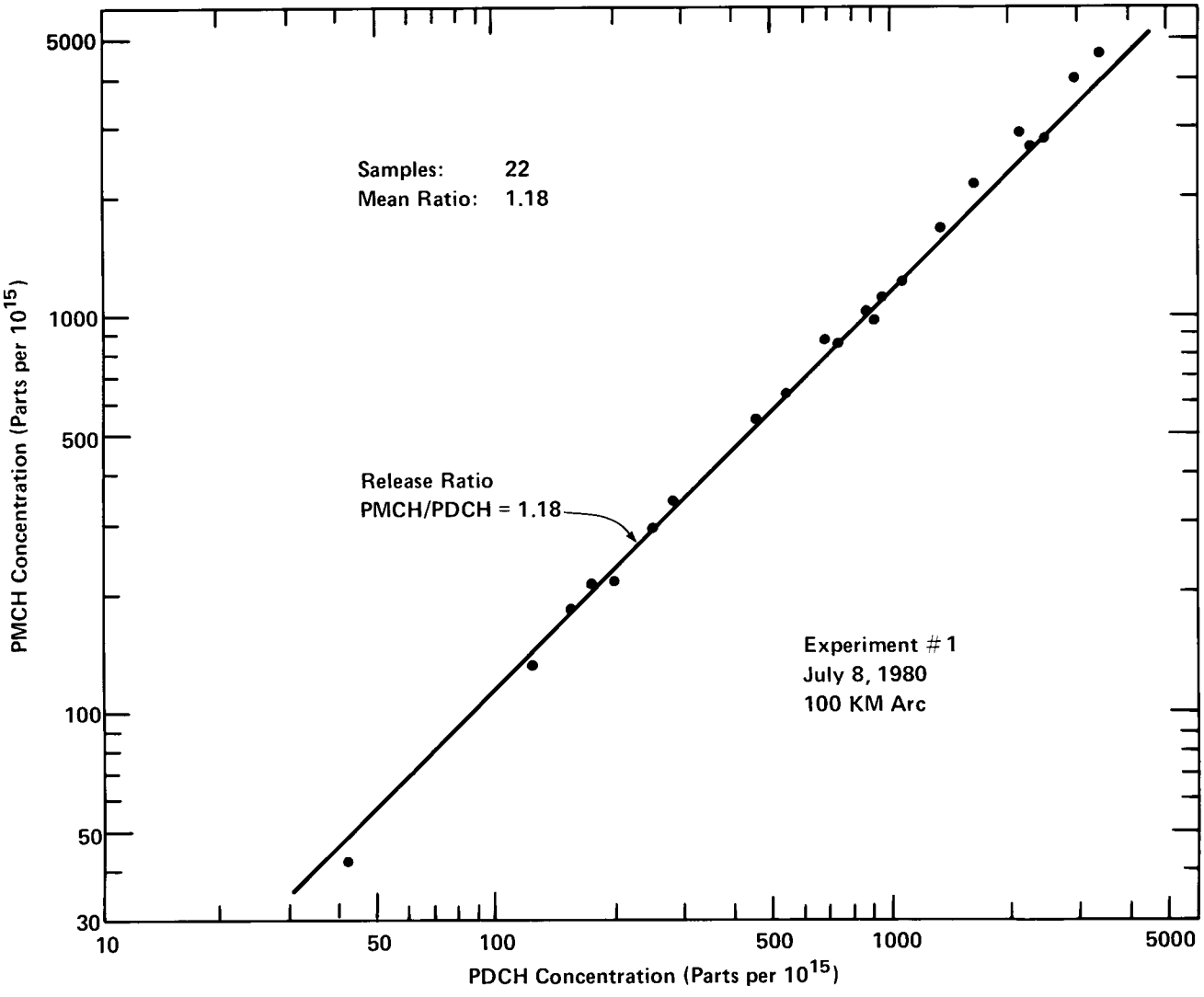

Figure 17. Comparison of PMCH and PDCH concentrations from the 100 km BATS samples on July 8.

