TRANSPORT OF ACIDIC AIR POLLUTANTS TO FORESTS AND ALPINE REGIONS OF THE SIERRA NEVADA (TAAPS)

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ABSTRACT

Two separate atmospheric tracer experiments were conducted in the summer and fall season of 1990 to study the transport of air pollutants from the San Joaquin Valley (SJV) into the Sierra Nevada Range. The experiments involved the release of three perfluorocarbon chemicals, used as atmospheric tracer gases, to track air mass movement during the breakdown of ozone episodes in the SJV. Forecasting and the determination of when to perform each test was made by ARB personnel. Sequential two-hour averaged concentration levels were sampled simultaneously at 31 preselected locations situated throughout the SJV and the Sierra Nevada Range. The summer test was performed during August 12-14, 1990 and the fall test was performed during October 24-27, 1990. Each test was designed to last 48 hours following the release of tracer gases from Stockton, Fresno, and Bakersfield. The Autumn test, however, involved a longer sampling time period due to unexpected equipment problems.

This study has provided some important findings concerning the transport of pollutants from the SJV. First, because air pollutant transport is dominated by winds aloft within the mixing layer, surface winds are a poor indicator of air mass transport. Secondly, pollutants born in the SJV are eventually transported into the upper Sierra. Return flow during nocturnal periods has little effect in removing pollutants from the Sierra foothill regions. Finally, transport mechanisms of air pollutants into the Sierra are not a simple process. In most instances, the pollutants are trapped along the foothill regions and slowly seep into the upper Sierra through major canyons and valleys. This decreases the peak pollutant concentration levels which impact the upper Sierra but can substantially prolong episodes of elevated concentrations.

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1.0 INTRODUCTION

The Atmospheric Acidity Protection Program (AAPP) requires the Air Resources Board to determine the extent of transport and deposition of acidic pollutants to mountainous areas and high elevation watersheds. The focus of AAPP is to perform research and monitoring to support the setting of atmospheric acidity and/or deposition standards, should they be needed to protect the public health and welfare (ARB RFP, (1989), "Transport of Acidic Air Pollutants to Forests and Alpine Regions of the Sierra Nevada").

In support of these goals, the Air Resources Board sponsored the Transport of Acidic Air Pollutants to Forests and Alpine Regions of the Sierra Nevada Study (TAAPS). The purpose of the study is to study the transport of pollutants from the San Joaquin Valley into the mountain areas and high elevation watersheds of the Sierra Nevada.

Tracer Technologies was contracted to conduct atmospheric tracer experiments which would (1) help identify pollutant pathways from the San Joaquin Valley into the Sierra Nevada, and (2) help determine the source attribution from Stockton, Fresno and Bakersfield to pollutant impacts in the Sierra Nevada.

Two intensive tracer experiments were planned, one experiment during typical summertime conditions and the second experiment during the tail end of a stagnant period followed by a cold frontal passage. One tracer experiment was conducted during a typical summertime day while the second experiment succeeded in catching stagnant conditions in the SJV but the approaching frontal passage weakened and failed to ventilate the valley. Tracer Technologies utilized three non-reactive perfluorocarbon tracer chemicals to determine transport in the study area. During each of the two intensives, three different tracer chemicals (abbreviated PMCH, PDCH, PTCH) were released over a four-hour period at three different locations: Stockton, Fresno, and Bakersfield.

Tracer Technologies' automated samplers were used to collect air samples at 31 sampling sites throughout the San Joaquin Valley, the elevated terrain of the Sierra, and at three locations on the valley floor east of the Sierra. The array of air samplers simultaneously collected sequential two-hour average samples for 48 consecutive hours. In addition, instantaneous "grab" samples were collected from a fixed wing aircraft over the mountain regions. All air samples collected were analyzed for tracer concentration using electron capture detector gas chromatography.

This report summarizes the field experiments according to a carefully developed measurement plan. Sections 2.0 through 4.0 highlight the field study activities and the

success in executing a comprehensive tracer experiment. Section 5.0 provides a brief summary of the meteorological setting which prevailed during each test. Section 6.0 presents an analysis of the tracer data, depicting tracer cloud movement from release to final measurement. A trajectory analysis is provided in Section 7.0. In this section, anticipated plume trajectories based upon surface wind data are compared to actual tracer data collected on this program. Section 8.0 discusses some data correlations between air quality measurements and the tracer data. Also discussed in this section are the source apportionment analysis and mass balance study. Finally, Section 9.0 outlines several technical conclusions formulated from the program data.

2.0 TEST DESCRIPTION

2.1 Test Objective

The primary objective of the TAAPS Study is to quantify the transport of air pollutants from the San Joaquin Valley to forests and alpine watersheds in the Sierra Nevada. This study examines the atmospheric transport of simultaneous tracer releases from major source areas and the impact which occurs at areas within the Sierra Nevada Range. With the above objective in mind, the tracer experiments were designed to specifically accomplish the following tasks:

1. Determine the source attribution from Stockton, Fresno and Bakersfield to pollutant impacts in the Sierra Nevada Range.

2. Identify pollutant pathways from the San Joaquin Valley into the Sierra Nevada Range.

Secondary technical objectives were anticipated with the conduct of this program. A better understanding of how pollutants are transported within the SJV may be an outcome of this program data. In the mesoscale, one may learn how air exchanges occur from the valley floor to upper Sierra regions. Impact severity may be addressed regarding leeward areas of the Sierra, such as the Owens Valley and desert regions.

2.2 Targeted Meteorology

During the summer months, mild upvalley flow persists in the San Joaquin Valley more often than any other time of the year; nearly 69% of the time (ARB, "California Surface Wind Climatology", 1984). Additionally, upvalley flow occurs more during daylight hours than during nocturnal periods. Ideally, tests were planned during the reversal of nocturnal drainage winds combined with a slight strengthening of the onshore pressure gradient. Relatively low and strong inversions were desired, which limit the vertical dilution of airborne contaminants. Hence releases occurred during the morning hours with the objective of intercepting upvalley flow which would then carry the tracer eastward into the Sierra Nevada.

The summertime climate of central and southern California is dominated by the presence of a semi-permanent high pressure system off the California coast. This characteristic high pressure system can be accompanied by relatively strong and low lying inversions. Under these conditions, winds are light to moderate, and are driven mainly by thermal heating effects caused by cloudless sky conditions occurring over the inland valleys and

deserts. During such conditions, pollutant levels along the central valley tend to build since transport is slow and ventilation is poor. Periodically, due to increased heating in the southwestern deserts, a thermal low develops and a resulting pressure gradient is created along the western United States. This condition promotes air movement out of the valley regions into the nearby mountain ranges. Under this scenario, air masses of relatively high pollutant levels are believed to be quickly transported into the Sierra Nevada from the central valley regions. During this transition, ideal conditions exist to perform transport studies from the central valley to the Sierra Nevada Region.

For the purposes of this research, the two meteorological conditions of interest can generally be characterized as:

1) Flow associated with the breakup of a pollution episode (stagnation breakdown) resulting in a flow of pollutants from the San Joaquin Valley into the Sierra Nevada.

2) Upvalley flow under normal summertime conditions during which ozone may be forming as the emissions from the valley floor move into the Sierra Nevada.

2.3 Tracer Release Scenarios

To accommodate these experimental objectives, two separate tests were designed with the following tracer release scenarios:

1. The first test was designed to characterize pollutant flow during normal upvalley flow conditions. Three tracers were released from Stockton, Fresno and Bakersfield. The Stockton and Fresno tracers were released at about midday from 1000 until 1400 PDT. The Bakersfield tracer was to be released in the early evening from 1900-2300 PDT.

2. The second test was designed to characterize pollutant flow during the breakdown of a stagnation episode during which a large build-up of pollutants occurred in the San Joaquin Valley. Three tracers were to be released from Stockton, Fresno, and Bakersfield from 1000-1400 PDT. Again, the Bakersfield tracer was released in the early evening from 1900-2300 PDT.

2.4 Tracer Release Summary

A tracer release summary is presented in Table 2-1. To better simulate pollutant generation from each area, mobile releases of the tracer gases were performed from the three release areas. For each tracer release, a technician was directed to release along a route encircling a designated city area. This ensured that the tracer release would

represent emissions from the urban center and not a particular point source within the designated city. Maps of each of the routes used to release the tracer are shown in Figures 2-1 through 2-3.

The first experiment (typical summertime transport scenario) was conducted between the 12th and 14th of August 1990. The second experiment (breakdown of poor air quality scenario) was executed during the period from 24 October 1990 through 27 October 1990. During the second experiment, equipment problems surfaced (sampler programming problems) which extended the sampling period. Fortunately, the instrumentation delay enabled capturing some of the transport that did occur later during the stagnant period.

TABLE 2-1. Summary of Tracer Releases

Test #	Site	Date	Time	Tracer	Amount (kg)
1	Bakersfield	8/12/90	1900-2335*	PTCH	21.4
1	Fresno	8/12/90	1000-1400	PDCH	29.1
1	Stockton	8/12/90	1000-1400	PMCH	29.1
2	Bakersfield	10/24/90	1900-2300	PTCH	27.7
2	Fresno	10/24/90	1000-1400	PDCH	33.9
2	Stockton	10/24/90	1000-1400	PMCH	22.5

* Release system was clogged at 22:30 and took 35 minutes to unplug.

2.5 Sampler Locations

Tracer samplers were stationed at 31 different ground sites in the defined study area. These sites are listed in Table 2-2 and are displayed in Figure 2-4. Most of the samplers were collocated with air quality and meteorological sites used in the San Joaquin Valley Air Quality Study (SJVAQS). The remainder of the sites were located at United States Forest Service (USFS) facilities chosen by the Air Resources Board. As can be seen, the locations span from Stockton in the northern part of the Valley to Lebec at the southern end of the Valley, and from the central part of the SJV in the west, to locations such as Mammoth, Bishop, and Edwards Air Force Base in the east. There were also collocated samplers at Auberry and, for test 1 only, at Academy. All samplers were to operate for 48 consecutive hours, collecting 24 two-hour averaged samples. The start time for all samplers was planned for 1000 PDT on the day that the tracer gases were released.

