DP-1469

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HEAVY METHANE-SF_6 TRACER TEST CONDUCTED AT THE SAVANNAH RIVER PLANT, DECEMBER 10, 1975

SAVANNAH RIVER LABORATORY
AIKEN, SOUTH CAROLINA 29801

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY UNDER CONTRACT AT(07-2)-1

Printed in the United States of America

Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

Price: Printed Copy $5.25; Microfiche $3.00

662713

DP-1469
Distribution Category: UC-11

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Approved by:

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Environmental Transport Division

Publication Date: April 1978

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ABSTRACT

Concern for man's impact on his environment requires an understanding of transport and dispersion of airborne pollutants on regional, continental or global scales. Collection of experimental data in which the transport and diffusion processes can be isolated from source and sink factors is needed in order to help this understanding. A test performed at the Savannah River Plant on December 10, 1975, to obtain this kind of data was part of a DOE-supported program in cooperation with other laboratories and groups. The object of this test was to obtain data by using several tracers which are inert and non-depositing in order to isolate the effects of long-range transport and diffusion. The tracers used in this test are sulfur hexafluoride, methane-20 and -21 (as developed by the Los Alamos Scientific Laboratory), and routine emissions of krypton-85.

Considerable experience was gained in release, sampling, processing and analysis of these tracers. Data from this test will allow the study of transport and dispersion of plumes to 100 km from a point source. Considerable data both on the ground and by aircraft at these distances were obtained. Collection of sulfur hexafluoride along with the two methane tracer systems were compared and a discrepancy between them was seen. The peak concentration and concentration summed over a sampling line show the methane to be low by about a factor of four relative to the sulfur hexafluoride. Sulfur hexafluoride appears to agree with the krypton-85 and mass balance calculations. Some explanations for the methane-sulfur hexafluoride discrepancy are given but no positive conclusion for this difference can be reached at this time. Conduct of the test and the data are described in this report.

FOREWORD

This report describes the results of a heavy methane-sulfur hexafluoride tracer test conducted December 10, 1975, as part of a number of tests performed at the Savannah River Plant (SRP) during the first 19 days of December 1975. This test was planned and executed by scientists from the Air Resources Laboratory (National Oceanic and Atmospheric Administration), Los Alamos Scientific Laboratory, Brookhaven National Laboratory, Lawrence Livermore Laboratory, and the Savannah River Laboratory. Personnel from Airco, Inc., and EG&G, Las Vagas, Nevada, took part in the test. An EG&G aircraft was used in the test.

Funds for the EG&G aircraft were provided by the Department of Energy (DOE) Division of Biomedical and Environmental Research in support of the Savannah River Laboratory (SRL) Atmospheric Release Advisory Capability - Southeastern United States (ARAC-S.E.U.S). The ARAC system has been developed by the Lawrence Livermore Laboratory (LLL) to provide support to ERDA sites in case of accidental releases to the atmosphere. The feasibility of ARAC was previously demonstrated at SRP with the EG&G radioactive tracking capability. The tests were designed to more fully validate the ARAC system by tracking the small amount of radioactive materials released to the atmosphere as a consequence of routine production at SRP as well as by tracking and measuring release of inert gases from the stacks at the SRP. Releases of this type are more nearly able to simulate accidental releases. Since the aircraft was scheduled to be at SRP awaiting weather conditions most appropriate for the ARAC tests, other tests, not discussed in this report, were planned to use this EG&G aircraft. These tests included:

a) The three ARAC tests (one of which was the December tenth joint test)

b) A test which monitored and photographed a controlled forest fire burn at SRP in cooperation with the U.S. Forest Service

c) A test which measured the three-dimensional concentration of tritium and tritiated water vapor downwind of the plant.

d) A flight measuring the natural and man-made radiation on the banks of the Savannah River between the plant and Savannah, Georgia, and within areas of the Savannah estuary

e) A series of flights which mapped the plantsite by using infrared scanning techniques and multispectral photography. The photographs are used for biological purposes.

Other reports and papers prepared by individuals at the different laboratories will evaluate the data obtained during the December tenth test and other tests mentioned above.

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INTRODUCTION

Concern for man's impact on his environment requires an understanding of transport and dispersion of airborne pollutants on regional, continental or global scales. The development of the requisite knowledge depends upon the collection of experimental data in which the transport and diffusion processes can be isolated from source and sink factors. Much of the currently existing data was gathered with effluents from multiple sources subjected to deposition, precipitation scavenging, and chemical transformation along the travel path. An inert, nondepositing tracer is needed to isolate the effects of long-range transport and diffusion.

The test performed on December 10, 1975, was part of an ERDA-supported effort in cooperation with several groups, each with expertise in particular aspects of the program. The test and data analysis were planned and carried out by scientists from the Air Resources Laboratories (ARL) of the National Oceanic and Atmospheric Administration (NOAA), Brookhaven National Laboratory (BNL), Los Alamos Scientific Laboratory (LASL) and the Savannah River Laboratory (SRL). In addition to these groups, personnel from Airco, Inc., and EG&G, Las Vegas, Nevada took part in the tests and in data processing and interpretation. An important program goal is to develop suitable tracer systems, to test them under field conditions, and ultimately to conduct tracer tests to test pollution models on all scales of interest.

A tracer should have a residence time in the atmosphere of at least several weeks or several years for a global experiment to be suitable for these purposes. The tracer should be nontoxic and not harmful to the environment; it should be relatively inexpensive, and the cost of sample analysis should not be prohibitive; it must be detectable at very low concentrations with almost no existing background in the atmosphere. In addition, simplicity of sample handling, a capability for short-duration sequential sampling, and speed of data reduction are desirable.

Several tracers have some of these properties. Sulfur hexafluoride (SF_6) has been used for medium-scale studies (out to about 100 kilometers), but a relatively high background from industrial uses makes it unsuitable for long-range studies.

Methane-20 and -21, used in this test, look promising. Cowan et. al.[1] report on long-range detection of methane-21 in a previous test. Another potential long-range tracer system, with perfluorocarbons, is being investigated by the Air Resources Laboratories (ARL) and was field-tested in the spring of 1977.

Goals of the Tracer Test

The test of December 10 had three specific objectives. The primary purpose was to determine if the SF_6 and methane tracer systems would give comparable results when the tracers were released and sampled simultaneously. This test provided an overall test of release, sampling, analysis procedures, and atmospheric behavior of both tracers. SF_6 was also planned for use as a standard to evaluate the perfluorocarbon tracer system in the follow-up experiment. The second objective was to study the transport and dispersion of the plume 100 kilometers from a point source. The third objective of this experiment was to gain experience in release, sampling, processing, and analysis of these tracers before proceeding to larger-scale experiments.

Design of Test

Three special tracers, SF_6 and two heavy methanes $^{12}CD_4$ and $^{13}CD_4$), were released over a four-hour period. The collected samples containing the heavy methanes were analyzed by a special mass spectrometer for minute quantities of the compounds (10^{-10} to 10^{-11} ppt of normal methane by volume). In addition, all samples were analyzed for krypton-85, which is routinely released from SRP in nuclear fuel reprocessing operations.

The general plan called for a line of surface air samplers laid out at a distance of about 100 kilometers from the source and spaced about three kilometers apart. Because the samplers had to be set out, turned on and off, and picked up the day of the experiment, placing them along a highway for quick access was necessary. Thus, the actual locations and distances from the source, both of which were governed by the highway locations, placed constraints on the acceptable wind conditions for the experiment.

The ground samplers collected both SF_6 and the methanes for inter-comparison. In addition, the vertical distribution of the plume was examined by means of aircraft sampling. The plan called for the EG&G aircraft to obtain profiles of the SF_6 plume at several altitudes and distances from the source, including one flight line over the ground samplers. Two electron-capture gas chromatographs, developed at BNL, were mounted in the aircraft

and provided nearly real-time measurements of SF_6. Also, a few large bags were filled on board the aircraft for subsequent analysis for SF_6, krypton, and the methanes. The flight plan for aircraft sampling had to be determined during the day of the experiment based on the wind speed and direction, the aircraft navigational capabilities, and fuel capacity.

Meteorological criteria entering into the test design were governed mostly by practical considerations. The tracer was to be transported from the source to the sampling line with a minimum of mesoscale complexities. Acceptable flying weather without major restrictions was required to vector the aircraft into the vicinity of the tracer plume. Major temporal or spatial changes in winds such as are present in frontal zones were to be avoided.

The planned sampling line dictated that the mean wind direction for transport of the tracer be between 210° and 330° azimuth. The logistics of activating the samplers required moderate wind speeds. A climatological summary was prepared from a review of eleven years of December surface charts. Geostrophic winds and observed surface winds at Augusta, Georgia, were estimated daily; and weather conditions which might affect flight operations or introduce unwanted complications into the flow field were tabulated. About 40% of the days had winds in the acceptable sector with fair weather. The additional constraint of moderate wind speed reduced the likelihood of acceptable test conditions to about 15%. The test plan allowed for continuous monitoring of the meteorological situation and required a system of alert notices with lead times as long as 36 hours. The option to cancel a test was retained until release time, or even 20% into the tracer release phase if meteorological conditions deteriorated.

The tracer test was carried out successfully, but a bias was found between the heavy methane and SF_6 results; methane concentrations were low relative to SF_6 by nearly a factor of four. Possible causes of this discrepancy are being investigated.

TRACER RELEASE

The three tracers (SF_6, $^{13}CD_4$, and $^{12}CD_4$) were released simultaneously over a four-hour period beginning at 10:25 A.M. EST on December 10, 1975. A total of 285.5 grams of methane-20, 85.5 grams of methane-21, and 154 kilograms of SF_6 was released. Calculations indicated that these amounts would be sufficient to permit delineation of the tracer plumes by the ground-level and airborne samplers at 100 kilometers from the source, if a reasonable safety margin for meteorological uncertainties and experimental error were allowed. The actual release rates are shown in Figure 1. Release rates of the two methane gases were monitored with precalibrated Matheson Gas Mass Flowmeters. Flowmeter calibrations were made with normal methane by displacing water to measure flow for either a fixed length of time or a fixed total volume. Methane was assumed to behave as an ideal gas at the temperatures and pressures used (17°C, 0.76 atm). No correction was made for the vapor pressure of water (14 mm at 17°C) in the calibration. The sulfur hexafluoride release was monitored with a gas rotameter. The rotameter rate, pressure, and temperature were recorded every ten minutes. The total mass of each tracer released was also determined by weighing the gas cylinders before and after release.

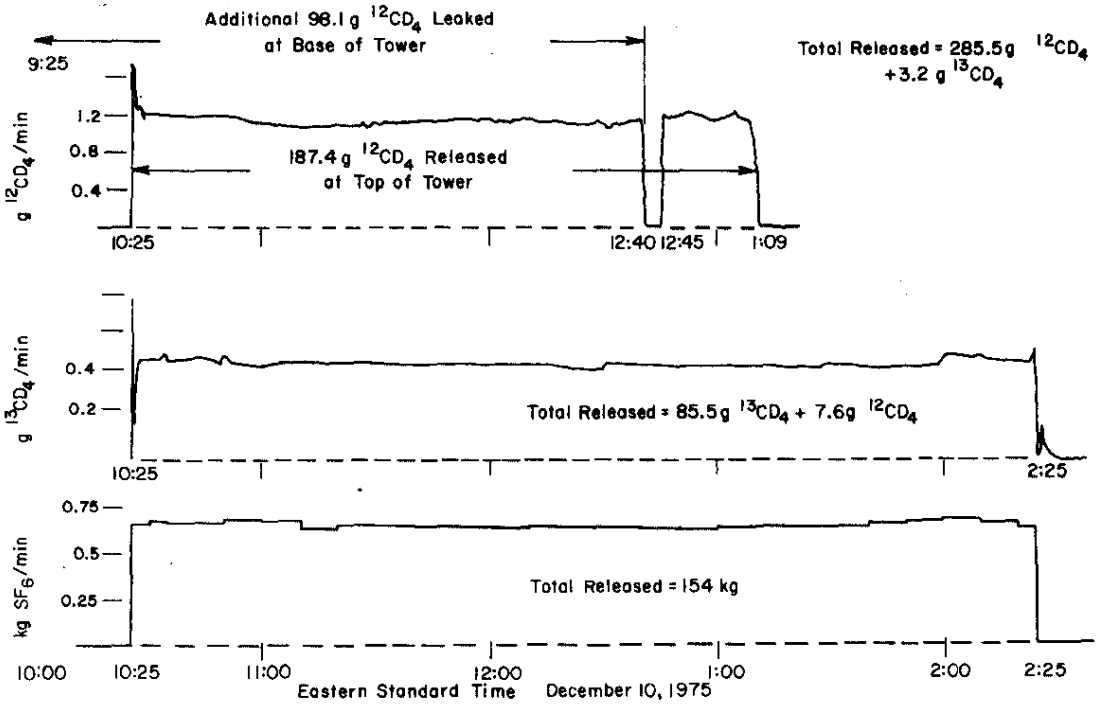

FIGURE 1. Matheson Mass Flow Meter Records for Methane-20 and Methane-21 Release Rates. Histogram of SF_6 Release Rate Constructed from Rotometer Flow Rate, Pressure, and Temperature Readings.

Methane-20 Gas

Methane-20 gas ($^{12}CD_4$) was released at the top of the A-Area 62-meter meteorological tower (Figure 2, tracer release location A. Areas of release are designated A, F, and H.) The methane, metered through a mass flowmeter, was mixed into a rapidly flowing stream of N_2 gas which was piped to the top of the tower, through a one-half-inch I.D. tygon tube (Figure 3). The methane-20 gas was contained in two compressed gas cylinders. The pressure regulator on one of the cylinders leaked 98.1 grams of methane-20 at the base of the tower between 09:25 A.M and 12:40 A.M. EST. 187.4 grams of methane-20 which was released at the top of the tower was metered through the mass flowmeter shown by the top release rate record in Figure 1. The methane-20 released also contained 3.2 grams of methane-21 which was released at the A-Area tower.

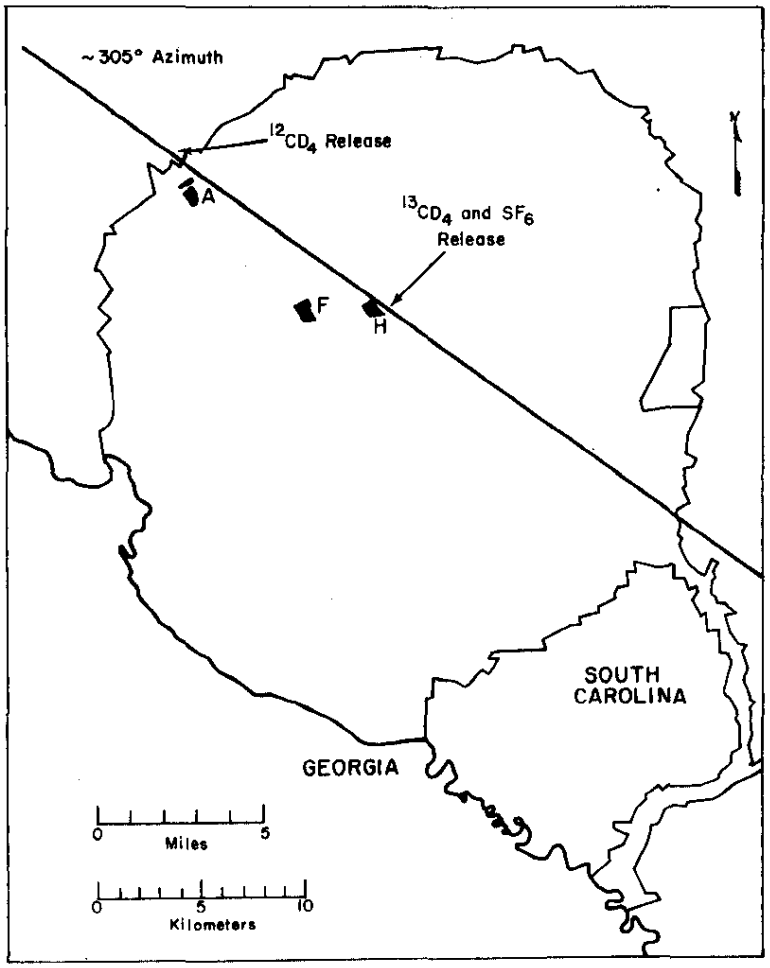

FIGURE 2. Tracer Release Locations (A and H) on the Savannah River Plantsite

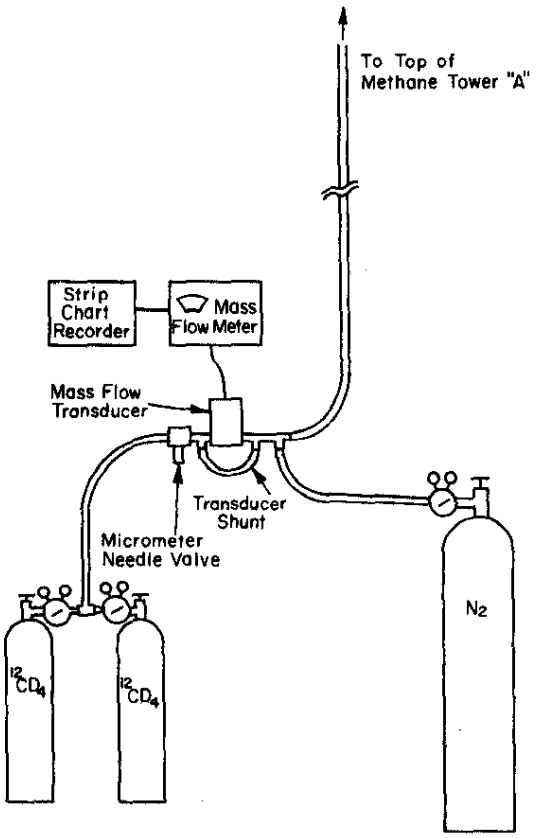

FIGURE 3. Methane-20 Release System

Methane-21 and SF_6 Gases

Methane-21 gas ($^{13}CD_4$) and sulfur hexafluoride (SF_6) were released into the top of the 62-meter exhaust stack at H Area. A Area is approximately 11 kilometers west-northwest of H Area on the 305° azimuth (Figure 2). On the day of the release, H Area was almost directly downwind of A Area. The methane-21 was metered through a mass flowmeter, and the SF_6 was metered through a rotameter. The two gases were mixed at the inlet of the SF_6 rotameter. They were routed to the top of the stack through a stack-gas sampling line (Figure 4). Flow in the sampling line was the reverse of that normally used for sampling. The 85.5 grams of methane-21 plus 7.6 grams of methane-20 were released at the rate shown by the mass flowmeter record (Figure 1). Due to a calibration error, only 154 kilograms (339 pounds) of SF_6 was released at the rate shown by the histogram constructed from rotameter readings (Figure 2). Fortunately, the safety margin built into the experimental design was sufficient to tolerate the reduced release amount.

