AD-764 893

LONG-RANGE TRANSPORT AND DIFFUSION EXPERIMENTS

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National Oceanic and Atmospheric Administration

Prepared for:

Advanced Research Project Agency

May 1973

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Final Report

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89

U.S. DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration
ENVIRONMENTAL RESEARCH LABORATORIES
Air Resources Laboratories
Silver Spring, Maryland 20910
June 12, 1973

Final Technical Report

Sponsored by

Advanced Research Projects Agency

ARPA Order No. 1841

Program Code No. 1F10

Name of Contractor: U. S. Department of Commerce
National Oceanic and Atmospheric Administration

Effective Date of Contract: 7 May 1971

Contract Expiration Date: 31 December 1972

Amount of Contract: $100,000

Contract No. VT/1416

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Short Title: BLUENOSE

ACKNOWLEDGEMENTS

This research was supported primarily by the Department of Defense, Advanced Research Projects Agency, through the Air Force Technical Applications Center (AFTAC). The advice and assistance of Major Frederick B. Buoni, AFTAC contract monitor, are gratefully acknowledged.

The field test could not have been conducted without the cooperation and assistance of many organizations and individuals. Field support (meteorological measurements, sampling and sample analysis) was provided by C. Ray Dickson and his staff at the Air Resources Laboratories Field Research Office, Idaho Falls, under contract to the Division of Reactor Development and Technology, U.S.A.E.C. Data analysis and interpretation reported here was supported by the Earth Sciences Branch, Division of Biomedical and Environmental Research, U.S.A.E.C.

Dr. Ray L. McCarthy and Dr. Clark Hoffman of E. I. DuPont de Nemours and Company provided much information on fluorocarbon tracer compounds and Dr. Hoffman also assisted in developing tracer release techniques. Dr. William J. Maeck and Joseph H. Keller of Allied Chemical Corporation provided facilities and carried out the tracer release.

Dr. Russell N. Dietz and Edgar A. Cote of Brookhaven National Laboratory, Department of Applied Science, provided a portable gas chromatograph for airborne SF_6 sampling. Mr. Cote operated the sampler during the tracer experiment and Dr. Dietz provided sample analyses, instrument calibration and advice on data interpretation.

Dr. James Lovelock of Brazzos, Ltd., designed a gas chromatograph for fluorocarbon analyses, assisted in setting up the instrument, suggested

the cryogenic sampling technique and provided other consultation. Dr. Peter Simmonds of Jet Propulsion Laboratory, working with Dr. Lovelock, also provided advice and assistance in setting up the chromatograph.

Analysis of the ^{85}Kr samples was under the supervision of Robert Bench of Airco, Inc., Murray Hill, New Jersey.

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

SUMMARY

The purpose of this project is to investigate the feasibility of conducting long-range atmospheric tracer experiments to study transport and diffusion of gaseous plumes over continental distances. Such experiments would be used to extend our understanding of the behavior of pollutant plumes to regional and continental scales, and improve our ability to relate the location and strength of pollutant sources to distant air concentration measurements.

This study considered the feasibility of a series of experiments in which a tracer gas would be released in the western U.S. and cross-country air sampling would be carried out to determine the distribution of the tracer as a function of time and distance from the source, at ground level and aloft. The feasibility of such large-scale experiments rests on the availability of a non-toxic tracer gas that can be detected at very low concentrations using relatively simple and inexpensive techniques. Ideally, the amount of tracer already present in the atmosphere should be below the level of detectability.

Two main alternatives ~~have been~~ were considered. The first involves taking advantage of a source of opportunity, ^{85}Kr emitted from a nuclear fuel reprocessing plant, to obtain long-range plume data. Drawbacks are the high cost of ^{85}Kr sampling and analysis, which limits the number of samples that can be processed, and the high probability that the plume would be lost in the general background levels of ^{85}Kr at the extreme ranges (thousands of km) of interest to this study. Calculations indicate that detection of a ^{85}Kr plume is feasible at distances to at least 1500 km.

The second ~~[illegible]~~ would use CF_2Br_2 or $C_2F_4Br_2$. A short range evaluation was made using SF_6 as a control tracer.

The second alternative is to develop new tracers and techniques for continental-scale experiments. Potential long-range tracers investigated in this study include sulfur hexafluoride (SF_6) and two fluorocarbons 12B2 (CF_2Br_2) and 114B2 ($C_2F_4Br_2$). All are detectable by electron-capture gas chromatography at extremely low concentrations.

The use of SF_6 as a long-range tracer appears impractical because of the high average background concentrations already in the atmosphere (on the order of 1 part in 10^{13}) and likely interference from many strong local sources. However, SF_6 is still an excellent tracer for distances up to several hundred kilometers.

A field experiment was conducted in September 1972 to test equipment and techniques for release, sampling and analysis of 12B2 and 114B2 and to obtain plume data to a distance of 90 kilometers. These tracers, along with SF_6, ^{85}Kr, methyl iodide, and uranine dye were released from a 76-meter stack over a 3-hr period. A detailed discussion of this experiment is provided in section 2 of this report.

Measurements of SF_6, 12B2 and 114B2 were made with a dual-chromatograph designed for this project. The limits of detection with this instrument were about 5 parts in 10^{13} (by volume) for SF_6, 1 part in 10^{12} for 12B2 and 3 parts in 10^{12} for 114B2. Detection limits can be lowered by preconcentration of the sample. A simple cryogenic technique for field concentration of samples was successfully demonstrated and concentration factors up to about 40 were achieved; factors up to 80 have been attained in laboratory experiments. Concentration factors on the order of 10^3 may be possible after further development work. This would permit measurement of air concentrations down to about 1 part in 10^{15}, sufficient for a cross-country experiment.

In situ measurements of SF_6 plume profiles were also made with an airborne chromatograph designed by the Brookhaven National Laboratory. This instrument proved very useful and could also be adapted for use with 12B2 and 114B2.

Although basic procedures for cryogenic sampling and chromatographic analysis of 12B2 and 114B2 were successfully demonstrated, problems were encountered which indicate that more development work will be needed. The time required to develop a reliable long-range capability with these tracers cannot be fixed with any certainty. Therefore the alternative experimental approach using ^{85}Kr is recommended for more immediate results.

Instead of extensive cross-country sampling of plumes from a relatively few releases of special tracers, it is proposed to institute more limited long-range sampling of the existing plume emanating from the National Reactor Testing Station in Idaho. Cryogenic sampling equipment will be installed at 10-15 National Weather Service stations along an arc from Minnesota to Texas, about 1500 km from the source. Twice-daily samples will be collected over a 4-month period. At this distance (about 2 days travel) the plume will go through diurnal cycles of wind and stability conditions and will also show the effects of passage over mountainous terrain. Sample concentrations will be related to source strength, meteorological trajectories, wind speed, and stability.

Results will be used to develop a model of plume transport and diffusion to a distance of several thousand kilometers.

1. Proposed Long-Range Tracer Experiment

Two alternatives for conducting continental-scale atmospheric tracer experiments were considered in this feasibility study. The first involves a series of releases of special gaseous tracers (fluorocarbons 12B2 and 114B2) with an extensive cross-country sampling program. Results of a short-range field trial, discussed in detail in the next section, indicate the need for further development work before these new tracers can be used operationally. Therefore, a second approach, taking advantage of an existing ^{85}Kr plume, is recommended.

Operations at the National Reactor Testing Station in Idaho are expected to provide a nearly continuous plume for a period of about four months during the winter of 1973-74. It is proposed to develop cryogenic sampling equipment to be installed at 10-15 National Weather Service stations. Twice-daily samples (8-12 hr duration) will be taken routinely at these stations, located along an arc from Minnesota to Texas, about 1500 km from the source. Plume travel time at this distance should be about 2 days so the plume will experience diurnal cycles of wind and stability conditions. It will also undergo the effects of mountainous terrain as it passes from the Rockies to the Great Plains. Both effects need to be studied.

Peak sample concentrations at this distance are expected to be about 40 percent above background, which should be readily distinguishable with existing analysis techniques. If the sampling arc were placed further to the east, interferance from other sources could be anticipated.

Sampling results will be analyzed in conjunction with meteorological data to develop an improved model of plume transport and diffusion over a distance of thousands of kilometers. Different techniques used to construct meteorological trajectories will be tested to determine which best explain the sampling measurements. This experiment should also indicate which synoptic scale weather conditions produce the highest air concentrations at this distance from a source and provide information on the range of pollutant dilution factors produced under different meteorological conditions.

2. Short-Range Field Trial

An atmospheric tracer experiment was conducted during the afternoon of September 22, 1972 at the National Reactor Testing Station (NRTS) near Idaho Falls, Idaho. The primary purpose was to field-test instrumentation and techniques for release, sampling, and analysis of two materials (fluorocarbons 12B2 and 114B2) previously identified in this study as potentially useful tracers of atmospheric motions to distances of at least several hundred km. The second objective of the experiment was to obtain date on plume behavior to a distance of about 90 km from the source.

2.1 Site Description

The location of the National Reactor Testing Station in southeastern Idaho is shown by the shaded area in figure 1. The rectangle surrounding the site (130 km long by 100 km wide) roughly defines the area of interest for the short range experiment. The southwest-northeast orientation follows the Snake River Valley which tends to channel low-level wind flow over the area. Computer programs (1) have been developed to provide wind flow patterns and air trajectories based on data from about 20 wind towers within this area.

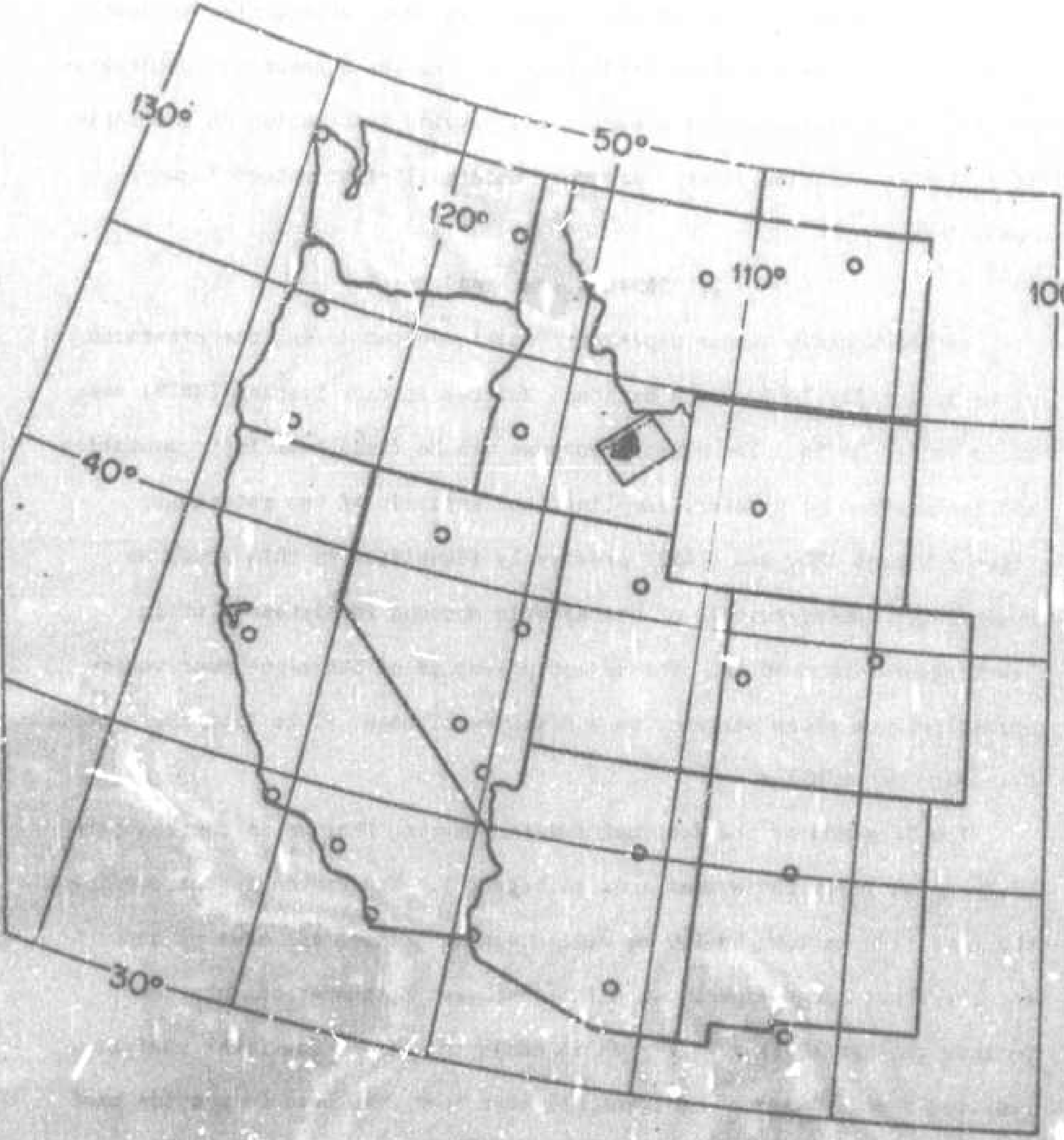


Figure 1. Location of National Reactor Testing Station (shaded area within rectangle).

The terrain at the test site is illustrated in figure 2 along with wind tower locations and the computational grid. The site is fairly level (mean elevation about 1500 m MSL) but bounded by rugged mountains to the northwest, northeast, and southeast with peaks from 2400 to 3000 m above sea level.

Four sampling "arcs" were set up at approximately 6, 18, 47 and 87 km downwind of the release point as shown in figure 3. Predetermined sampling positions on each arc are also indicated (7 on arc A, 9 each on arcs B and C, 14 on arc D). The sampling program is described in section 2.4.

2.2 Tracer Release

Six tracer materials were released simultaneously from the 76-meter stack of the NRTS chemical plant. Multiple tracers were used to allow intercomparisons and cross-checks of the behavior of different tracers and to indicate the accuracy and reliability of the various sampling and analysis techniques. Planned and actual total release amounts for the four tracers discussed in this report are shown in Table I. Small amounts of methyl iodide and uranine dye were also released. It was intended to release each tracer uniformly over a 3-hr period. The release began at 1233 MST.

Table I
Tracer Release Amounts

Tracer	Planned Release	Actual Release
SF_6	270 lbs.	274 lbs.
12B2*	390 lbs.	212 lbs.
114B2**	480 lbs.	116 lbs. (45 min.)
^{85}Kr	1000 Ci	1093 Ci

*CF_2Br_2 (manufactured by Imperial Chemicals, Inc. - UK)

**$C_2F_4Br_2$ (manufactured by Dupont - USA)

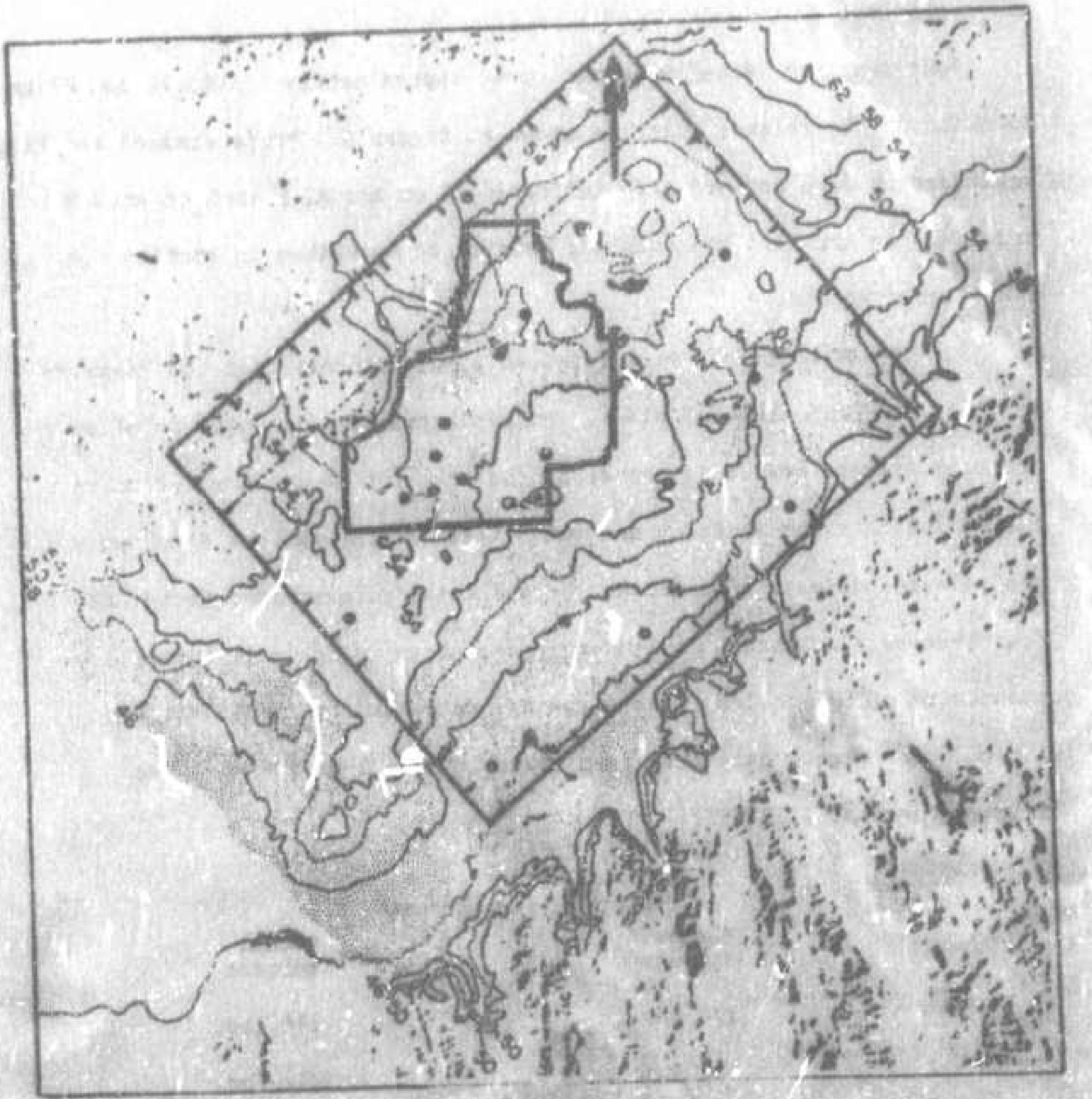


Figure 2. Relief map of the NRTS site. Contour values are in hundreds of feet. The area below 5000 ft. (1500 m) MSL is stippled. Tick marks along the sides of the rectangle indicate the computer grid spacing (about 7.6 km). Solid dots are wind tower locations.