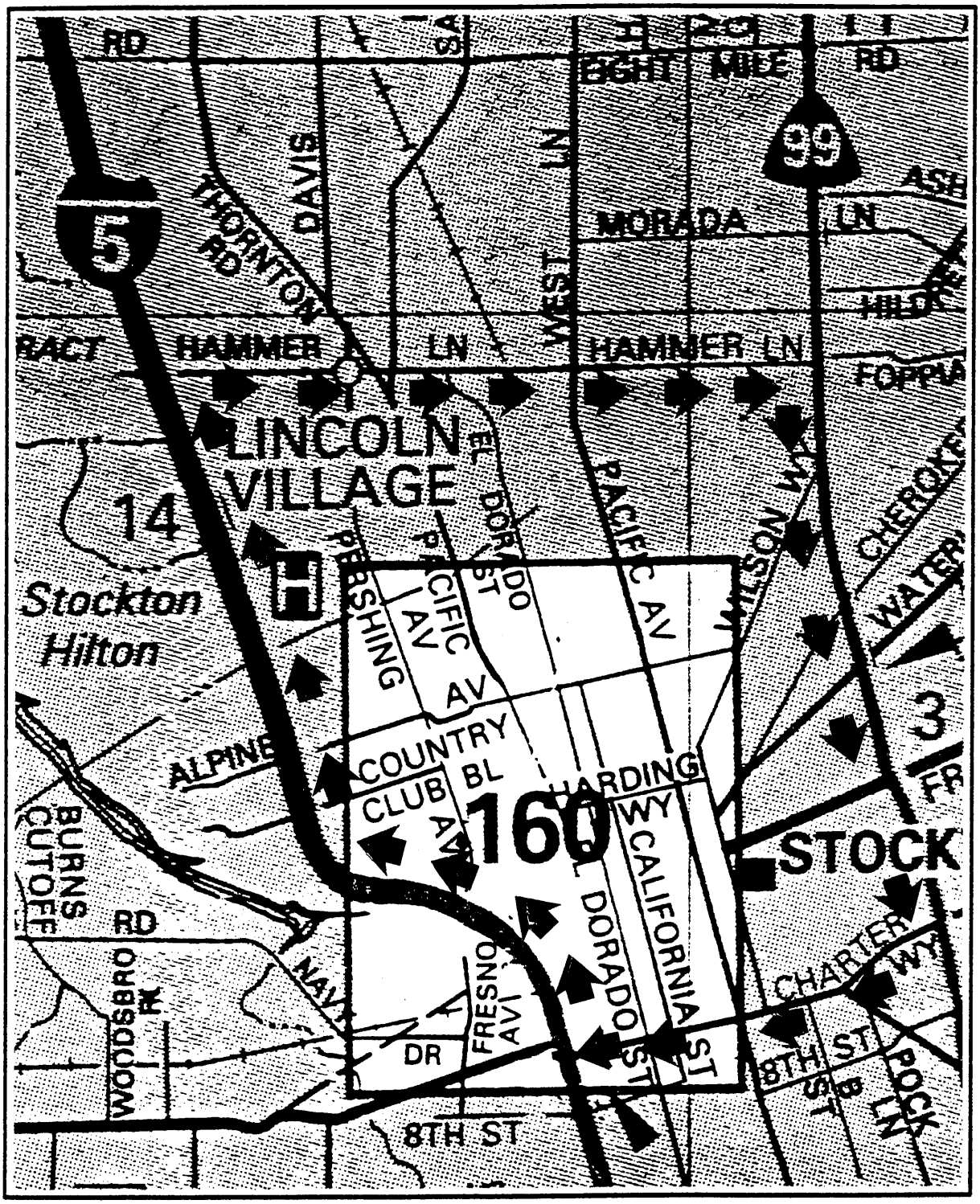


FIGURE 2-1 - STOCKTON AREA TRACER RELEASE ROUTE

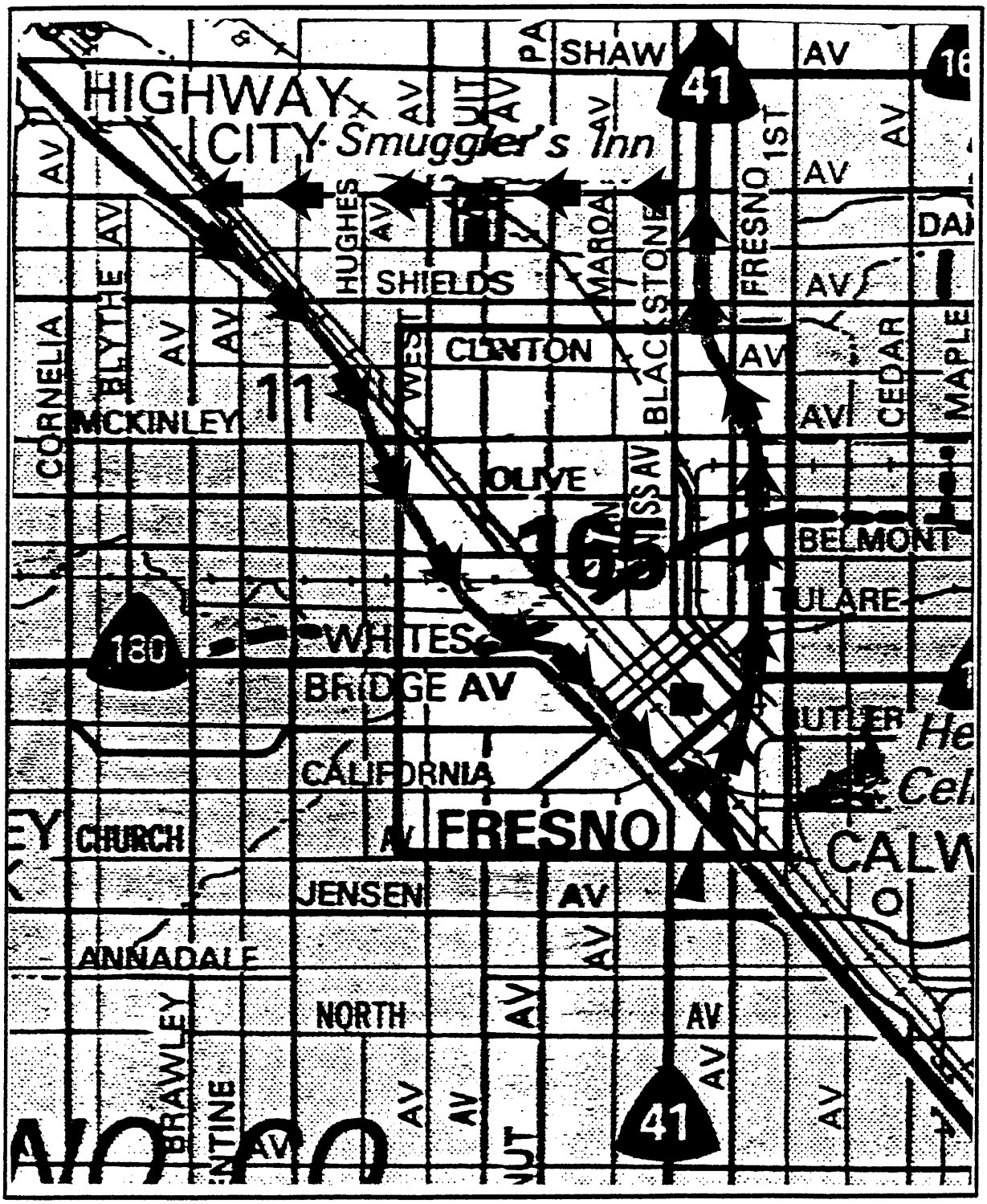


FIGURE 2-2 - FRESNO AREA TRACER RELEASE ROUTE

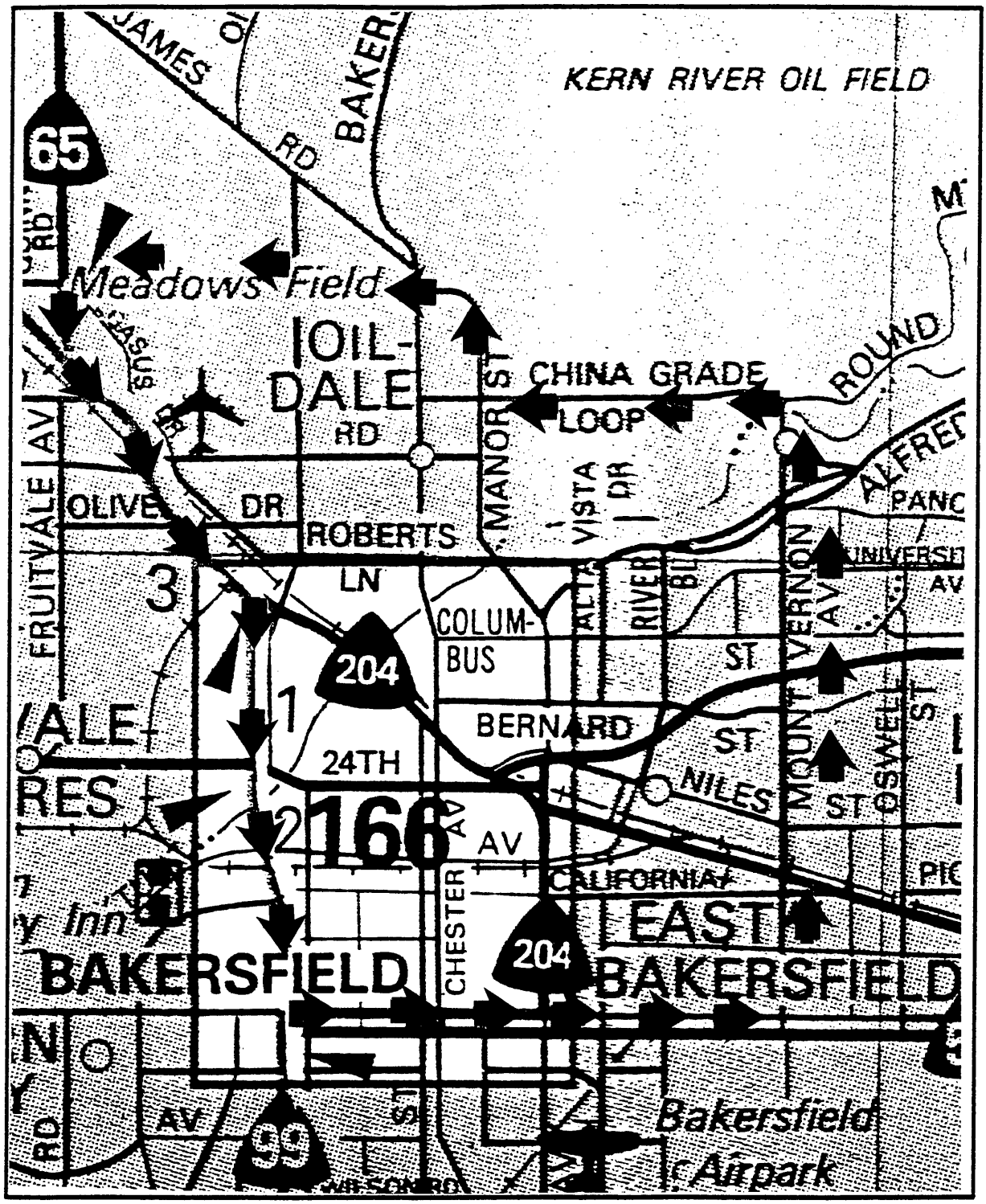


FIGURE 2-3 - BAKERSFIELD AREA TRACER RELEASE ROUTE

TABLE 2-2. Ground Sampling Sites

Site #	Site Name	Latitude	Longitude	Elevation (ft MSL)
1	Academy	36° 53.26'	119° 32.25'	750
3	Angel's Camp	38° 06.43'	120° 32.07'	1000
12	Corcoran	36° 08.19'	119° 34.34'	200
14	Delano	35° 45.25'	119° 16.69'	300
17	El Nido	37° 11.83'	120° 33.77'	150
21	Giant Forest	36° 34.01'	118° 46.70'	6500
29	Mariposa Reservoir	37° 20.00'	120° 16.10'	500
31	Modesto	37° 39.46'	121° 01.69'	90
34	North Fork King's R.	36° 48.25'	119° 23.40'	650
41	Raisin City	36° 35.31'	119° 54.54'	250
46	Tehachapi	35° 10.00'	118° 29.00'	4000
47	Terra Bella	35° 57.84'	118° 58.36'	500
52	Visalia	36° 19.56'	119° 17.25'	320
55	Woodward Reservoir	37° 50.56'	120° 52.45'	230
56	Yosemite	37° 40.16'	119° 48.33'	1800
62	Ash Mountain	36° 30.10'	118° 49.70'	2000
63	Auberry	37° 06.70'	119° 29.10'	2100
65	Cedar Grove	36° 47.00'	118° 39.50'	4900
66	Cherry Lake	37° 58.25'	119° 54.80'	4500
67	Democrat Station	35° 31.80'	118° 37.40'	2400
68	Dinkey Creek	37° 04.80'	119° 11.20'	6300
70	Kaiser Diggings	37° 22.00'	119° 17.00'	3500
71	Lebec	34° 50.25'	118° 51.50'	3900
72	Mammoth Mountain	37° 38.35'	119° 02.20'	9800
73	Onyx	35° 43.70'	118° 08.50'	3000
74	Road's End	35° 56.60'	118° 28.50'	6300
75	Strawberry	38° 11.40'	120° 00.10'	5600
76	Tuolomne Meadows	37° 52.20'	119° 20.00'	8700
77	Westfall Station	37° 27.10'	119° 39.00'	4900
89	Edwards	34° 47.90'	117° 50.30'	2300
90	China Lake	35° 42.50'	117° 38.30'	2300
91	Bishop	37° 21.70'	118° 23.50'	4100
99	Auberry (collocated)	37° 06.70'	119° 29.10'	2100
100	Academy (collocated)	36° 53.26'	119° 32.25'	750

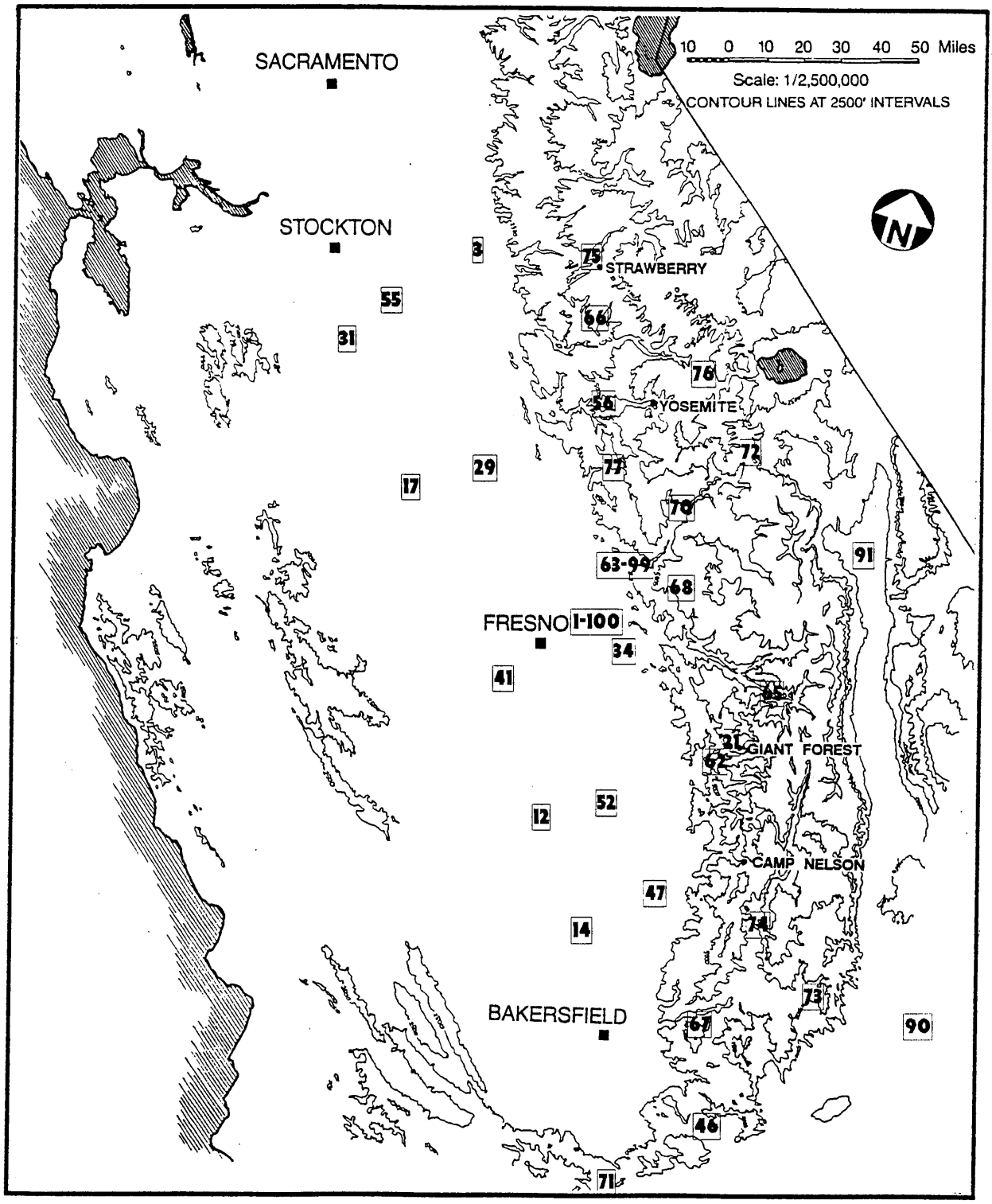


FIGURE 2-4. GROUND SAMPLER LOCATIONS
(1-100, 63-99, are collocated sites)

During the October test, a problem with the sampler software prevented the samplers from starting at the prescribed time. All samplers were re-programmed in the field and as a result, a majority of the samplers did not start sampling until the next evening and following morning. A list of the sampler start times for the second intensive are presented in Table 3-3.