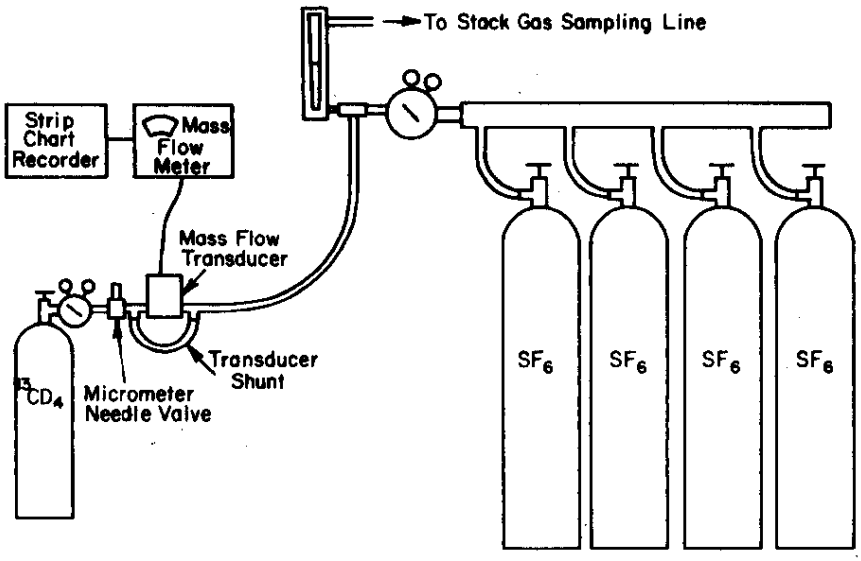

FIGURE 4. SF_6 and Methane-21 Release Mechanism

Krypton-85

As a result of routine plant operations on the day of the experiment, krypton-85 was released from the H-Area stack and from a 62-meter stack in F Area, about three kilometers to the west. Estimates of the combined hourly krypton-85 release amounts during the day are given in Table 1.

TABLE 1

Total Hourly Releases of Kr-85 from the Savannah River Plant on December 10, 1975

Time EST	*Kr-85 Release,*[a] *Curies*	*Time EST*	*Kr-85 Release, Curies*
1:00 (A.M.)	454	10:00	152
2:00	408	11:00 (A.M.)	127
3:00	352	12:00 (Noon)	110
4:00	257	1:00 (P.M.)	94
5:00	138	2:00	81
6:00	72	3:00	70
7:00	45	4:00	64
8:00	38	5:00	56
9:00	108	6:00 (P.M.)	24

a. Estimated amount released from 30 minutes before to 30 minutes after the indicated time.

GROUND LEVEL AIR SAMPLING

Whole air sampling was accomplished by pumping air into 45-liter *Saran* bags during plume passage at 30 locations on or near Interstate 95 (I-95) from mile post 76 southward to the intersection with South Carolina Highway 336 (Figure 5). Portions of the sample in each bag were later transferred to two cylinders, one for SF_6 analysis and the other for methane and krypton-85 analyses. Bag samplers were also operated at two sites where routine cryogenic sampling of krypton-85 was done.

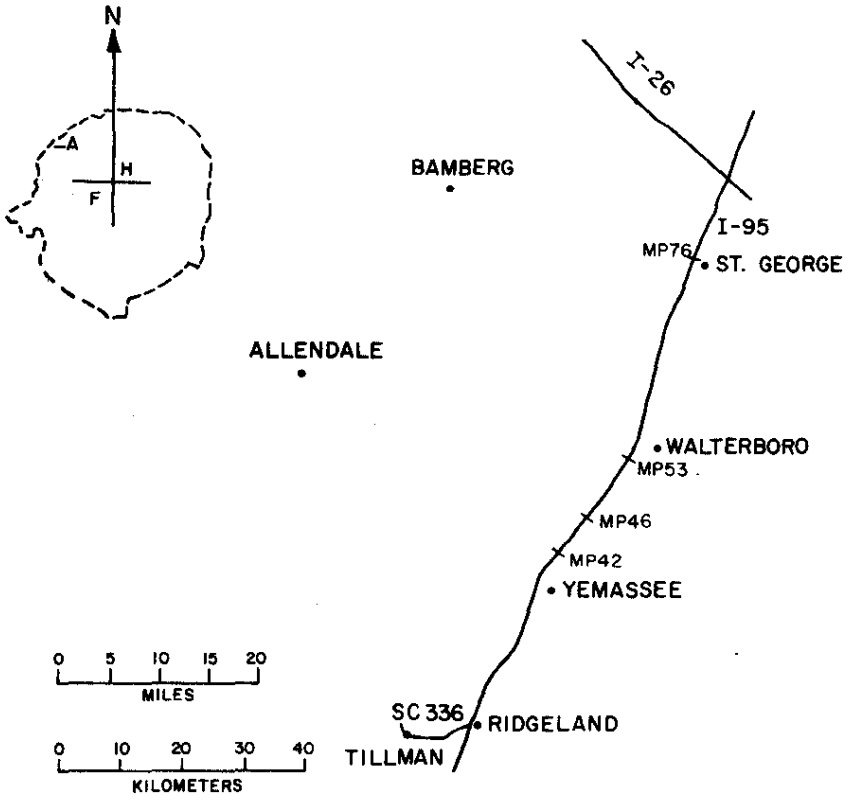

FIGURE 5. Location of Sampling Line. Samplers Extended on Interstate-95 from Mile Post 76 Southward to South Carolina Highway 336. Cryogenic Samplers were Located at Bamberg, St. George, and Ridgeland.

SF_6 and Methane Background Measurements

Background measurements of SF_6 were obtained between September 22 and October 1, 1975, on the plantsite and along Interstate 26 about 100 kilometers northeast of the plant. Ten

spot samples (five to ten minutes each) were taken in 900 cc steel cylinders. Concentrations by volume ranged from 0.4 to 0.9 ppt with an average concentration of 0.54 ppt, except for one sample of 5.9 ppt which was later found to be caused by a contaminated cylinder.

Although no background concentrations of the heavy methanes were detected, the concentration of normal methane ($^{12}CH_4$) in the samples must be known in order to calculate the heavy methane concentrations in air. Methane concentrations in 23 samples taken in the vicinity of the plant at various times before the tracer experiment varied from 1.1 to 2.2 ppm with an average of 1.64 ppm. Three spot samples taken between 9:00 A.M. and 9:00 P.M. EST on December 10, in the vicinity of the sampling line all had concentrations of 1.70 ppm, which is assumed to be the concentration in all samples taken during this experiment.

Bag Samplers

A whole-air sample of at least ten liters (preferably 30) was required to provide a sufficient sample for processing the heavy methane components. Large 16-inch-diameter and 32-inch-high plastic barrels were fitted with a *Teflon** pump (Science Pump Corp., Model D-200) connected with one-fourth inch outside diameter (O.D.) by one-eighth-inch diameter (I.D.) amber, natural rubber surgical tubing to a 45-liter *Saran*** bag. Power was provided by a NEDA 918 (or equivalent) six-volt dry cell battery. A small (0.1- to 0.5-inch length) 1/8-inch O.D. by 0.015-inch capillary stainless steel tubing provided the necessary restriction on the pump outlet to give the desired sampling times of either 8 or 11 hours to fill a bag. Connection of the amber rubber tubing to the *Saran* tube of the bag was accomplished with a three-inch length of amber tubing (3/8-inch O.D. by 1/4-inch I.D.) between the two. A pinch clamp on the short piece of amber tubing provided a leak-tight seal before sampling and after collecting the air sample. Before the bags were used, they were purged with zero air (air containing <0.5 ppt SF_6), rolled flat, and closed with the pinch clamp to prevent any possible SF_6 contamination.

The sampling bag fill rate from the pump was set to a value of 100 mL/min for the eight-hour samplers (about 60 mL/min for the 11-hour samplers at the cryogenic sites) by varying the number of capillary inserts placed between the pump and the bag. At the proper time after placing the barrel samplers, the sampler pumps were turned on and off manually by an internal switch.

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* Trademark of E. I. du Pont de Nemours and Company.

** Trademark of Dow Chemical Company, Midland, Mich.

Tests of Bags and Transfer Cylinders

Before the test, the *Saran* bags were individually checked for leaks; and several were tested for their ability to retain SF_6 mixtures without loss to the walls. After the bags were filled with helium and compressed slightly with a weighted plate, the bags were leak-checked with a portable thermal conductivity detector. About one out of every five bags had leaks at a seam or fold and were discarded.

The results of the sulfur hexafluoride tests are shown in Table 2. *Saran* bags were filled with different test mixtures of SF_6 in air and analyzed for several days. A portion of the gas in the bags was then transferred to steel cylinders (as the field samples would be) and analyzed 18 days later. The concentrations determined were within a few percent of the starting mixtures. One 45-liter bag was purged of the 38 ppt mixture, filled with zero gas, and analyzed 24 hours later. Residual SF_6 from the previous mixture was not indicated.

TABLE 2

Sample Bag and Cylinder Tests
(*Saran* bags; steel cylinders)

Sample Container No.	*SF_6 Test Gas, ppt*	*Days Elapsed after Filling*	*Meas SF_6 Conc, ppt*
45-1	Zero gas	1	0.05
(45-liter bag)		6	0.04
45-2	1.90	0	2.02
		5	1.87
		5	1.96
45.3	38.0	0	41.1
		5	38.9
		5	40.7
34 (steel cylinder)	from 45-1	18	0.04
29	from 45-2	18	2.01
		18	1.97
33	from 45-3	18	38.0
		18	38.7
45-3	Zero gas	0	0.03
		1	0.03

Placing of Samplers

On the morning of the December 10 test, the samplers were taken to Walterboro (Figure 5) and positioned along Interstate 95 and South Carolina Highway 336 in accordance with the latest wind information. Samplers were placed at three-mile intervals from Walterboro north to St. George, two-mile intervals from Walterboro south to Ridgeland, and at three-mile intervals west on South Carolina Highway 336. Sampling locations, times, and other pertinent information are given in Table 3.

Generally, the terrain in which the samplers were located was a forested, gently rolling landscape. The samplers were positioned as close as possible to the edge of the highway right-of-way (50 to 100 feet from the highway). The samplers were to run 7.5 hours and were to be picked up in the same order as they were put out.

During the sample collection period, several of the sampler units were checked; all but one was functioning normally. One unit (Sample No. 46) had stopped as a result of a jammed air pump. The pump was cleaned and restarted.

The position of the plume centerline was determined from the aircraft sampling data, and three postplume samplers were started at six-mile intervals near the estimated centerline. These samplers were run for two hours to provide information on any plume material passing the sampling line after the regular sampling was terminated. Information on these samplers is shown in Table 4. All samples were finally returned to the Savannah River Plant at about 11:00 P.M. EST.

Cryogenic Sampling Sites

As part of an ongoing program, cryogenic samplers were obtaining weekly concentrations of krypton-85 at 13 sites within about 125 kilometers of the Savannah River Plant. Since three of these sites, St. George, Ridgeland, and Bamberg (Figure 5) were near the sampling line, special samples of shorter duration were requested. In addition, bag samplers were operated with the cryogenic samplers at St. George and Ridgeland. All samples were analyzed for krypton-85 and the heavy methanes.

TABLE 3

Ground-Level Sampling Locations and Times

Sample I.D. No.[a]	Sampler Position,[b] mi	Collection Time EST Start	Stop	Collection Duration, hr	Spacing,[g] mi	Checks During Collection Time, EST	Inflation of Bag
30	I-95 ~76[c]	11:49	7:12	7.38	-		
18	~73	11:46	7:02	7.27	3		
25	~70	11:39	6:53	7.23	3		
31	~67	11:27	6:46	7.32	3		
6	~64	11:15	6:36	7.35	3		
59	61	11:04	6.30	7.43	3		
63	58	10:55	6:20	7.42	3		
2	56	10:40	6:10	7.50	2		
57	54	10:51	6:20	7.48	2		
65	52	10:59	6:30	7.52	2		
40	50	11:08	6:38	7.50	2		
60	48	11:15	6:45	7.50	2		
48	46	11:22	6:55	7.55	2		
4	44	11:31	7:05	7.57	2		
8	42	11:46	7:16	7.50	2	4:05	1/2 full
52	40	11:55	7:24	7.48	2	4:15[h]	1/2 full
46	38	12:05	7:35	7.50	2	4:20[h]	--------
51	36	12:14	7:44	7.50	2	4:37	1/2 full
44	34	12:23	7:53	7.50	2		
10	32	11:19	7:27	7.13	2	3:00	1/3 full
5	30	11:26	7:33	7.12	2	2:56	--------
64	28	11:33	7:41	7.13	2		
3	26	11:41	7:47	7.10	2	2:48	--------
55	24	11:49	7:53	7.07	2	2:44	1/4 full
49	U.S. 17 ~22[d]	11:56	7:00	7.07	2		
53	Route 336[e]	12:08	7:07	6.98	2		
35	Route 336	12:17	7:18	7.02	3		
47	Route 336	12:26	7:27	7.02	3		
61	(336)[f]	12:34	7:36	7.03	3		
56	(336)	12:42	7:44	7.03	3		

a. The sample I.D. is the number of the Bag in the Sampler.

b. Samplers were positioned off the highway at the Interstate mile markers indicated.

c. Miles 64 through 76 were on an unopened section of I-95, and no mile markers were present. In these cases Odometer readings were used.

d. Sampler No. 49 was placed on U. S. Highway 17 parallel to I-95 at the 22-mile marker on I-95.

e. No mile markers were placed on S. C. Highway 336; Odometer readings were used for placement.

f. The road west from Tillman, S. C., has no number but is a natural extention of S. C. Highway 336; Odometer readings were used.

g. Distance to next Sampler farther north.

h. At 4:20 P.M. found not operating -- cleaned pump and restarted at 4:30 P.M. had about 1 hr of sample in it when found stopped.

TABLE 4

Post-Plume Samples

Sample I. D. No.	Sampler Position, mi	Collection Start time, EST	Collection Time, hrs.	Comments
1	I-95, 46	6:57	2:12	Sample lost in transit.
39	40	7:26	1:90	
54	34	7:55	1:67	Barrel frosted at pickup time.

SAMPLE PROCESSING

At SRL, samples were immediately transferred from the sampling bags to cylinders for shipment to Brookhaven National Laboratory (SF_6 analysis) and Airco, Inc. (krypton-85 and methane).

SF_6 Sample Processing

Approximately one liter of air was transferred from each bag to a pre-evacuated steel cylinder which was then transported back to Brookhaven for analysis. Several cylinders were not used in order to determine their integrity during transport. At Brookhaven, these bottles were rechecked for vacuum, filled with zero gas, and analyzed for SF_6, which was always below the detectable level (<0.02 ppt).

Details of the laboratory analysis of SF_6 in the steel canisters have been described elsewhere.[2,3] To determine the low SF_6 levels present in these samples at the 100-kilometer downwind distance (<10 ppt), a laboratory chromatograph system with a four-inch-long 13X molecular sieve concentrator trap, a three-foot precut column, and a 17-foot analytical column (both with 5A molecular sieve) was used. A sample of air from the steel bottles was expanded into the evacuated 40-cc sample loop to a known pressure and then flushed into the concentractor trap at dry ice temperature. After the trap was isolated and heated to 200°C, the SF_6 was flushed into the precut column and into the analytical column. Immediately after the SF_6 eluted into the analytical column, the precut column was backflushed to remove the remaining constituents of the air sample. With this procedure, total cycle time for each determination was ten minutes with a limit of detection of 0.02 ppt for a 40-cc sample.