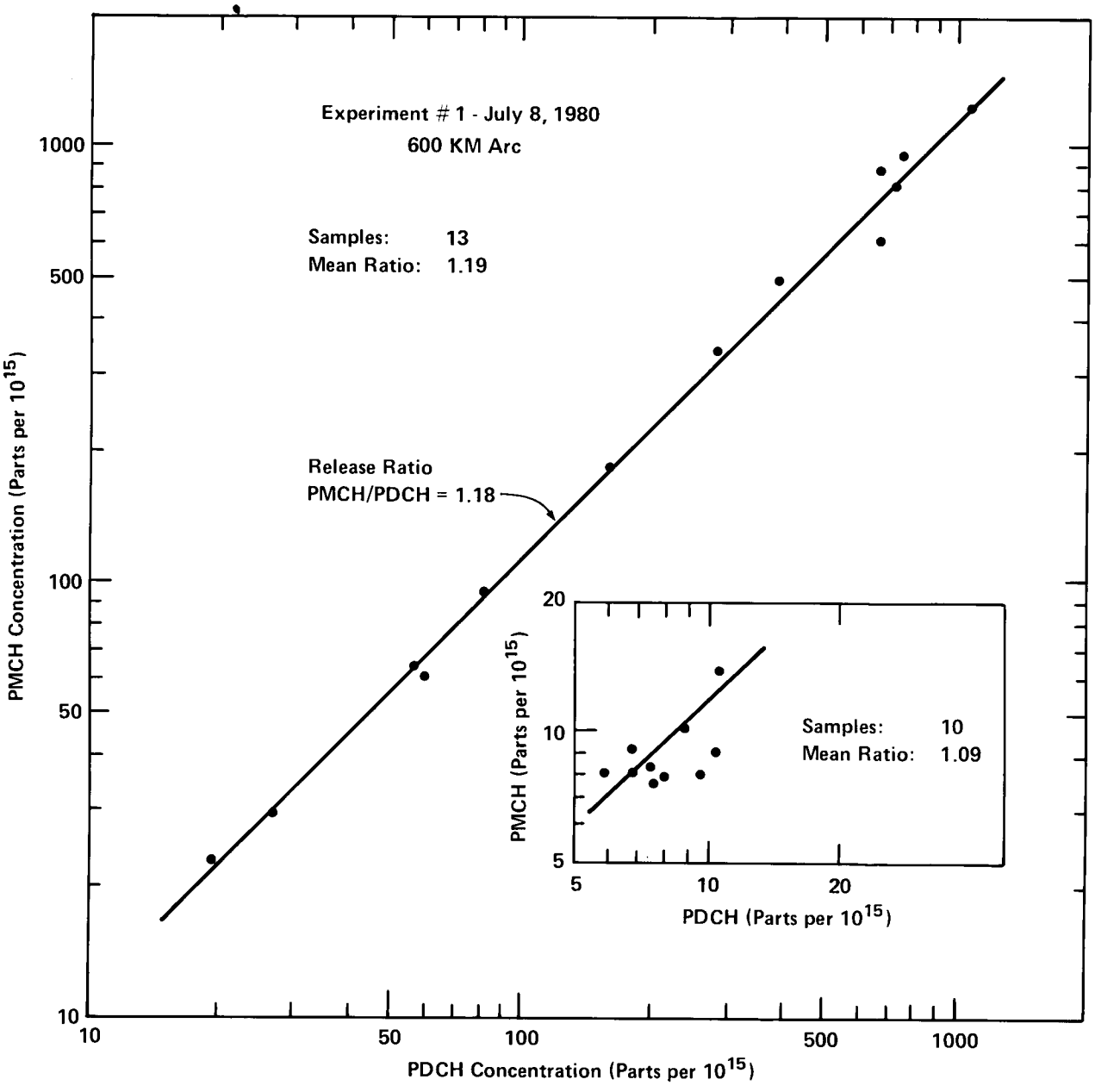

Figure 18. Comparison of PMCH and PDCH concentrations from the 600 km BATS samples.