In addition to ground sampling, aircraft sampling was also performed. Beginning shortly after noon on the second day of each intensive, two air sampling flights were conducted simultaneously, one over the northern half of the study area and one over the southern half. The time intervals during which the aircraft samples were obtained were approximately 1335 through 1640 PDT for the August test and from 1435 to 1640 PDT for the October test. The aircraft sample locations and identification numbers (used for sample tracking) are listed in Table 2-3 and are depicted in Figure 2-5.

2.6 Tracer Selection

Three perfluorocarbon tracers (PFTs), abbreviated PMCH, PDCH, and PTCH, were chosen for use in this study. The specific chemical names and molecular weights of these compounds are presented in Table 2-4. Perfluorocarbons have been demonstrated as the tracer of choice where long-range transport is required (Dietz, R.N., "Perfluorocarbon Tracer Technology", 1986). Primary reasons for their success is the low global background of PFTs and the excellent analytical resolution which can be achieved through electron capture detector (ECD) gas chromatography. Since the industrial use of PFTs is limited, the global background levels can be 100 to 1000 times less than other tracer chemicals. PFTs can also be detected in concentrations less than 10 femtoliters of tracer per liter of air (fl/l, 10^{-15} liters/liter). This superior detectability combined with low global backgrounds provide an atmospheric detectability that is 1000 times greater than other popular tracers such as sulfur hexafluoride. Thus long range tests can be conducted using a minimal amount of the PFTs resulting in a substantial cost savings over other tracers.

The PFT chemicals are also physically and chemically inert. This prevents their loss in the atmosphere and makes them biologically inactive and thus harmless to the environment. Because of their low solubility in water and moderate vapor pressure, they are not readily scavenged or deposited on the ground. (ISC Division, "Materials Safety Data Sheet", 1989).