To insure accurate determination of SF_6 concentrations, calibration of the chromatograph with a prepared gas standard of 10 ppt and a working standard of 1.75 ppt was necessary. Linearity of the calibration to less than ambient levels was confirmed by the analysis of a 60-fold dynamic dilution of the working standard. Comparison of samples with the Health and Safety Laboratory (HASL) of ERDA agreed well, less than five percent relative standard deviation between laboratories. The reproducibility of the measurements is demonstrated by the analyses of four samples in triplicate, which were analyzed on two separate days (Table 5). The concentrations indicate the SF_6 background level during the experiment. The precision at these ambient levels could be improved by using double injections, i.e., 80-cc total sample size.

TABLE 5

Background SF_6 Measurements from Field Samples of December 10, 1975

Sample No.	*SF_6 Concentration ±σ,[a] ppt* 4-14-76	4-16-76
18	0.50 ±0.04	0.49 ±0.01
22[b]	0.50 ±0.01	0.49 ±0.03
56	0.55 ±0.02	0.56 ±0.01
30	0.50 ±0.04	0.49 ±0.03

a. σ is the standard deviation of triplicate determinations and does not include that for the working standard (1.75 ±0.03 ppt).

b. Sample 22 was collected at the St. George cryogenic site.

Methanes and Krypton-85

After transferring the fraction for SF_6 analysis, the remainder of the gas in the bags was transferred to a one-liter stainless steel cylinder by condensation with liquid nitrogen. The cylinders were then shipped to Airco's Central Research Laboratory at Murray Hill, New Jersey, for separation of the krypton and methanes from each sample and measurement of the krypton specific activity. The methane fractions were sent to Dr. Norman Daly, Atomic Weapons Research Establishment in Aldermaston, England, for mass spectrometric analysis of the heavy methane content.

Before the test krypton and methane "spikes" had been measured into each cylinder at Airco. This addition of these gases was necessary since the anticipated 30-liter air volumes would contain insufficient material to physically isolate in a pure state. A nominal 10 cc of krypton and 0.5 cc of methane were expanded into each cylinder after it had been evacuated to 0.1 millitorr. The volumes were measured from mercury-filled gas burettes readable to 0.025 cc. Essentially dead krypton (0.01 dpm/cc) from the immediate post-World War II era was used as a carrier. The methane was obtained from Matheson as ultra pure grade (99.97%).

The volume of each air sample was determined by weighing the full cylinders before processing and the evacuated cylinders, after processing. Weighings were made with a Voland HCE 50 equal arm balance, Class P stainless steel weights and a stainless cylinder without valve as a counterpoise. The dew point of the air at the collection sites was reported as 30°F. This is equivalent to 0.3% water by weight which would be subtracted from the air weight if results on a dry basis were required. However, considering the overall errors involved, the quantity is insignificant; and no moisture correction was made to the reported air weights.

Airco performed an initial concentration step by adsorption on charcoal at liquid oxygen temperature. The krypton and methane were then separated by gas chromatography on a mixed charcoal molecular sieve column with helium as the eluting gas. The krypton and methane were isolated from the eluting gas by condensing each fraction in separate freezeout traps at the triple point of nitrogen (63°K). This process produces krypton samples in the ten-cc range with less than 100 ppm impurities and 0.5-cc methane fractions with purities of 97 to 99%. Each methane sample was sealed into a 25-cc Pyrex breakseal bulb for shipment to England.

The krypton was loaded into Geiger counters and counted for 1000 minutes. Each sample was counted twice in two different counters. Data from these analyses are presented in Table 6

TABLE 6

Ground-Level Air Sample Processing Data
(Methane and Krypton from Bag Samples)

	AIR SAMPLE		KRYPTON				METHANE			
Sample, I.D. No.	*Weight, g*	*Volume, L*[d]	*Spike, cc*	*Natural,*[g] *cc*	*Recovered, cc*	*Recovery Efficiency, %*	*Spike, cc*	*Natural,*[h] *cc*	*Recovered, cc*	*Recovery Efficiency, %*
30	16.99	14.3	9.12	0.016	7.5	82	0.58	0.024	0.59	98
18	22.84	19.3	9.24	0.022	7.9	85	0.61	0.033	0.46	72
25	46.30	39.1	9.50	0.044	8.7	91	0.66	0.066	0.62	86
31	13.32	11.2	7.81	0.013	6.6	84	0.64	0.019	0.60	91
6	55.28	46.6	8.69	0.052	7.5	86	0.58	0.079	0.60	91
59	42.08	35.5	9.12	0.040	8.3	91	0.59	0.060	0.56	86
63	19.40	47.5[e]	9.27	0.053	2.9	31	0.45	0.081	0.16	30
2[a]	19.06	33.2[e]	8.83	0.037	3.9	44	0.72	0.056	0.41	53
57	38.52	32.5	9.20	0.036	8.0	87	0.48	0.055	0.46	86
65	39.63	33.4	8.89	0.038	7.9	89	0.66	0.057	0.65	91
40	16.50	49.1[e]	8.66	0.055	2.3	26	0.57	0.083	0.20	31
60	38.51	32.5	8.81	0.036	7.9	89	0.59	0.055	0.60	93
48	47.85	40.4	9.04	0.045	8.3	91	0.56	0.069	0.60	95
4	31.37	33.1[e]	9.00	0.037	6.5	72	0.72	0.056	0.52	67
8	12.91	34.9[e]	8.87	0.039	2.5	28	0.51	0.059	0.20	35
52	25.79	21.8	8.90	0.024	7.8	88	0.47	0.037	0.46	91
46	12.97	14.0[e]	8.94	0.016	6.3	70	0.62	0.024	0.47	73
51	33.50	31.6[e]	9.05	0.035	7.3	80	0.59	0.054	0.50	78
44	31.72	26.7	8.90	0.030	7.9	89	0.62	0.045	0.66	99
10	42.43	35.8	8.88	0.040	8.1	91	0.50	0.061	0.50	89
5	21.84	38.6[e]	8.71	0.043	3.4	43	0.69	0.066	0.35	46
64	48.62	41.0	8.67	0.046	8.0	92	0.74	0.070	0.78	96
3	28.06	23.7	8.84	0.027	7.8	88	0.65	0.040	0.64	93
55	36.49	30.8	8.96	0.034	7.3	81	0.74	0.052	0.72	91
49	37.71	31.8	8.86	0.036	7.9	89	0.57	0.054	0.46	74
53	32.06	27.1	8.97	0.030	8.0	89	0.48	0.046	0.44	84
35[b]	27.22	23.0	8.67	0.026	7.7	89	0.57	0.039	0.50	82
47	7.84	6.6	8.64				0.65			
61	29.77	59.5[e,f]	8.91	0.067	3.4	38	0.59	0.100	0.21	30
56	20.11	17.0	9.25	0.019	7.9	85	0.60	0.029	0.66	105
23[c]	33.93	28.6	8.87	0.032	7.2	81	0.64	0.049	0.57	83
22	14.97	12.6	9.16	0.014	7.5	82	0.64	0.021	0.62	94

a. Kr lost in counting.

b. Sample too small.

c. 23 Ridgeland, 22 St. George

d. All gas volumes corrected to 25°C; 760 mm Hg (air density = 1.185 gms/liter)

e. Cylinder leaked; air volume corrected assuming 90% recovery efficiency for Krypton.

f. Bad sample; maximum capacity of bag was about 48 liters.

g. Abundance of atmospheric krypton = 1.112 ppm (V/V).

h. Abundance of methane at SRP = 1.70 ppm (V/V).

(sample identification numbers are the same as in Table 3). The second column gives the actual weight of the air sample in the cylinder. The third column converts this weight to sample volume at 25°C and 760 millimeters of mercury. The nine starred samples show that the cylinders had leaked, and part of the original air condensed into the cylinders was lost along with the spike material. In each case, when the krypton recovery was below 80%, a check of the cylinder after processing the sample indicated the presence of a leak. The volume of air obtained by weight was corrected for these samples based on the original amount of krypton spike added with the assumption of a 90% recovery efficiency.

Column 4 lists the volume of added methane (spike). Column 5 gives the volume of atmospheric krypton contained in the sample volume given in Column 3 if the natural krypton concentration in air is assumed to be 1.112 ppm by volume. The volume of krypton recovered from each sample is given in Column 6, and the recovery efficiency in Column 7. The last four columns give the same information for methane.

The last two bag samples were taken at the cryogenic sites; bag 23, at Ridgeland; and bag 22, at St. George.

AIRCRAFT SAMPLING

Two portable automatic gas chromatographs[3,4] developed at Brookhaven National Laboratory (BNL) were operated onboard the EG&G Martin 404 aircraft by a BNL technician. Crosswind passes were made through the plume, and profiles of SF_6 concentration were obtained with the BNL instruments. Eleven passes were made at altitudes between 500 and 2000 feet above the ground at 16, 40, and 90 kilometers from the release points. Four five-minute bag samples were also collected onboard the aircraft for analysis of SF_6, methanes, and krypton-85.

SF_6 Chromatographs

Both BNL SF_6 Chromatographs were mounted onto a rack in the aircraft with two portable recorders, two spare batteries, and two battery chargers for emergency use. Each of these instruments uses a pump to continuously compress the air being sampled through a chromatograph column (molecular sieve 5A) and into an electron capture detector. After sulfur hexafluoride is eluted, oxygen is eluted. The column is then automatically back-flushed before the next measurement. Generally, the longer the chromatograph column, the longer the length of the continuous SF_6 sampling window. For example, one instrument has a 16-foot column which provides a continuous measurement of SF_6 for approx-

imately 3½ minutes. However, the increased column length increases the delay time before SF_6 is first eluted, decreases the resolution, and requires longer backflush times before the next analysis can be made. Total cycle time with this instrument is 12 minutes.

The second instrument used in this experiment has a shorter column which provides a 90-second continuous sampling window. This instrument requires only a three-minute backflush time; total cycle time is about five minutes. This instrument also has a rapid response time (for better resolution of the plume) as shown in Figure 6, where a recorder trace is obtained when

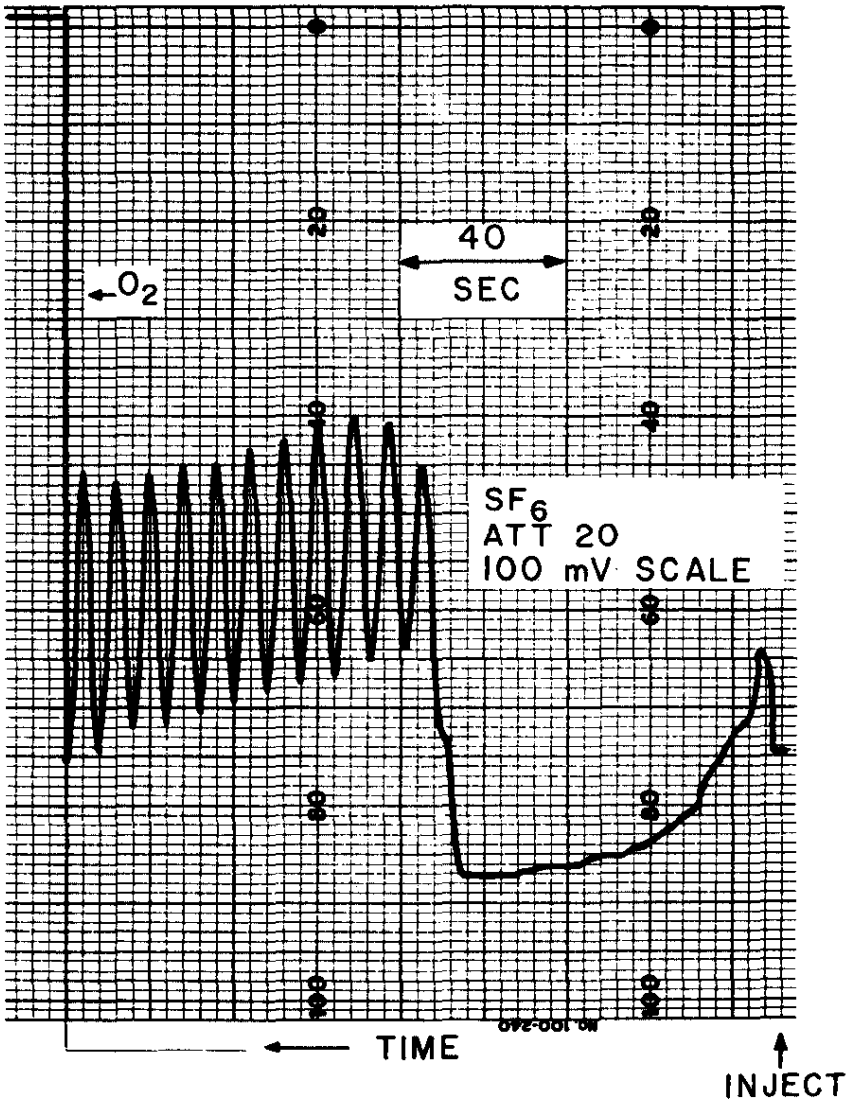

FIGURE 6. SF_6 Trace when Cycling Every Four Seconds Between a 100-ppt and a 10-ppt Standard

cycling every four seconds between a 100-ppt and a 10-ppt standard. The limit of detection at a signal-to-noise ratio of three is about 0.5 ppt.

The instruments' 20-amp-hour battery is sufficient for about an eight-hour continuous operation and the one-liter gas cylinder is sufficient for several days. Electronic components were mounted on either the electrometer or timer plug-in printed circuit boards for rapid field exchange in the event of failure. Dewar flasks, which serve as insulated ovens for the detector and column, allowed the detector and columns to be baked out periodically while in the instrument; normal operation was at room temperature.

Calibration chromatographs were performed with a ten-ppt primary standard while the instruments were on the ground and with a 38-ppt working standard when the instruments were airborne. A linear response with concentrations up to 100 ppt was observed, but a slight decrease in response with altitude (about 10% at 5000 feet) occurred.

Profiles obtained on the recorders were later converted to SF_6 concentration versus crosswind distance or time with the aid of a digitizer-plotter system. The two instruments had different delay periods for SF_6 to elute from the columns (about two minutes and 40 seconds for one and about 54 seconds for the other). Therefore, finding a common point in real time on the scans to compare the results of simultaneous or serial operation of the two was necessary. When the 90-second instrument was turned on and also when it was automatically turned off, an event marker was automatically made on the recorder of the 3½-minute instrument recorder. From these marks and the known delay period for each instrument, matching the outputs of both instruments to within two seconds of real time in most cases was possible.

To convert the recorder traces to concentration plots, a digitizer cursor with crosshair window was manually moved along the recorder trace, and points were either manually or continuously entered into the calculator of the plotter system. Four consecutive points (Y_1, Y_2, Y_3, Y_4) are used to compute the best slope for three straight line segments to be drawn from Y_2 to Y_3. Thus, as each new location is entered into the plotter calculator, three lines are drawn between the previous two points. At the same time, the area under the curve is summed to obtain the crosswind integral of plume concentrations.

Bag Samples

The sampler inlet ports on the aircraft were adapted to accommodate gas bags for obtaining whole air samples. These bags were provided by LASL. Flow rates were adjusted on the air sampling ports to provide the desired air sample volume for heavy methane analysis. The gas bags, produced by LASL from ten-mil polyethylene plastic sheets, were fitted with a valve stem which allowed tham to be filled from the aircraft sampling port. Approximately 100 liters of air were collected over a five-minute period. Some 50 to 100 liters of each sample were cryogenically condensed and transferred to cylinders and processed in the same manner as the ground level air samples. Processing data on the four samples collected on board the aircraft are given in Table 7. The krypton and methane processing data are the same as in Table 6, and the same comments apply. Aircraft locations on each pass and sampling results are discussed under "Preliminary Results." Aircraft speed and altitudes are approximate values from the sampling log; more precise data will be obtained from the magnetic tape record.

TABLE 7

Processing Data on Aircraft Bag Samples

Sample No.	A/C-1	A/C-2	A/C-3	A/C-4
Cylinder No.	W4929	W4785	W4780	W4754
Pass No.	0	1	8	11
Time, EST Sample Started	0918	1131	1618	1746
Altitude, Ft. above ground	500	500	500	2000
Aircraft Speed, KtS	150	150	180	180
Sample				
Weight, g	59.97	113.6	105.7	98.54
Volume, L	50.6	95.9	89.2	83.2
Krypton:				
Spike, cc	8.99	8.99	8.75	8.63
Natural, cc	.057	0.11	0.10	0.093
Recovered, cc	8.1	8.3	8.2	8.1
Efficiency, %	90	91	93	93
Methane:				
Spike, cc	0.72	0.63	0.55	0.62
Natural, cc	0.086	0.16	0.15	0.14
Recovered, cc	0.75	0.66	0.50	0.70
Efficiency, %	93	84	71	92

METEOROLOGICAL DATA

Brief Description

All meteorological data obtained at SRL during the tracer tests consist of the following: 1) wind speeds, directions, and temperatures (including deviations) from the WJBF-TV Tower (seven levels) and the seven-tower system on SRP for December 5, 6, 10, 13, 18, and 19; 2) surface weather data (every hour) for December 10, 18, and 19 for South Carolina, Georgia, North Carolina, Florida (in part), and Alabama (in part); 3) upper air wind speeds, directions, pressures, and temperatures from Georgia, South Carolina, and North Carolina for December 5, 6, 10, 13, and 18; and 4) wind speeds, directions, temperatures, and relative humidity recordings from the Georgia and South Carolina Forestry Lookout Towers for December 10, 18, and 19. In addition to these sets of data, a table of the dates, times and mileage between ground sampler locations (on I-95), along with the aircraft path and measurements recorded in flight, are also listed in Volume 2 of this report.