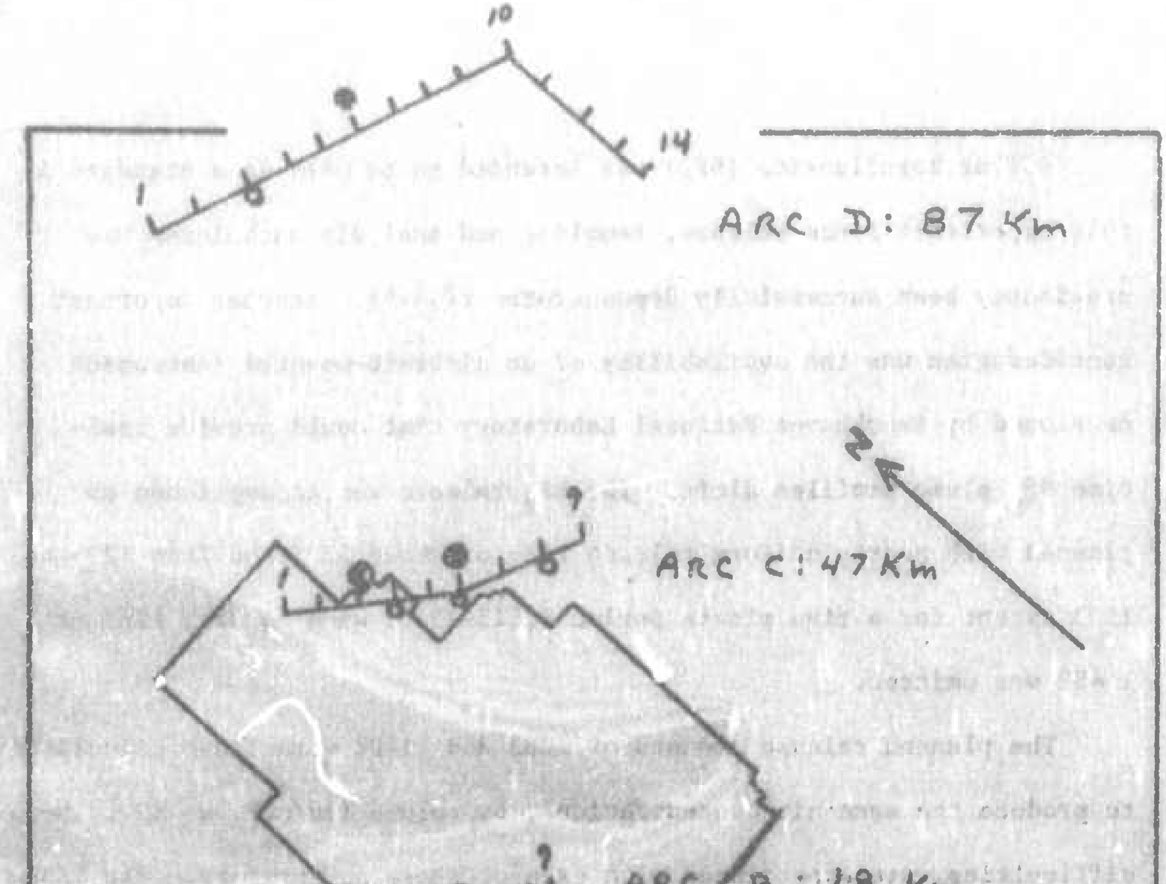


Figure 3. Sampling positions on the four arcs.

Sulfur hexafluoride (SF_6) was intended to be used as a standard in this experiment since release, sampling and analysis techniques had previously been successfully demonstrated (2,3,4). Another important consideration was the availability of an aircraft-mounted instrument developed by Brookhaven National Laboratory that could provide real-time SF_6 plume profiles aloft. The SF_6 release was accomplished as planned with nearly uniform release rate of about 12 g/sec from 1233 to 1533 except for a five minute period (1315-1320) when no SF_6, 12B2 or 114B2 was emitted.

The planned release amounts of 12B2 and 114B2 were those calculated to produce the same air concentrations, by volume (cc/cc), as SF_6. Some difficulties were experienced with each of these new tracers. The 12B2 was released at a fairly constant rate of about 9 g/sec during the same period as SF_6. The rate and total amount released were about one-half (0.53) that of SF_6 on a volume basis. Improper connector threadings on one of the 12B2 cylinders was responsible for the reduced release rate (only 2 of 3 cylinders were usable). The 114B2 was released at the desired rate (about 20 g/sec) during the early part of the release period (1233 - 1305 MST). At 1305 the dispensing pump failed, terminating the flow of 114B2. Flow was subsequently restored for approximately 3-minute periods at 1345, 1400, 1405, and 1408 MST. Some physical properties of 12B2 and 114B2 are given in Table 2.

Table 2

Physical Properties of Tracer Materials

	12B2	114B2
Formula	CF_2Br_2	$C_2F_4Br_2$
Molecular Weight	210	260
Boiling Point (°C)	22.8	47.3
Freezing Point (°C)	-141.5	-110.5
Critical Temp. (°C)	198.3	214.5
Critical Press. (psia)	593	506
Critical Density (g/cc)	.836	.790
Heat of Vaporization (cal/g)	28.3	~25

The radioactive gas, ^{85}Kr (half-life 10.7 years), is also under consideration as a long-range tracer. About 1090 Ci were released through the stack with the other tracers from 1236 to 1530 MST at an average rate of 6.3 Ci/min.

Total amounts of SF_6, 12B2, and 114B2 released were determined by weighing the containers before and after release; accurate flowmeters were used to monitor release rates. The tracers were injected into a stack airflow of approximately $3.1 \times 10^3 m^3$ per minute.

2.3 Meteorology

The spacing of routine upper-air measurement stations is suited to the definition of wind flow on a much larger scale than that of interest for this experiment. This may be seen in figure 1 where open circles indicate locations of the synoptic upper-air sounding stations of the National Weather Service. For this experiment, routine upper-air data were augmented by data from the NRTS wind tower network and trajectory information from radar-tracked tetroons.

The 700 mb charts for 1200 GCT (0500 MST) on September 22 and 0000 GCT, 12 hours later, are shown in figures 4 and 5. These charts show that at 700 mb (about 1500 m above the ground) the geostrophic wind flow was steady from the west-southwest during the experiment (1230-1730 MST). The 850 mb geostrophic wind (not shown) was nearly parallel to the 700 mb flow over the test site during this period.

The main features of the 3-hourly surface weather charts are shown in figures 6 - 8. The direction of plume travel is shown by a dashed arrow originating at the release point. On the day of the experiment, a cold front passed the test site at about 0330 MST and then stalled about 100 km to the south. Surface wind data measured at stations on the Snake River plain are plotted along with isobars indicating the surface geostrophic wind flow over the region. Winds in the surface layer tended to follow the shape of the Snake River Valley from Boise (BOI) to West Yellowstone (WEY). Thus, the flow was from the southwest or south-southwest over NRTS, apparently opposite to the geostrophic direction at 1800 GCT. Actually the surface wind flow was influenced by a meso-scale low pressure center in the extreme upper end of the Snake River Valley that was not detected in the synoptic scale pressure analysis. This situation is typical of many observed at the NRTS site.

Hourly average surface winds from the CFA tower (Table 3a), just south of the tracer release site, show strong steady flow from the 30° sector centered on southwest throughout the day. Upper winds (Table 3b) tended to become more westerly with increasing altitude. This is an interesting case illustrating the fact that synoptic scale geostrophic

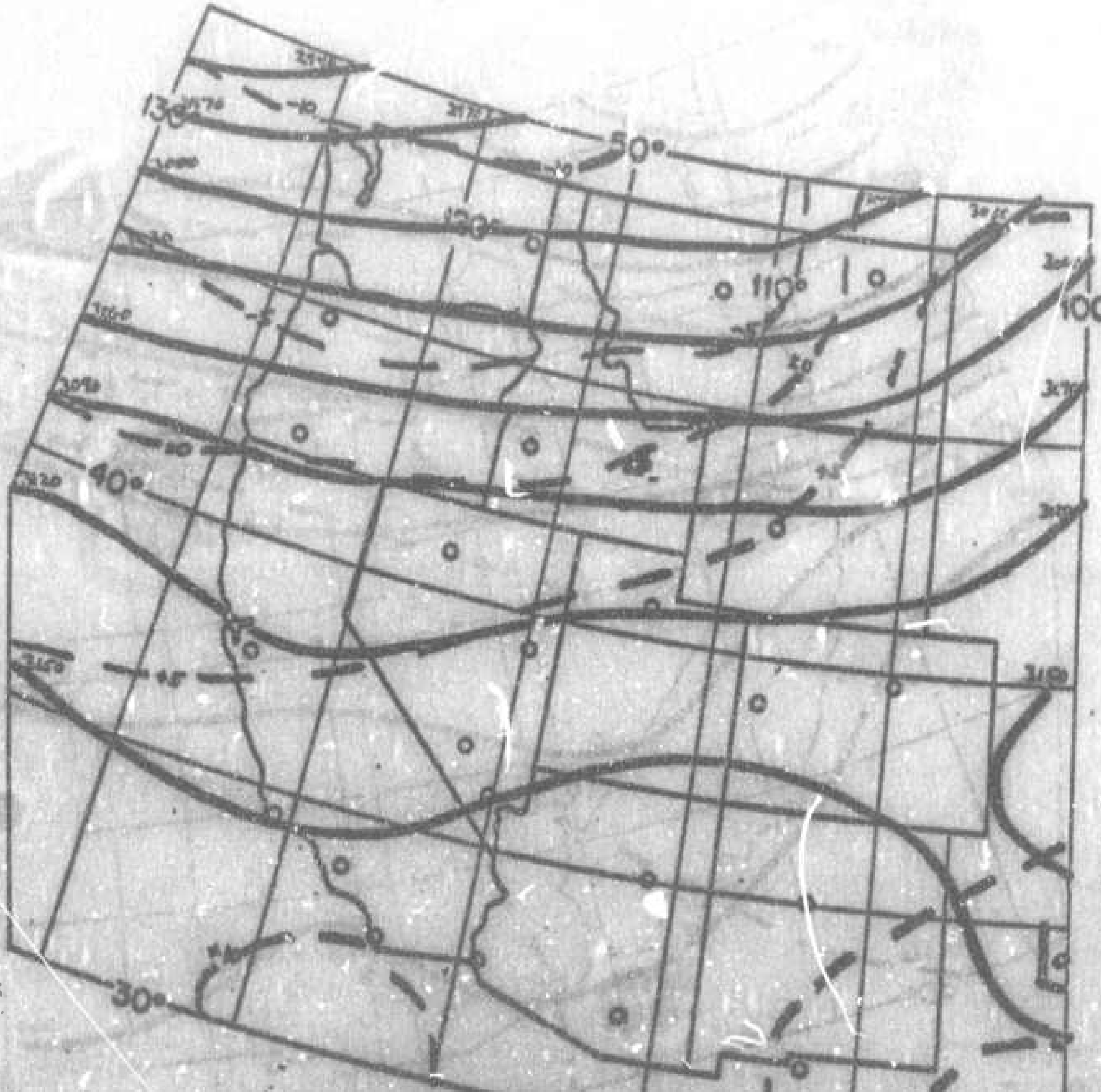


Figure 4. 700mb chart for 1200 GCT (0500 MST) on September 22, 1972.

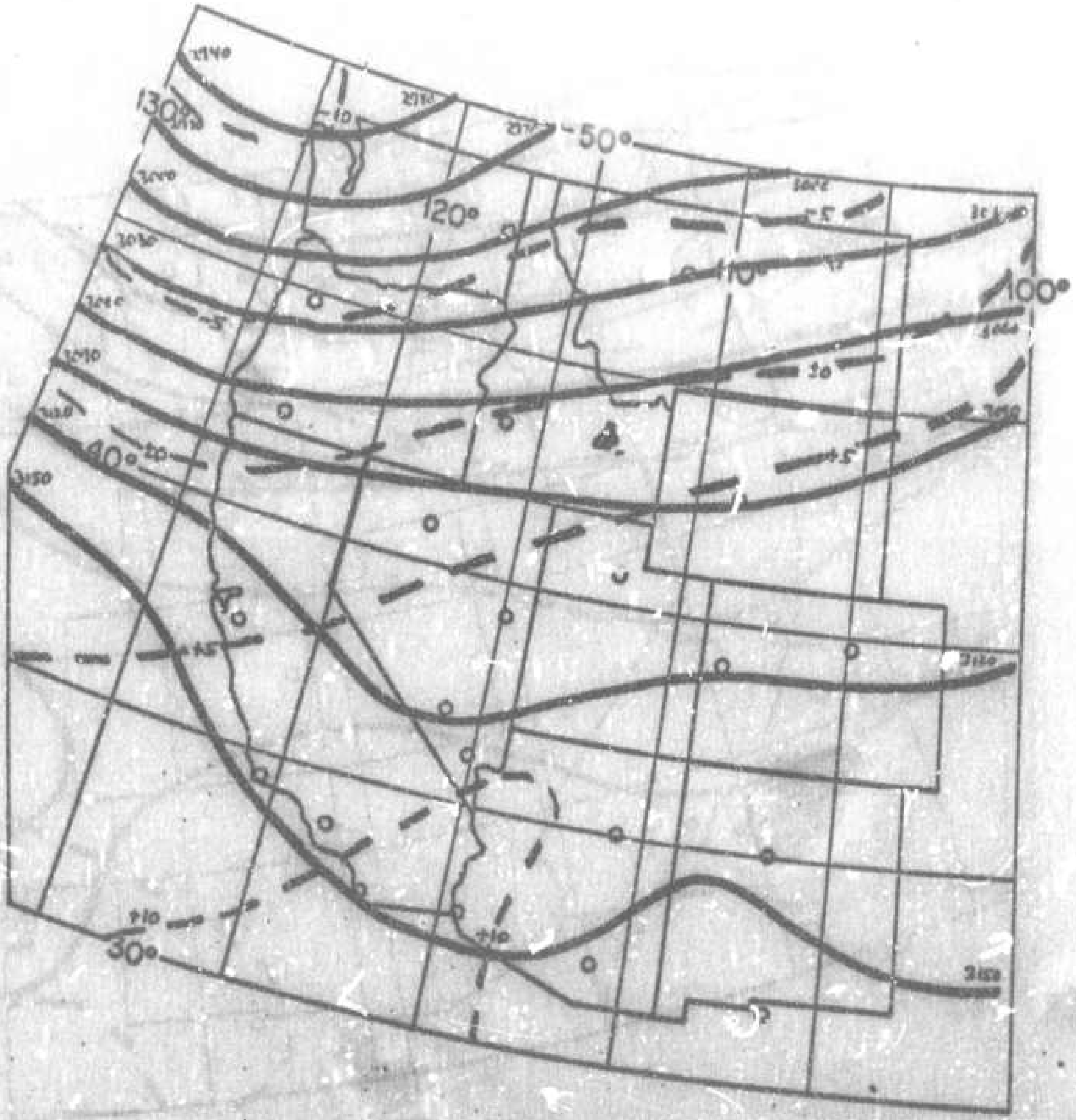


Figure 5. 700mb chart for 0000 GCT (1700 MST on September 22, 1972).

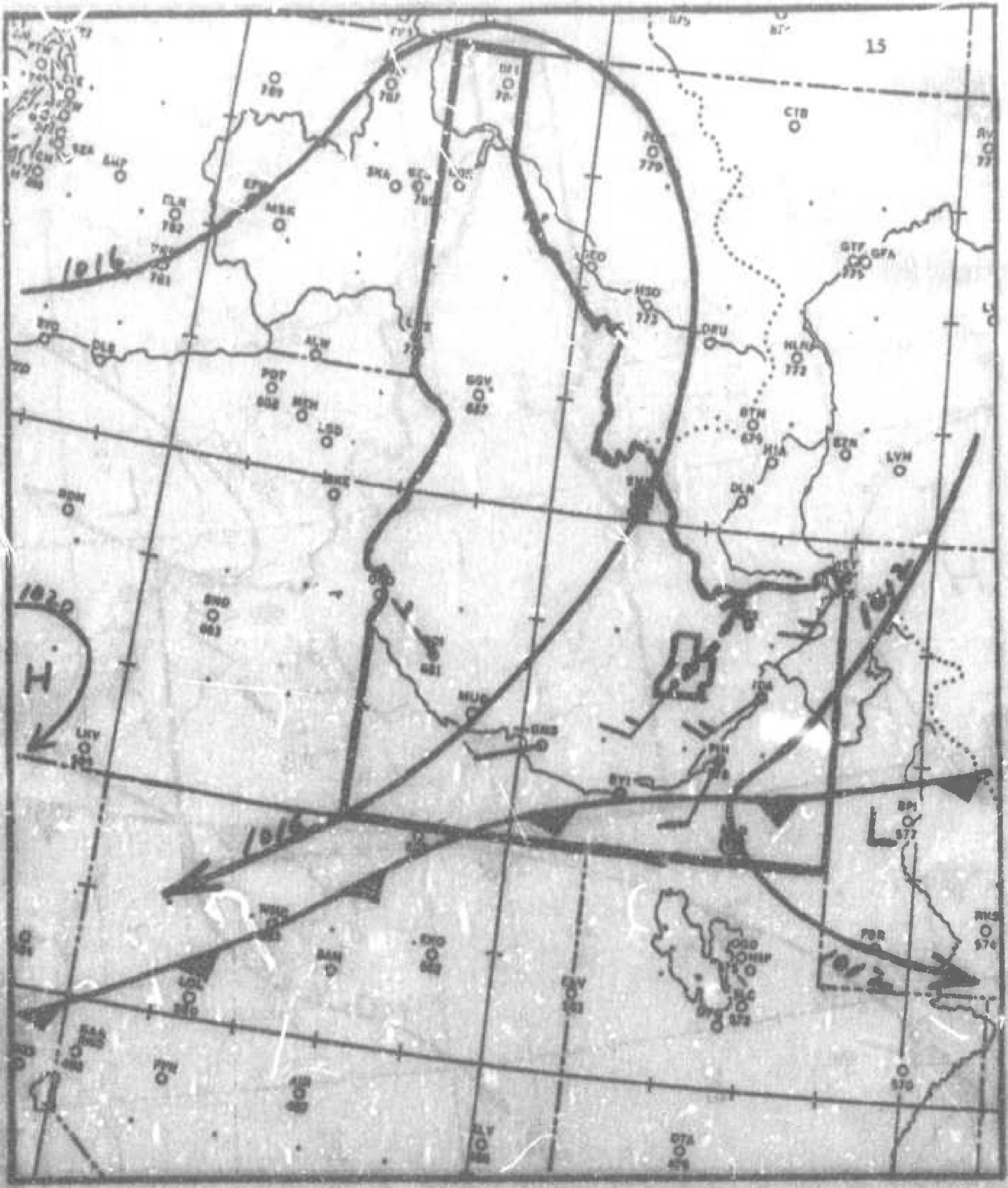


Figure 4. Surface weather features and wind flow over southern Idaho at 1100 MST on September 22, 1972.