TABLE 2-3. Aircraft Sampling Sites

Site #	Site Name	Latitude	Longitude
2	Shaver Lake	37°07.00'	119°8.00'
4	20 mi. S/E of Shaver Lake	36°50.00'	119°9.00'
5	S/E of Orosi	36°30.00'	119°0.00'
6	20 mi. S/E of Wood Lake	36°09.00'	118°1.00'
7	S/E of Lake Success	35°49.00'	118°4.00'
8	S. of Breckenridge Mt.	35°27.00'	118°6.00'
9	E. of Arvin	35°13.00'	118°2.00'
10	E. of Wheeler Ridge	35°01.00'	118°7.00'
11	Lebec	34°50.00'	118°1.00'
13	N/E of Wheeler Ridge	35°05.00'	118°0.00'
15	N/E of Caliente	35°21.00'	118°2.00'
16	Lake Isabella	35°39.00'	118°3.00'
18	30 mi. N/W of L. Isabella	36°04.00'	118°1.00'
19	60 mi. N/W of L. Isabella	36°28.00'	118°9.00'
20	N/E of Wood Lake	36°43.00'	118°4.00'
22	Cherry Gap	36°58.00'	118°8.00'
23	E. of Shaver Lake	37°10.00'	118°2.00'
24	Thomas Edison Lake	37°23.00'	118°8.00'
25	Huntington Lake	37°13.00'	119°1.00'
26	Bass Lake	37°17.00'	119°2.00'
27	Ahwahnee	37°23.00'	119°7.00'
28	Mariposa	37°30.00'	119°8.00'
30	Lake Mc Clure	37°34.00'	120°1.00'
32	Don Pedro Reservoir	37°43.00'	120°9.00'
33	Melones Reservoir	37°51.00'	120°2.00'
35	Calaveras	38°02.00'	120°7.00'
36	Hogan Reservoir	38°09.00'	120°6.00'
37	Mokelumne Hill	38°18.00'	120°2.00'
38	S. of West Point	38°20.00'	120°8.00'
39	Dorrington	38°22.00'	120°4.00'
40	Lake Alpine	38°26.00'	120°0.00'
42	Hummer-6 M.O.A.	38°15.00'	119°8.00'
43	Cherry Lake	38°01.00'	119°5.00'
44	Mather	37°52.00'	119°0.00'
45	Yosemite Valley	37°43.00'	119°40.00'
48	10 mi. N. of Sugar Pine	37°34.00'	119°38.00'
49	10 mi. N. of Bass Lake	37°25.00'	119°35.00'
50	Friant	36°59.00'	119°43.00'
51	Shaver Lake	37°07.00'	119°18.00'

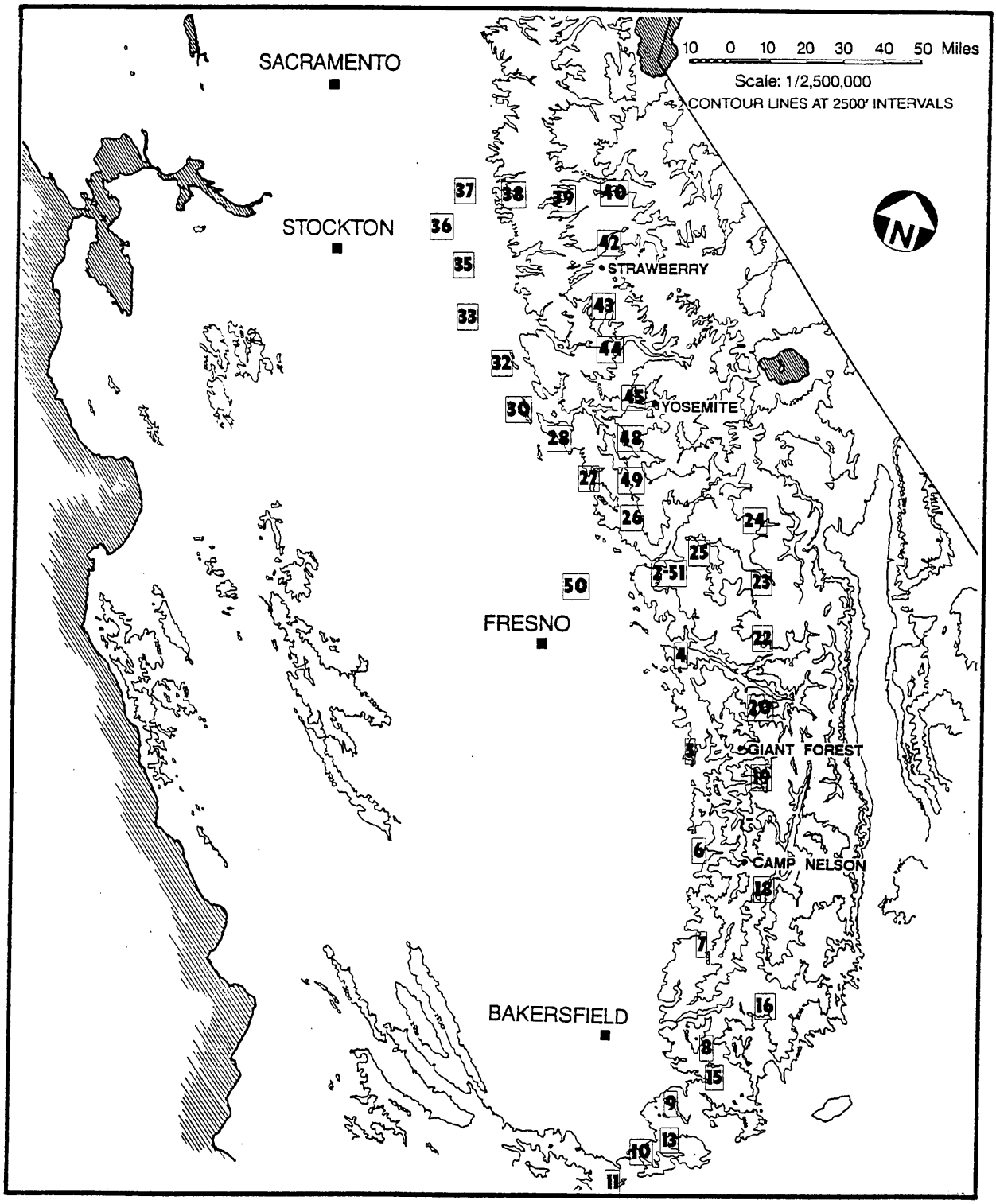


FIGURE 2-5. AIRBORNE SAMPLE LOCATIONS

TABLE 2-4 - Perfluorocarbon Tracer Properties

	Tracer Chemical Name	Abbreviation	Molecular Wt.
1	Perfluoromethylcyclohexane	PMCH	350
2	Perfluor-1,2-dimethylcyclohexane	PDCH	400
3	Perfluorotrimethylcyclohexane	PTCH	450

3.0 FIELD OPERATIONS

The objectives of the field operations were (1) to accurately release a predetermined amount of tracer chemicals from the three different release locations, and then (2) to collect properly documented air samples from both ground level and aircraft sites throughout the study region. Tracer Technologies' field operations were conducted from three locations. The central coordinating office was located in Fresno and two other field offices were located in Stockton and Bakersfield.

All tracer chemicals and related equipment were delivered to interim storage areas in Pittsburgh, Fresno, and Bakersfield prior to the start of the first test. As a quality assurance check, documentation was maintained on the amount of stored PFTs to note if there was an inadvertent loss or accidental release of any of the tracers during storage. Gravimetric readings were collected on all stored tracer materials before and after each test period. The performance of each tracer release system was documented and reported to the field manager after each release was completed.

3.1 Tracer Release Operations

Two independent tests were performed on this contract: one in August 1990 and the other in October 1990. During each test, three tracers were released; one at each of three locations in the San Joaquin Valley. A listing of the tracer release sites and a summary of the tracer releases is presented in Table 3-1. All tracer releases were performed as area releases to simulate pollution or precursor flow from the city area into the Sierra Nevada. During Test 1, the Bakersfield release took thirty five minutes longer to complete because the release system got clogged and it took thirty minutes to unplug the system.

TABLE 3-1. Test Summary of Tracer Releases

Test #	Site	Date	Time	Tracer	Amount (kg)
1	Bakersfield	8/12/90	1900-2335	PTCH	21.4
1	Fresno	8/12/90	1000-1400	PDCH	29.1
1	Stockton	8/12/90	1000-1400	PMCH	29.1
2	Bakersfield	10/24/90	1900-2300	PTCH	27.7
2	Fresno	10/24/90	1000-1400	PDCH	33.9
2	Stockton	10/24/90	1000-1400	PMCH	22.5

3.1.1 Tracer Release Equipment

The objective of the release system was to accurately release a predetermined amount of tracer as a fine atomized mist. This fine mist will rapidly vaporize resulting in a gas cloud which will be transported by the ambient winds. To accomplish this objective, the tracer release system consisted of five main components: a compressed air source, a tracer reservoir, a flow control valve, a flow meter, and a spray nozzle. A schematic of the tracer release system is presented in Figure 3-1. Stainless steel tubing was used for connections throughout the system. To perform a release, the compressed air source was used to pressurize the tracer reservoir and then the flow control valve was opened. The difference in pressure between the tracer reservoir and the atmosphere caused the tracer chemical to flow through the system and out the discharge nozzle. To aid in vaporization of the tracer, the nozzle was adjusted to spray the tracer into the ambient air.

3.1.2 Tracer Release Calibrations

Prior to use in the field, the flowmeter in each release system was calibrated for a specific tracer. The calibration curves were generated by determining the mass flow rates for several specific flowmeter readings. This was accomplished by attaching a Mylar™ bag to the tracer discharge line downstream from the flowmeter and adjusting the system to a specific rotameter setting. The tracer was then collected in the bag for a measured time period. The bag was weighed prior to and after each test run, and several test runs were performed for each flowmeter setting. From these data points a calibration curve of mass flow rate versus flowmeter reading was calculated.