Tower Data

The meteorological tower network at SRP consists of seven 62-meter towers located throughout SRP and the WJBF-TV Tower located approximately 20 kilometers northwest of the center of SRP. The TV tower is instrumented at seven levels, beginning with ten meters and extending to 335 meters. Wind speeds, wind direction, and temperatures are recorded every 5.2 seconds. The data are placed on magnetic tape at SRL and are also transmitted to LLL. Data from the 62-meter towers were likewise recorded by SRL and LLL every 5.2 seconds. Values for σ_A [standard deviation of the horizontal wind direction (azimuth) in degrees], σ_E (standard deviation of vertical wind direction in degrees), and mean wind direction and speed from the tower data are calculated as a function of sampling time (normally every 60 minutes). Hard copy prints of the wind speeds, directions, σ_A, σ_E, and temperature are made every hour.

Meteorological data from the SRP tower network were recorded for the flights made on December 5, 6, 10, 13, 18, and 19. All times in this report are in Eastern Standard Time (EST).

Surface Hourly Data

Hourly surface data were obtained from the following stations for December 10, 18, and 19:

South Carolina:	AND, GSP, CAE, SPA, FLO, CRE, CHS
Georgia:	AGS, AHN, MCN, ATL, RMG, CSG, FTY
North Carolina:	AVL, CLT, ECG, EWN, FAY, GSO, HKY, ILM, ROU RWI, INT
Alabama:	ANB, BHM, DHN, HSV, MGM, MOB, MSL, TCL
Florida:	CEW, DWB, EYW, FLL, FMY, MCO, MIA, MLB, ORL, PBI, PIE, PNS, SRQ, TPA, VRB

Data were transmitted every hour to LLL during the following periods:

December 9	6:00 P.M. EST
December 10	7:00 P.M. EST
December 18	10:00 A.M. - 5:00 P.M. EST
December 19	4:00 A.M. - 11:00 A.M. EST

Upper Air Data

Upper air wind speeds, directions, temperatures, pressures, and heights were recorded for December 5, 6, 10, 13, and 18. Data were received from the following stations at 12-hour intervals:

South Carolina:	CHS
Georgia:	AHN, AYS
North Carolina:	GSO, HAT

Meteorological Summary

The tracer experiment was conducted in a northwesterly flow behind a well-defined cold front with clear skies and strong northwesterly winds at the surface. Figure 7 shows time-height cross sections of wind direction and speed obtained by visual theodolite tracking of pilot balloons released near the tracer release point.

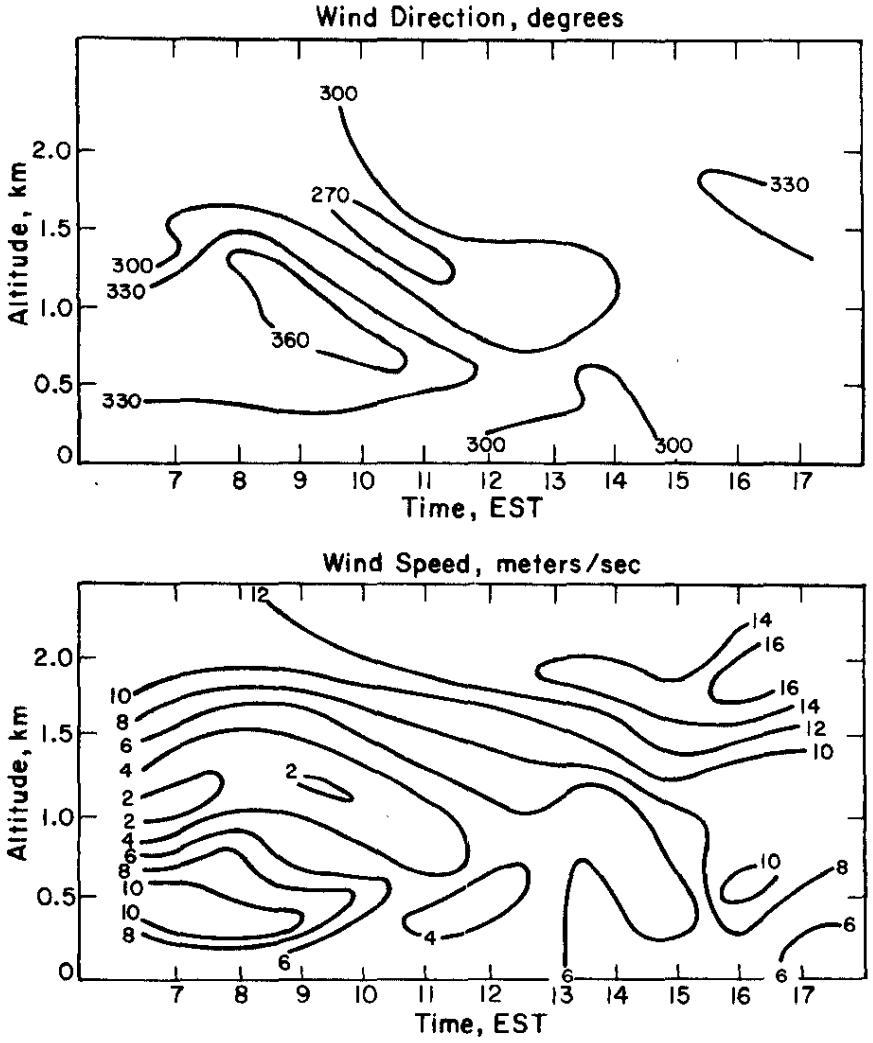

FIGURE 7. Height-time Cross Sections of Wind Direction and Speed from PIBALS Tracked from the Tracer Release Area

The wind veered to a northerly direction at about 1.5 kilometers at 8:00 A.M. EST, and this veering propagated down to 0.5 kilometers. The wind field at 1.5 kilometers then backed to 270° azimuth and propagated downward by 11:00 A.M. EST. After 11:00 A.M. EST, this transient feature had passed, and the wind field settled into a relatively steady northwesterly flow at seven to 10 meters/second in the 1.5-kilometer layer in which the tracer plume was transported. The tracer release began at 10:30 A.M. EST, and was virtually unaffected by the transient wind disturbance.

Analysis of the vertical temperature structure allows the height of the layer through which the plume was mixed and the intensity of mixing in the layer to be estimated. The closest upper-air sounding data are from Athens, Georgia, at 7:00 A.M. EST (1200Z). Figure 8 shows this sounding and estimated soundings

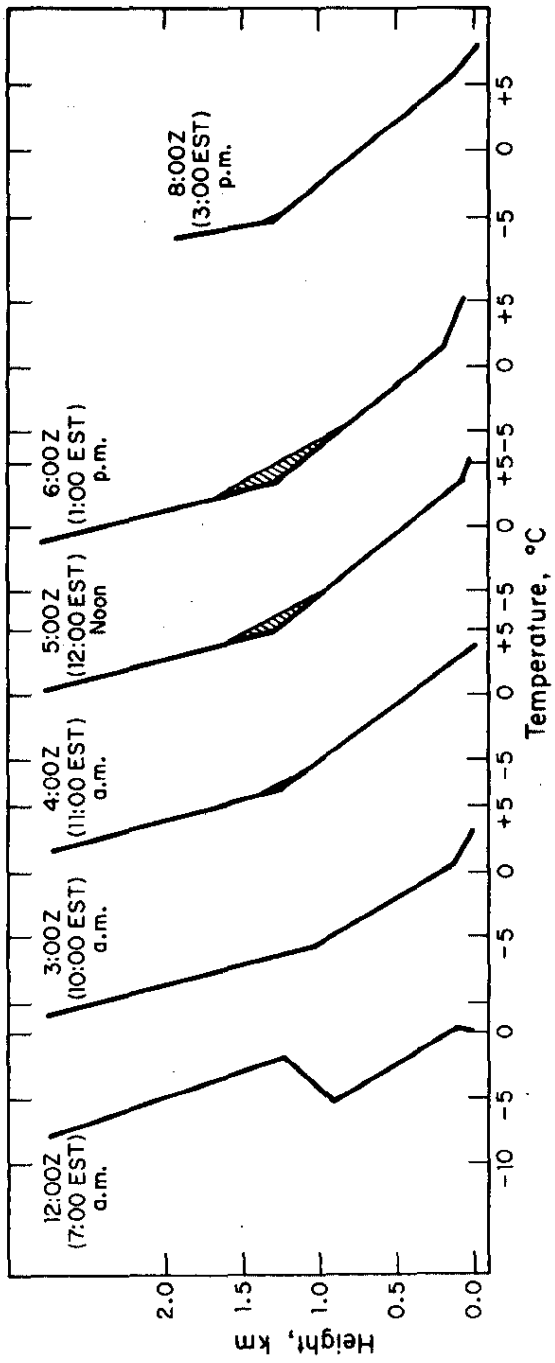

FIGURE 8. Observed 12:00Z Sounding at Athens, Georgia, and Estimated Soundings at Later Times During the Day. (Crosshatched Area Indicates Potential Energy Released Because of Moist Convection.)

during the experiment based on observed hourly surface temperature and advected temperature fields at 850 and 700 millibars. These soundings show the initiation of moist convection at 11:00 A.M. EST, a maximum at 1:00 P.M. EST, and an ending at 3:00 P.M. EST. This convection coincides very closely with the observed clouds which were first noted at 10:30 A.M. EST. The clouds reached 4/8 sky cover at 1:00 P.M. EST, and dissipated completely by 5:00 P.M. EST. Figure 9 shows the estimated mixing depth derived by following a dry adiabatic temperature curve from the estimated surface temperature to its intersection with the evolving sounding. After the onset of moist convection, the mixed depth is the estimated top of the convection. Also plotted in Figure 9 are the growth curve estimates for the front edge of the tracer cloud and the trailing edge. The effective mixing associated with convective turbulence transports tracer material to the top of the mixed layer within a few hours. The plume was assumed to mix fairly uniformly throughout the 1.5-kilometer layer.

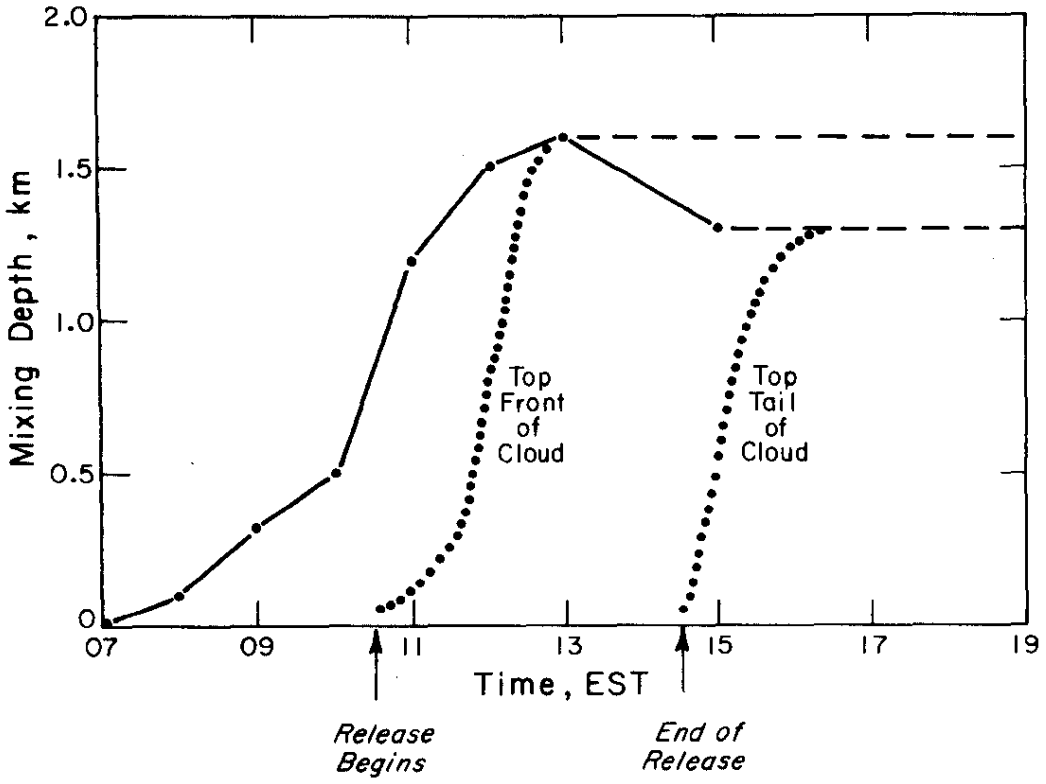

FIGURE 9. Estimated Mixing Depths Derived from Soundings in Figure 8

PRELIMINARY RESULTS

Ground Sampling Data (Highway Samplers)

Results of the analysis of bag samples on Interstate 95 and South Carolina Highway 336 are shown in Tables 8 (krypton-85 and SF_6) and 9 (methanes). The time of collection of each sample is given in Tables 3 and 4. Analysis and interpretation of preliminary data will be presented in subsequent reports.

Krypton-85 Concentrations

The krypton-85 concentrations along Interstate 95 are plotted in Figure 10. Background krypton-85 concentration was about 14 pCi/SCM. The concentration of krypton-85 in air (pCi/SCM) was obtained by first measuring the krypton-85 radioactivity in the total krypton isolated from the transfer cylinder (reported in Table 8 as dpm/cc of krypton). This concentration was then adjusted for the volume of the krypton spike in

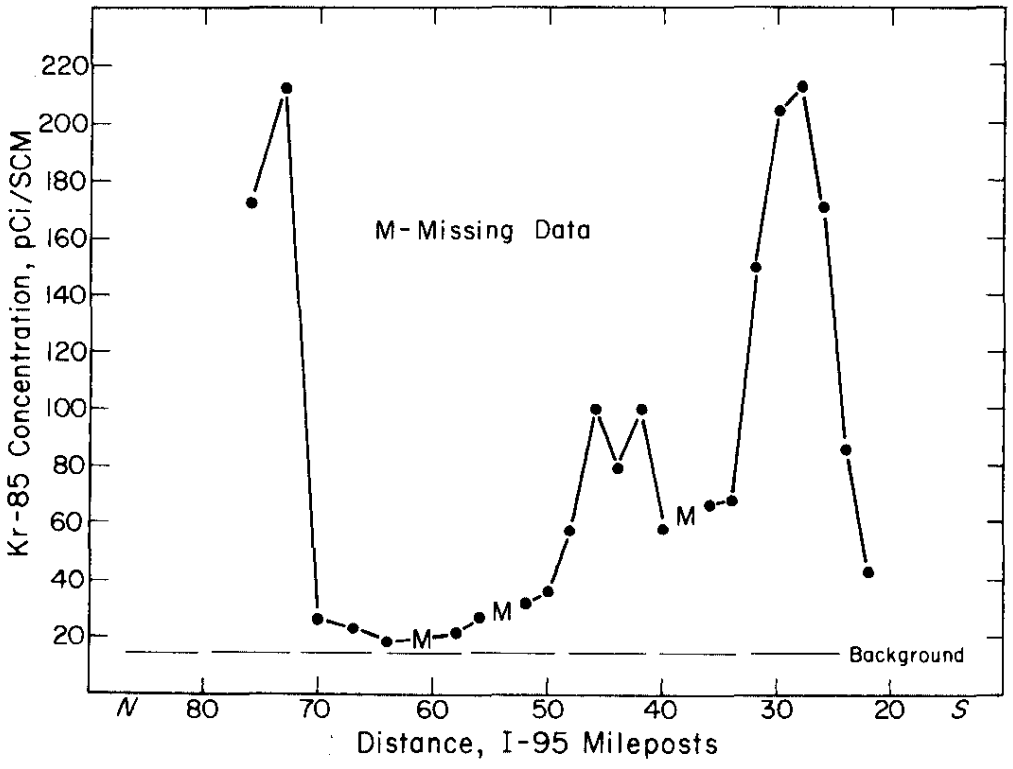

FIGURE 10. Time-Averaged Krypton-85 Plume Profile Along Interstate-95

the transfer cylinder and for the abundance of normal krypton in the atmosphere. Thus,

$$C_a = C_{Kr} \frac{\text{pCi/SCM}}{\text{dpm/cc}} \frac{V_s + V_n}{V_n} A_{Kr} \quad (1)$$

where

C_a = concentration of krypton-85 in air sample (pCi/SCM)

C_{Kr} = concentration of krypton-85 in krypton from sample (dpm/cc)

$\frac{\text{pCi/SCM}}{\text{dpm/cc}}$ = conversion factor = 0.45×10^6

V_s = volume of spike (cc)

V_n = volume of normal krypton in cylinders (cc)

A_{Kr} = abundance of normal krypton in air (1.112×10^{-6} by volume)

So that,

$$C_a = 0.5\ C_{Kr} \frac{V_s + V_n}{V_n} \quad (2)$$

Also note that

$$V_n = A_{Kr}\ V_c \quad (3)$$

where

V_c = volume of air sample in the cylinders.