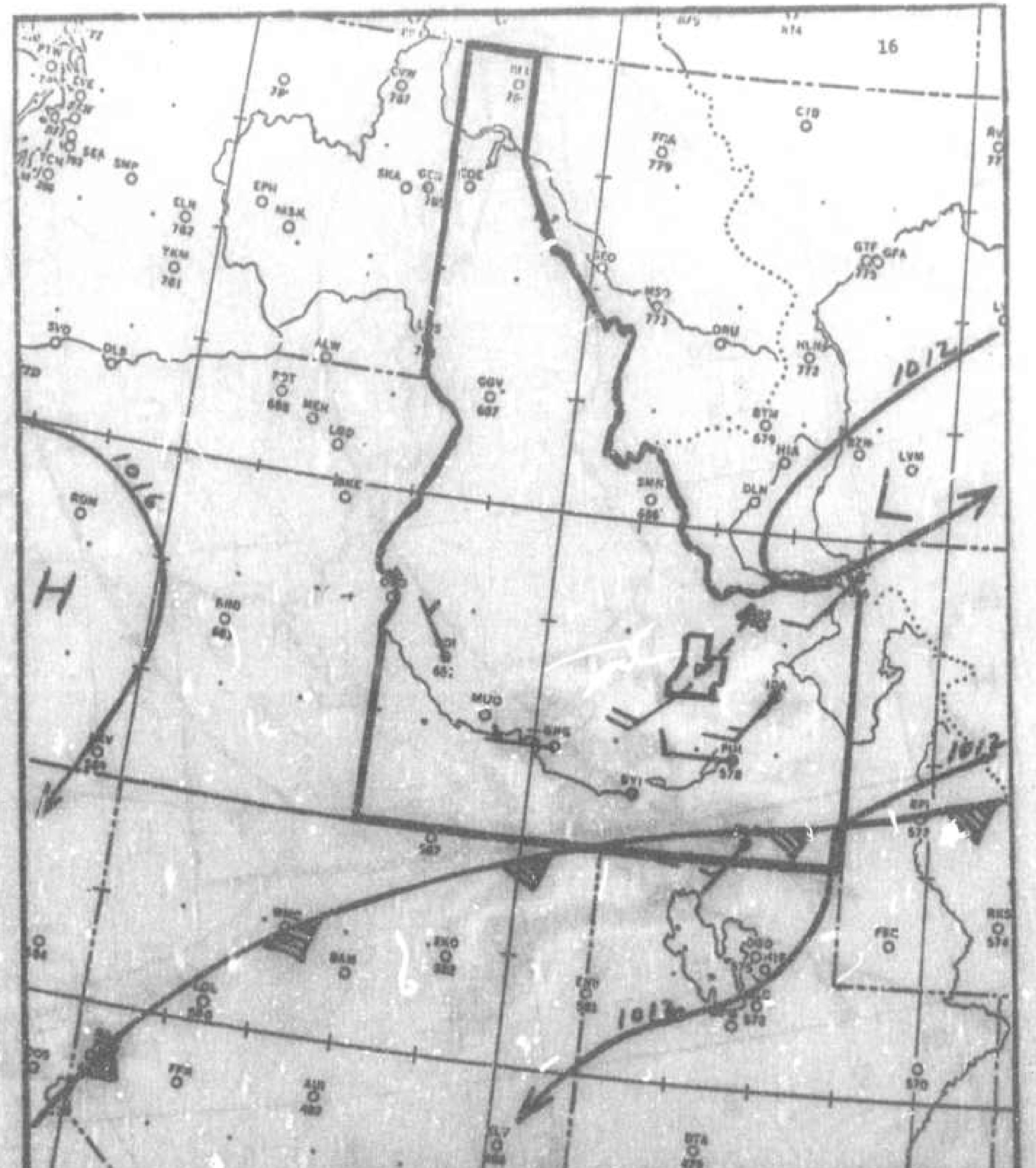


Figure 7. Surface weather features and wind flow over southern Idaho at 1400 MST.

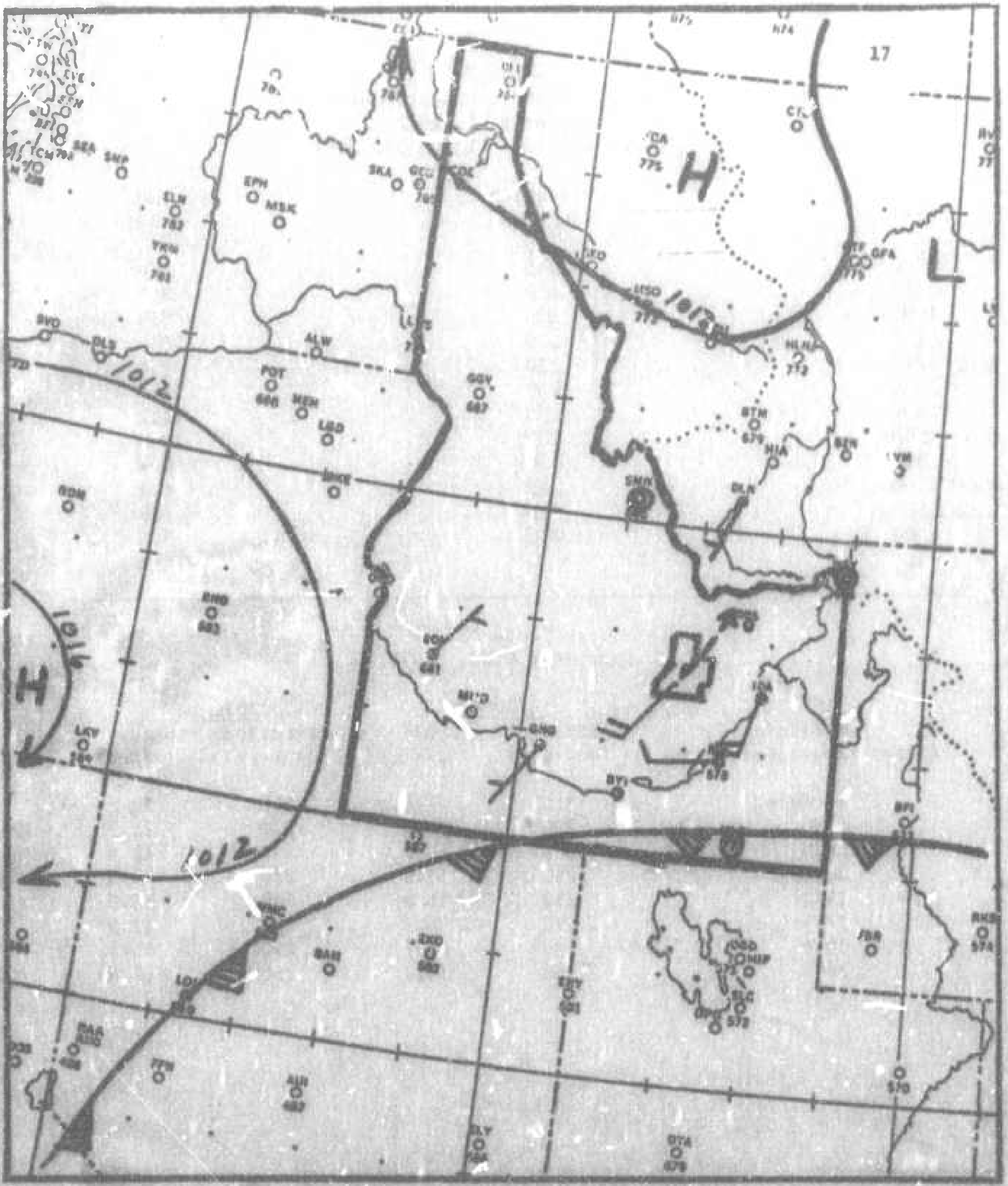


Figure 8. Surface weather features and wind flow over southern Idaho at 1700 MST.

Table 3a
Surface Winds (6-meter tower)
September 22, 1972
(Tracer Release: 1230-1530 MST)

Time (MST)	Direction (degrees)	Speed (m/sec)
0800	240	8.0
0900	230	8.9
1000	220	8.9
1100	220	8.0
1200	230	9.8
1300	230	11.6
1400	230	11.2
1500	230	10.3
1600	230	9.4
1700	220	8.9
1800	220	7.6
1900	210	5.4

Table 3b
Upper-Air Winds (NRTS)

Altitude (meters above sea level)	0730 MST		1510 MST	
	Direction (degrees)	Speed (m/sec)	Direction (degrees)	Speed (m/sec)
Surface	230	5.8	220	12.5
1680	230	14.7	220	16.5
1830	250	14.7	230	20.6
2130	260	15.2	230	18.3
2440	260	16.5	230	12.5
2740	270	14.3	240	12.5
3050	270	16.1	240	15.6
3660	250	16.1	250	11.6

flow can be a very poor approximation to actual wind flow in the surface layer, particularly in mountainous terrain.

Computer-calculated surface wind flow over the site at 1300, 1600 and 1900 MST is shown in figure 9. The NRTS tower wind data were used to calculate hourly average winds. Wind arrows are plotted at each tower site (each barb represents 10 mph). An interpolation scheme (1) is then used to calculate a wind vector at each grid point. Vector length is plotted proportional to wind speed.

Tetroons were launched near the tracer release point at half-hour intervals during the release period and tracked by radar to provide estimates of plume trajectories. Tetroon trajectories and computer-calculated surface wind trajectories (1) for the same starting times (MST) are shown in figure 10. Letters along each trajectory (upper-case for surface winds, lower case for tetroons) denote successive 15-minute positions (i.e., A denotes position 15 minutes after start, B denotes position 30 minutes after start, etc.). A very steady wind flow pattern during the experiment is evident with trajectories starting toward the northeast and gradually curving toward the north. Tetroon trajectories are consistently a little to the right of the surface wind trajectories and about 50% faster. The entire 3-hr plume apparently passed over all 4 sampling arcs. Travel time to the last sampling arc (about 90 km) was almost 2 1/2 hrs near the ground and about 1 1/2 hrs aloft. Arc-crossing positions, mean travel times and travel speeds to each arc, as determined from tetroon trajectories, are provided in Table 4.

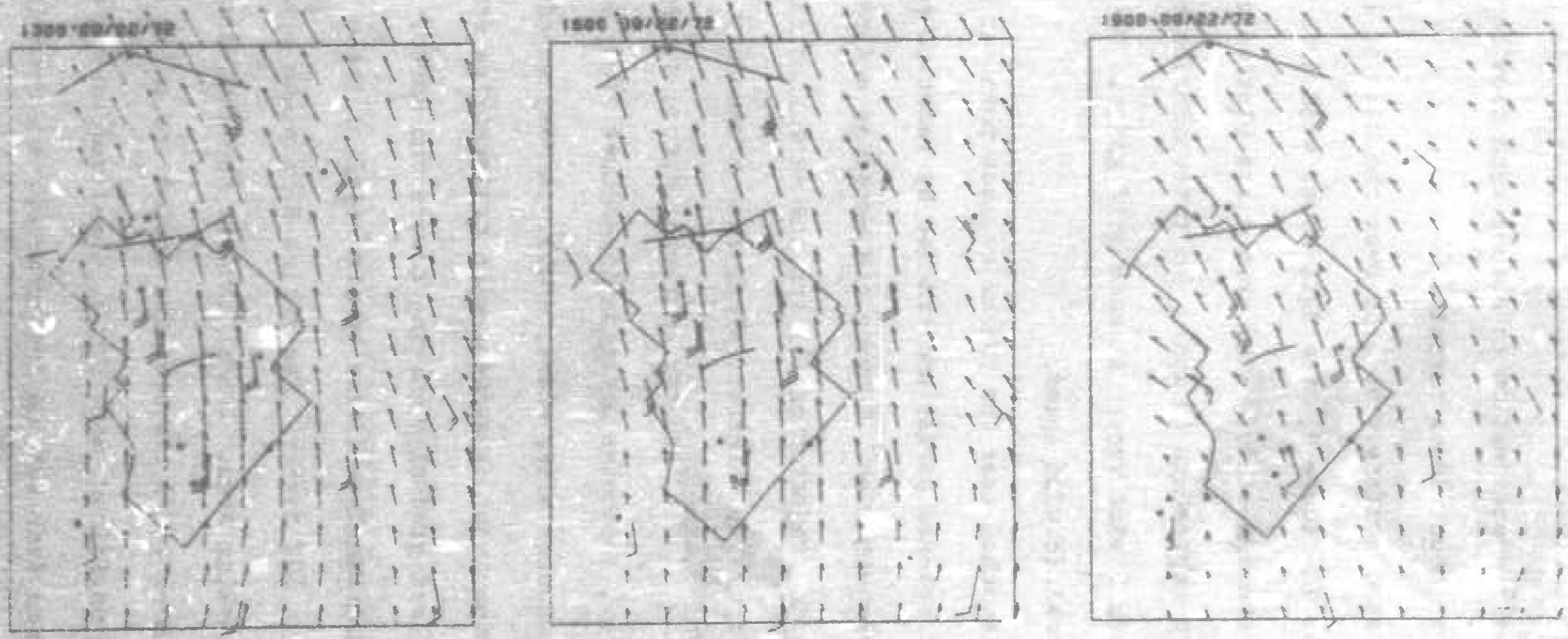
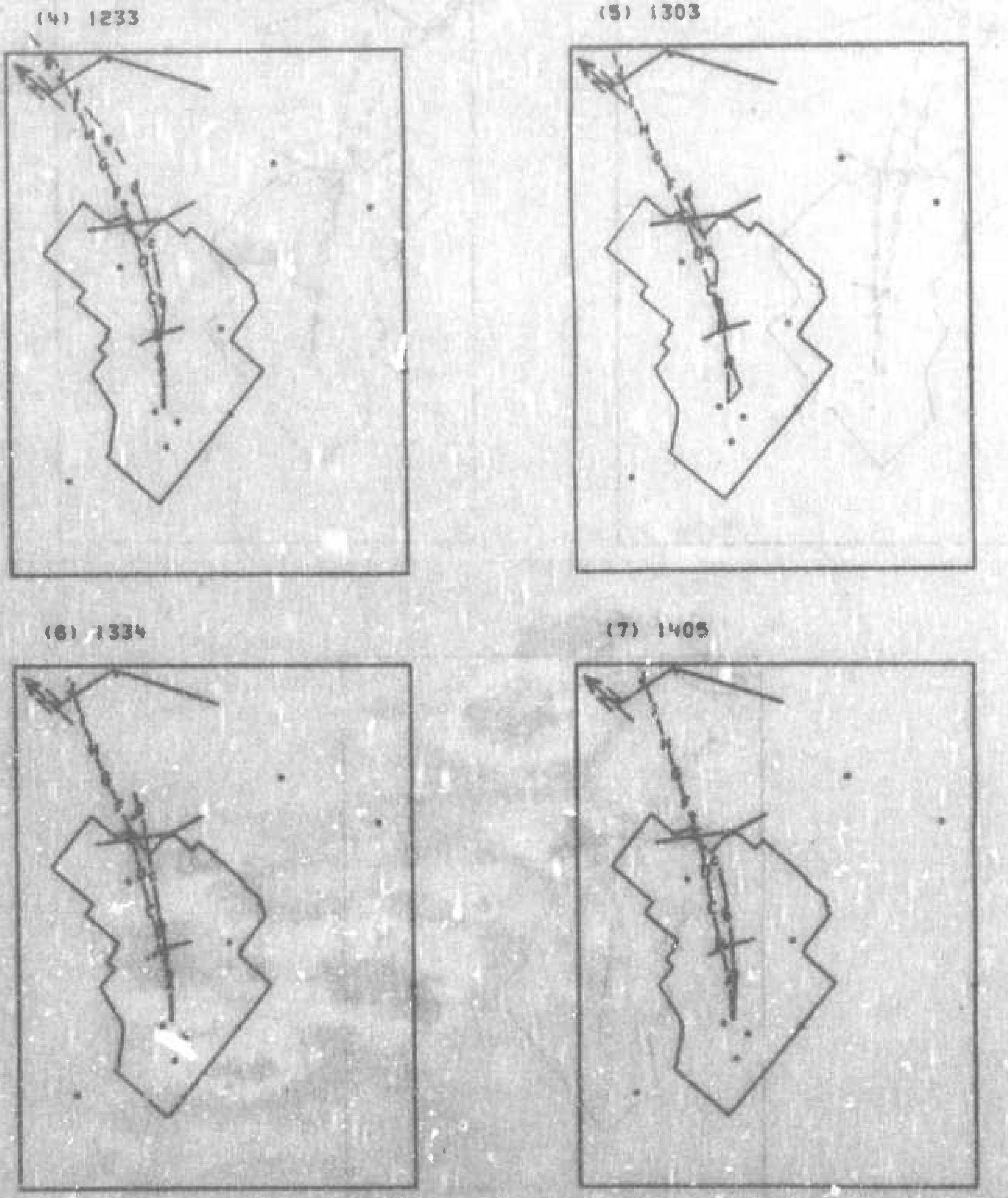


Figure 9. Computer-calculated surface wind fields (times are MST).



(4) 1233

(5) 1303

(6) 1334

(7) 1405

Figure 10a. Tetroon (lower case letters) and surface wind (upper case) trajectories during the tracer release period. Starting time (MST) is indicated above each picture.

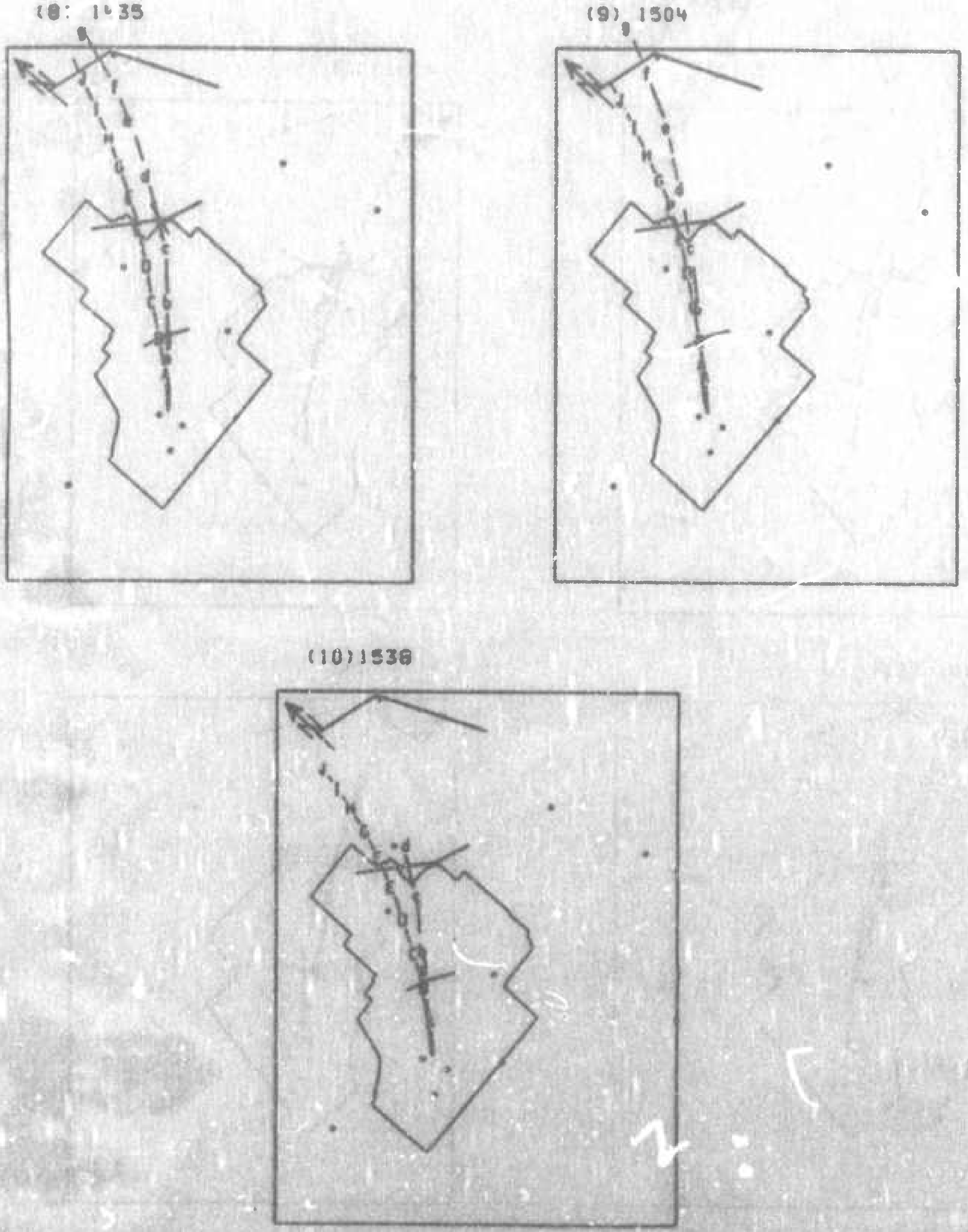


Figure 10b. (Same as 10a).