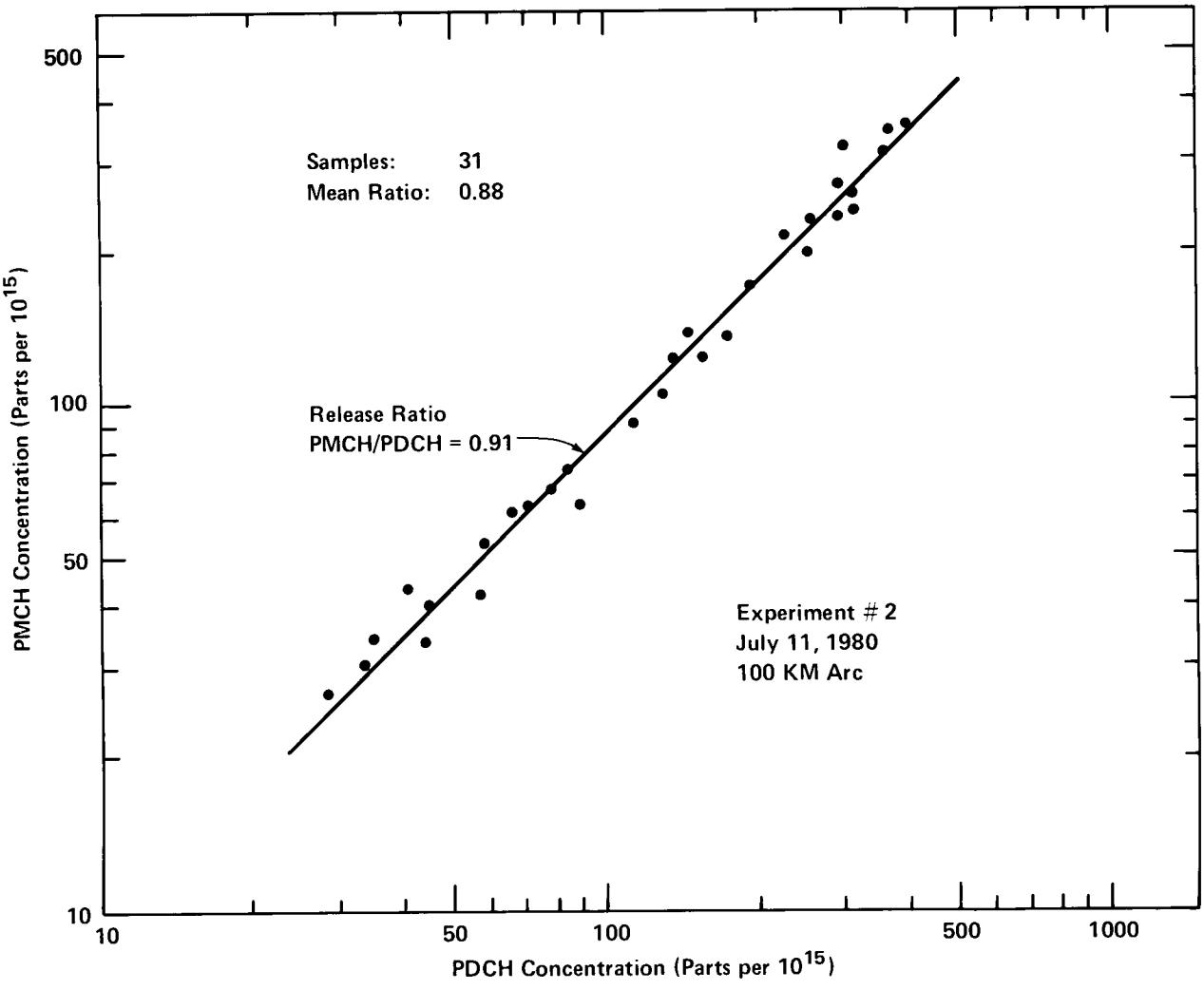

Figure 19. Comparison of PMCH and PDCH concentrations from the 100 km BATS samples on July 11.

5.4 Comparison with Other Tracers

Whole-air samples were collected in plastic bags at sequential sampling sites on the 100 km arc in the July 8 experiment in order to compare SF_6, and heavy methane tracer measurements. Unfortunately, most of the whole-air sample aliquots sent to BNL for analysis became contaminated with PFTs and SF_6 (apparently at BNL) to an extent that made them useless for tracer intercomparisons. It should be noted that the BATS sequential samplers were designed to avoid the contamination problems that had been encountered previously in handling whole-air samples.