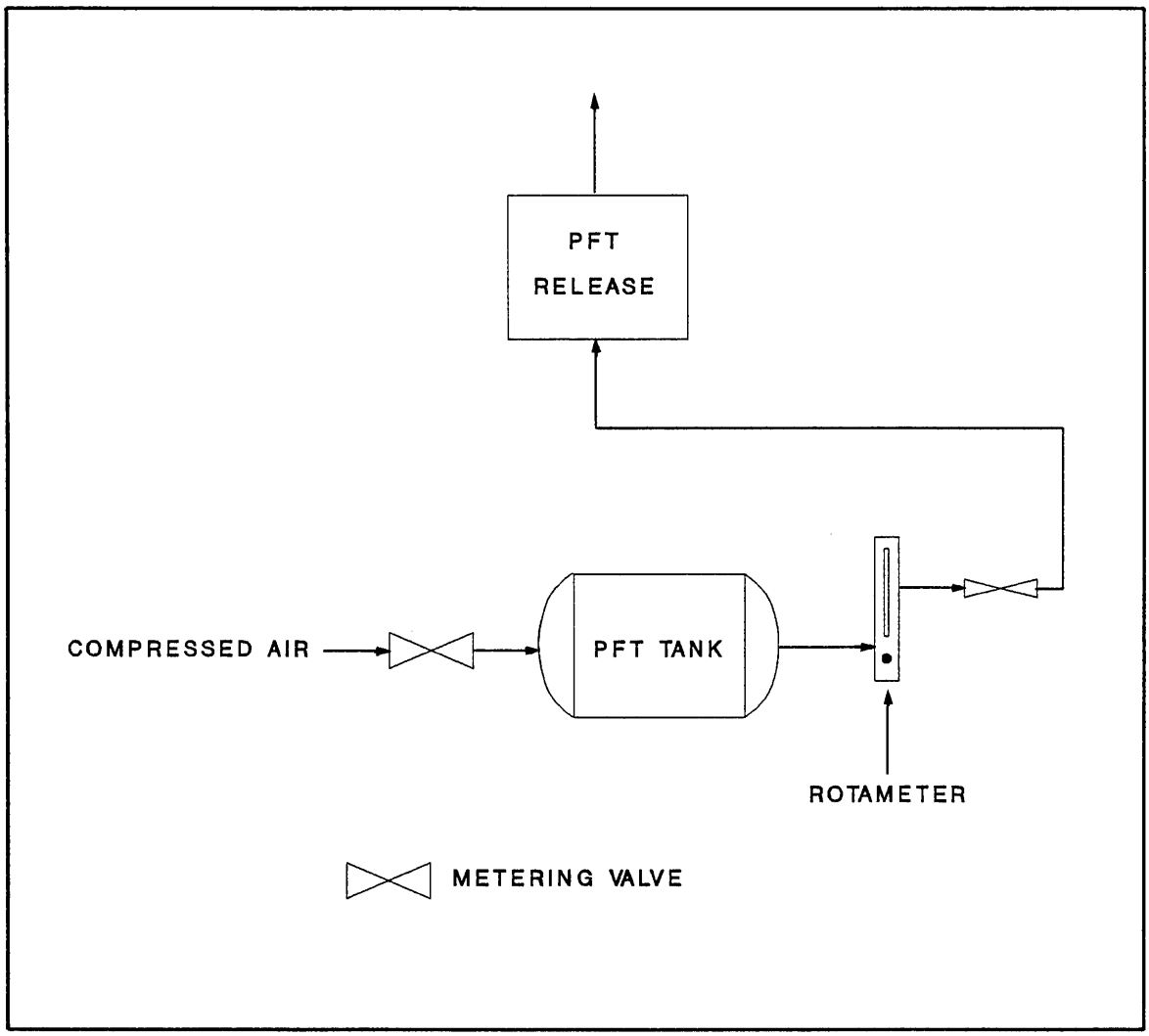
3.1.3 Tracer Release Logistics

Several logistical issues were addressed regarding the shipment and storage of tracer chemicals, the operation of tracer release equipment, and the deployment of release technicians and equipment during the study.

Three storage lockers were used to store the tracer chemicals used during the study. The storage lockers were located in three cities, Pittsburg (Bay Area), Fresno, and Bakersfield. Approximately one week prior to the beginning of the study, all tracer chemicals and release systems were transported to the field. Tracer chemicals were allocated to the individual storage lockers in each city where respective releases would occur. Each type of tracer chemical was transported inside an aluminum canister capable of holding approximately 10 kilograms; these canisters were in turn packed into cardboard boxes. Empty tracer canisters were also stored in their respective storage lockers until the end of the study.

FIGURE 3-1

TRACER RELEASE SCHEMATIC



The three PFT release systems designed for this study were also stored in the tracer storage lockers. The release system for Stockton was stored in the Pittsburg locker, while the other two systems were stored in Fresno and Bakersfield respectively.

When an intensive alert was announced, all release technicians were notified. The alert for an intensive was given approximately 36 hours before the actual tracer release. Upon a final "go" from the ARB project manager, all release technicians were sent into the field to retrieve the appropriate tracer release systems and tracer chemicals. Once the equipment had been retrieved, the release engineers then traveled to their designated release locations to prepare for the respective release.

As previously stated, all tracer releases in this study were performed as mobile releases. Each release system, after appropriate servicing, was loaded into a motor vehicle and transported to a predetermined starting location. At the appointed release start time, the release technician began operating the release system which discharged the tracer through a manifold wand projecting from the vehicle. The tracer release operation then continued for the next four hours, as the vehicle was driven continuously along a prescribed route around the perimeter of its designated release city. The release routes for each of the three cities are shown on maps in Figures 2-1 through 2-3.

During each tracer release, the technicians operated and monitored the equipment performance on a continuous basis. Flow meter readings and gravimetric analysis of the PFT release were coordinated every 5 and 30 minutes respectively, to provide an additional check on the amount of tracer being released. After the release was completed, the weight of the tracer container was documented, shutdown procedures were performed, and the release system was returned to the appropriate storage locker. The release technicians also reported the amount of tracer released to the field manager, and archived the release data sheet.

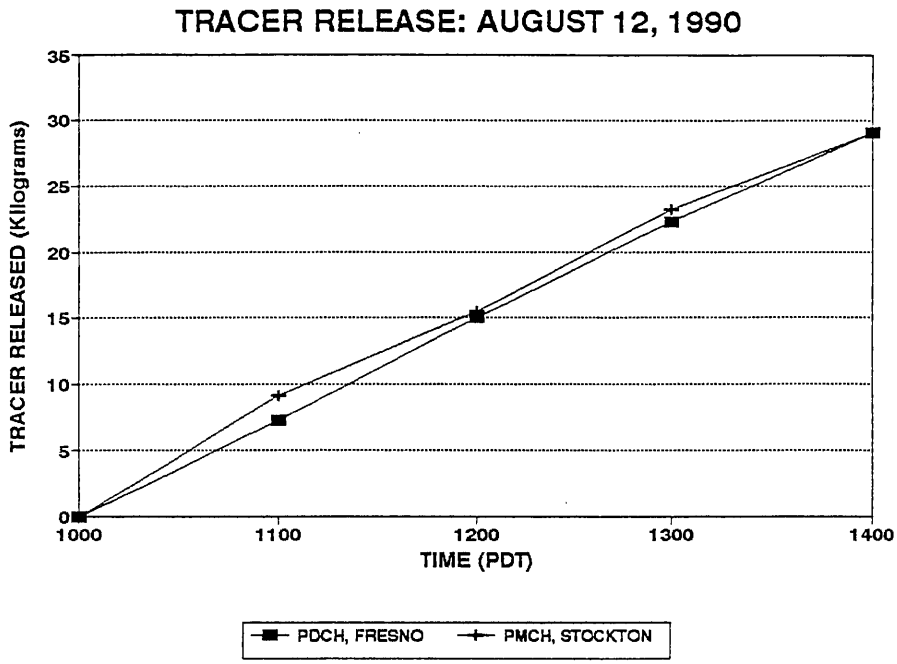
Time series plots of the cumulative tracer releases for each test are shown in Figures 3-2 and 3-3. Tracer release rates are determined from the slopes of the curves in Figures 3-2 and 3-3.

3.2 Sampling Operations

Sampling operations were coordinated through three temporary field offices in the San Joaquin Valley: Fresno, Stockton, and Bakersfield. Each office served as a base for sampler crews and as an intermediate delivery point for sampler equipment and collected air sample bags.

All ground level sampling was performed using Tracer Technologies' automated samplers and aluminized Mylar™ sampling bags. The air samplers collected sequential two-hour time averaged samples for the designed 48 hour sampling period.