Table 4
Tetroon Trajectory Data

Arc	Mean Crossing Point*	Range of Crossing Points	Width (km)	Mean Travel Time (minutes)	Mean Travel Speed (meters/sec)
A	2.6	2.1-2.8	1.08	5	16.6
B	4.9	4.0-5.8	2.46	21	14.6
C	5.0	4.4-5.7	4.28	52	14.9
D**	3.8	2.5-4.8	8.34	94	15.8

*Crossing points are indicated by ground sampling position numbers (see figure 3).

**Trajectories were extrapolated for those tetroons that were not tracked as far as arc D.

Tetroons respond to vertical as well as horizontal air motions but the restoring force on a tetroon tends to damp its vertical oscillations. A preliminary indication of vertical air motion during the experiment is shown by the tetroon vertical motions in figure 11. Knowing the restoring force on each tetroon, actual air motions can be calculated from these data. The restoring force increases as the tetroon is carried away from its pre-set float level and apparent vertical velocities may be in error by as much as ±50%. Nevertheless, these tetroon flights indicate strong vertical motions with excursions up to about 900 meters above the terrain. This was borne out also by aircraft sampling; tracers were detected as high as 1450 meters over arc B.

2.4 Sampling Program

Sampling stations were set up along four arcs downwind of the source (see figure 3). Time averaged crosswind profiles of the plume at ground

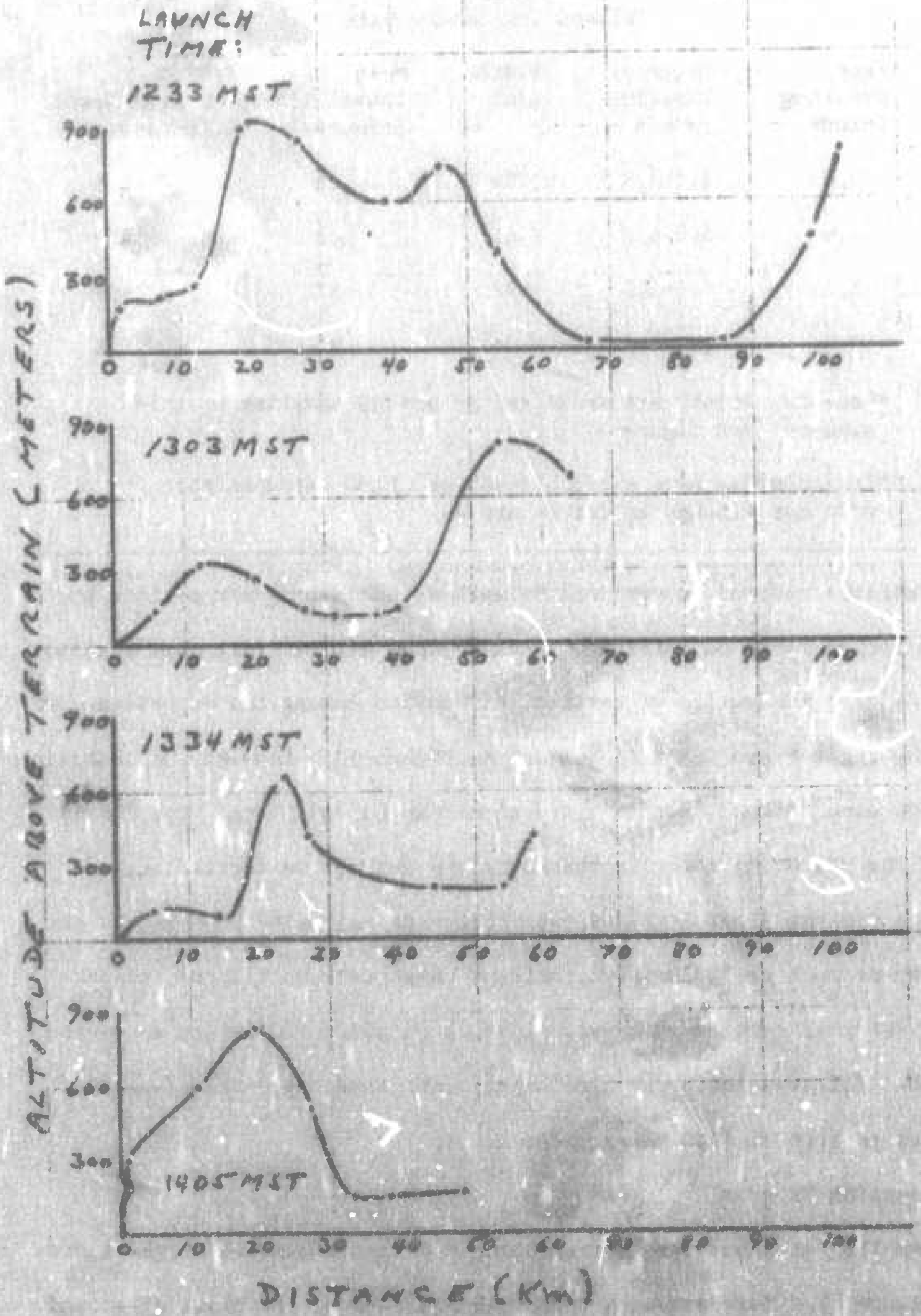


Figure 11a. Tetroon vertical sections.

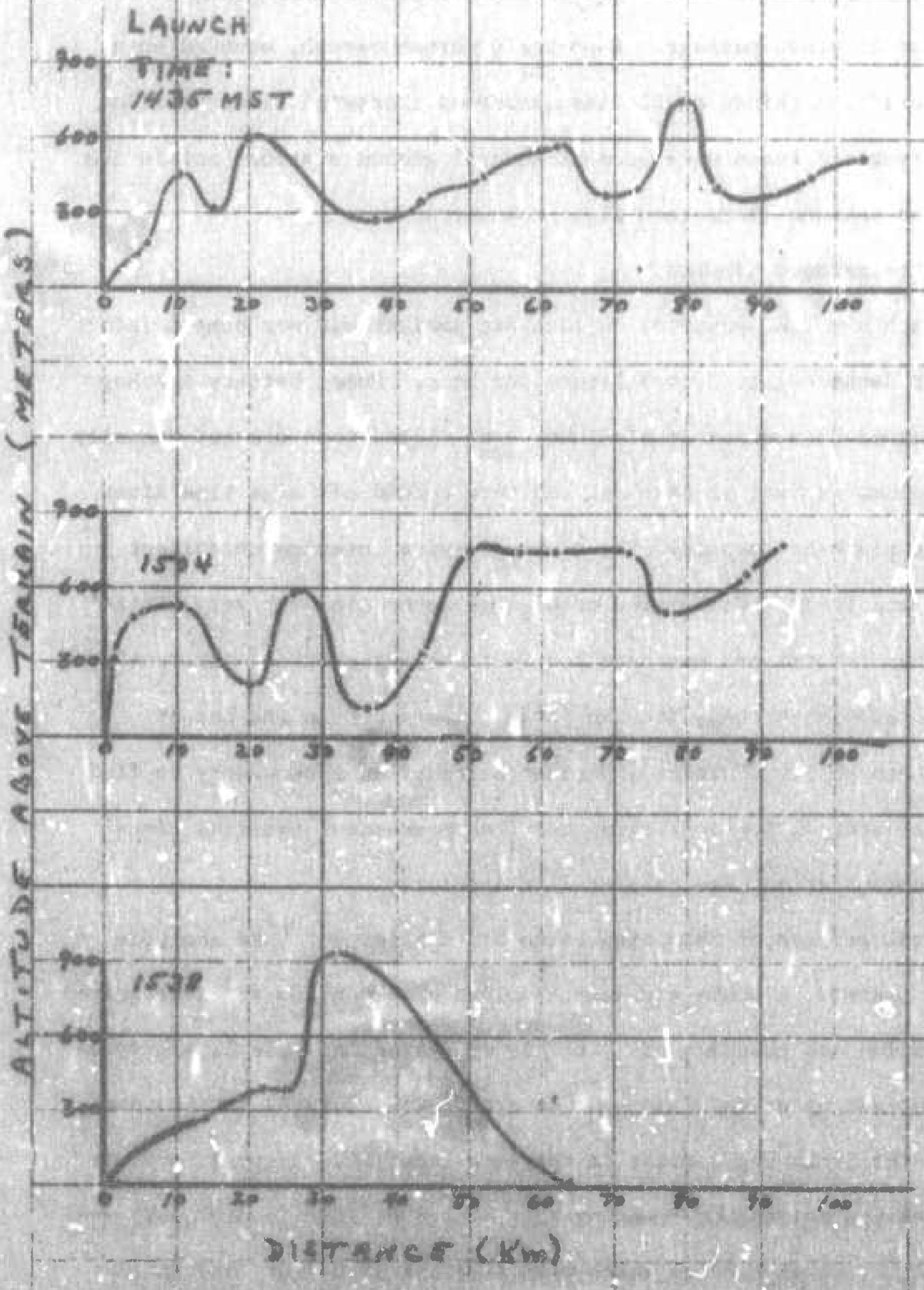


Figure 11b (Same as 11a).

level were obtained along each arc. Samples were obtained at each station by pumping ambient air into plastic bags and balloons during the entire time of plume passage. A portable chromatograph, mounted in a small aircraft, obtained nearly instantaneous crosswind plume profiles aloft. Cryogenic traps were used at several ground stations and in the aircraft to measure short-term plume concentrations.

2.4.1 Time-averaged Samples

At each sampling position on each arc ambient air was pumped into a 48-liter Saran bag at 2 to 3 liters per hour. Pump, battery and bag were contained in a portable aluminum case. Pumps were started manually prior to plume arrival at each arc and were turned off some time after the entire plume had passed. These samples were intended to collect SF_6, 12B2 and 114B2. Collection of SF_6 was successful but very little of the other two tracers was detected in these bag samples. Evidently, the fluorocarbons reacted with the Saran, plated out in the bag or migrated through it. Further experimentation will be necessary to find a suitable material for collecting the fluorocarbons. Sampling times and SF_6 concentrations are tabulated in Appendix A.

Several methods of obtaining large air samples for ^{85}Kr analysis were also tested. A whole-air sample volume of about 200 ft^3 is required for separation and counting of ^{85}Kr. As indicated in Table 5, a krypton sampler was set up on each arc (two on arc C) and operated for the same period as the Saran bag sampler at the same location. At position C-6 a high-pressure compressor (pumping rate of 1.8 ft^3/min to 3100 psi) was used to fill 4 steel spheres (each with a volume of 0.7 ft^3 and rated capacity of 3000 psi) in sequence. Unfortunately, this sample was lost during laboratory analysis.

Table 5
^{85}Kr Sampling Results

Arc	Position	Sampling Method	Concentration (pCi/SCM)
A	4	Plastic balloon	1380
A	4	Neoprene Balloon	burst
B	4	Plastic balloon	339.2
C	3	Plastic balloon	13.8
C	3	Neoprene balloon	low volume
C	6	Steel Sphere	lost sample
C	6	Neoprene balloon	296
D	[illegible]	Neoprene balloon	157.4

At the other sampling positions, small, low-pressure pumps were used to slowly inflate either standard weather balloons (neoprene rubber) or large plastic balloons. Later, the high-pressure compressor was used to transfer air samples from the balloons to steel spheres for shipment to the laboratory.

Replicate samples were planned at positions A-4, C-3, and C-6 to check retention of krypton by rubber and plastic balloons. As is evident from Table 5, mishaps prevented our obtaining any replicate krypton concentrations. Nevertheless, four of the five successful collections contained concentrations one to two orders of magnitude above the background of about 14pCi/SCM. Comparisons with SF_6 concentrations are discussed in section 2.7.1.

2.4.2 Cryogenic Sampling of 12B2 and 114B2

Several hundred small cryogenic sampling traps were fabricated for use in this experiment. Each cryotrap consisted of a stainless steel tube, about 9 cm long, internal diameter about 5mm, crimped and welded shut at one end. The other end was silver soldered to a smaller bore copper tube about 7 cm in length.

To obtain a cryogenic air sample with this simple apparatus, the tube is lowered into a dewar flask containing liquid nitrogen. Air in the tube is liquefied after about 30 seconds and more air is continuously sucked into the tube until the submerged portion is filled with liquid air. A 30 cm length of teflon tubing was fitted over the open end of the copper tube during sampling to ensure that the air drawn into the tube would not be unduly contaminated by nitrogen vapor from the flask. In a few minutes several hundred milliliters of air are drawn into the tube and liquefied. The tube is then removed from the liquid nitrogen and the trapped air is allowed to boil off as the trap warms. The tracers 12B2 and 114B2, as well as other trace constituents with relatively high boiling points will be largely retained in the tube. The end of the copper tube is then crimped and the trap is stored in the liquid nitrogen flask until it is returned to the laboratory for analysis (see 2.5.1)

Approximately 3-minute cryogenic samples were taken every 15 minutes at positions A-4, B-4, C-4, C-6, C-8 and D-3. Once each hour duplicate samples were taken as nearly simultaneously as possible at each position.

The same technique was used to obtain about 20 cryogenic samples in the aircraft as it traversed the plume over each sampling arc. Ground-level cryogenic sampling results are tabulated in Appendix B and airborne cryotrap data are in Appendix C.

2.4.3 Airborne Chromatograph Plume Profiles

An electron-capture gas chromatograph, developed (2,3) at Brookhaven National Laboratory, was mounted in a small aircraft (Cessna 206) for this experiment. A 3-man crew was used; pilot, chromatograph operator, and cryotrap sampler. Calibration of the chromatograph was partially performed at NRTS with lecture bottles containing 10^{-10} and 10^{-11} parts of SF_6 per part of air. It was discovered, however, that the instrument response was sensitive to barometric pressure and in a non-linear way. Since the atmospheric pressure at Idaho Falls was about 635 mm Hg at ground level (1.5 km above mean sea level) and analyses were performed at altitudes up to 1.4 km above ground level (2.9 km MSL) where the pressure was 535 mm Hg, additional calibration was found to be necessary. This was performed in the High Altitude Test Chamber at the Health and Safety Laboratories (HASL) of the AEC in New York City. Simulated barometric pressures as low as 550 mm Hg were achieved during analyses with standard mixtures of 10^{-9} and 10^{-10} cc/cc. The combined results of the calibration at the NRTS site and at HASL were correlated by least squares approximation and plotted, for various altitudes, as shown in figure 12. The circles represent the averages of data measured at three concentrations and four simulated altitudes. At 1.5 x 10^{-9} cc/cc the sensitivity decreased by a factor of three going from sea level to 10,000 feet, but at $10^{-1[illegible]}$ cc/cc the change was almost 13-fold. In the future the instrument will have a constant pressure (sea-level or higher) within the detector to improve sensitivity.

Frontal chromatography was used for sampling instead of the more usual finite injection sampling. A continuous stream of ambient air was passed through a nitrogen oxide-treated molecular sieve column as the aircraft traversed the plume. The column separates the SF_6 from the oxygen, nitrogen, and other air components. About 40 seconds after sampling begins, the SF_6 starts to emerge from the column in a continuous stream which is passed through an electron-capture detector. In the detector, the SF_6 absorbs some of the electrons produced by a small radioactive source, reducing the electric current in proportion to the amount of SF_6. The continuous trace of the detector output quantitatively depicts the actual profile of SF_6 in the plume during the aircraft traverse. About 46 seconds after the SF_6 begins to emerge from the column, the oxygen starts to appear and the sampling must be stopped to backflush the column. This instrument provides 46-second sampling windows separated by about 3 minutes required for backflush. Further development of this instrument would allow continuous sampling over any desired time interval by automatically switching chromatograph columns during backflush. The instrument requires 150 watts (120 volt AC)

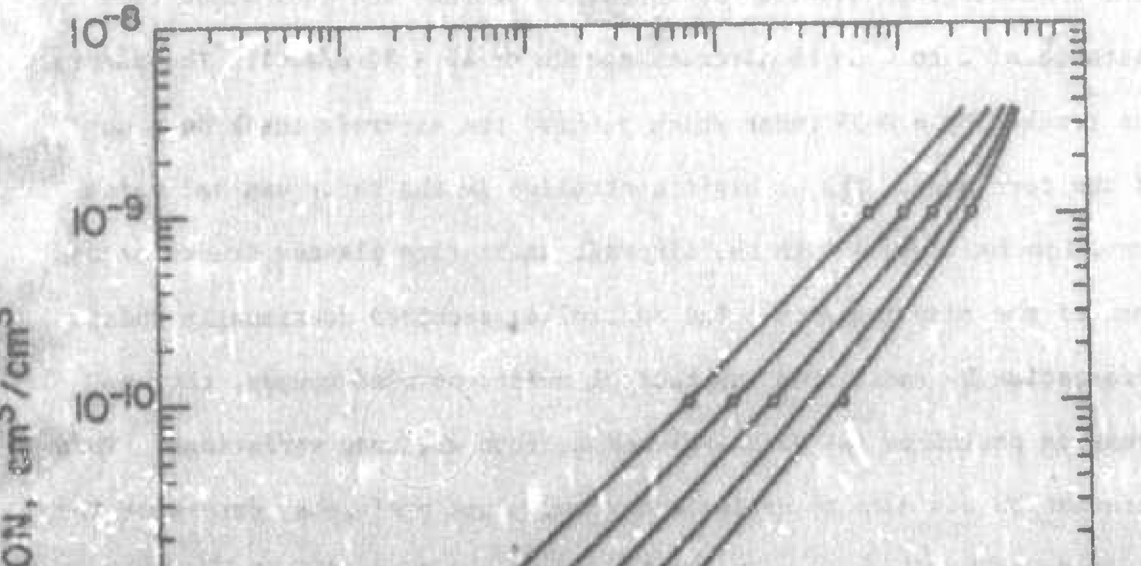


Figure 12. Airborne chromatograph calibration curves for various altitudes.

continuously and an additional 200 watts momentary surge for activating a solenoid switching valve.

Since the plume was not visible, the success of the aircraft sampling program was dependent on accurate estimates of plume location (the chromatograph sampling period of 46 seconds was equivalent to a distance of 2 to 4 km at aircraft speeds of 40 - 80 m/sec). The aircraft was tracked by a M-33 radar which plotted the aircraft track on a map of the test area. The aircraft controller in the radar van had voice communication (radio) with the aircraft as it flew planned tracks across each of the sampling arcs. The controller received continually updated information by radio from the control point, on wind speeds, tetroon crossing positions (at each arc) and tetroon altitude variations. This information was used to estimate current plume positions, determine the altitude to be flown on each sampling run, and determine where along the arc to start each chromatograph sample. The chromatograph operator relayed his results (from his recorder chart trace) back to the controller. The start and finish of each cryotrap sample was also directed from the radar and sampling positions were marked on the radar plot of the aircraft track.

At least two sampling runs were planned at each of several altitudes over each sampling arc. The aircraft sampling program was quite successful on the whole, although unexpectedly strong winds and operational difficulties (primarily radio communications problems and an unscheduled landing to replace a depleted battery) prevented the full attainment of all sampling goals. On arcs A and B, where the entire plume cross-section could be seen within the 46-second window, cryotraps were used to overlap chromatograph samples. Cryotrap sampling periods ranged from 2 to 5 minutes, providing average concentrations of 12B2 and 114B2 over distances from about 5 to 12 km. On arcs C and D where the entire plume could not be traversed in 46 seconds, cryotraps and chromatograph profiles were taken alternately along each traverse, occasionally with some overlap, in an attempt to obtain as much information as possible.

Two samples of SF_6 profiles obtained with the airborne chromatograph are shown in figure 13. The original traces have been computer processed to remove background noise and correct for altitude. Note that the entire plume is included in profile 4A but the aircraft was still in the plume at the end of the 46-second sampling period in profile 21C.