In spite of the contamination problem, some good data have been salvaged from the whole-air samples. Aliquots were sent to LASL for analysis of heavy methanes and SF_6. Seven of the samples collected in the aircraft flight over the 100 km arc, that were analyzed at LASL, appeared to be free of PFT contamination when analyzed at BNL. After subtraction of appropriate background values: 2.4×10^{-15} for PMCH, 26×10^{-15} for PDCH and 600×10^{-15} for SF_6 (Me-21 background is nil), the tracer concentrations were plotted in Figure 20. On the upper left, PMCH is plotted against PDCH. The PMCH/PDCH ratios are quite good in these samples with a mean value of 1.08 and little scatter about the line representing the release ratio of 1.18.

On the upper right, PMCH concentrations determined at BNL are plotted against SF_6 concentrations determined at LASL. The mean SF_6/PMCH ratio in these samples is 3.08 compared to the releae ratio of 3.41 and the individual sample ratios show only slightly more scatter than the PMCH/PDCH ratios.

The lower graph in Figure 20 shows PMCH concentrations plotted against Methane-21. The mean PMCH/Me-21 ratio is 131, very close to the release ratio of 137 and again the scatter is small. Considering that the heavy methane and perfluorocarbon determinations are made by totally different analysis techniques (mass spectrometry for the methanes, gas chromatography for the PFTs) these excellent results inspire confidence in both tracer systems.

In all three comparisons shown in Figure 20, the mean of the measured tracer ratios is within 10% of the release ratio and all individual sample ratios are well within a factor of two of the release ratio. We can conclude from these data that all tracers behaved the same in the atmosphere, faithfully following the air motions with no significant depletion mechanism out to 100 km from the source. We would expect the same to hold true at 600 km and beyond. We hope to confirm this with a total of ten whole-air samples, collected at two LASL cryogenic sites within the plume at the 600 km arc, which have not yet been analyzed.

5.5 Comparison of BATS with Whole-Air Samples

It was intended that PFT concentrations from the BATS sequential samplers on the 100 km arc would be compared with those from the co-located whole-air bag samples. Contamination of the aliquots sent to BNL from the bag samples rendered them useless for intercomparison of perfluorocarbon measurements. However, the analyses of SF_6 and Me-21 concentrations, done at LASL, are available for five of the bag samples, along with PFT analyses from the BATS sequential sampler at the same locations. The PMCH and PDCH concentrations from the 45-minute BATS sequential samples were averaged over the time interval that the whole-air sample was collected at each location. The concentration of each tracer is shown in the upper part of Table 16. Background concentrations were subtracted from each value and tracer ratios were determined as shown in the lower portion of the table. The mean