In the cases where the cylinders leaked, the air sample and the spike were assumed to be lost in the same proportion, and the ratio of the apparent krypton-85 recovery efficiency to the expected efficiency (90%) was used to adjust the sample volume V_c and the volume of normal Kr, V_n (Table 6).

SF_6 Concentrations

Since no spike was involved in SF_6 processing the air concentrations in Table 8 were obtained directly by chromatographic

TABLE 8

Concentration of Kr-85 and SF_6 in Highway Bag Samples

Sample I. D., No.	*Position, mile, No.*	*Kr-85*		*SF_6, ppt by vol*
		dpm/cc	*pCi/SCM*	
30	I-95: ∿76	0.60	172	0.50
18	∿73	0.99	212	0.50
25	∿70	0.24	26	0.61
31	∿67	0.07	23	0.58
6	∿64	0.21	18	0.57
59	61	----	---[c]	0.61
63[a]	58	0.23	21	0.56
2[a]	56	0.23	27	1.20
57	54	----	---[c]	1.58
65	52	0.26	32	1.94
40[a]	50	0.45	36	2.81
60	48	0.47	57	4.04
48	46	1.00	100	5.57
4[a]	44	0.66	79	3.17
8[a]	42	0.87	100	3.06
52	40	0.32	58	1.88
46[a,b]	38	0.06	17	0.58
51[a]	36	0.52	66	1.24
44	34	0.46	68	0.82
10	32	1.35	150	0.77
5[a]	30	2.03	205	0.60
64	28	2.25	213	0.63
3	26	1.03	171	0.57
55	24	0.66	86	1.12
49	∿22	0.35	43	1.02
53	SC 336: 2	0.16	23	0.67
35	5	0.10	17[d]	0.54
47	8	----	---[d]	0.59
61[a]	11	5.00	334[e]	12.3[f]
56	14	0.20	49[d]	0.63
39	I-95: 40	----	---[d]	1.64[g]
54	34	----	---[d]	0.55[g]

a. Transfer cylinder (for krypton) leaked.

b. Sampler malfunctioned (Table 3, Note *h*).

c. Krypton Lost in counting.

d. Sample too small to process for krypton.

e. Bad data (See Table 6, Note *f*).

f. Bad data (contaminated cylinder).

g. Post-plume SF_6 Samples.

analysis of the sample. The standard deviation of duplicate determinations on each sample ranged from 0.00 to 0.04 ppt. The SF_6 concentrations along Interstate 95 are shown in Figure 11. The main plume crossed the highway between Mile Post 30 and Mile Post 58. Sampling results appeared very consistent and showed a background concentration of 0.5 to 0.6 ppt and a peak plume concentration of 5.6 ppt. The SF_6 seen at Mile Posts 22 and 24 probably resulted from the more northerly winds that existed for a short period after the release began. Samplers on Highway 336 (not plotted) west of Mile Post 22 showed essentially background concentrations.

Of the two postplume samples obtained after the regular sampling was terminated (Table 4), Sample 54 at Mile Post 34 showed background; but Sample 39 at Mile Post 40 had 1.6 ppt of SF_6, almost as much as the earlier sample at that position. Further analysis is needed to determine whether a significant fraction of the release might have arrived at the sampling line after the samplers were turned off.

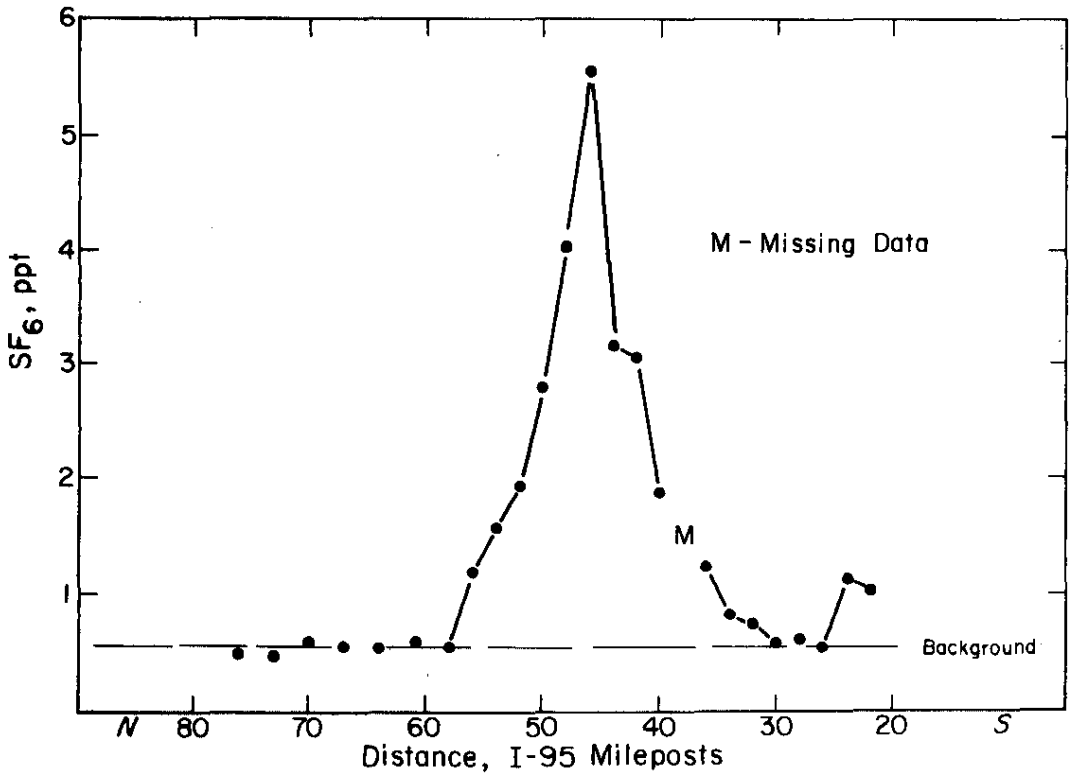

FIGURE 11. Time-Averaged SF_6 Plume Profile Along Interstate-95

Heavy Methane Concentrations

The results of mass spectrometric analysis for methane-20 ($^{12}CD_4$) and methane-21 ($^{13}CD_4$) are shown in Table 9 for the highway bag samples.

The table indicates errors associated with the mass spectrometric measurements alone. Another error is associated with the assumed constancy of the methane concentration at the experimental site. Although this concentration has been observed to vary from 1.1 to 2.2 ppm at SRP, measurements on the day of the experiment indicated a constant value of 1.70 ppm in all three samples taken for this purpose.

TABLE 9

Heavy Methane Concentrations From Highway Bag Samples

Position I-95 mile No.	*(20/16)meas* (cc/cc) × 10^{+11}		*(20/air)*, (cc/cc) × 10^{+16}		*(21/16)meas* (cc/cc) × 10^{+11}		*(21/air)*, (cc/cc) × 10^{+16}	
76[a,b]	935.0	±6.0	3935.0	±25.3	98.5	±2.0	414.5	±8.4
73[a,b]	260000.0	±300.0	866000.0	±999.2	10200.0	±20.0	34000.0	±66.7
70	1.02	±0.30	1.9	±0.56	0.10	±0.30	0.186	±0.557
67	3.18	±0.38	18.71	±2.24	1.36	±0.34	8.00	±2.00
64	0.99	±0.33	1.40	±0.47	0.54	±0.33	0.764	±0.467
61	0.64	±0.35	1.17	±0.64	-0.17	±0.30	-0.311	±0.550
58	4.47	±0.72	4.99	±0.80	0.83	±0.52	0.927	±0.581
56[a]	11.4	±0.60	52.9	±2.78	5.40	±0.40	25.0	±1.85
54	13.8	±0.60	22.73	±0.99	9.43	±0.49	15.53	±0.81
52	16.9	±0.60	36.27	±1.29	7.70	±0.47	16.52	±1.01
50	49.4	±1.20	65.75	±1.60	19.00	±0.80	25.29	±1.06
48	64.0	±1.00	127.0	±2.0	20.80	±0.60	41.29	±1.19
46	160.0	±2.0	249.0	±3.1	37.0	±0.80	57.57	±1.24
44	37.8	±0.90	88.64	±2.11	9.88	±0.49	23.17	±1.15
42	45.2	±1.1	73.72	±1.79	11.80	±0.60	19.24	±0.98
40[a]	20.8	±0.6	48.4	±1.40	6.73	±0.42	15.6	±0.97
38[a,c]	15.0	±4.0	6.9	±1.84	0.44	±0.32	2.0	±1.45
36	27.8	±0.90	56.63	±1.83	1.86	±0.37	3.79	±0.75
34	17.6	±0.60	43.86	±1.50	0.74	±0.32	1.84	±0.59
32	40.4	±0.90	59.1	±1.32	1.86	±0.36	2.92	±0.57
30	9.75	±0.50	38.2	±1.96	0.70	±0.35	2.79	±1.40
28	5.27	±0.39	10.42	±0.77	0.57	±0.30	1.13	±0.59
26	1.80	±0.20	5.24	±0.58	0.50	±0.30	1.46	±0.88
24	0.90	±0.28	2.32	±0.72	0.27	±0.31	0.695	±0.798
22[a]	1.20	±0.40	2.35	±0.78	0.70	±0.30	1.37	±0.59
SC 336 2[a]	1.50	±0.40	2.91	±0.78	0.60	±0.30	1.16	±0.58
5[a]	1.92	±0.33	5.08	±0.87	-0.04	±0.26	-0.11	±0.72
8								
11[a]	2.64	±0.40	66.5	10.07	0.94	±0.34	23.7	±8.57
14[a,b]	536.0	±4.0	1980.0	±14.78	166.5	±2.0	616.0	±7.40
St. Geo. Cryo Bag[a,b]	48.5	±0.09	255.0	±0.47	7.9	±0.46	41.5	±2.42

a. Standard was ~40% higher than on previous run. (Data not normalized.)

b. Samples were transferred later and were contaminated.

c. Sampler pumps stopped during portion of plume passage.

The reported concentrations of methane-21 in air (21/air) are derived from the abundance ratios of methane-21 to methane-16 measured by the mass spectrometer, $(21/16)_{meas}$, from the relationship:

$$(21/air) = (21/16)_{meas}\left(\frac{V_s}{V_c} + A_{CH_4}\right) \quad (4)$$

where

V_s = volume of CH_4 spike

V_c = volume of air sample in the cylinder

A_{CH_4} = abundance of CH_4 in air (1.7×10^{-6} by volume).

The volumes V_s and V_c for each sample are given in Table 6. Equation 4 was also used to determine the methane-20 concentration in air (20/air) from the measured methane-20 to methane-16 ratios, $(20/16)_{meas}$.

To a good approximation, the fractional error in the concentration of methane-21 in air is the same as the fractional variation in either V_s or V_c. On the other hand, the uncertainty in the value of $(21/16)_{air}$ arises mainly from the uncertainty of the value of A_{CH_4}.

The creditable measured values of (21/16) in the mass spectrometer ranged from $(-0.17 \pm 0.30) \times 10^{-11}$ to $(37 \pm 0.8) \times 10^{-11}$ for the samples from highway I-95. The peak signal-to-noise ratio in this experiment was thus greater than 100 in the case of methane 21. The four lowest values can be used to lower the limit on the present background value of (21/16) in atmospheric methane to $(1.2 \pm 1.5) \times 10^{-12}$.

For methane-20, the four values corresponding to those used for the background values of methane-21 average $(1.0 \pm 0.17) \times 10^{-11}$. Whether or not this background of the atmosphere and/or spike is real is not clear. In any case, the peak value of the (20/16) mass ratio observed in this experiment $(160 \pm 2) \times 10^{-11}$ again corresponds to a peak-to-noise ratio >100.

The heavy methane concentrations analyzed to date are plotted in Figure 12. Note the different scales used for methane-20 and methane-21.

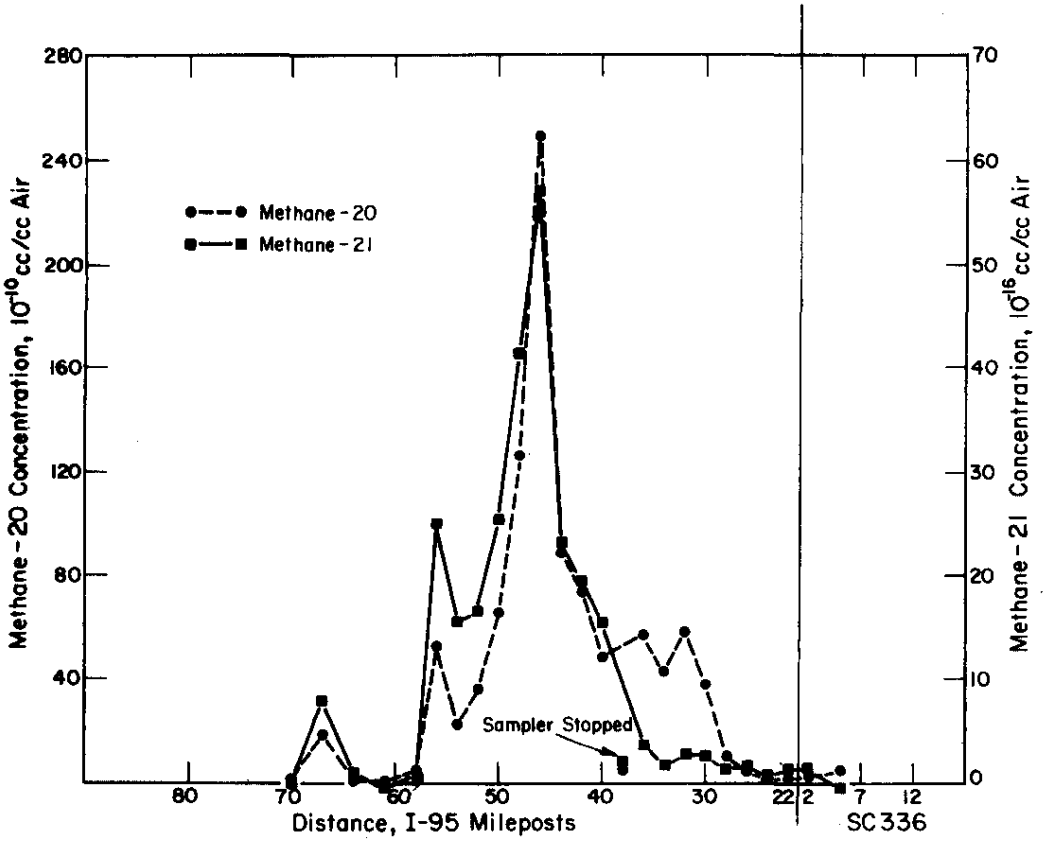

FIGURE 12. Heavy Methane Concentrations (20/air) and (21/air) Along Interstate-95

Tracer Comparisons

The concentration profiles of the two heavy methanes and SF_6 along Interstate 95 appear very similar and all three tracers show the highest concentration in the samples taken at Mile Post 46. However, when the concentrations are normalized to the same release amount, the methane concentrations are low by about a factor of four compared with SF_6. The cause of this discrepancy is not yet understood, but some of the possibilities being investigated are discussed in the section *"Tracer Concentration Ratios."*

Gaussian Model Fits to the Highway Sampling Data

The crosswind concentration distributions were fitted with a Gaussian model plus a constant function of the form given by Equation 5 with a least squares criterion.

$$c = (1/\sqrt{2\pi})\ (A/\sigma)\ \exp - \left[\frac{(x-x_0)^2}{2\sigma^2}\right] + B \qquad (5)$$

The curves are shown in Figure 13, and selected parameters of the fitted distributions are presented in Table 10. The SF_6 profile

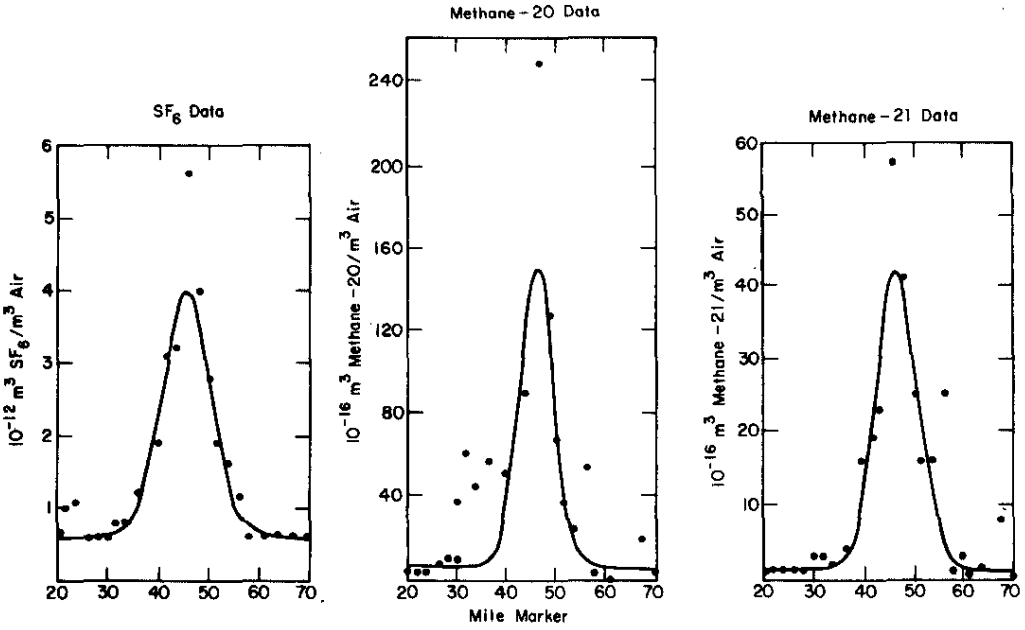

FIGURE 13. Gaussian Plus Constant Fit to SF_6, Methane-20 and Methane-21 Data. (Curves are calculated data points, and dots are measured data points.)