Aircraft cryotrap data and chromatograph profile data are given in Appendix C. A complete set of profile plots is available from the Air Resources Laboratories, Silver Spring, Md.

2.5 Sample Analysis

Whole-air samples collected in balloons were compressed into high-pressure spheres and shipped to Airco, Inc. in Murray Hill, New Jersey for separation and radio-assay of ^{85}Kr.

All other samples collected were analyzed for SF_6, 12B2 and 114B2 by ARL at the NRTS using chromatographs based on a prototype designed by Lovelock (3). The Lovelock instrument fabricated for this project is actually a parallel chromatograph system with two columns, two detectors and two electronic systems, one for analysis of SF_6, the other

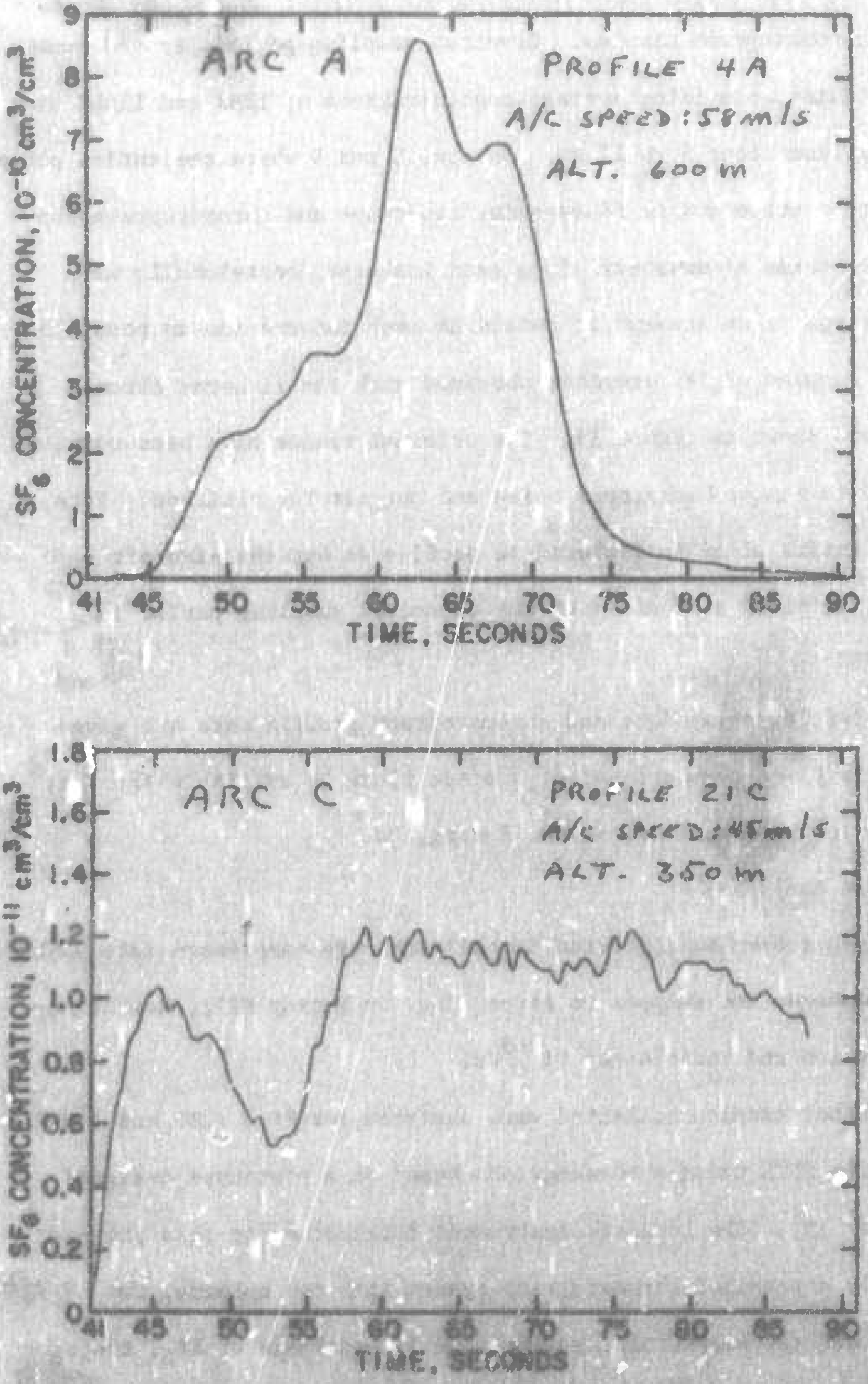


Figure 13. Airborne SF$_6$ plume profiles.

for 12B2 and 114B2. The column material used for SF_6 separation was Linde 5A Molecular Sieve, 80-100, while Durapak Low K Carbowax 400 on Porasil F 100-120 mesh was used for separating the fluorocarbons. The detectors used 15 mCi ^{63}Ni radioactive sources and pure nitrogen was used as the carrier gas. The system was operated under gas phase coulometric conditions.

At present, the practical limits of detection with this chromatograph are about 5 parts in 10^{13} for SF_6, about 1 part in 10^{12} for 12B2 and about 3 parts in 10^{12} for 114B2. The simple cryogenic trapping procedure used in this experiment (including subsequent dilution with pure nitrogen) produced concentration factors between 3 and about 40 (average factor was about 20) for 12B2 and 114B2. The detection limits for cryotrapped samples were, therefore, lowered by the same factor. The lowest air concentrations actually measured from cryotraps were 4×10^{-14} for 12B2 and 8×10^{-13} for 114B2. Only a small fraction of the samples contained measurable 114B2 because of the relatively short release period.

2.5.1 Analysis Procedure

Time-integrated samples were analyzed for SF_6 by removing 5cc of air from the Saran bag collector with a hypodermic syringe. The sample was then injected directly upstream of the chromatograph column. The instrument measures the amount of SF_6 in the sample and since the volume was known (5cc) the concentration was readily obtained. An absolute measure of the amount of electron-absorbing substance (SF_6, 112B2, or 114B2) passing through the detector may be obtained only if the efficiency of the detector is known. Efficiencies determined by Lovelock for this instrument design and operating condition are given in Table 6.

Table 6
Chromatograph Detector Efficiencies

Tracer	Efficiency
SF_6	0.44
12B2	0.50
114B2	0.30
Freon-11*	0.40
CCl_4*	0.66

*Used to determine sample volumes (see 2.5.2)

In attempting to verify these efficiencies, it was found that many more variables are involved than were anticipated. The values in Table 6 were used to obtain all concentrations reported in the Appendices. Efforts are continuing to verify Lovelock's efficiencies for this particular instrument and operating procedure. If significant changes result from this work, they will be reported.

Cryotraps were removed from the dewar flasks in the laboratory and maintained at a reduced temperature while the copper tube was cut below the crimp. A gas-tight fitting with a septum was placed over the open end and the sample was warmed to ambient temperature. A hypodermic syringe was used to mix 6 cc of pure nitrogen with the air sample in the cryotrap (about 1 cc) until the sample was equilibrated with the nitrogen. Five cc of the diluted sample was then withdrawn in the syringe and injected into the chromatograph column. As before, the amount of tracer (12B2 and 114B2) contained in the 5 cc sample was measured. To obtain the original concentration in the air, the effective volume represented by the sample had to be determined.

2.5.2 Cryotrap Volume Determination

Effective sample volumes were determined indirectly by measuring the Freon-11 (CCl_3F) and carbon tetrachloride (CCl_4) concentrations in each sample. Air concentrations of both substances may be assumed constant over the time and space frame of this experiment and both are electron absorbers that are readily separated and measured by the same column material used for 12B2 and 114B2 analysis. Measured background concentrations averaged 7.6×10^{-11} cc/cc for Freon-11 and 7.0×10^{-11} for CCl_4. All four substances have boiling points well above that of liquid nitrogen (-196°C) or oxygen (-183°C); 12B2 boils at 22.8°C; Freon-11 at 23.8°C; 114B2 at 47.3°C; and CCl_4 at 78.8°C. For purposes of calculating effective volumes, it was assumed that 12B2 follows the behavior of Freon-11 in the cryotrap procedure and 114B2 follows CCl_4. Fractionation between Freon-11 and CCl_4 was almost always less that a factor of two as can be seen in figure 14.

The effective volume represented by the sample injected into the chromatograph, with Freon-11 as the standard, is

$$V_{eff} = \frac{C_m}{C_b} \quad V_{inj} \qquad \text{Eq. 1}$$

where C_m is the measured concentration of Freon-11 in the sample

C_b is the background concentration of Freon-11 in the atmosphere

V_{inj} is the volume of the injected sample (usually 5 cc).

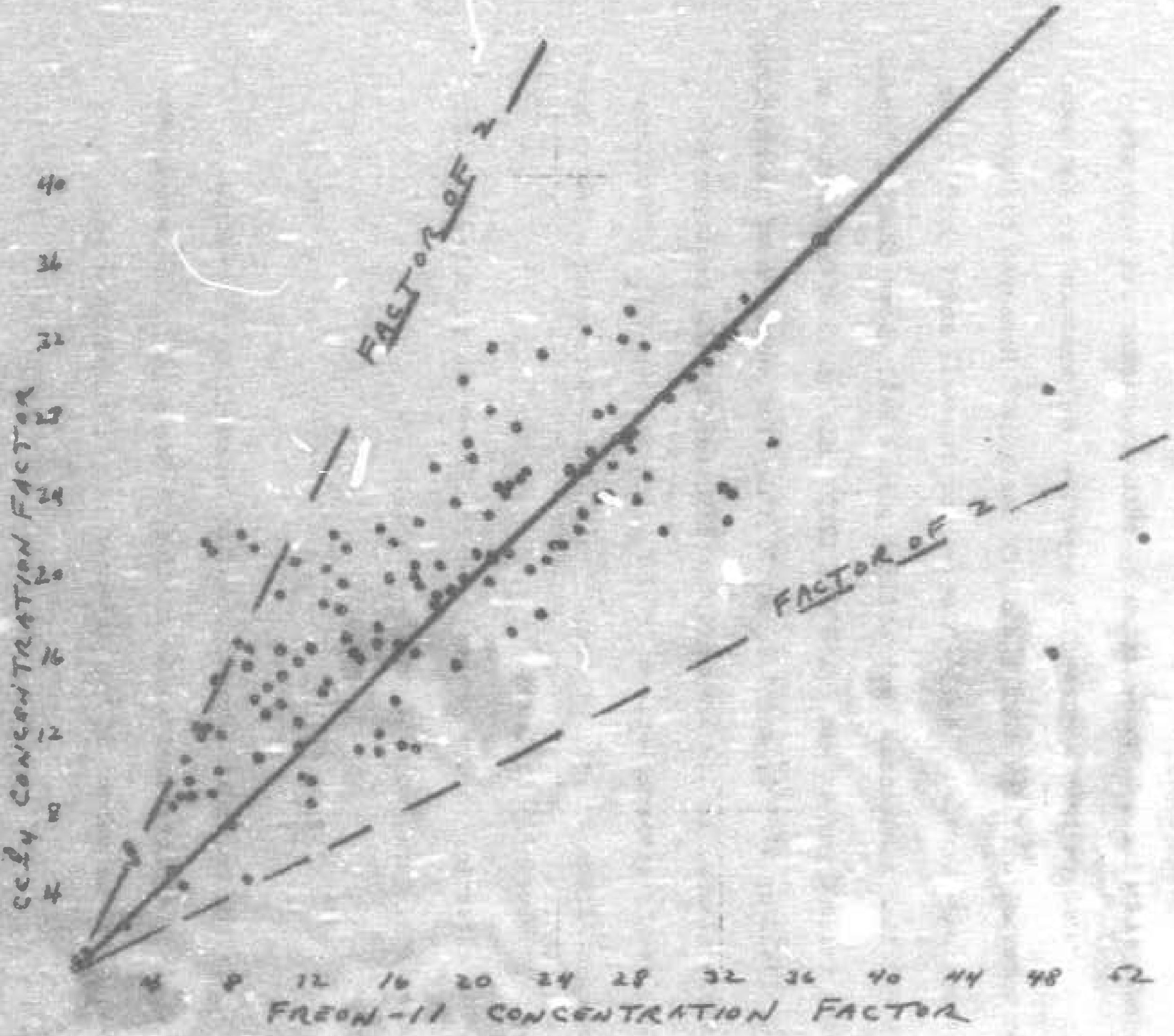


Figure 14. Sample concentration factors for Freon-11 and CCl_4.

For each sample injected into the chromatograph, the measured amount of 12B2 (cc) was divided by the effective volume (cc) to obtain the 12B2 concentration in the ambient air originally sampled. A similar calculation was made for each sample, using CCl_4 as a standard, in order to determine the effective volume and concentration of 114B2.

The ratios C_a/C_b or V_{eff}/V_{inj} represent the effective concentrating factor achieved by cryotrapping as subsequently diminished (mixed with 5 cc of N_2) during removal of the sample from the cryotrap. Concentration factors with respect to Freon-11 and CCl_4 are plotted in figure 14 for all cryotrap samples. The scatter in the data indicates that a high degree of precision cannot be expected with these experimental procedures. In general, concentration factors appear to be slightly greater for CCl_4 than for Freon-11 but only a few points show more than a factor of two difference. The line of one-to-one correspondence and the factor of two range are shown. These data indicate an average concentration factor of about 20. Presumably, if the cryotrap volume were 5 cc rather than 1 cc, and the samples could be introduced directly into the chromatograph without dilution with N_2 an average concentration factor of almost 100 should be achieved. To date, concentration factors up to 80 have been attained in laboratory experiments.

If much larger samples were collected under rigid procedures with all dilutions avoided, it appears that a two-stage cryotrap procedure might achieve concentration factors of 1000 or more. This might be achieved for example, by first cryotrapping into a 1 liter container, allowing the nitrogen and oxygen to boil off, and then cryotrapping the remaining air and trace constituents into a 5 cc trap. It is planned to continue experiments (not ARPA-funded) with this and other concentrating techniques to determine the practical limits of concentrating 12B2 and 114B2.

2.6 Analysis of SF_6 Plume Data

Release, sampling and analysis of SF_6 were generally successful and good definition of the plume was achieved both at the ground with time-integrated samples and aloft with nearly instantaneous crosswind profiles. As might be expected, some difficulties were experienced in the first field trial of the two new tracers, 12B2 and 114B2. Release of 12B2 was successful although the release rate was about one-half the planned rate. The major problem with 12B2 was the inability of the Saran bags, used for ground-level integrated samples, to retain this tracer (or 114B2). Very little data were obtained with 114B2 because of this problem and the relatively short release achieved with this tracer. On the positive side, both tracers were successfully cryotrapped and both were detected at the most distant sampling arc (about 90 km downwind).

Since the SF_6 sampling data set was the most complete, it was used for analyses of plume behavior which are summarized in this section. Evaluations of 12B2, 114B2, and ^{85}Kr data were made, wherever possible, by comparison with SF_6 data and results are presented in section 2.7.

2.6.1 Material Balance Calculations

Ground-level concentrations of SF_6 collected in Saran bags over the entire duration of plume passage on each arc are listed in Appendix A. Crosswind concentration profiles on each arc are plotted in figures 15 and 16. There was a surprisingly steep drop in peak concentration from

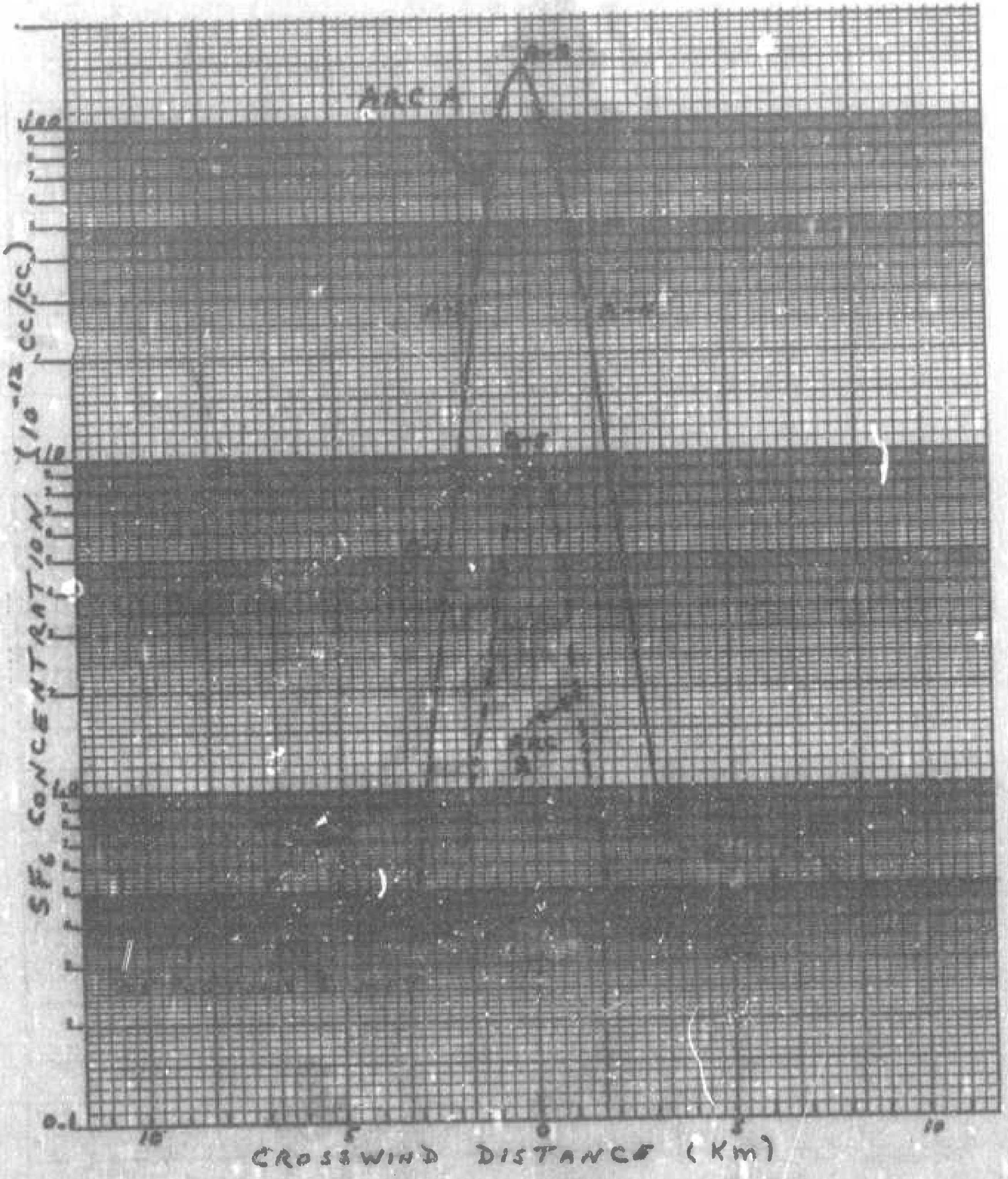


Figure 15. Ground-level SF_6 profiles on arcs A and B.