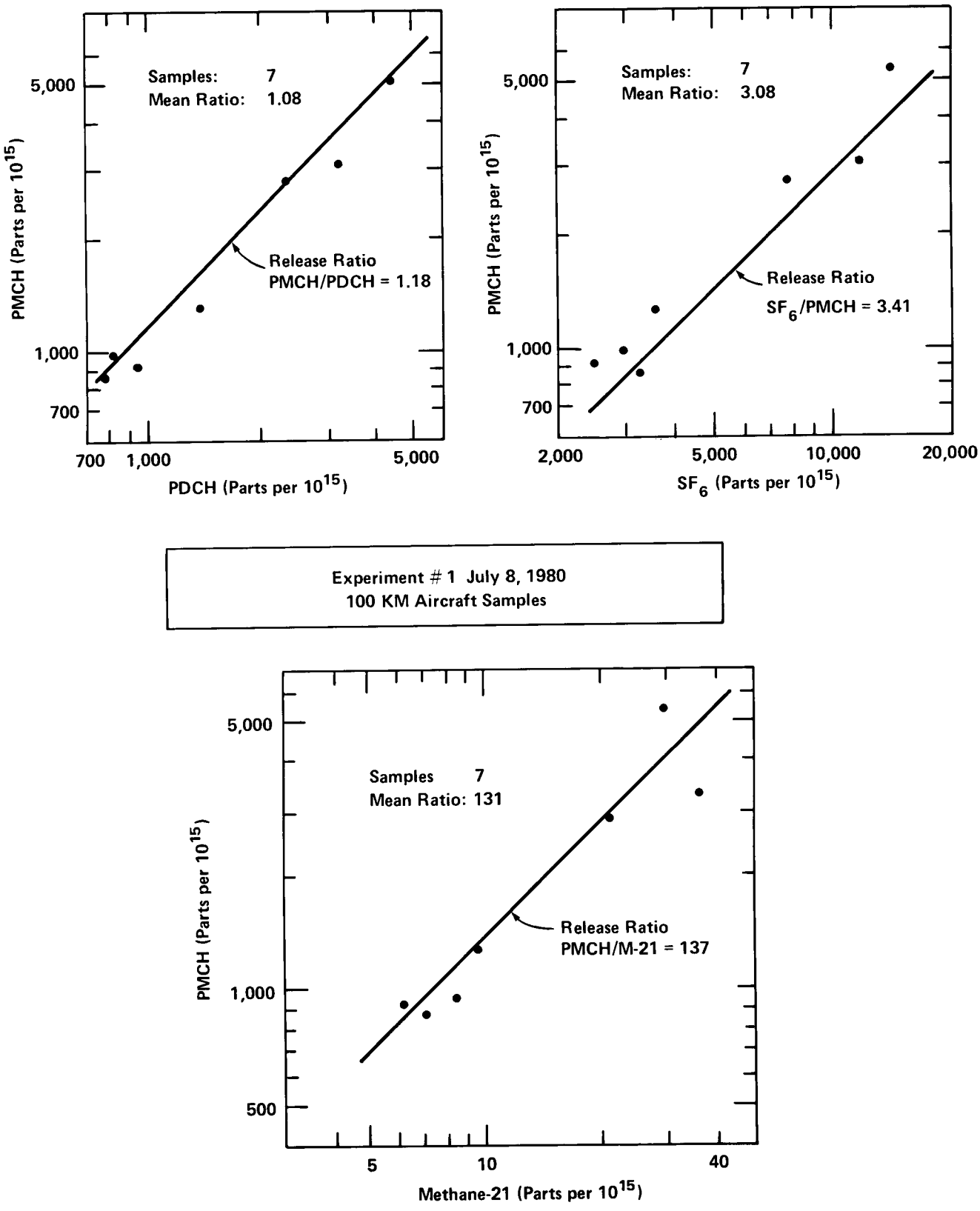

Figure 20. Comparisons of tracer concentrations in whole-air samples collected in the flight over the 100 km arc on July 8.

Table 16. Comparison of BATS sequential samples with whole-air samples at the 100 km arc (July 8, 1980).

Site	Whole Air Bag Sampling Period (GMT)	Tracer Concentrations (parts per 10^{15}) PMCH[1]	PDCH[1]	SF_6[2]	Me-21[2]
12	2130-0435	1030	810	3250	7.93
13	2121-0427	1090	950	3530	8.10
14	2012-0418	700	570	4030	9.37
16	2032-0401	450	410	2060	3.92
17	2001-0357	700	600	2720	5.50

(1) BATS (sequential air sampler) concentration averaged over the period of the whole air bag sample (analysis by BNL).

(2) Whole air sample (analysis by LASL).

Tracer Ratios

Site	PMCH/PDCH	SF_6/Me-21	SF_6/PMCH	PMCH/Me-21
12	1.31	332	2.58	129
13	1.17	362	2.69	134
14	1.28	366	4.93	74
16	1.15	372	3.29	113
17	1.21	385	3.04	127
Mean Ratio	1.22	363	3.31	115
Release Ratio	1.18	467	3.41	137

PMCH/PDCH ratio from the BATS samplers is very close to the release ratio and the individual values are within ±10% of the mean. The SF_6/Me-21 ratios from the whole-air samples are consistent though they are about 20% lower than the release ratio. The mean ratio between SF_6 from the whole-air samples and PMCH from the BATS samplers is 3.31, very close to the release ratio of 3.41 although the scatter of individual ratios is relatively large. The mean ratio between PMCH (BATS) and Me-21 (whole-air) is 115, about 15% lower than the release ratio. One reason for the discrepancy between the BATS results and the whole-air sampler results may be the failure of the whole-air sampler to pump air at a constant rate. It was discovered during the experiment that the bag sampler pumping rate was erratic, probably because it was not designed for the extreme heat encountered in this experiment. In spite of this problem, the correspondence between the BATS and whole-air sampler results is good; all measured tracer ratios are well within a factor of two of the release ratios.