FIGURE 3-2
TIME HISTORY OF TRACER RELEASES - AUGUST 12, 1990



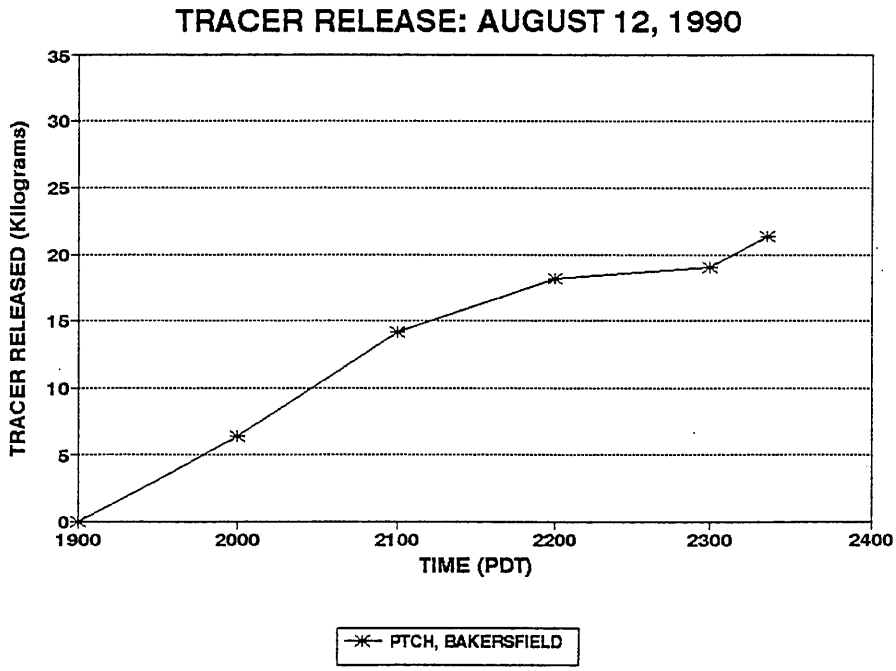
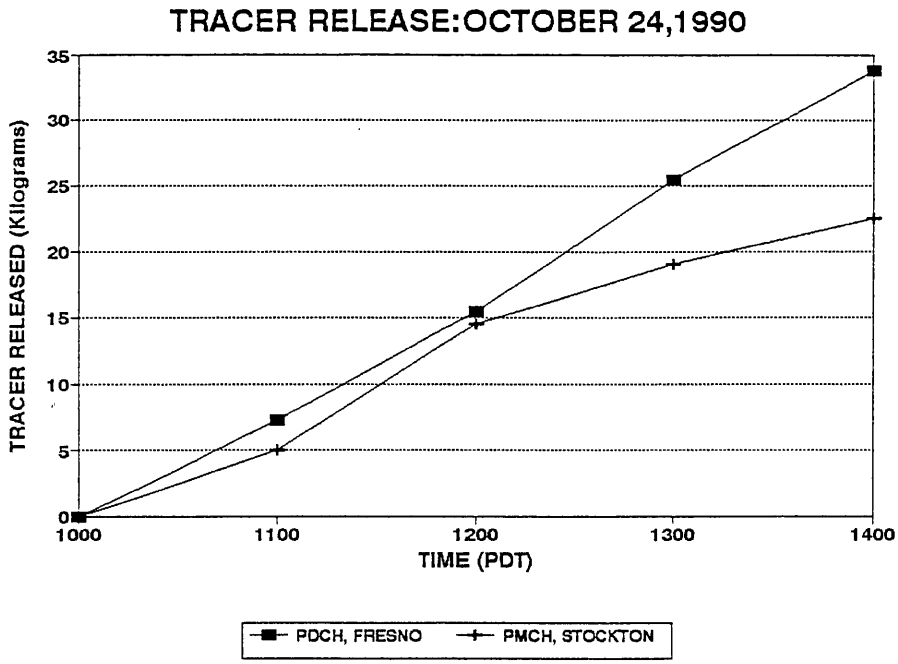
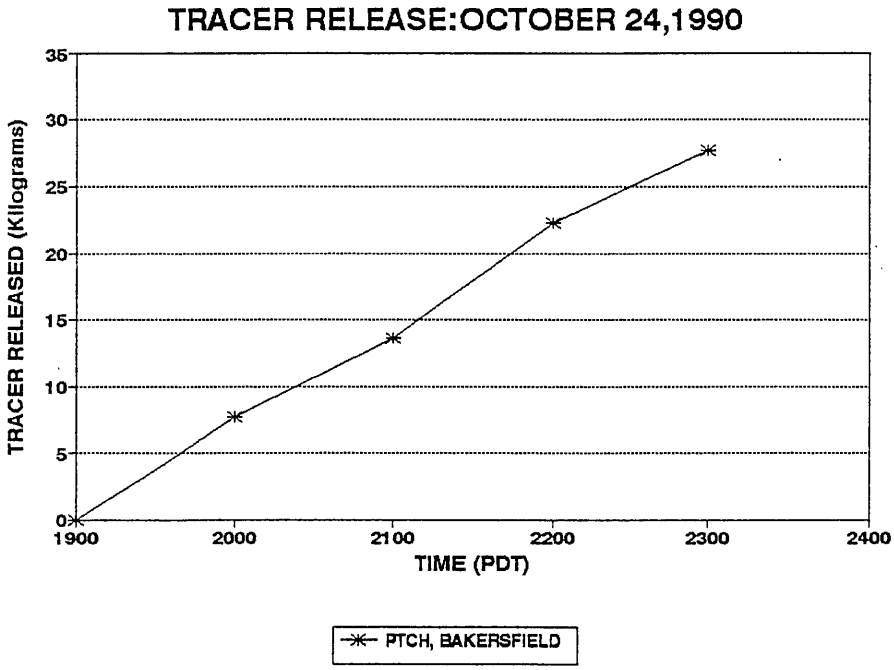


FIGURE 3-3
TIME HISTORY OF TRACER RELEASES - OCTOBER 24, 1990





3.2.1 Ground Level Sampling Sites

Tracer sampling was conducted at 31 air quality sampling sites for 48 sequential hours during each intensive. Twenty five of these sites were a combination of SJVAQS and Atmospheric Utility Signatures, Predictions, and Experiments (AUSPEX) sites while 6 of the sites were USFS facility sites as chosen by the Air Resources Board. Two sites were designated as collocated quality control sites: the Academy and Auberry sites served as collocated sampler locations. A listing of the ground sampling sites is presented in Table 2-2 and a map of the ground site locations is shown in Figure 2-4.

All test releases were conducted from 1000-1400 except for the Bakersfield releases which were conducted from 1900-2300. The Bakersfield releases were conducted later during the day to prevent a scenario whereby the tracer, under prevalent daytime north to south flow, would move south out of the sampling network within a few hours of the release.

Although the listing in Table 2-2 is applicable to both tests, some exceptions apply to each of the tests conducted:

1) The site at Road's End was not operational during the August intensive sampling period due to fires in the southern Sierra Nevada.

2) Five sites were not operational during the October intensive sampling period. The samplers at North Fork of the King's River and the collocated Academy site were unavailable because the samplers had been stolen. The Edwards, China Lake, and Bishop sites were not used because the Department of Defense person responsible for the sites was unavailable during the testing and it was not possible to coordinate a substitute person to activate those samplers.

The sampler start and stop times for the first test are presented in Table 3-2. The samplers used in the first intensive (12 August 1990) were installed by Tracer Technologies' technicians one week prior to the beginning of the test. All samplers remained in the field between the first and second tests.

During the October test, a problem with the sampler software prevented the samplers from starting at the prescribed time. All samplers were re-programmed in the field and as a result, most of the samplers did not start sampling until the next evening and following morning hours. Samples were collected for a period of 48 hours. A list of the sampler start times for the October test are presented in Table 3-3.

This turned out to be beneficial to the program since the anticipated breakdown never occurred and the prolonging of the sampling period enabled the documentation of worst case transport during a stagnation period.

TABLE 3-2. Sampler Start Times, Test 1, August 12-14, 1990

Site #	Site Name	Sample Period	Start Time	End Time
1	Academy	8/12-14	1000	1000
3	Angel's Camp	8/12-14	1000	1000
12	Corcoran	8/12-14	1000	1000
14	Delano	8/12-14	1000	1000
17	El Nido	8/12-14	1000	1000
21	Giant Forest	8/12-14	1000	1000
29	Mariposa Reservoir	8/12-14	1000	1000
31	Modesto	8/12-14	1000	1000
34	North Fork King's R.	8/12-14	1000	1000
41	Raisin City	8/12-14	1000	1000
46	Tehachapi	8/12-14	1000	1000
47	Terra Bella	8/12-14	1000	1000
52	Visalia	8/12-14	1000	1000
56	Yosemite	8/12-14	1000	1000
62	Ash Mountain	8/12-14	1000	1000
63	Auberry	8/12-14	1000	1000
65	Cedar Grove	8/12-14	1000	1000
66	Cherry Lake	8/12-14	1000	1000
67	Democrat Station	8/12-14	1000	1000
68	Dinkey Creek	8/12-14	1000	1000
70	Kaiser Diggings	8/12-14	1000	1000
71	Lebec	8/12-14	1000	1000
72	Mammoth Mountain	8/12-14	1000	1000
73	Onyx	8/12-14	1000	1000
74	Road's End	Not started due to fires in southern Sierra		
75	Strawberry	8/12-14	1000	1000
76	Tuolomne Meadows	8/12-14	1000	1000
77	Westfall Station	8/12-14	1000	1000
89	Edwards	8/12-14	1000	1000
90	China Lake	8/12-14	1000	1000
91	Bishop	8/12-14	1000	1000
99	Auberry (collocated)	8/12-14	1000	1000
100	Academy (collocated)			

TABLE 3-3. Sampler Start Times, Test 2, October 24-27, 1990

Site #	Site Name	Sample Period	Start Time	End Time
1	Academy	10/24-26	1400	1400
3	Angel's Camp	10/26-28	1800	1800
12	Corcoran	10/25-27	0400	0400
14	Delano	10/24-26	0600	0600
17	El Nido	10/25-27	0200	0200
21	Giant Forest	10/25-27	0800	0800
29	Mariposa Reservoir	10/25-27	1200	1200
31	Modesto	10/24-26	1000	1000
34	North Fork King's R.	Sampler Stolen		
41	Raisin City	10/24-26	2200	2200
46	Tehachapi	10/25-27	0800	0800
47	Terra Bella	10/25-27	0200	0200
52	Visalia	10/25-27	0600	0600
56	Yosemite	10/25-27	1200	1200
62	Ash Mountain	10/25-27	0800	0800
63	Auberry	10/25-27	0200	0200
65	Cedar Grove	10/25-27	1000	1000
66	Cherry Lake	10/25-27	0800	0800
67	Democrat Station	10/25-27	0600	0600
68	Dinkey Creek	10/25-27	0200	0200
70	Kaiser Diggings	10/25-27	1200	1200
71	Lebec	10/25-27	0200	0200
72	Mammoth Mountain	10/25-27	1800	1800
73	Onyx	10/25-27	0800	0800
74	Road's End	10/26-28	0000	0000
75	Strawberry	10/25-27	1800	1800
76	Tuolomne Meadows	10/25-27	1400	1400
77	Westfall Station	10/25-27	1000	1000
89	Edwards	Was not started		
90	China Lake	Was not started		
91	Bishop	Was not started		
99	Auberry (collocated)	10/25-27	0200	0200
100	Academy (collocated)	Sampler stolen		

3.2.2 Airborne Sampling

Instantaneous "grab" samples were collected at predetermined time intervals from fixed wing aircraft in the Sierra Nevada. Aircraft sampling was conducted approximately 24 hours after the initial release of PFTs. Aluminized mylar sample bags were inflated with "ram" air collected by a forward facing probe affixed to the aircraft fuselage.