TABLE 10

Distribution Parameters for 100-km Surface Data

A. Gross Statistical Parameters

Tracer	$\bar{X}^a$	σ, *km*	*Kurtosis*
Methane-20	44.2	12.7	3.7
Methane-21	47.3	11.6	5.5
SF_6	45.0	11.6	6.0

B. Parameters From Fitted Gaussian + Constant[b]

Tracer	$\bar{X}^a$	σ, *km*	*Peak, m^3/m^3 Air*	*B, m^3/m^3 Air*
Methane-20	46.0 ±0.5	5.5 ±0.9	(144 ±32) x 10^{-16}	(6.9 ±3.5) x 10^{-16}
Methane-21	46.8 ±0.4	6.6 ±0.7	(40.9 ±6.0) x 10^{-16}	(1.3 ±1.0) x 10^{-16}
SF_6	45.9 ±0.4	7.4 ±0.6	(3.4 ±0.4) x 10^{-12}	(0.64 ±0.04) x 10^{-12}

a. $\bar{X}$ = Peak position in terms of I-95 mile markers

b. $C(X) = \frac{A}{\sqrt{2\pi\sigma^2}} \exp - \left[\frac{(X-X_0)^2}{2\sigma^2}\right] + B$

was the most nearly Gaussian of the three tracers and fitted well in the region of the main concentration peak. The additive constant (B) in the fit, 0.64×10^{-12} cc/cc of air, represented the SF_6 background. The value of B obtained for the methanes may not represent an actual background, but probably reflects the noise on the low-level concentration values on the wings of the distribution. The methane tracers did not appear to enjoy the same close fit to the Gaussian function, mainly because of a higher kurtosis (sharper peak with broader wings). The normalized least squares curve-fit criterion indicates the quality of fit to the methane-20 and methane-21 profiles to be similar. Qualitatively, the methane-21 profile appears to be more satisfactory fit than the methane-20. Although the Gaussian function offers a useful basis of comparison among the three tracers, departures from this shape are not unexpected for a single cloud with a length on the order of the travel distance.

Tracer Concentration Ratios

Air concentrations of the four tracers may be directly compared by dividing the concentrations χ expressed in grams/SCM (pCi/SCM for krypton-85) by the respective release amounts Q. The estimated background concentrations of 0.55 ppt for SF_6 and 14 pCi/SCM for krypton-85 were subtracted before normalizing the measured concentrations. Release amounts were

SF_6	1.54×10^5 g
methane-20	2.93×10^2 g
methane-21	8.86×10^1 g
krypton-85	4.12×10^2 Ci

For this comparison, the krypton-85 emitted during the four-hour tracer release (412 Ci) was used although krypton-85 was also released before and after this period.

The normalized concentrations χ/Q along Interstate 95 are shown in Figure 14. Since SF_6 and methane-21 were released simultaneously through the same stack, their concentration profiles should coincide if no flaws occurred in the release, sampling, processing, or analysis procedures; the two tracers behaved the same in the atmosphere. The methane-20 would be expected to have a somewhat different profile with a slightly lower peak concentration since it was released about ten kilometers upwind of the SF_6 and methane-21 release.

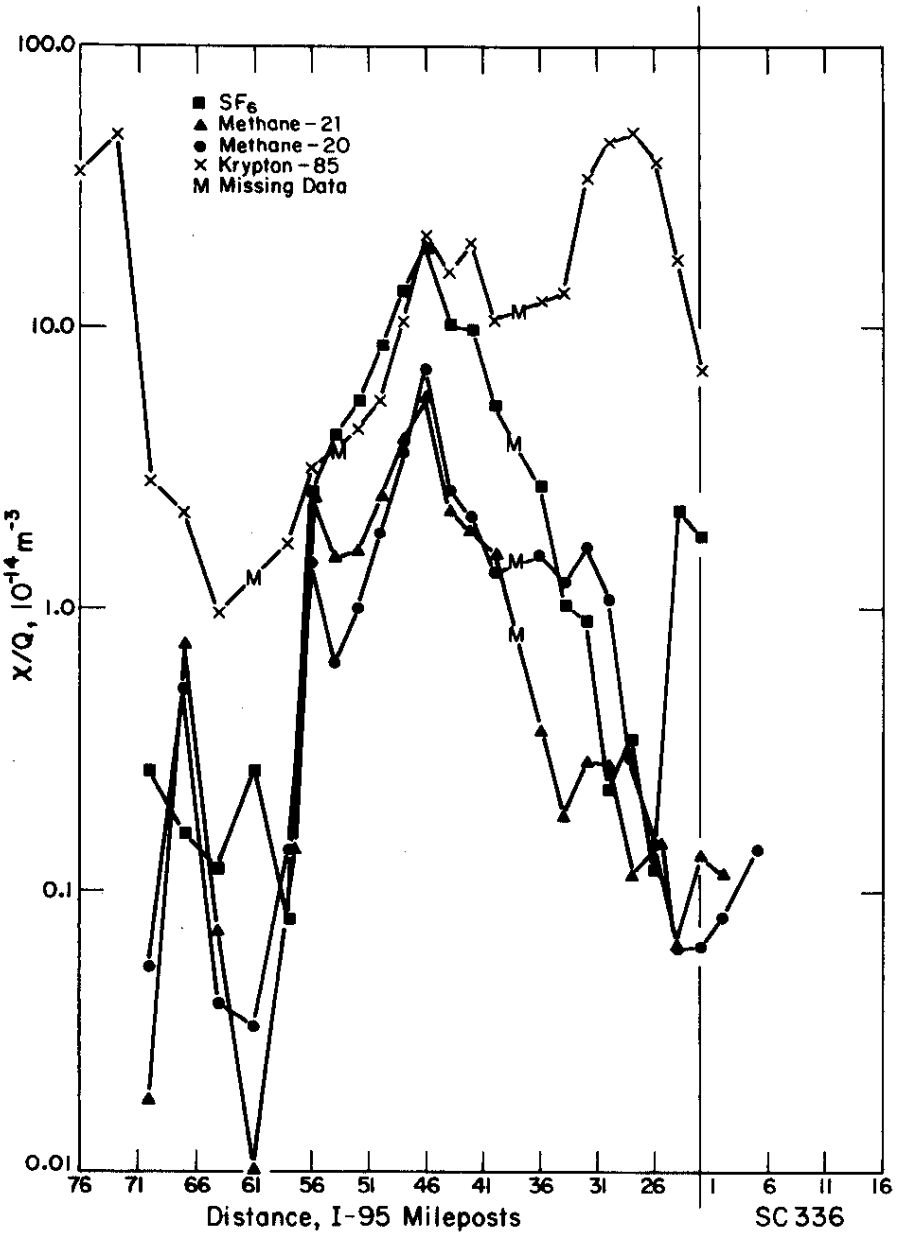

FIGURE 14. Normalized Tracer Concentrations Along Interstate-95

All four tracers agree on the position of a peak shown at Mile Post 46; SF_6 and krypton concentrations agree well, and the methanes are a factor of three to four lower. Note that the krypton is high relative to SF_6 on the south side of this peak and low on the north side. Because wind data indicate the plume shifted from south to north along the sampling line with time, data qualitatively agree with the decrease in krypton-85 release rate during

the tracer release period. The large krypton-85 peak to the south appears to be readily explainable by the krypton released prior to the other tracers (Table 1) as the samplers were turned on early enough to catch this material. The krypton-85 peak at the north end of the sampling line may be due to krypton-85 emitted after termination of the other releases, but more detailed analysis is needed to account for its arrival before the samplers were turned off.

In addition to the agreement on the position of the peak at Mile Post 46, all four tracers show a relatively high concentration at Mile Post 42. However, both methanes show a definite peak at Mile Post 69 that is absent in the SF_6 data while the SF_6 shows a peak at Mile Posts 22 and 24 that is absent in the methane data. No explanation for these differences has been uncovered.

The major problem revealed in this experiment is the discrepancy between the methane and SF_6. Both the peak concentrations and the concentrations summed over the sampling line show the methanes to be low by about a factor of four relative to SF_6. The SF_6 appears to agree with krypton-85, and mass balance calculations also tend to confirm the validity of the SF_6 measurements. On the other hand, the two methanes appear to agree well with each other. The ratio of the methane-20/methane-21 concentrations summed over the sampling line is 3.6 which agrees well with the ratio of molecules released 3.5.

Some possible explanations for the methane-SF_6 results which have been considered are the following:

a) Loss of methane from the plastic bags before transferring to cylinders. This loss had been checked before the experiment by using mass-16 methane and appeared to be negligible.

b) Solubility of the methane and/or exchange with dissolved methane in the plastic. According to typical solubilities of methane in organic solvents, this solubility should be negligible.

c) Reaction of methane-21 with the processing stack gases or in their radiation field. This reaction may be ruled out by the agreement of the methane-21 results with the methane-20 results which was released under chemically clean and radiation free conditions.

d) Destruction of the methanes in the atmosphere. The possibility of destruction occurring during the several hours of plume travel would be ruled out by the apparent three-to four-year lifetime of atmospheric methane.

e) Exchange of deuterated methane with ordinary methane in the atmosphere or with the methane spike. The homogeneous exchange of hydrogen atoms in methane is very slow. The catalytically induced exchange on the walls of the metal cylinders is being studied. However, no clear dependence of the methane-21/SF_6 ratio on the residence time in the cylinders is apparent. For example, the data from Stations 50 and 52, which show essentially the same methane-21/SF_6 ratio, were processed 61 and 37 days after collection. Experiments are under way to explore further the possibility of exchange under the conditions of the SRP experiment.

f) Possible drastically different behavior of the SF_6 from that of the methanes at the source. A hint of this behavior appears in the dependence of methane-21/SF_6 ratio on the position of the collecting station. The ratio generally increases from south to north along the sampling line. Possible flaws in the release technique are being investigated, but no credible mechanism for separation of the tracers during the release has been uncovered to date.

Sampling at Cryogenic Sites

Results of the cryogenic sampling of krypton-85 at St. George, Bamberg, and Ridgeland are shown in Table 11A. The St. George sample on the night before the experiment showed a high concentration of krypton-85, and the sample starting at 10/0900, shortly before the start of the tracer release, also showed krypton-85 in excess of the background concentration. However, the bag sample taken simultaneously with this cryogenic sample (Table 11B) showed only background SF_6, indicating that the krypton seen at St. George must have been emitted before the tracer release. Note also that the bag sample has a concentration of 37 pCi/m^3 compared with 19.2 pCi/m^3 in the simultaneous cryogenic sample. The low volume reported for the bag sample (Table 6) suggests that the pump might have malfunctioned, and that most or all of this sample was collected during the first few hours of the sampling period when the krypton-85 plume was in the vicinity of St. George.

The plume was not seen at Bamberg during the period of experiment. Krypton-85 was definitely above background at Ridgeland and SF_6 in the bag sample also appeared to be slightly above background.

TABLE 11

SF_6 and Kr-85 Concentrations at Cryogenic Sites

A. Kr-85 From Cryogenic Samplers

Location	*Bottle No.*	*Day/Time, On*	*EST, Off*	*pCi/m³*
St. George	1591	9/6:00 P.M.	10/8:00 A.M.	785
	0025	10/9:00 A.M.	10/5:00 P.M.	19.2
	2420	10/6:00 P.M.	11/8:00 A.M.	15.4
	1294	11/9:00 A.M.	11/5:00 P.M.	23.0
Bamberg	1748	9/11:30 A.M.	9/5:00 P.M.	17.0
	0152	9/6:00 P.M.	10/8:00 A.M.	16.4
	1246	10/9:00 A.M.	10/5:00 P.M.	14.0
	2065	10/6:00 P.M.	11/8:00 A.M.	14.4
Ridgeland	1047	9/11:30 A.M.	10/9:00 A.M.	15.1
	0891	10/9:00 A.M.	11/9:00 A.M.	16.5
	0079	11/9:00 A.M.	15/9:45 A.M.	15.3

B. SF_6 and Kr-85 Bag Samplers

Location	*Bag No.*	*Day/Time, On*	*EST, Off*	*Kr-85, pCi/m³*	*SF_6, ppt by vol*	*Methane-20/ air*	*Methane-21/ air*
St. George	22	10/9:00 A.M.	10/5:00 P.M.	37	0.49	255.0×10^{-16}	41.5×10^{-1}
Ridgeland	23	10/9:00 A.M.	10/5:00 P.M.	24	0.64	3.2×10^{-16}	0.62×10^{-1}

Aircraft Sampling

The approximate locations of the aircraft sampling passes are shown in Figures 15 (passes 1 through 5) and 16 (passes 6 through 11). These plots are based on the log kept by the sampling team onboard the aircraft; more precise positioning should be possible by using the magnetic tape record of location, time and SF_6 concentration. All five passes shown in Figure 15 were flown on flight path A-A. The dashed portion of each pass indicates the segment over which the SF_6 instruments were turned on; the solid portion indicates the segment where the plume was found. The arrows indicate the direction of travel on each pass. A plume profile was obtained on four of the five passes. As shown in Figure 16, the two passes made in the vicinity of Allendale (along flight path B-B) recorded the plume as did three of the four passes along path C-C near Interstate-95.

The plume profiles obtained with the two BNL instruments are shown in Figures 17 through 24. These profiles were derived from the instrument recorder plots described in the section "SF_6 Chromatographs." Table 12A gives the altitude (above terrain), aircraft speed, and time each SF_6 instrument was started on each

pass. Also shown is the SF_6 crosswind integral (conc x time) obtained from the concentration plots. These data can be used to estimate the total amount of SF_6 crossing the flight line. The peak SF_6 concentration recorded on each pass is given in the last column.

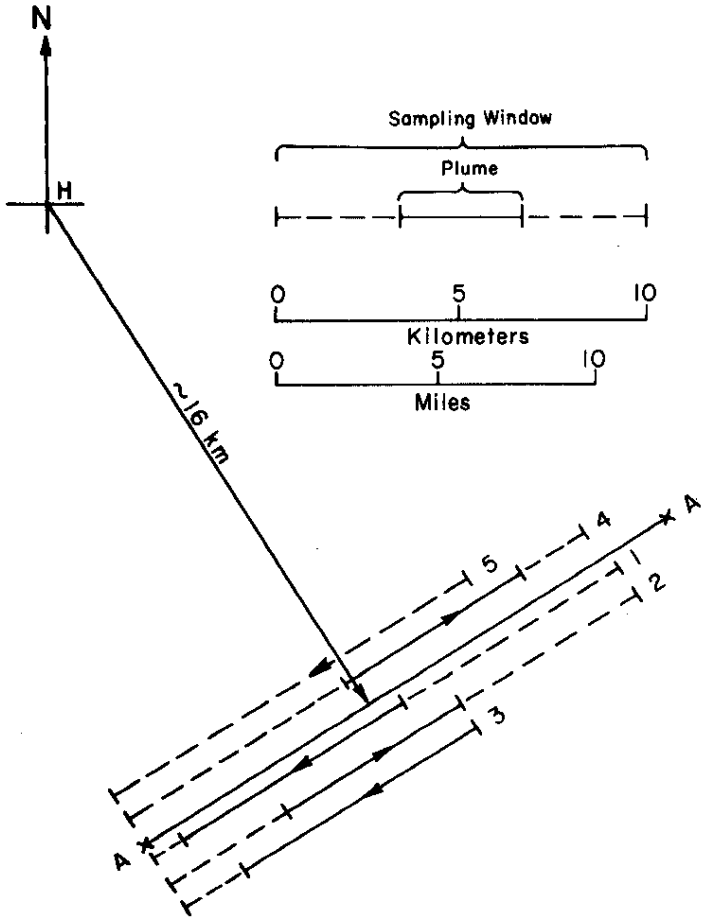

FIGURE 15. Aircraft Sampling Passes at About 16 km Downwind of SF_6 Release Point