5.6 Performance of Real-Time Samplers

The real-time continuous PFT monitor, intended for use in the sampling aircraft, was not available because of various malfunctions. Efforts to repair the instrument in the field were unsuccessful. The difficulties appear to be correctable and efforts are continuing to develop this instrument into a reliable continuous airborne monitor.

The Dual-Trap sampler functioned well and was used to provide field analyses of some of the whole-air bag samples as well as real-time tracer concentration measurements on the 100 km arc. Some difficulty was experienced in positioning the Dual-Trap sampler within the tracer plume because of shifting wind conditions at the arc. However, an excellent set of 5-min plume concentrations was obtained alongside of a BATS sampler (see Table 9). Concentrations obtained with these two samplers show very good agreement. The Dual-Trap sampler was later used extensively in the ASCOT drainage wind experiments and provided hundreds of 5-minute samples with real-time readout of PMCH and PDCH concentrations.

6. SUMMARY

These experiments have successfully demonstrated the capabilities of the perfluorocarbon tracer system and the feasibility of carrying out atmospheric transport and dispersion experiments over distances of 1000 km or more. A release of 65 kg/hr of PMCH produced concentrations at the 600 km arc almost three orders of magnitude above the background value of 2.4 parts per 10^{15}. This suggests that a PMCH release rate of about 10 kg/hr should be sufficient to provide plume measurements out to 100 km from the release point.

Reliability of the BATS sequential samplers is judged to be very good for the first trial of a completely new system. About 12% of the 1121 scheduled samples were lost because of sampler malfunctions. Another 11% were lost in analysis. Modification of the BATS pump and relatively minor changes in the analysis apparatus should significantly improve the reliability of the BATS system.

Simultaneous measurements of PMCH and PDCH concentrations with the BATS system were remarkably consistent. The PMCH/PDCH ratios in all samples were very close to the tracer release ratio; most measured ratios were within ±5% of the release ratio.

Most of the whole-air samples, intended for comparison of PFT measurements with SF_6 and heavy methane tracers, were of no use because of contamination of the bag samples. However, a small number of samples, that could be analyzed for all five tracers, showed generally good agreement, sufficient to establish that all tracers behaved the same in the atmosphere.

Deployment of many samplers over the large area involved in a long-range experiment can be very costly and present difficult logistics problems. One of the objectives of this experiment was to test the feasibility of using the National Weather Service sub-station network of over 12,000 sites to deploy the BATS sequential samplers. Substation specialists delivered the samplers to 39 selected sites on the 600 km arc where cooperative observers, who take routine temperature and precipitation measurements for the NWS, operated the samplers. The 600 km sampling program was very successful as the cooperative observers carried out their assigned role with competence and enthusiasm. Future long-range tracer experiments should take advantage of the capability inherent in the NWS sub-station network.

7. ACKNOWLEDGMENTS

This work was supported by the Office of Health and Environmental Research, Department of Energy and the Environmental Protection Agency.

Development of the perfluorocarbon tracer system has been carried out by the Air Resources Laboratories, NOAA, in collaboration with the Dept. of Energy's Environmental Measurements Laboratory and Brookhaven National Laboratory.

We wish to acknowledge our debt to Dr. James E. Lovelock who first conceived the perfluorocarbon tracer system and designed the prototype samplers and analyzer.

The success of this experiment would not have been possible without the cooperation of the many individuals, from the different agencies and laboratories, listed at the beginning of this report.

To Dr. Edwin Kessler, Director, National Severe Storms Laboratory, we owe a debt of gratitude not only for the support he and his staff provided but also for the hospitality extended to the experimenters stationed at Norman, OK and the spirit of cooperation that prevailed.

To Dr. Harold Meyers, Superintendent of the Agronomy Research Station, Oklahoma State University, we wish to express our appreciation for the assistance he and the OSU students provided in shipping, storing, and operating sampling equipment along the 100 km arc and also for providing work space at considerable personal inconvenience.