The aircraft sampling sites are listed in Table 2-3 and are depicted in Figure 2-5. Two airplanes were sent simultaneously from the Fresno Airport on two separate routes. Each aircraft traversed the foothill regions of the Sierra and then sampled along the upper Sierra regions. In all cases each aircraft flew at about 2000 feet above ground level. The foothill traverse followed the 2000 foot (asl) contour and the upper Sierra traverse followed the 6000 foot (asl) contour. From the Fresno area, one aircraft travelled north towards Lake Tahoe and then returned on a 6000 ft. contour (asl) of the Sierra Nevada. The second airplane traveled south along the 2000 ft contour of the Sierra foothills until Lebec and then returned on a 6000 ft. contour of the Sierra Nevada. Samples were taken approximately every five to twelve minutes depending upon the sample route while the aircraft traveled at a constant speed. The position identified in Figure 2-5 are the determined positions from each technician's sample log.

3.2.3 Sampling Equipment

All ground level sampling was conducted using Tracer Technologies' automated samplers. Each sampler has a control module and two holding enclosures for the sample bags. The air sampling intake was located approximately 3 feet above ground level. A schematic of the air sampler is shown in Figure 3-4.

The control module consisted of a microprocessor that controlled a pump and 24 valves. The sampler system required 110 VAC at approximately 1 amp of current, and was self-starting on power-up. When the processor powered up, the clock was read and the system began pumping to port #1 at the beginning of the next hour. The pump ran continuously at a rate of about 25 ml/min. Every two hours, on the hour, the microprocessor switched valves on a main manifold to select the next appropriate port.

The two holding enclosures for sample bags were 36 inches wide by 24 inches high and 18 inches deep. They were made of sheet metal with a hinged door on the front. Each enclosure weighed approximately 40 pounds. A diagram of the sampler system assembly is shown in Figure 3-5.

All air samplers were tested prior to being transported to the field. These tests included the cycling of each sampler through a four day sampling period plus one period of the fifth day.

3.2.4 Sample Collection and Transportation

All ground sample collection was performed by Tracer Technologies' technicians. Before collecting each bag, the technician checked the label on the bag for its correctness, such as site number, port number, test identification number, and site name. The technician was also responsible for bar-coding each sample with the sample number, the period number, and the site number. An example sample label is presented in Figure 3-6. As each bag was collected, the sampler performance record was filled out accordingly, to document the condition of the bag at that time. An example sampler performance record is shown in Figure 3-7. Each site produced 24 sample bags which were designated as a lot.

When the field technician completed a route, all samples were transported in lots to one of the Tracer Technologies' field offices in Stockton, Fresno, or Bakersfield. Once there, a Tracer Technologies staff scientist received the samples, assigned a lot number to each sample package according to site and test number, and recorded the lot number on the chain of custody record. The field office manager receiving the individual lots of samples also signed the chain of custody forms and checked each sample for correct labeling and bar-coding. The manager then updated the sampler performance record with the current status of the sample.

When all samples were verified, they were transported from the field office to the Tracer Technologies laboratory in Escondido. During the loading of the sample lots, the chain of custody list of lot numbers was verified.

3.3 Laboratory Operations

Upon arrival at the analytical laboratory and prior to gas chromatograph analysis, all sample bags were logged-in to a master database and were then transferred to a pre-analysis retainment area. When a lot was analyzed, it was taken from the pre-analysis retainment area, checked off on the chain of custody record and brought into the gas chromatograph (GC) laboratory. All samples collected were analyzed using an electron capture detector (ECD) Gas Chromatograph (GC). A Baseline™ data acquisition system was used to control all gas chromatograph operating parameters and to integrate and store chromatogram records.

3.3.1 Sample Log-in

Upon arrival at the laboratory, the sample transport driver was met by the sample custodian to unload the sample lots into the sample retainment area. The driver dated and initialized the chain of custody record for each lot released to the sample custodian. The sample custodian then initialed and dated the chain of custody for every lot received.