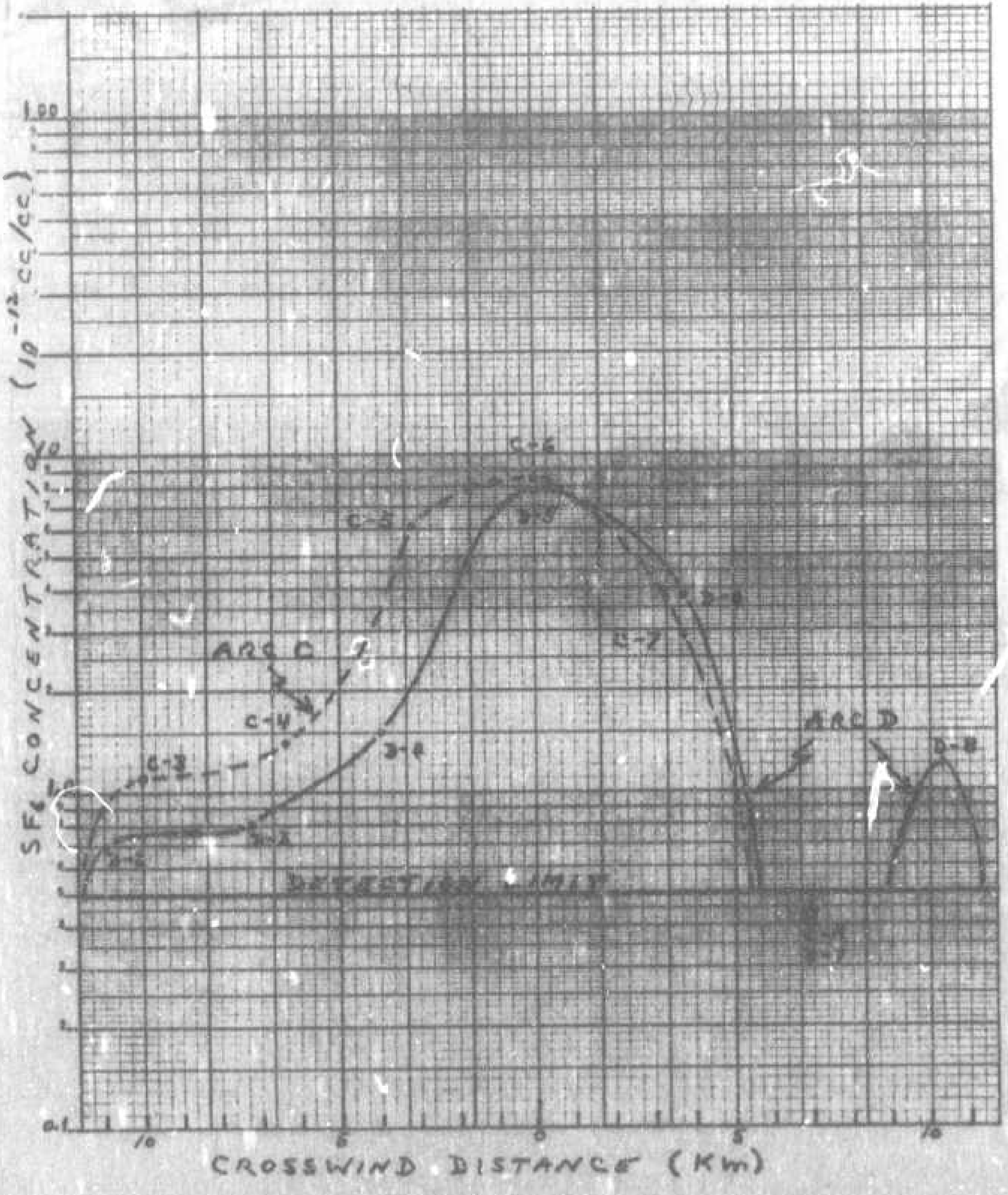


Figure 16. Ground-level SF$_6$ profiles on arcs C and D.

arc A (6 km downwind) to arc B (12 km). The comparatively long sampling duration on arc B (see Appendix A) can account for only a small part of this decrease. Peak concentrations on arcs C and D (about 47 and 89 km downwind, respectively) were only slightly less than on arc B, although the time-averaged plume had broadened considerably.

The total amount of SF_6 that passed each arc between the surface and a height of 30 meters, was calculated assuming uniform concentration in the vertical within this layer, a mean wind speed of 11 m/sec, and using the average sampling durations on each arc from Appendix A.

Calculated amounts, in grams of SF_6, are as follows:

Arc A	7.6×10^3
Arc B	7.6×10^2
Arc C	1.64×10^3
Arc D	1.74×10^3

The amount of SF_6 passing through this layer would be expected to decrease slowly with distance as the plume mixes upward to increasing heights. The data again show a large decrease from arc A to arc B and even more surprising, an increase of about a factor of two at arcs C and D over the total at arc B. The arc B surface sampling data appear to be out of line but the reasons for this behavior are not readily apparent.

Crosswind profiles obtained with the airborne chromatograph (Appendix C) were used in conjunction with the ground sampling data in an effort to obtain a complete material balance at each arc. Given the aircraft speed on each sampling run (from radar tracking data) and the mean wind speed aloft (16 m/sec; from tetroon tracking data) the crosswind integral of each profile over arcs A and B was used to calculate the total SF_6 passing through a 30-meter layer centered at each sampling altitude. It was necessary to assume that each nearly instantaneous profile is representative of the concentrations during the entire 3-hr period of plume passage. Since only one aircraft was used, simultaneous profiles at different altitudes could not be obtained, further adding to the uncertainties in material balance calculations. The resulting vertical profiles of total SF_6 per 30-meter slice over arc A and arc B are shown in figure 17. Each point plotted represents a single crosswind profile except that at 600 meters over arc A, which is an average of two profiles (1.3×10^4 and 1.9×10^4 g/30m) taken 8 minutes apart. This indicates that fluctuations of at least 50% occurred in the crosswind integral at a given altitude at arc A (only 5 minutes travel time from the source). Such fluctuations leave the actual shape of the vertical profile very much in doubt. However, it is clear that the plume had mixed upward to nearly 1000 meters at arc A and to over 1500 meters at arc B. No tracer was detected at 1000 meters above arc A (cryotrap data confirm the negative result obtained with the airborne chromatograph). The top of the plume at arc B is uncertain since high concentrations were found at the highest sampling altitude (1430 m).

Integrating the areas under the vertical profiles, the total SF_6 was calculated to be 4.07×10^5 g passing arc A and 1.06×10^5 g passing arc B. This compares with the total SF_6 release of 275 lbs or 1.25×10^5 g. The integral calculated at arc A is more than 3 times the actual release amount. Since the sampling data are believed to be accurate to much better than a factor of 3, it is conjectured that plume fluctuations in the

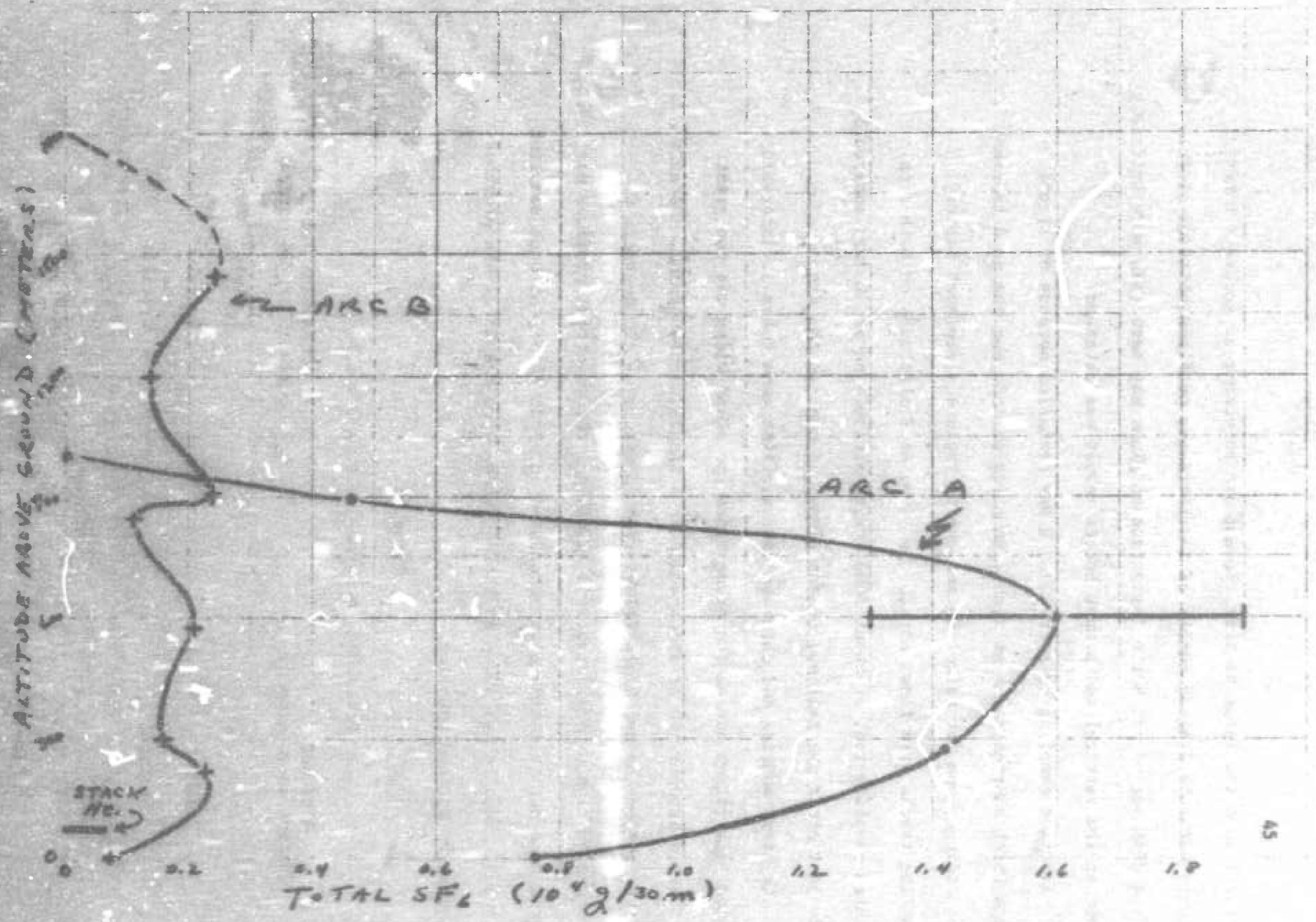


Figure 17. Vertical profiles of total SF_6 passing arcs A and B.

vertical were too large at this closest arc to permit an accurate material balance with the limited number of instantaneous profiles obtained aloft. At the distance of arc B the instantaneous plume may have been more uniformly mixed in the vertical and a much better result was obtained.

Aircraft sampling on arcs C and D was curtailed because of strong winds which shortened the available sampling period, and the need to make two landings, one for refueling and one to replace a depleted battery. Sampling tracks were flown across the plume at 2 altitudes on both arcs. A third sampling run, at about 1000 meters altitude on arc D, was apparently made just after the tail end of the plume had cleared the arc.

Cryotrap samples and chromatograph profiles were taken at intervals during each flight across the plume since the plume width was too great, at these distances, to be encompassed in a single sample period. Details of the sampling on arc D are illustrated in figure C-1 in Appendix C. Information from several cryotraps (12B2) and chromatograph profiles was pieced together to estimate the crosswind integral of SF_6 at each sampling altitude. Results are shown in Table 7 along with the integrals previously obtained by surface sampling.

Table 7

Crosswind Integrals on Arcs C and D

Arc	Altitude (Meters above ground)	Crosswind Integral (grams of SF_6/30 meters)
C	275	1.61×10^3
C	330	1.48×10^3
C	Surface	1.64×10^3
D	225	1.68×10^3
D	440	1.45×10^3
D	Surface	1.74×10^3

It is interesting to note that the two aircraft sampling runs on arc C were made about an hour apart. All the data show essentially the same crosswind integral, an average of about $1.6x10^3$ g/20m on both arcs. If we assume this value remains uniform with altitude, a plume top at 2340 meters would give the proper material balance (total of $1.25x10^5$ g of SF_6). This height appears reasonable when compared to the height of at least 1800 meters estimated at arc B and in light of the fact that surface air concentrations changed very little from arc B to arc D.

2.6.2 Estimates of Crosswind Standard Deviation

Estimates of the crosswind standard deviation (σy) of the plume were calculated from the ground sampling data (figs. 15 and 16) and the airborne chromatograph profiles. With the strong winds and fairly strong insolation, stability conditions during the experiment were estimated to lie between Pasquill categories C and D (slightly unstable). Curves of σy as a function of plume travel distance for these conditions are shown in figure 18 along with the values obtained in this experiment. These curves as presented by Turner (6) were extrapolated from experimental data largely confined to travel distances of a few km with sampling durations on the order of 3 minutes. The aircraft profiles represent nearly instantaneous "snapshots" of the plume while the ground sample profiles represent the result of superimposing many such "snapshots" taken over a 3-hr period, thus incorporating the effects of plume meander at each arc. As expected, the aircraft "snapshots" yield relatively small values of σy and the time-averaged distributions yield much larger values.

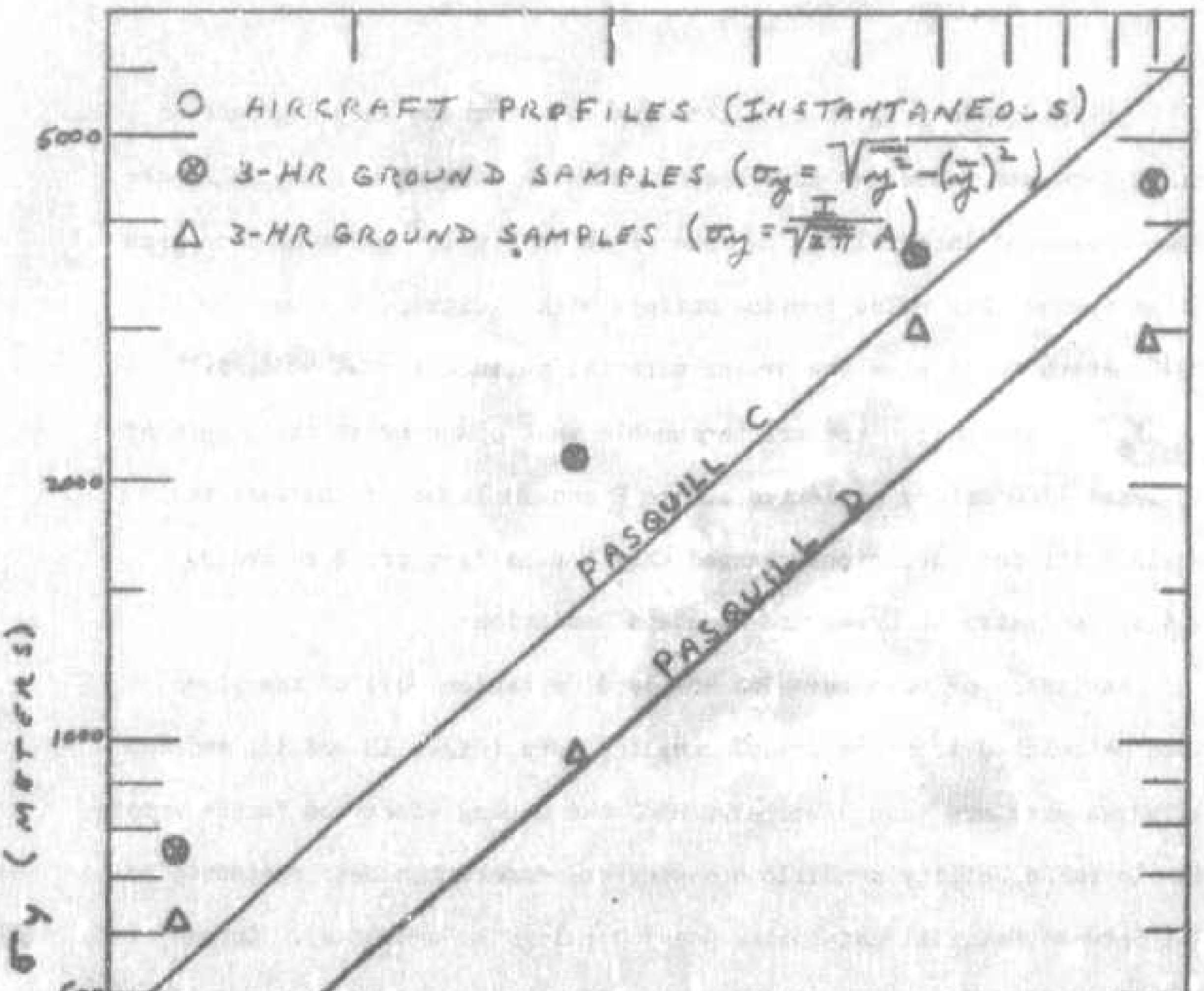


Figure 18. Estimates of σ_y from plume measurements.

The points indicated by crosses (3-hr samples) were calculated using a standard formula for the standard deviation of a frequency distribution:

$$\sigma y^2 = \overline{y^2} - (\bar{y})^2 \qquad \text{eq. 2}$$

where $y^2 = \Sigma \chi y^2 / \Sigma \chi$

$(\overline{y})^2 = (\Sigma \chi y / \Sigma \chi)^2$

and values of y (crosswind distance) and χ (concentration) are determined at unit intervals of y.

The σy's measured for the 3-hr sampling duration at arcs A and B are larger than those estimated for 3-minute samples (represented by the range between curves C and D). However, the measured 3-hr values on arcs C and D appear to approach the 3-minute expected values. This may result from the unusually small amount of plume meander during the experiment; as the diffusion component of the horizontal spread grew larger with increasing distance, the component due to plume meander became less significant.

Since σy values measured in diffusion experiments are usually applied to a Gaussian plume model, it is interesting to compute σy from these measurements, assuming a Gaussian distribution. Under this assumption:

$$\sigma y = \frac{I}{\sqrt{2\pi}\, A} \qquad \text{eq. 3}$$

where I is the measured crosswind integral (area under the curves in figures 15 and 16) and A is the amplitude or peak concentration.

The solid triangles plotted in figure 18 represent σy values calculated from eq. 3. Presumably a Gaussian plume model would better reproduce the observed peak concentrations using these "effective" σy values. This raises a question as to the most efficacious way to derive σy estimates from experimental data where distributions are not truly normal. Results for the two methods illustrated here differ by more than a factor of two on arc B.

The standard deviations from aircraft profiles (open circles) were derived from eq. 3. Numbers in parentheses indicate that 3 separate profiles gave the indicated σy value. On arcs C and D the plume was too wide to obtain σy estimates from airborne sampling.