Without the excellent cooperation and dedication of the National Weather Service, and the cooperative observers listed in Table 4, this experiment would not have been possible. We extend our thanks to Bernard Spittler, Chief Substation Management Branch, NWS, and his associates who were instrumental in setting up the 600 km sampling program and instructing the cooperative observers in the operation of the sequential samplers.

We wish to express our appreciation to Dr. Jeremy Hales, Battelle Pacific Northwest Laboratories, for his cooperation in providing a DC-3 aircraft and knowledgeable crew for airborne tracer sampling missions.

We wish to thank Paul Guthals and his colleagues at the Los Alamos Scientific Laboratory for participating in our 600 km experiment and providing heavy methane and SF_6 analyses for comparison with perfluorocarbon measurements.

Special thanks are extended to Col. Van Louven, Chief M/Sgt. Greening and the members of the 6th Air Weather Squadron, USAF, for taking special rawinsondes that provided data vital to the experiments.

8. REFERENCES

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Lovelock, J.E. (1974): Improvements in the Experimental Methods for a Long-Range Tracer Experiment. Unpublished report. Available at the Air Resources Laboratories, NOAA, Silver Spring, MD 20910.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/7-81-006		

4. TITLE AND SUBTITLE
Demonstration of a Long-Range Tracer System Using Perfluorocarbons - Final Report

5. REPORT DATE
January 1981

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Gilbert J. Ferber, Kosta Telegadas, Jerome L. Heffter, C.Ray Dickson, Russell N. Dietz, Philip W. Krey

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
National Oceanic and Atmospheric Administration
Air Resources Laboratories
8060 13th Street
Silver Spring, MD 20910

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
EPA-IAG-D5-0693

12. SPONSORING AGENCY NAME AND ADDRESS
U.S. Environmental Protection Agency
Office of Research & Development
Office of Energy, Minerals & Industry
Washington, D.C. 20460

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE
EPA-ORD

15. SUPPLEMENTARY NOTES
This project is part of the EPA-planned and coordinated Federal Interagency Energy/Environment R&D Program.

16. ABSTRACT

Regional-scale tracer experiments are needed to validate atmospheric dispersion aspects of air pollution models. The capability of a new system, using perfluorocarbon tracers (PFTs), for long-range dispersion experiments at reasonable cost, was demonstrated in two experiments. Two PFTs were released simultaneously with SF_6 and two heavy methanes.

The PFT system uses automatic sequential samplers and provides rapid, inexpensive analyses down to .002 ppt. PFT concentrations were measured 600 km away, up to three days after release. Performance of the PFT system was excellent and a very consistent set of tracer data was obtained.

17. KEY WORDS AND DOCUMENT ANALYSIS (Circle One or More)

a. DESCRIPTORS			b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Ecology	Hydrology, Limnology	Energy Conversion		6F 8A 8F
Environments	Biochemistry	Physical Chemistry		
Earth Atmosphere *	Earth Hydrosphere	Materials Handling		8H 10A 10B
Environmental Engineering	Combustion	Inorganic Chemistry		
Geography	Refining	Organic Chemistry		7B 7C 13B
Other:		Chemical Engineering	Atmospheric Tracers Dispersion Experiments	

18. DISTRIBUTION STATEMENT
Release unlimited.

19. SECURITY CLASS *(This Report)*
Unclassified

21. NO. OF PAGES
64

20. SECURITY CLASS *(This page)*
Unclassified

22. PRICE

EPA Form 2220-1 (9-73)

☆ U.S. GOVERNMENT PRINTING OFFICE: 1981—777-002/1216 Region No. 8

DEMONSTRATION OF A LONG-RANGE TRACER SYSTEM
USING PERFLUOROCARBONS - FINAL REPORT

ERRATA SHEET

1. p.6, Section 3, line 2; ... and two heavy methane tracers.

2. p.8, Section 3.2.1, 1st ¶, last line; ... 45-minute samples starting at 2100 GMT.

3. p.13, Table 4, Station No. 7 (Lincoln); 40.85°N 96.75°W.

4. p.37, Section 4.2, line 7; ... and tubes 12-20 exposed on July 11.

5. p.52, Summary, 1st ¶, last line; ... out to 1000 km from the ... .