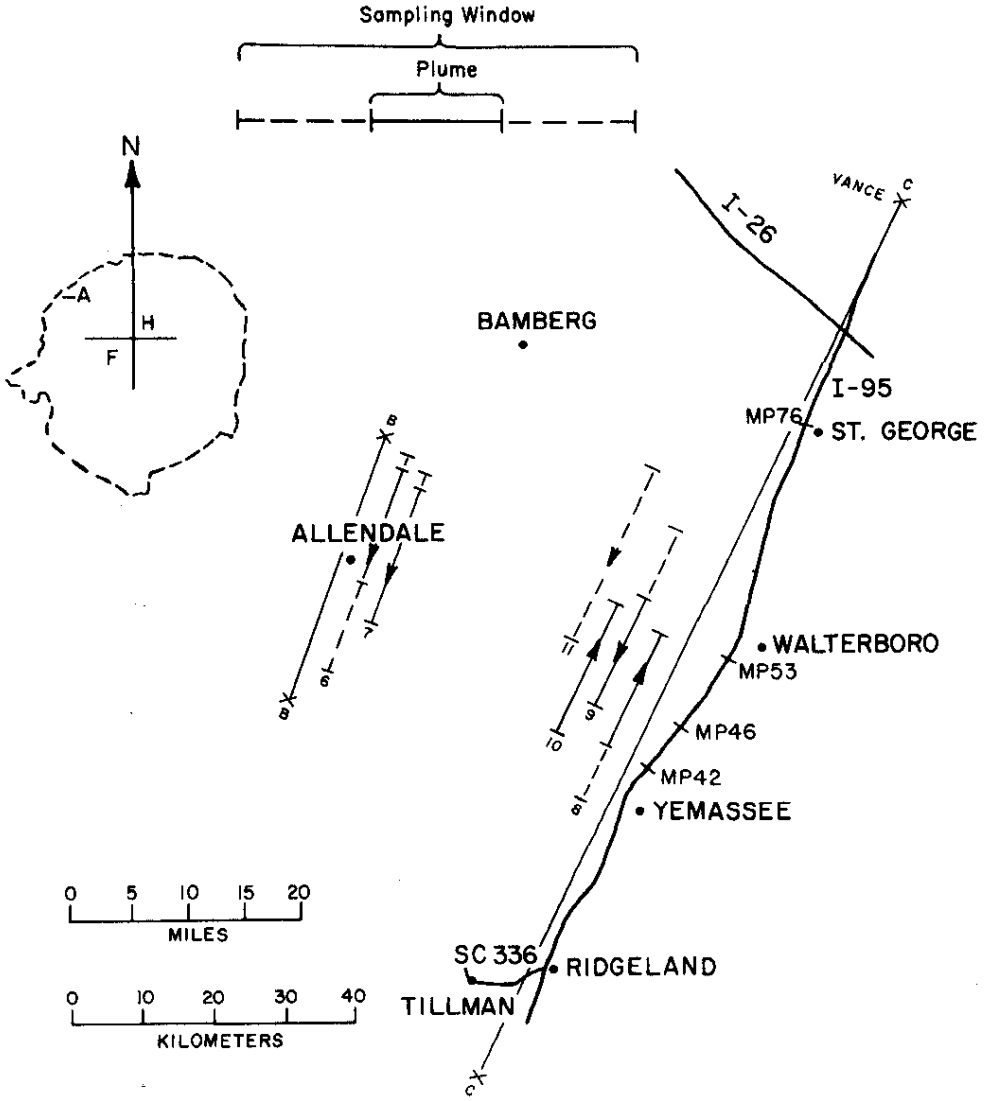

FIGURE 16. Aircraft Sampling Passes at 42 and 92 km from SF_6 Release Point

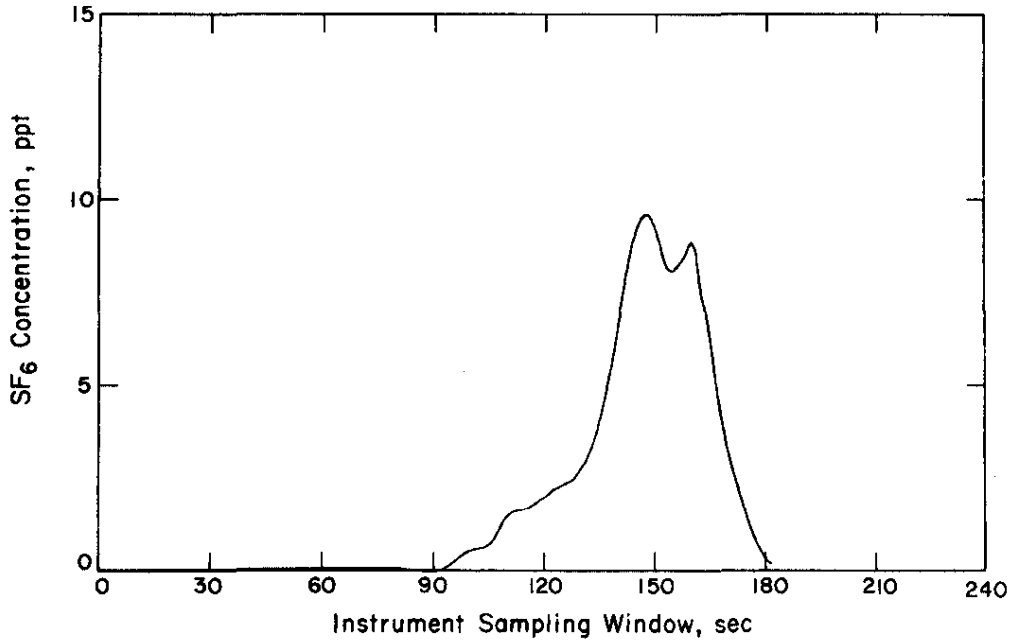

FIGURE 17. Pass 1 Plume Profile from Instrument 1 (3-min Window)

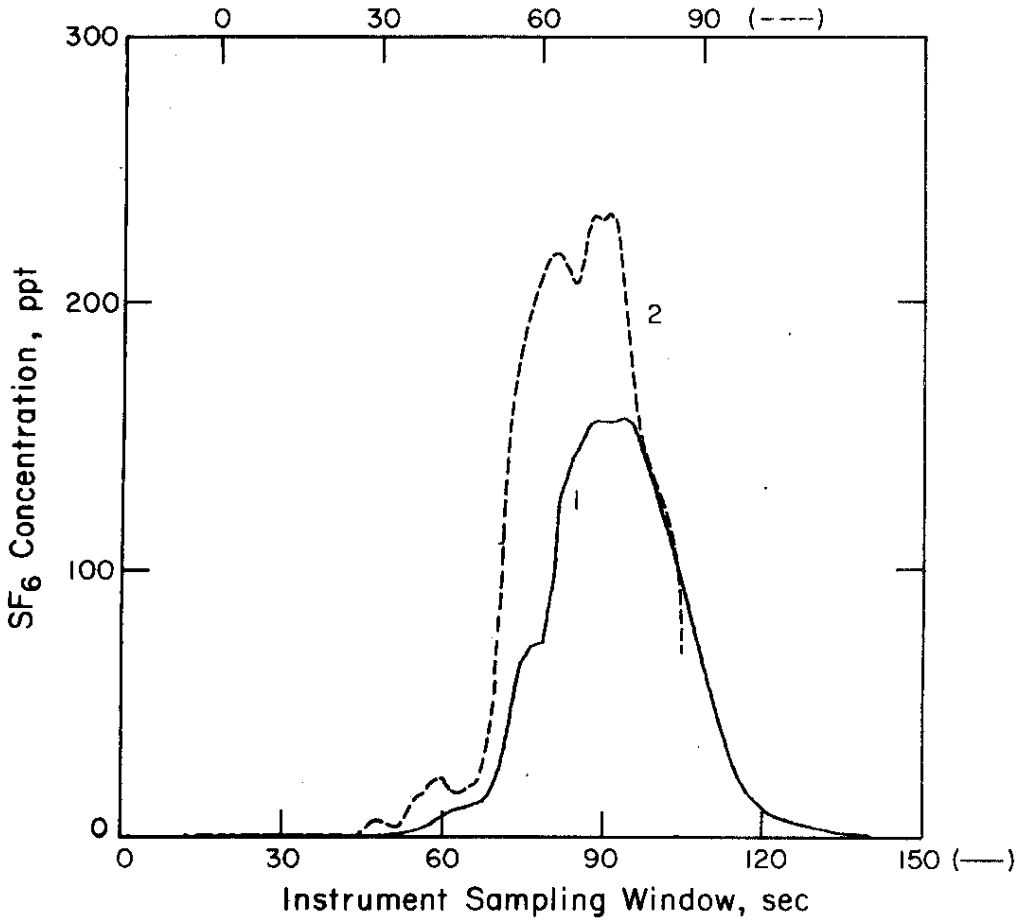

FIGURE 18. Pass 2 Plume Profiles from Instrument 1 (3-Min Window) and Instrument 2 (90-sec Window)

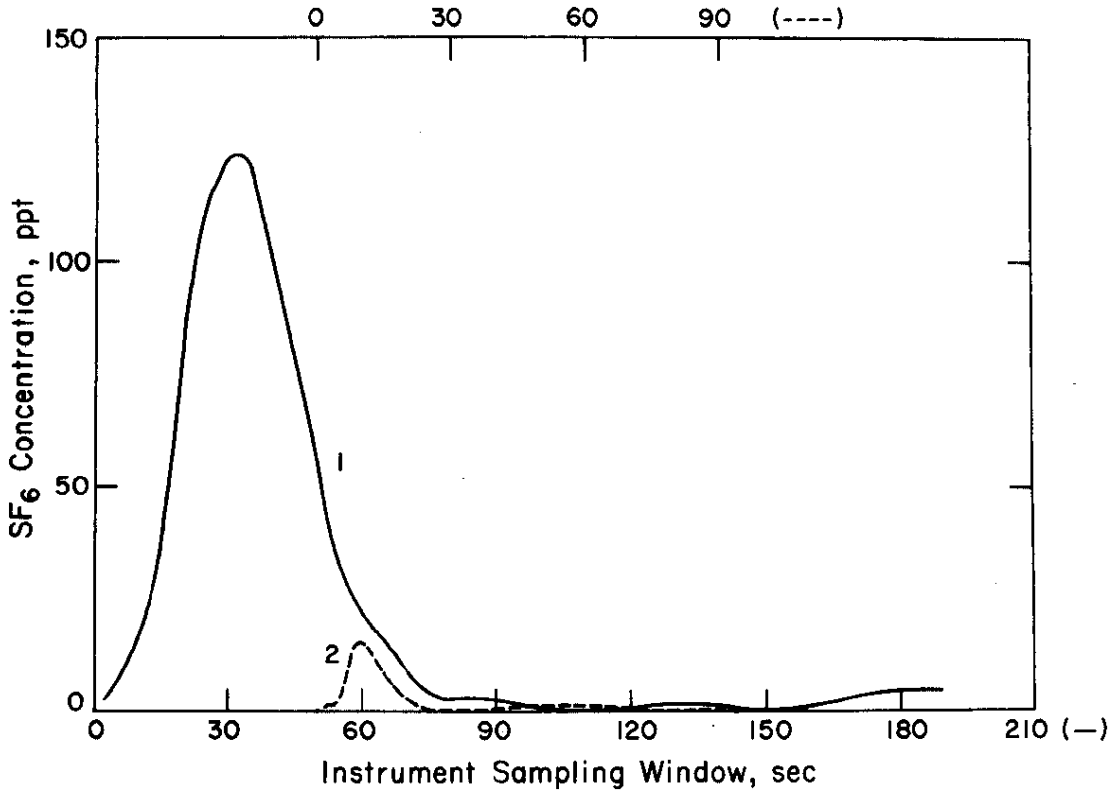

FIGURE 19. Pass 3 Profiles from Both Instruments

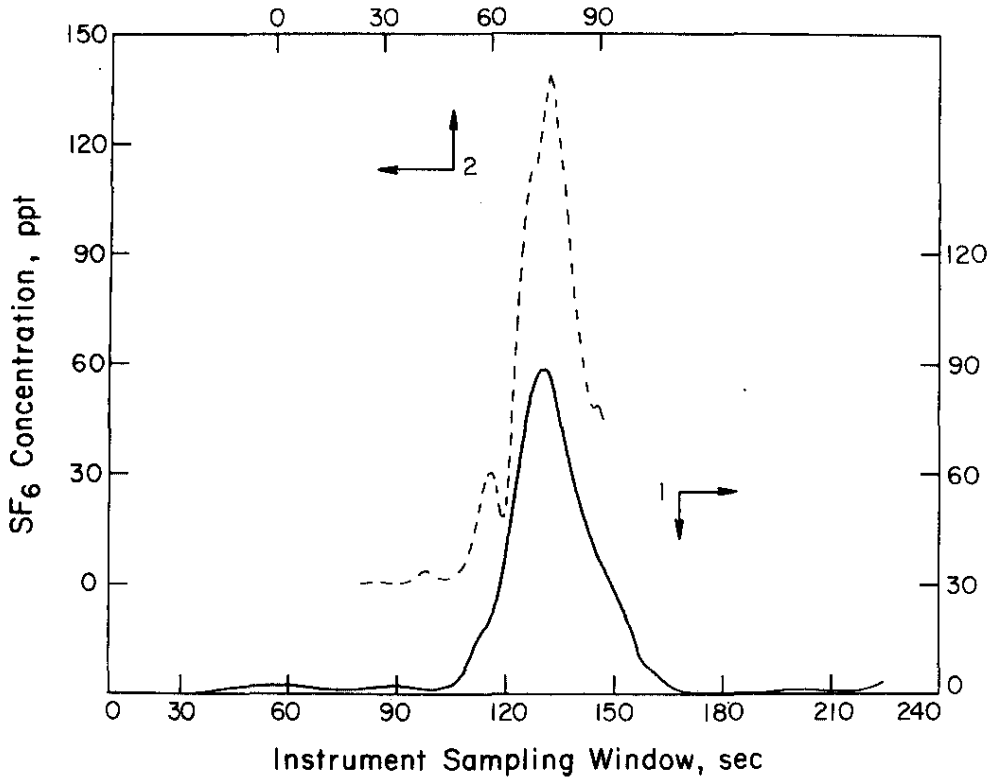

FIGURE 20. Pass 4 Plume Profiles from Both Instruments

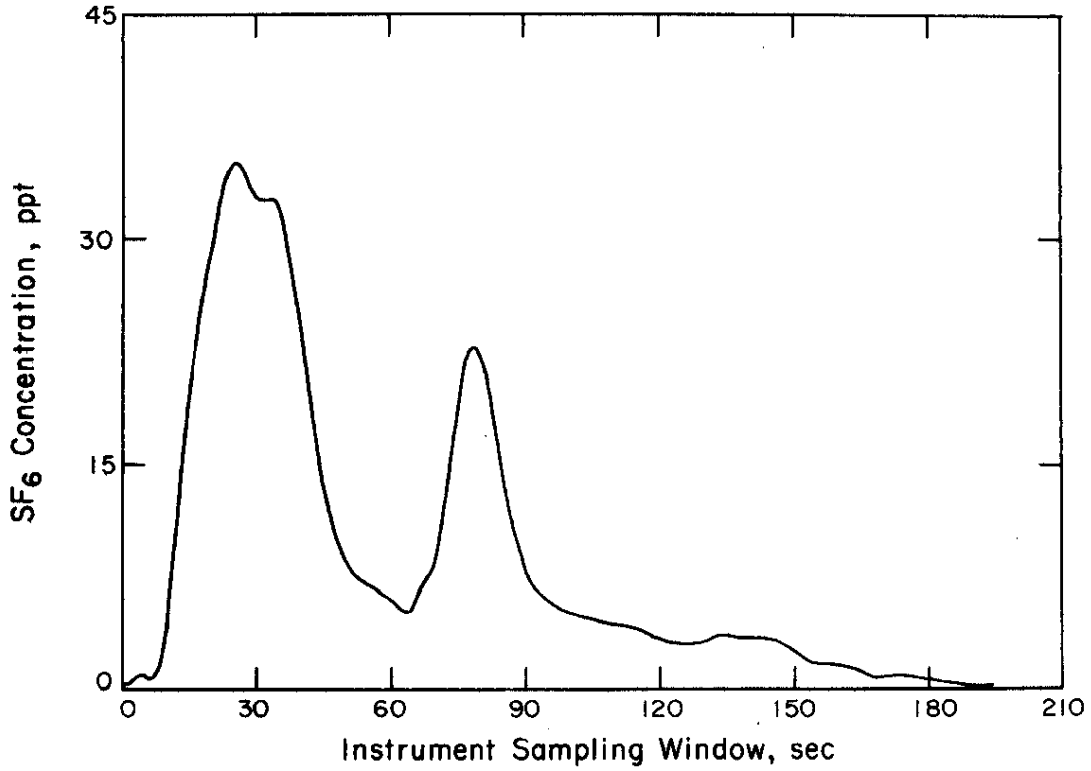

FIGURE 21. Pass 6 Plume Profile (Instrument 1)