2.6.3 Calculated and Measured Peak Concentrations

Peak ground level SF_6 concentrations expected from a continuous Gaussian plume may be calculated at each sampling arc from

$$\chi = \frac{Q}{\pi\sigma_y\sigma_z u} \exp\left[-1/2 \left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{eq. 4}$$

where χ = peak concentration (g/m^3)

Q = emission rate (11.6 g/sec)

u = mean wind speed (13m/sec)

H = initial plume height (76m)

σy, σz = horizontal and vertical standard deviations (m)

Estimated values of σy and σz (meters) for stability conditions mid-way between Pasquill categories C and D are (6):

Arc	σy	σz
A	420	170
B	1100	380
C	2600	750
D	4500	1100

These σ values, based on approximately 3-min sampling data were used in eq. 4 to calculate the 3-min peak concentration plotted (cross in circle) in figure 19. Although the relationship between concentrations obtained over different sampling periods is complex (dependent on the relative effects of turbulent diffusion and trajectory meander) these values can be adjusted for a 3-hr sampling period using an approximate relationship, suggested by Turner (6), based on experimental data

$$X_s = X_k \left(\frac{t_k}{t_s}\right)^{.17} \quad \text{eq. 5}$$

where t is sampling period and the subscript s denotes the desired period and k denotes the period for which the concentration is known. This indicates 3-hr peak concentrations would be one-half the 3-min values. Calculated peak concentrations adjusted to a 3-hr sampling period are plotted as a solid curve in figure 19. The dashed curve gives the peak concentrations from the time-integrated ground samples adjusted to a 3-hr sampling period (concentrations multiplied by the ratio of actual sampling period to 3 hrs). The shapes of the two curves are quite different. Measured and calculated peak concentrations agree well at arc A but the measured peak at arc B is more than a factor of three lower than the calculated value. This difference appears to be the result of much greater

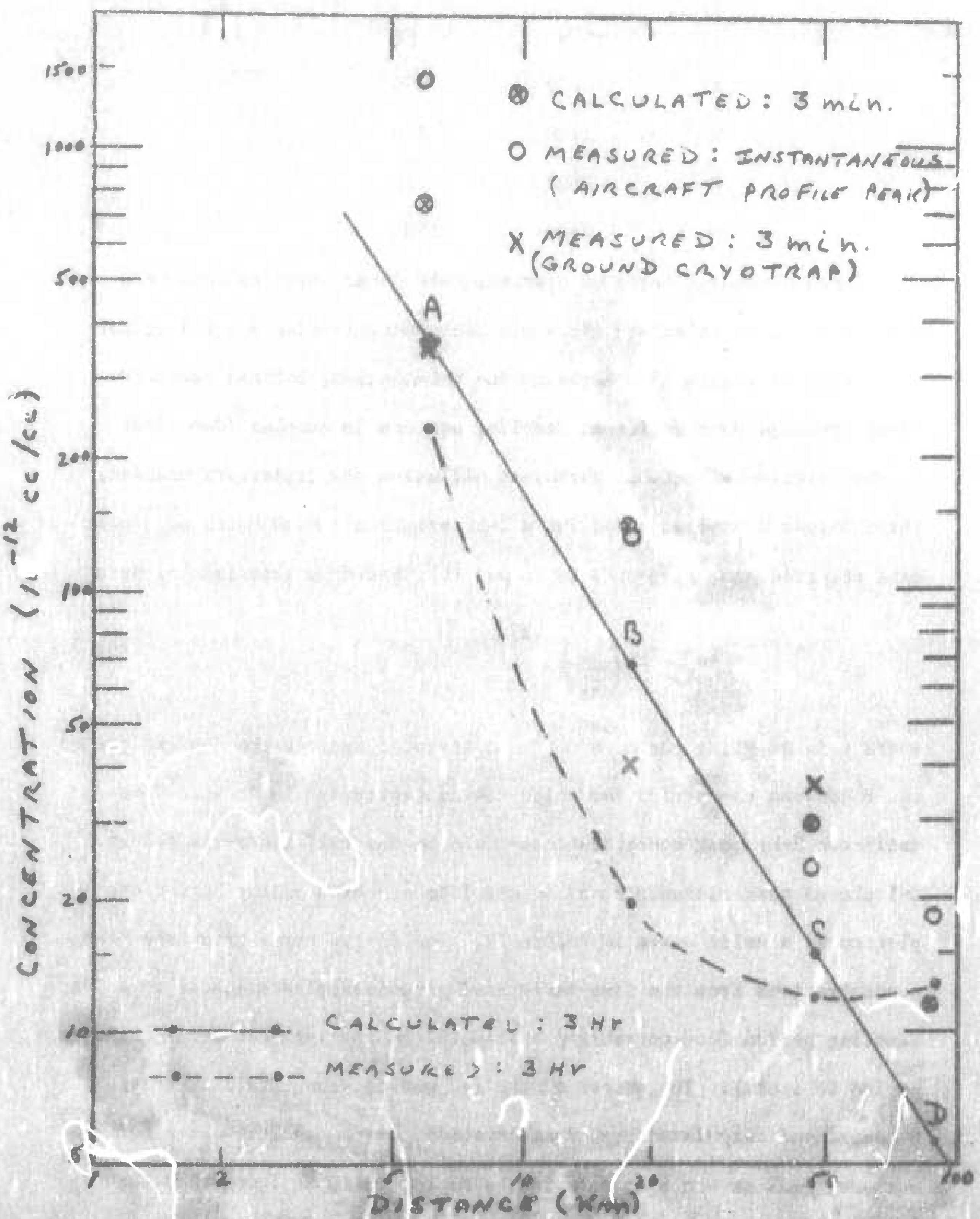


Figure 19. Measured and calculated peak SF_6 concentrations.

vertical spreading of the plume at arc B than assumed in the calculations. As mentioned earlier, material balance calculations suggest that the vertical spread of the plume increased only slightly from arc B to arc D. As a result, the calculated and measured concentrations agree well at arc C and the measured peak at arc D is actually higher than calculated. Note that the adjusted (3-hr) peak concentration on arc D is slightly greater than on arc C.

Calculated 3-min concentrations may be compared with the peak concentrations observed in approximately 3-min cryogenic samples at the ground (crosses) and with instantaneous peak concentrations obtained in the aircraft plume profiles (open circles). Calculated and measured peaks agree within about a factor of two except for the ground-level cryotrap on arc B.

2.7 Tracer Intercomparisons

Direct comparison of 12B2 and 114B2 concentrations with SF_6 was prevented by the failure of the Saran bag samplers to retain the fluorocarbons. However, indirect comparisons of SF_6 with ^{85}Kr, 12B2, and 114B2 were made wherever possible.

2.7.1 Comparison of ^{85}Kr with SF_6

Whole-air samples (balloons) analyzed for ^{85}Kr and Saran bag samples analyzed for SF_6 were available at the positions listed in table 8. Both systems sampled continuously during the time of plume passage and were turned on and off at the same time. The expected ratio of ^{85}Kr (pCi/SCM) to SF_6 (10^{-12}cc/cc) is 55, based on the release amounts (background of 15 pCi/SCM was subtracted from ^{85}Kr values). Some deviation from this ratio would be expected because of a difference of a few minutes in the respective release periods and deviations from the average release rates (about ±35% for ^{85}Kr). This cannot explain the large discrepancies at B-4 and C-3. Cryogenic samples at B-4 suggest that the SF_6 measured at that position is low by about a factor of 2 but adjustment for this would still leave a discrepancy of more than a factor of 2 in the $^{85}Kr/SF_6$ ratio. At C-3 there is nothing to indicate which measurement is correct. ^{85}Kr might have been lost during collection or later handling of the sample.

Table 8

Comparison of ^{85}Kr and SF_6 Samples

Sampling Location	^{85}Kr (pCI/SCM)	SF_6 (10^{-12}cc/cc)	$^{85}Kr/SF_6$ Ratio
A-4	1365	29	47
B-4	324	1.2	270
C-3	Background	1.1	----
C-6	281	8.4	33
D-6	142	3.8	37

2.7.2 Cryogenic Sampling Results (12B2 and 114B2)

Cryogenic sampling was intended only to augment the more precise data obtained from Saran bag collections at the ground and the SF_6 profiles aloft. When the Saran bags failed to retain the fluorocarbons, the cryotraps became the only source of data on 12B2 and 114B2 concentrations.

Cryotrap samples were taken every fifteen minutes at one location on each sampling arc (3 locations on arc C). Data are provided in Appendix B. An illustration of the plume concentration fluctuations with time at a fixed sampling position (C-6) is shown in figure 20. When duplicate samples were taken, both the range and the mean are shown.

Simultaneous cryotrap samples were taken once each hour at the sampling positions listed in Table 9. Sample pairs are listed only when at least one positive reading was obtained. In general, the 12B2 sample pairs reveal the lack of precision inherent in the cryotrap techniques used in this experiment. Although some pairs of simultaneous samples show good agreement, others differ by a factor of 4 or more. Two steps in the sampling and analysis procedure are believed to have caused most of the trouble. First, allowing most of the O_2 and N_2 to boil off before crimping the cryotrap may have allowed fractionation to occur; that is, different fractions of 12B2 and Freon 11 may escape from the trap. This problem may have been most severe with the duplicate samples because of the difficulty in handling two samples simultaneously. The 12B2-SF_6 comparisons (Tables 10 and 11) show better agreement than the duplicate samples.

Only 2 pairs of 114B2 simultaneous measurements were obtained but they show agreement well within a factor of two. Based on release rates, 114B2, when present in a sample, should show about twice the 12B2 concentration.

An indirect comparison may be made between 12B2 and SF_6 concentrations. At those sampling positions where cryotraps were taken, the SF_6 in the Saran bag collection can be used to calculate the average 12B2 concentration during the collection period ($12B2/SF_6 = 0.53$). By averaging the cryotrap concentrations taken every 15 minutes during plume passage, one can also

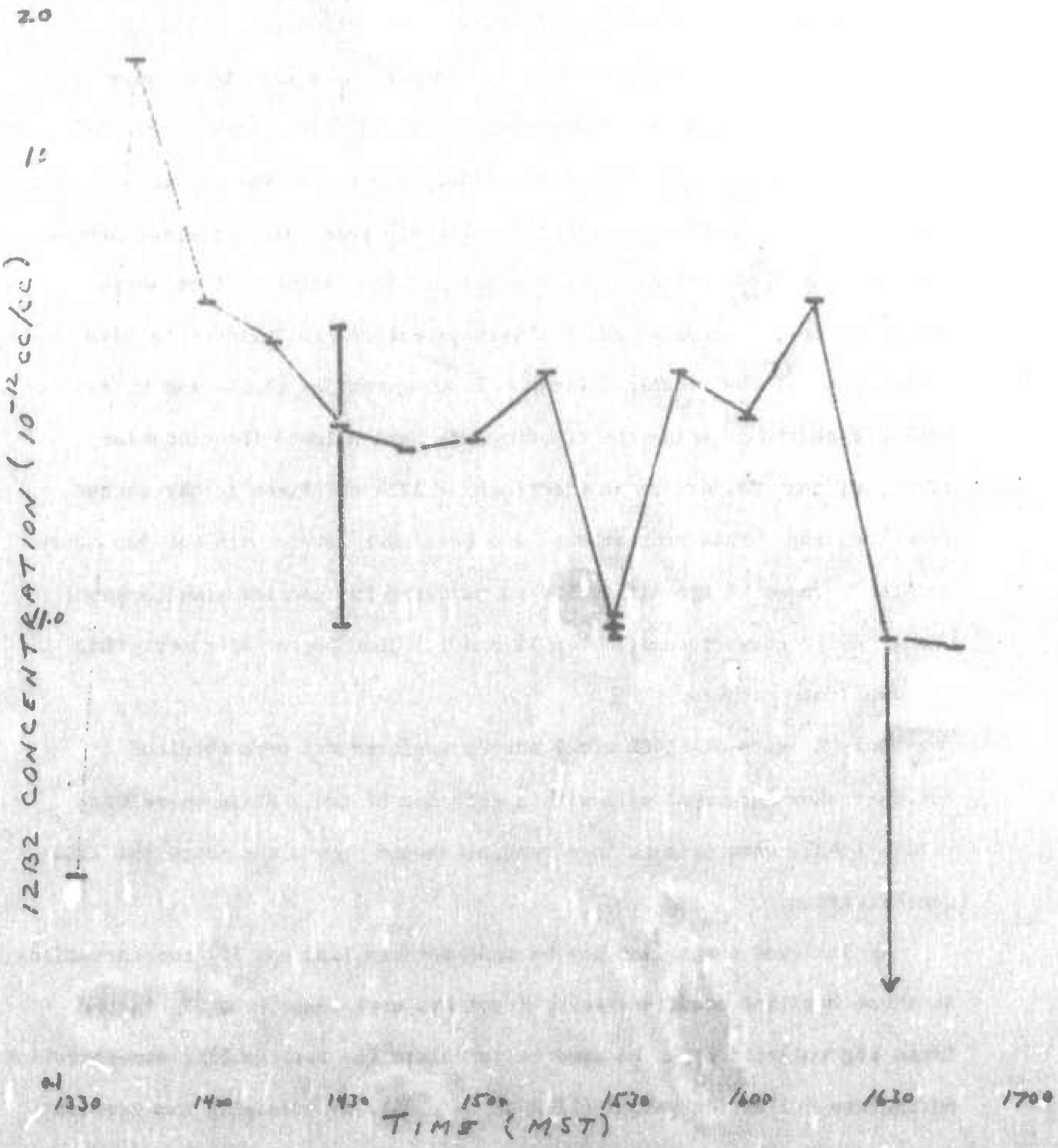


Figure 20. Variation of concentration with time at position C-6.

Table 9
Cryotrap Sample Replicates
(Ground-Level Samples)

Sampling Position	Time (MST)	12B2 (10^{-12} cc/cc)	114B2 (10^{-12} cc/cc)
A-4	1320	13.6	-
		29.4	-
A-4	1420	5.9	-
		1.6	-
A-4	1520	0.11	-
		<0.15	-
B-4	1500	18.1	-
		14.1	-
C-4	1330	6.6	8.2
		2.6	5.1
C-4	1430	0.77	-
		<0.21	-
C-4	1530	2.6	-
		3.1	-
C-6	1330	[illegible]	-
		[illegible]	-
C-6	1430	1.0	-
		4.4	-
C-6	1530	0.94	-
		1.03	-
C-6	1630	0.92	-
		<0.16	-
D-6	1400	<0.34	-
		0.15	-
D-3	1435	1.6	6.4
		5.3	8.5

estimate the average 12B2 concentration during the Saran bag collection period. Results of these two estimates are compared in Table 10.

Table 10

Comparison of Cryotrap Samples (12B2) with Time-Integrated Samples (SF_6)

Sample Position	Estimated 12B2 Concentration in Saran Bag (10^{-12} cc/cc) From SF_6 in bag	From Cryotraps
A-4	16	18
B-4	0.64	1.2
C-4	0.75	0.58
C-6	4.5	3.1
C-8	Not detectable	Not detectable
D-3	0.43	0.30

Agreement is rather good in every case. This may indicate that while the cryotrap procedures were subject to rather large random errors, as indicated by the duplicate sample results shown in table 9, the average of a series of cryotraps was much more reliable.

On arcs A and B, individual aircraft chromatograph profiles of SF_6 and cryotrap samples (12B2 and 114B2) both encompassed the entire plume cross-section. Since the cryotraps sampled for a longer period (1 to 3 minutes compared to 46 seconds) the cryotrap concentrations should be lower than the average concentration in the corresponding SF_6 profile. The SF_6 profile area (sec cc/cc) divided by the cryotrap duration (sec) for each pass gives the expected SF_6 (or 114B2) concentration in the cryotrap. Adjusting for release rates by multiplying by 0.53 gives the expected 12B2 in the cryotrap. Table 11 compares the measured 12B2 and

Table 11

Comparison of Aircraft Cryotrap Measurements (12B2 and 114B2) with Chromatograph Profiles (SF_6)

Cryotrap Sample	Profile Number	Altitude (Meters)	Concentration (10^{-12}cc/cc) 12B2	Calc from SF_6	Ratio Meas/Calc	Concentration (10^{-12}cc/cc) 114B2	Calc from SF_6	Ratio Meas/Calc
21	1A	270	24	44	0.55	109	82	1.3
23	3A	610	34	38	0.89	97	72	1.3
24	4A	600	24	110	0.22	57	210	0.27
26	6A	890	36	13	2.8	—	—	—
28	8B	220	2.2	4.8	0.46			
29	9B	300	3.2	3.7	0.87			
30	10B	220	2.7	2.3	1.2			
31	11B	580	2.0	3.7	0.54			
32	12B	590	4.3	1.3*	3.3*			
34	13B	910	1.4	4.8	0.29			
33	14B	850	2.9	3.7	0.78	2.8	7.0	0.40
35	15B	1200	5.2	2.7	1.9			
36	16B	1450	0.7	5.1	0.14			

* SF_6 crosswind integral appears to be low - profile 12B may cover only part of the plume.

114B2 cryotrap concentrations with the expected concentrations calculated from the SF_6 profiles. Basic data are provided in Appendix C. The agreement between measured and calculated values is surprisingly good considering the uncertainties involved. The onset time of cryotrap sampling (after the cryotrap was immersed in liquid N_2) is known to have been variable and the flow-rate into the trap after sampling began was not uniform. In the rapidly changing concentration field encountered as the aircraft traversed the plume, is is estimated that these factors could affect the measured concentration by ±30 percent. Other uncertainties involved in the cryotrap sampling and analysis procedures have already been discussed.

2.8 Conclusions

This first field test of instrumentation and techniques for release, sampling and analysis of two new atmospheric tracers achieved most of its objectives. Feasibility of a simple, inexpensive cryogenic sampling procedure for fluorocarbons 12B2 and 114B2 has been demonstrated. Concentrations down to 4 parts in 10^{14} of air were cryotrapped in the field and measured by an electron-capture gas chromatograph. Several problems were uncovered which indicate the need for further development work before a completely satisfactory meteorological experiment can be conducted with these tracers.

The most complete set of data was obtained with the SF_6 tracer using previously tested techniques. The use of an airborne chromatograph greatly enhanced the information obtained by ground-level sampling. Results, problems encountered, and areas where further development is needed, are summarized below.

2.8.1 Plume Transport and Diffusion

Plume trajectory and horizontal spread were well delineated to a distance of almost 90 km by ground-level SF_6 samples and airborne chromatograph profiles. Radar tracking of tetroons launched near the tracer release point proved very useful in locating the narrow plume and directing aircraft sampling. Dependence of the horizontal standard deviation (σy) on sampling duration is clearly seen in comparing instantaneous values from airborne sampling with long-term average values from continuous ground-level samples. More such data are needed to develop a functional relationship dependent on stability, wind speed, and plume travel time or distance. Another problem encountered in the analysis involves the estimation of σy from experimental data that are non-normally distributed. On the 18-km arc, for example, σy of the actual crosswind distribution at ground level differed by more than a factor of two from the σy obtained by assuming a Gaussian distribution. Since experimental values are intended for use in a Gaussian plume model, it seems logical to use the Gaussian assumption in estimating σy from plume concentration data. It is suggested that more attention be given to effects of sampling duration and methods of estimating σy so that experimental data from different studies could be placed on a truly compatible basis.

Sampling profiles aloft indicated that the plume had mixed upward to nearly 1000 meters at the 6 km arc but the calculated total amount of SF_6 passing this arc was about a factor of 3 too high when compared to the release amount. This suggests that the instantaneous plume was not spread through the 1000 meter layer, but rather, a more narrow plume experienced vertical oscillations within the layer that resulted in an unrepresentative vertical profile being obtained from non-simultaneous crosswind profiles at different altitudes. This hypothesis could be checked with another tracer experiment under similar meteorological conditions, using several aircraft to obtain a series of simultaneous profiles at several altitudes over the arc. Another possibility might be to visually observe and photograph a plume of smoke or dye under similar conditions.

Crosswind profiles and material balance considerations suggest that the plume had spread fairly uniformly in the vertical, to about 2000 meters at 18 km and about 2300 meters at 40-90 km. Unfortunately, with strong winds blowing the plume rapidly past the arcs, there was insufficient time to directly establish the altitude of the top of the plume beyond the first arc. The use of two aircraft in future experiments of this type would involve little additional expense, while greatly enhancing the prospects for attaining all objectives of the experiment.

2.8.2 Tracer Release, Sampling and Analysis

Several problems were encountered in release, sampling and analysis of 12B2 and 114B2. None of these difficulties appear to be insurmountable.

There were no serious problems in the release of SF_6 or 12B2. However, release of 114B2 was terminated when the dispensing pump failed. This was a mechanical problem that should be overcome by equipment changes.

Saran bag sample collectors that worked well with SF_6 were found to retain 12B2 and 114B2 very poorly. It is likely that some other plastic will prove suitable for these tracers; otherwise a different long-term sampling system would have to be devised.