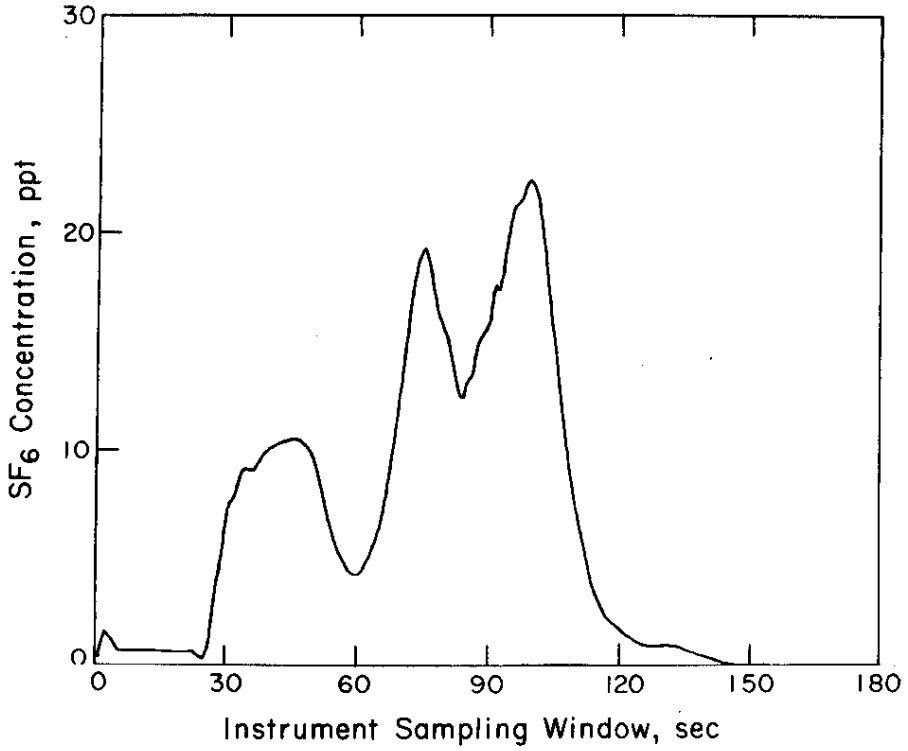

FIGURE 22. Pass 7 Plume Profile from Instrument 1

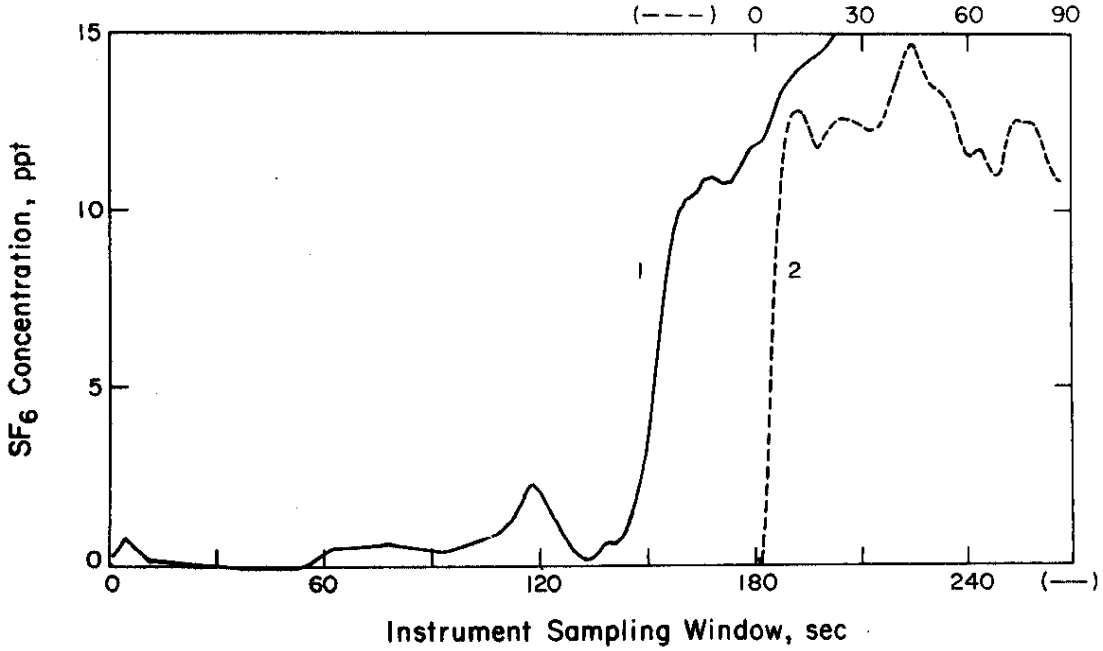

FIGURE 23. Pass 8 Plume Profiles from Both Instruments

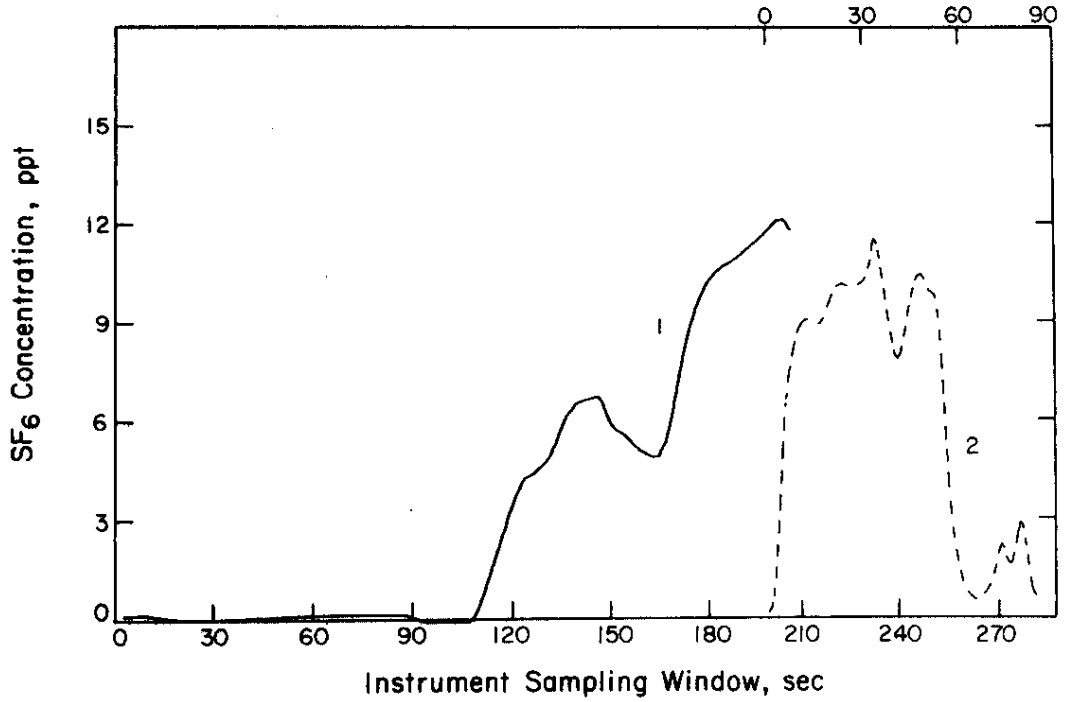

FIGURE 24. Pass 9 Plume Profiles from Both Instruments

Figure 17 shows the profile of SF_6 concentration (ppt of air) versus time (seconds) during pass 1. Only instrument 1 (three-minute sampling window) was used on this pass.

Figure 18 (pass 2) shows the overlapping plots obtained from the two instruments. The SF_6 signal overloaded the amplifier of instrument 1 near the peak so that the actual peak was not recorded by this instrument. In general, where the traces overlap, instrument 2 (90-second window) should be used since it has the better response time and greater resolution.

On pass 3 (Figure 19) the entire plume is again traversed within the three-minute sampling window and the 90-second instrument was turned on just in time to see the tail end of the plume profile.

On pass 4 (Figure 20), the better resolution of the 90-second instrument is again evident. In this instance, the three-minute instrument underestimates the narrow peak by about 30 percent.

On pass 5 (not shown), both instruments gave background readings. The aircraft, at 1500 feet may have been above the plume, or the instruments may have been turned on a little late on this pass (see Figure 15).

Passes 6 and 7 (Figures 21 and 22) at 42 kilometers downwind show a broader plume with multiple peaks. On both passes, the entire plume was traversed during the three-minute sampling window as confirmed by background readings on the nine-second instrument which was started at the end of the three-minute sampling period.

On passes 8 and 9 (Figures 23 and 24), at 92 kilometers downwind, the instruments were again operated sequentially in anticipation of a broad plume. On pass 8, the aircraft was still in the plume at the end of the sampling window; on pass 9, a complete plume profile appeared to be obtained with the two instruments.

On pass 10 (not shown), the three-minute instrument saw the plume; but a problem with baseline drift prevented a quantitative measurement. On pass 11 (now shown), both instruments showed only background. Whether or not the plume mixed up to a height of 2000 feet cannot be established as the result of this single pass.

Table 12-A gives additional information concerning passes 1 through 11. Table 12-B gives the results of the bag samples taken onboard the aircraft. These five-minute samples were started at about the same time as the three-minute BNL scan on passes 1, 8,

TABLE 12

Aircraft Sampling Data

A. Plume Profiles

Pass No.	Downwind Distance, km	Altitude Above Ground, ft	Aircraft Speed, m/sec	Start of 3-min Profile, EST	3-min SF_6 Integral, ppt-sec	Start of 90-sec Profile, EST	90-sec SF_6 Integral, ppt-sec	Peak SF_6 Conc, ppt
1	16	500	77	11:31	339	-----	-----	9.5
2	16	500	77	11:51	4940	11:51	6700	220
3	16	500	77	12:12	4250	12:13	199	124
4	16	1000	77	12:28	2400	12:29	2650	139
5	16	1500	77	12:54	Background	12:54	Background	Background
6	42	1000	93	3:21	1740	3:24	Background	35
7	42	1000	93	3:50	1340	3:52	Background	22
8	92	500	93	4:18	445	4:21	1045	15
9	92	1000	93	4:50	677	4:54	526	12
10	92	1000	82			5:20	Background	16
11	92	2000	93	1746	Background	5:49	Background	Background

B. Bag Samples

Pass	Sample No.	SF_6, ppt	Kr-85, pCi/m^3	(21/air), (cc/cc) $\times 10^{+16}$	(20/air), (cc/cc) $\times 10^{+16}$
0	A/C-1	0.52	986	9.81	320
1	A/C-2	2.30	364	90.0	990
8	A/C-3	6.10	113	21.5	145
11	A/C-4	1.28	21.5	12.9	15.6

and 11. Sample A/C-1 was a background sample taken at 500 feet over SRP at 9:18 A.M. EST before the start of the tracer release. The SF_6 concentration is consistent with other background measurements, and the high krypton-85 value is not surprising since krypton-85 was being released at the time (Table 1) and the aircraft was not far from the stack. The other three bag samples all show SF_6 well above background. Note that the BNL instruments did not see the plume on pass 11 (combined sampling time of about 4.5 minutes) while sample A/C-4 (five-minute sample) caught some plume. The profiling instruments might have just missed the plume on this pass, and the plume might have extended to at least 2000 feet over I-95.

The only aircraft sample (A/C-3) to be analyzed for heavy methanes to date was taken at 500 ft over I-95. The calculated air concentration of 21.5×10^{-16} cc/cc, when adjusted for the relative release amounts, is low by about a factor of ten compared with the SF_6 concentration in the same sample. (The bag was 10-mil polyethylene.)

EVALUATION OF THE EXPERIMENT

The primary objective of the experiment, a test of the release, sampling, processing, and analysis procedures for the heavy methane tracers with SF_6 as a standard, was accomplished. The use of methane-20 as a meteorological tracer was demonstrated for the first time. Methane-21 had been used once before in a 1974 experiment and detected out to 2500 km, but results had not been checked quantitatively with simultaneous release of another tracer.

Air concentrations of all three tracers were measured at the ground and aloft out to 90 km from the release points. The BNL continuous SF_6 analyzers obtained plume profiles on 9 of the 11 crosswind passes attempted.

The release of less than 300 g of methane-20 and 100 g of methane-21 both gave signal-to-noise ratios of better than 100 to 1 at a distance of about 90 km from the source. If larger samples are collected (on the order of 500 liters) so that dilution with a methane "spike" is unnecessary, about 30 g of methane-21 would be sufficient to give the same response.

All three tracers showed the peak concentration at the same location and generally similar concentration profiles along the sampling line. However, heavy methane concentrations, were low by about a factor of four compared with SF_6 after normalization for the different release amounts. Possible causes for this discrepancy are being investigated, but the problem has not yet been resolved. A flaw may possibly be somewhere in the release, sampling, or processing procedures rather than a difference in the behavior of the tracers in the atmosphere.

Suggested Improvements

In addition to the unresolved questions concerning the methane/SF_6 ratio, various operational problems were encountered which suggest improvements for future experiments.

Tracer Release

A leaky pressure regulator resulted in the uncontrolled release of a portion of the methane-20 tracer. The apparatus for release of SF_6 and methane-21 functioned well; both tracers were released at uniform rates over a four-hour period, as planned. However, a calibration error resulted in the release of only one-third of the planned amount of SF_6. The planned

release amount provided sufficient safety margin to compensate for the lower-than-expected release. The problems are easily corrected and will not recur.

Placing of Samplers

Samplers were properly placed to intercept the plume in spite of communications problems. Commercial telephones provided intermittent communications with the field personnel deploying the sampling array. This arrangement was marginally satisfactory and would not suffice if experiments were conducted in less populated areas. Commercial mobile phones were not very satisfactory because of short range and a lack of good relaying stations in the area.

If at all possible, continuous communication between the control point and the sampling teams should be provided in future experiments.

Pump and Bag Samplers

The bag samplers were generally successful in collecting samples but improved design and functional features are indicated. The pumps appear to be temperature-sensitive and difficult to adjust to a desired sampling rate. The *Saran* bags were susceptible to changes in temperature, and some surface cracks were observed after exposure to cool temperatures. The mechanical fragility of the bags is an inherent problem which demands extreme care in handling. Leak-testing each bag before the experiment is a laborious, time consuming, but necessary effort. A simpler, more rugged sampling system is being sought. A sequential sampler would have obvious advantages in developing a better understanding of plume behavior in the atmosphere.

Sample Transfer to Cylinders

The transfer of samples immediately at the conclusion of whole air sampling from the bags to steel cylinders to maintain sample integrity until they could be analyzed appears to have been a wise decision. Transfer procedures worked well except for one flaw. The cylinders used for cryogenic transfer of samples for analysis of krypton and the methanes had valves on both ends. Immersion of one end of the cylinder in liquid nitrogen during the transfer appears to have affected the seal, causing leaks in some of the cylinders. In the future, a cylinder valved at one end only should be used. The other steps in the complex sample processing and analysis procedure appear to have worked well.

Aircraft Sampling

The aircraft used in this experiment, with its sophisticated navigational equipment, probably represented an "overkill" for our air sampling requirements. However, the aircraft was available because of its use on other experiments that required this sophistication.

Although excellent sampling results were obtained, a smaller aircraft flying pre-determined sampling tracks could have provided more sampling passes in the time it takes the plume to pass a sampling line. Arrangements should be made well in advance to provide for proper installation of sampling equipment and appropriate working space for the sampling team.

Attempting to obtain complete plume profiles by using instruments that had only a limited sampling window was a significant problem at 100 kilometers from the release point. In addition, the delay period associated with the Brookhaven semicontinuous instruments and the lengthy back-flush time required before the next scan could be made was responsible for reducing the effectiveness of the method. Continuous detection methods for SF_6 and perfluorocarbon tracers, which are at the prototype stage, would significantly improve plume profiling capabilities.

FUTURE PLANS

SRL and LLL will publish separate reports with the data gathered during these tracer tests to validate their concentration prediction models. Models of varying degrees of sophistication will be checked against the results obtained from this tracer experiment and those performed on December 18 and 19. A future joint test is planned between LLL and SRL to test their models, emergency response capabilities, and timing under differing and complex meteorological conditions out to as large a distance as possible downwind of the plant site taking into consideration the tracer, meteorological conditions and aircraft capability. The emphasis by SRL during the next year will be toward evaluating the data already obtained in this and other SRL data gathering programs.

The potential usefulness of heavy methanes as long-range meteorological tracers is readily apparent. However, a less costly tracer system which would allow simpler, automatic sample collection and processing would be desirable. With this goal in mind, ARL, BNL and the DOE-HASL Laboratory are engaged in a cooperative effort to develop a perfluorocarbon tracer system based on prototype sampling equipment developed for ARL by J. Lovelock in England. At the same time LASL is continuing development of the heavy methane system.

Another interlaboratory field test was conducted during the spring of 1977 in Idaho. This test involved the first field test of the perfluorocarbon tracers along with another methane release. SF_6 was again used as a standard to test both new tracer systems in a simultaneous release.

The Brookhaven National Laboratory is continuing work on the development of a continuous, real-time SF_6 monitor. Three techniques under investigation appear promising. In one, a PTFE perm-selective membrane which preferentially permeates O_2 at a rate more than an order of magnitude higher than SF_6 not only leads to a removal of oxygen but also an enrichment in SF_6 since some N_2 also permeates. In the second method, oxygen in air is continuously reduced below 10 ppm, while SF_6 is unaffected by bubbling through alkaline pyrogallol solution. Good response time is achieved because SF_6 is extremely insoluble in water. The third method, based on perfluorocarbon instruments, involves the catalytic removal of oxygen by reaction of the air sample with hydrogen over a palladium surface.

The DOE-supported laboratories involved in the SRP experiment gained valuable experience in working together and coordinating their efforts toward a common program goal. Future cooperative experiments with one or more of these new tracers are envisioned. Eventually a mass of data will be obtained at distances from 100 to several thousands of kilometers from a source for air pollution model verification. Experiments would be conducted at various locations with different types of terrain and under a variety of meteorological conditions.

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