A better controlled cryotrapping technique should be developed. A controlled release, in the laboratory, of the O_2 and N_2 in the cryotrapped sample would be preferable to boiling off these constituents in the field. A larger cryotrap, at least 5cc, should be used. Procedures for achieving greater concentration of the sample should be investigated further. In principle, a concentrating factor of 10^3 seems attainable by a 2-stage cryotrap procedure as suggested in section 2.5.2. This could extend the range for detection of these tracers to 1000 km or more.

The airborne chromatograph is being further developed at Brookhaven to permit continuous sampling over any desired time (by automatically switching chromatographic columns during backflush). This development will greatly enhance its usefulness in meteorological tracer work. Some additional work would be required to adapt the instrument to 12B2 and 114B2 rather than (or in addition to) SF_6.

Finally, the efficiency of a gas chromatograph for a given trace compound can be precisely established (6) so that concentration measurements are absolute. Lovelock's calibrations for the instrument used in this experiment have not yet been confirmed. Efforts to resolve this problem, in consultation with Lovelock, are continuing.

2.8.3 Feasibility of Long-Range Experiments

If the difficulties brought to light in this field test can be overcome by further development work, it may be feasible to use these tracers for a cross-country diffusion experiment. Assuming that a 2-stage cryotrap or some other concentrating procedure could lower the detection limit to a few parts in 10^{13} of air, the amount of tracer needed for a cross-country experiment would depend on the existing background concentration in the atmosphere. Estimated background concentrations and calculated tracer amounts required for a cross-country experiment are shown in Table 12 for SF_6, 114B2 and 12B2. Background values for SF_6 are based on actual measurements which indicate great variability due to many large local sources. Background values for 114B2 and 12B2 are based on the assumption that the total production to date resides in the atmosphere and is uniformly distributed. This assumption appears reasonable for 12B2 but information from Dupont indicates that 114B2 is probably destroyed in use and background concentrations may be comparable to 12B2. Background measurements should be attempted when an adequate concentration technique is developed.

Tracer requirements were calculated assuming a 12-hr release in the western U.S. and four days travel time to the east coast where the desired peak concentration in a 12-hr sample is 50 times background. Amounts required per experiment vary from about 1000 lb of 12B2 to more than 17 tons of SF_6. The tracer cost of about $6000 per experiment would make the use of 12B2 feasible. If the background proved to be as low as Dupont believes, the cost for 114B2 would be about the same as for 12B2.

In summary, SF_6 is the tracer of choice, at present, for distances to several hundred km, however, the high, and rapidly increasing, background concentration precludes its use on a cross-country scale. The fluorocarbons, 12B2 and 114B2, both appear promising as long-range tracers. Background is believed to be very low and there is a reasonable expectation that measurement down to 1 part in 10^{15} of air should be

Table 12

TRACER COMPARISON

Tracer	Molecular Weight	Cost/lb	Background Tons in Atmosphere	Current Annual Input (Tons)	Estimated Background Conc. (10^{-16}cc/cc)	Tons/experiment (Peak = 50 BKGD on E. Coast)	Tracer Cost
SF_6	146	$2.25	>3000	Increasing	>300	>17	>$76,000
114B2	260	3.25	850*	<50*	100*	10*	65,000*
12B2	210	5.75	35	<5	7	0.5**	5,750**

* Based on assumption that entire production remains in the atmosphere, however, 114B2 may be destroyed in use so that the amount required and cost may be comparable to 12B2.

** Assumes present detection capability can be improved significantly (see text).

possible. More work is needed on procedures for release, sampling, and precise measurement of these new tracers. Basic procedures for cryotrapping and chromatographic analysis of the tracers were successfully demonstrated in this field trial.

3. REFERENCES

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Appendix A

Ground-Level SF_6 Samples

Ambient air was slowly pumped at a uniform rate into Saran bag collectors during the entire time of plume passage at each arc. Since the samplers had to be turned on and off manually with limited manpower available, some samplers operated much longer than others, thus diluting the collected sample concentration.

Samplers marked with a star on arc D operated for less than the full period of plume passage due to mechanical trouble. Sampling times at these positions (D-1, 2, and 8) are uncertain and results are doubtful.

ND indicates SF_6 was not detectable (less than about 5×10^{-13}cc/cc).

Ground-level SF_6 sampling data are plotted in figures 15 and 16.

Table A-1

Ground-Level SF_6 Samples

(Saran Bag Collections)

Sample Location	Time (MST) On	Time (MST) Off	Sampling Duration (Minutes)	SF_6 Concentration (10^{-12}cc/cc)
A-1	1234	1722	288	4.9
A-2	1228	1716	288	28.7
A-3	1221	1709	288	140
A-4	1211	1655	284	29.2
A-5	1204	1647	283	0.6
A-6	1158	1642	284	ND
A-7	1149	1632	283	ND
B-1	1207	1825	378	0.7
B-2	1200	1813	373	ND
B-3	1206	1805	359	ND
B-4	1224	1755	331	1.2
B-5	1145	1747	362	9.0
B-6	1135	1730	355	1.3
B-7	1132	1720	348	ND
B-8	1125	1707	342	ND
B-9	1118	1635	337	0.7

Table A-1 (con't.)

Sample Location	Time (MST) On	Off	Sampling Duration (Minutes)	SF_6 Concentration (10^{-12} cc/cc)
C-1	1300	1730	270	ND
C-2	1305	1718	253	ND
C-3	1309	1710	241	1.1
C-4	1308	1702	234	1.4
C-5	1305	1711	246	6.1
C-6	1301	1715	254	8.4
C-7	1315	1734	259	2.9
C-8	1300	1707	247	ND
C-9	1307	1720	253	ND
D-1	1537	1742	125	ND*
D-2	1245	1545	180	0.7*
D-3	1254	1756	302	0.8
D-4	1300	1802	302	1.5
D-5	1306	1807	301	7.9
D-6	1320	1850	330	3.8
D-7	1329	1825	296	ND
D-8	1646	1825	99	1.2*
D-9	1343	1820	277	ND
D-10	1413	1836	263	ND
D-11	1324	1812	288	ND
D-12	1253	1737	[illegible]	ND
D-13	1230	1720	290	ND
D-14	1219	1705	286	ND

Appendix B

Ground-Level Cryotrap Sampling Data

Cryotraps were used to take approximately 3-minute samples every 15 minutes at the indicated positions on each arc (see figure 3 for sampling locations). Note that two samples were taken simultaneously once per hour at each location. Concentrations are given in parts per 10^{12} of air by volume (cc/cc). A sample was collected and analyzed for 12B2 and 114B2 for every time shown. Where no concentration is shown the concentration was below the detection limit. The minimum detectable concentration varied from sample to sample, depending on the concentration factor achieved with each cryotrap, but the limit was usually less than $5x10^{-13}$ for 12B2 and less than $1x10^{-12}$ for 114B2.

Based on average emission rates, concentrations of 114B2 should have been about twice those of 12B2 when 114B2 was present in the plume. Except for several bursts of a few minutes duration, 114B2 was released only during the first half-hour of the 3-hour release period (see section 2.2). Relatively few samples were taken when 114B2 was present.

Table B-1

Ground-Level

Cryotrap Sampling Data

Position: A-4			Position: B-4		
Time (MST)	Concentration ($X10^{-12}$) 12B2	114B2	Time (MST)	Concentration ($X10^{-12}$) 12B2	114B2
1226			1245		
1226			1300		
1235			1300		
1250	0.93	4.2	1315		
1305	0.66	1.1	1330		
1320	13.6		1345		
1320	29.4		1400		
1335	95.5		1400		
1350	165.5	0.81	1415		
1405	59.7	68.6	1430	0.19	
1420	5.9		1445	2.0	
1420	1.6		1500	18.1	
1435	0.37		1500	14.1	
1450			1515	10.4	
1505			1530	0.37	
1520	0.11		1545		
1520			1600		
1535	5.4		1600		
1550	0.11		1615		

Table B-1 (con't.)

Position: C-4			Position: C-6		
Time (MST)	Concentration (X10^{-12})		Time (MST)	Concentration (X10^{-12})	
	12B2	114B2		12B2	114B2
1313			1310		
1330	6.6	8.2	1330	0.29	
1330	2.6	5.1	1330		
1345			1345	16.8	
1400			1400	5.0	
1415			1415	4.1	
1430	0.77		1430	1.0	
1430			1430	4.4	
1445			1445	2.4	
1500			1500	2.5	
1515			1515	3.5	
1530	2.6		1530	0.94	
1530	3.1		1530	1.03	
1545			1545	3.48	
1600			1600	2.77	
1615			1615	4.88	
1630			1630	0.92	
1630			1630		
1645			1645	0.88	
1700					

Position C-8: Sampled from 1320 to 1700 MST; only positive measurement was 0.13x10^{-12} (12B2) at 1500 MST.

Table B-1 (con't.)

Position: D-6

Time (MST)	Concentration ($X10^{-12}$) 12B2	114B2
1400		
1400	0.15	
Moved to Position <u>D-3</u>		
1435	1.6	6.4
1435	5.3	8.5
1450	0.38	
1505	1.1	
1520	1.0	
1535		
1535		
1550		
1605	0.04	
1620		
1635		
1635		
1650	0.06	
1705		
1720		

Appendix C

Airborne Sampling Data

Cryotrap samples (12B2 and 114B2) and chromatograph profiles (SF_6) were taken as the aircraft made passes over each arc at several altitudes. Cryotrap data are given in table C-1 and chromatograph data in table C-2.

Sampling altitudes are given as height above terrain. Approximate mean terrain height (meters) above sea level at each arc is:

Arc A	1490
Arc B	1490
Arc C	1460
Arc D	1550

The aircraft made nearly straight-line passes over each arc. Aircraft positions are indicated by the nearest ground-sampling position on arcs A and B, and estimated to the nearest tenth of the distance between positions on arc C. For example, C 2.9 indicates a position nine-tenths of the way from C-2 to C-3 (see figure 3). On arc D, the straight-line flight path departed significantly from the sampling arc so aircraft sampling positions are shown in figure C-1. The reader is cautioned that sampling times and locations are only approximate; not precise enough, for example, to determine the plume tilt with altitude.

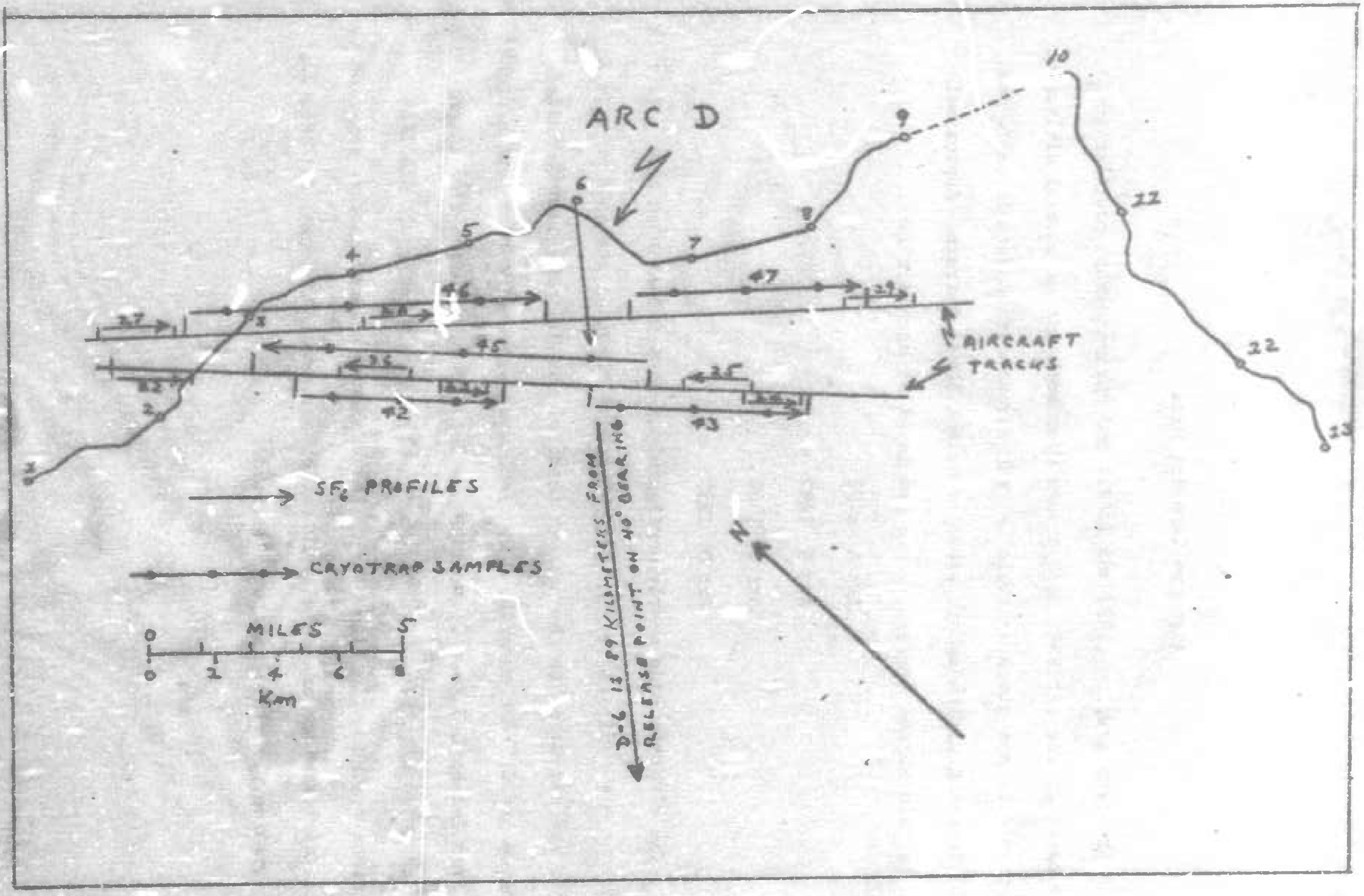

Figure C-1. Approximate aircraft sampling positions on arc D.

Table C-1

Aircraft Cryotrap Data

Notes

Laboratory tests indicated that the cryotrap began to draw in outside air an average of 30 seconds after immersion in liquid nitrogen. Therefor sample starting times, here given to the nearest minute, are assumed to be 30 seconds after the cryotrap is immersed in the flask of liquid nitrogen. Sample duration is given as total time of immersion less 30 seconds.

*Sample 25A: There is some doubt about the location of this sample due to radio trouble and loss of radar contact. If the sampling path is correct, it indicates that the plume was not present at 850 meters at this time.

ND indicates tracer was not detectable.

Table C-1

Aircraft Cryotrap Data

Sample Number	Start Time (MST)	Sample Duration (sec)	Altitude Above Ground (meters)	Arc Location	Aircraft Speed (m/sec)	Average Concentration (10^{-12} cc/cc) 12B2	Average Concentration (10^{-12} cc/cc) 114B2
21A	1252	90	270	A2-A5	72	24.2	109
22A	1300	90	210	A4-A2	55	6.2	8.7
23A	1306	90	610	A2-A5	77	34.4	97.2
24A	1313	60	600	A4-A2	58	23.6	57.1
25A*	1321	195	850	A1-A7	--	ND*	ND*
26A	1327	135	890	A4-A1	54	35.8	ND
27A	1336	120	1000	A3-A7	75	ND	ND
28B	1347	150	220	B3-B9	66	2.2	ND
29B	1352	150	260	B7-B2	59	3.2	ND
30B	1359	120	220	B2-B7	63	2.7	ND
31B	1408	150	580	B3-B9	68	2.0	ND
32B	1414	90	590	B7-B4	60	4.3	ND
34B	1420	150	910	B3-B9	69	1.4	ND
33B	1427	105	850	B7-B4	60	2.9	2.8
35B	1433	150	1200	B4-B9	69	13.6	ND
36B	1441	180	1450	B9-B3	55	0.70	ND
37C	1456	105	280	C2.9-C4.3	51	ND	ND
38C	1500	108	270	C5.7-C8.0	41	1.6	ND
39C	1505	120	330	E of C9	42	ND	ND
40C	1600	150	310	C7.6-C5.7	42	3.1	ND

Table C-1 (con't.)

Sample Number	Start Time (MST)	Sample Duration (sec)	Altitude Above Ground (meters)	Arc Location	Aircraft Speed (m/sec)	Average Concentration (10^{-12} cc/cc)	
						12B2	114B2
41C	1605	150	240	C3.9–C2.1	43	ND	ND
42[illegible]	1646	150	240	See fig. C-1	43	0.36	ND
43D	1650	150	210	"	45	3.7	ND
44D	1654	45	210	East of D-8	45	ND	ND
45D	1659	270	490	See fig. C-1	47	1.9	ND
46D	1709	240	1000	"	49	ND	ND
47D	1714	150	1070	"	47	ND	ND

Table C-2

Aircraft Chromatograph Profiles

Notes

Profile Area is the integral under the trace of SF_6 concentration versus time (crosswind integral). Profiles are available from Air Resources Laboratories, Silver Spring, Md.

Profile 2A: Missed the plume (chromatograph sampled too far to the east). Cryotrap 22A sampled over a longer interval and "saw" the plume on this pass.

Profile 5A: No chromatograph sample taken due to radio trouble.

Profile 7A: Position of chromatograph sample unknown due to radio trouble. Cryotrap 27A confirms no plume detected at this altitude.

Profiles 11B and 16B: Still in plume at end of 46 sec sampling period. Values in parenthesis are estimates of total area under extrapolated profile.

ND indicates SF_6 was not detectable.

Profiles 22D, 24D, 26D, and 29D: "Barely detectable" indicates concentrations on the order of 1 to $3x10^{-12}$cc/cc with the instrument attenuation setting used on arc D.

Profiles 26D-29D: Sampling after 1700 MST probably took place after the main plume had cleared arc D. The plume certainly extended above 400 m on arc D but sampling was performed too late.

Table C-2

Aircraft Chromatograph Profiles (SF_6)

Profile Number	Start Time (MST)	Altitude Above Ground (meters)	Profile Location	Aircraft Speed (m/sec)	Profile Area (10^{-10} sec cc/cc)
1A	1251	270	A2-A4	72	76.3
2A	1259	210	A5-A3	55	ND
3A	1305	610	A2-A4	77	64.5
4A	1313	600	A4-A2	58	127.0
5A	—	850	—	—	No Sample
6A	1327	890	A4-A2	54	33.0
7A	1335	1000	?	75	ND
8B	1346	[illegible]	B4-B6	66	13.6
9B	1352	300	B8-B6	59	10.5
10B	1402	220	B4-B6	63	5.2
11B	1408	580	B4-B7	68	10.3 (11.6)
12B	1414	590	B8-B6	60	2.2
13B	1420	910	B4-B7	69	13.6
14B	1428	850	B8-B6	60	7.4
15B	1433	[illegible]	B6-B8	69	7.7
16B	1441	1450	B9-B7	55	12.9 (17.2)
17C	1454	280	C1.3-C2.1	51	ND
18C	1459	280	C4.4-C5.1	47	7.9
19C	1503	290	C8.4-C9.0	42	ND
20C	1558	330	C9.0-C8.4	40	ND

Table C-2 (con't.)

Profile Number	Start Time (MST)	Altitude Above Ground (meters)	Profile Location	Aircraft Speed (m/sec)	Profile Area (10^{-10} sec cc/cc)
21C	1603	350	C5.6-C4.9	45	4.6
22D	1643	280	See Fig. C-1	54	Barely detectable
23D	1648	230	"	39	4.7
24D	1652	210	"	45	Barely detectable
25D	1657	400	"	47	2.4
26D	1702	510	"	48	Barely detectable
27D	1708	960	"	48	ND
28D	1712	1000	"	49	ND
29D	1716	1070	"	47	Barely detectable