FIGURE 3-4

AIR SAMPLER SCHEMATIC

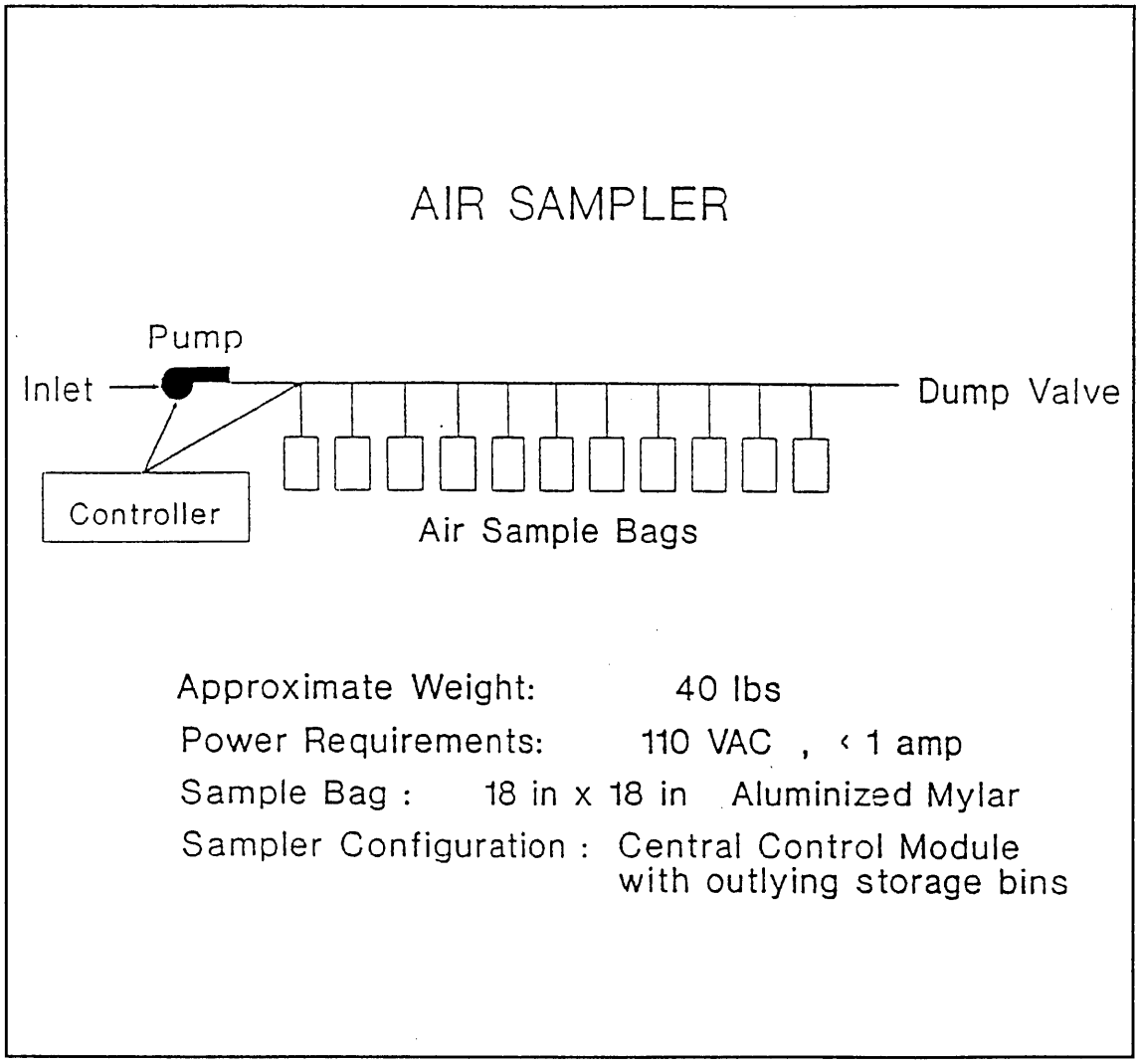


FIGURE 3-5

SAMPLER SYSTEM ASSEMBLY

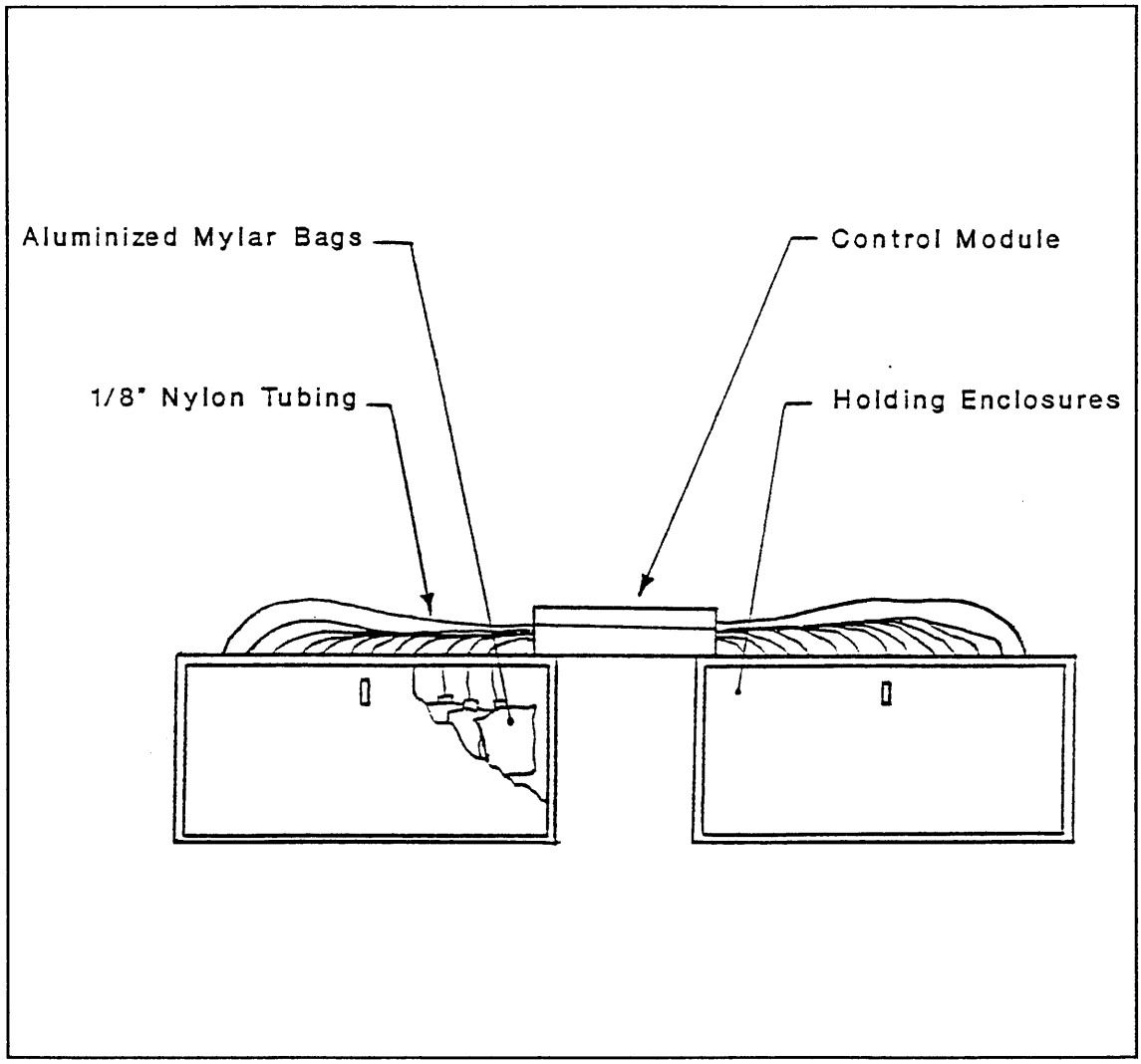


FIGURE 3-6

SAMPLE BAG LABEL

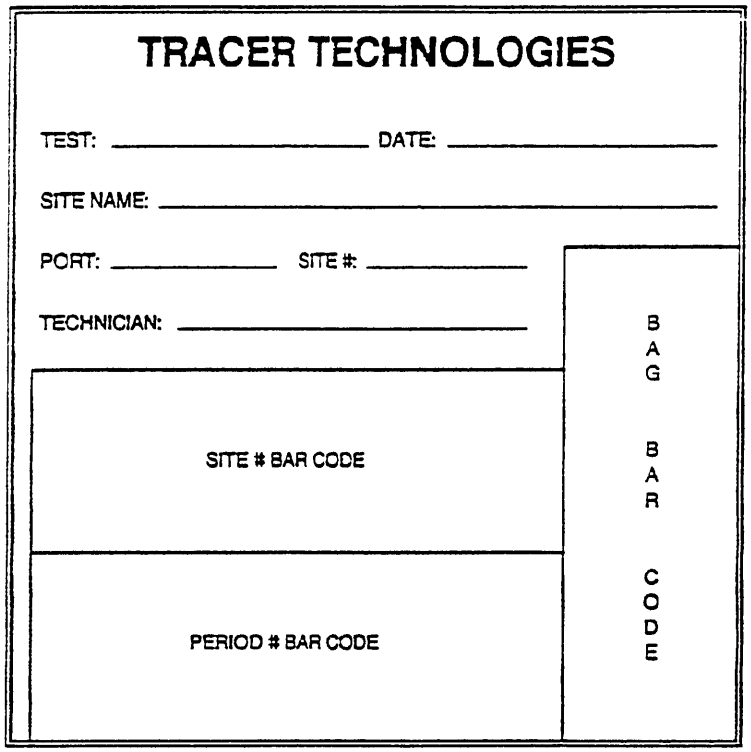


FIGURE 3-7

SAMPLER PERFORMANCE RECORD

SAMPLER PERFORMANCE RECORD		TRACER TECHNOLOGIES QUALITY ASSURANCE

SAMPLES COLLECTED (TIME/DATE) _____

SITE #: _____ SAMPLER ID #: _____ OPERATOR: _____

NEW BAGS SET ON PORTS ___ TO ___ CURRENT PORT: _____

SAMPLING BAG CONDITION				
PORT #	SAMPLE SITE	CENTRAL OFFICE DATE/INITIAL	LAB RECEIVING DATE/INITIAL	LAB ANALYSIS DATE/INITIAL
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				
21				
22				
23				
24				

LEGEND: (F)LAT BAG (F)ILLOWED BAG (M)ISSING BAG (G)OOD BAG (L)OW

COMMENTS ON BACK YES ___ NO ___

Revision 1/16/90

Once the entire shipment was received and accounted for, the sample custodian logged the sample bags into the computer data-base system by reading the coded bag labels with a bar-code reader. The sample custodian then generated a computerized sample inventory list for each lot. After all of the lots had been logged-in and verified, they were transferred to the pre-analysis retainment area.

3.3.2 Gas Chromatographic Analysis

For each lot analyzed, the GC operator would retrieve a lot from the pre-analysis retainment area and bring it into the laboratory. Only one lot was allowed into the laboratory at any one time. The operator would set up a sample queue in the data acquisition system, and then analyze a reference and blank on the gas chromatograph. If the reference was within 15% of the calibration curve, analysis of the lot was continued.

The ECD/GC analysis was performed by first preparing each sample through pre-concentration on a carbon absorbent followed by thermal desorption. Next, a silicon OV101 column, operated at 50°C was used for separation. A Valco™ ECD was used to quantify the tracer compounds. The output signal was then recorded by the Baseline™ data acquisition system. In addition, a stripchart recorder was used to provide a backup record of the chromatographs.

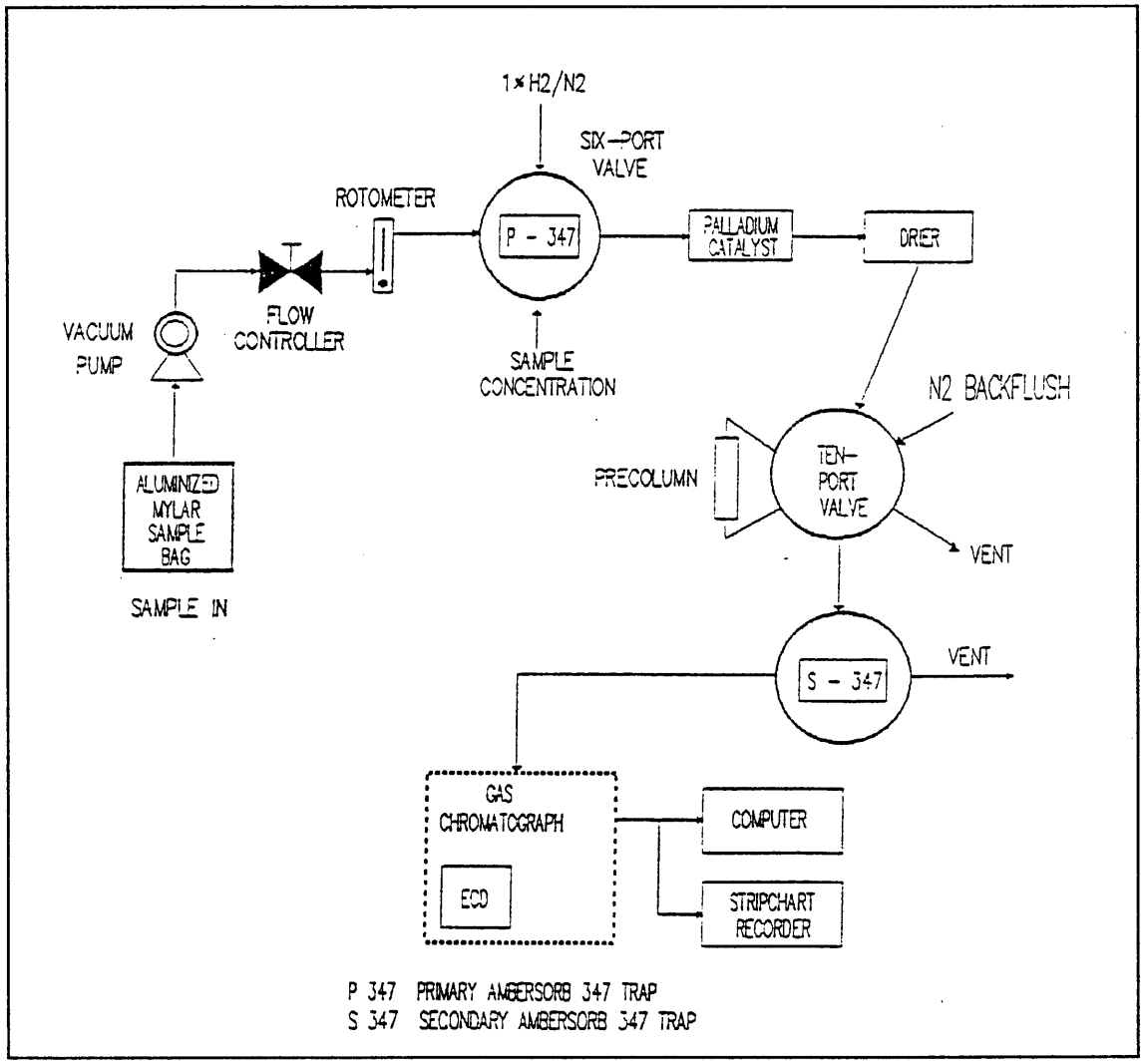
To analyze a sample, the technician had to attach the sample bag to the sample input valve of the chromatograph and start the data acquisition system. The system then prompted the technician for the sample number. The technician entered the sample number with a bar-code reader and labeled the strip chart with the sample number. All operation of the analysis system, such as valve switching, heating, and sample injection, was fully controlled by the Baseline™ control and data acquisition system. Once the sample was analyzed, the system prompted the technician for another sample. A schematic of the GC is shown in Figure 3-8.

3.3.3 Perfluorocarbon Analysis Calibrations

Calibration of the GC system was performed on a weekly basis or whenever operation conditions were changed. Prior to the beginning of analysis, a four point calibration curve was obtained and response factors for each tracer were calculated from this curve. All calibration runs were performed using the same procedures as a normal analysis run. In addition, a reference standard in the middle range of the response curve and a blank were run, once during every lot of twenty four samples, to check instrument performance. If there was more than a 15% variation in the response of the reference sample from the calibration curve, a new calibration was performed. All reference and blank analyses data are shown in Section 4.

FIGURE 3-8

GAS CHROMATOGRAPH SCHEMATIC



All standards were prepared by the Scott-Marrin Company. Arrangements were made with Brookhaven National Laboratories to audit the standards that were used in this test. Samples of the Scott-Marrin standards were analyzed by Brookhaven to certify their final concentrations. Results of the Brookhaven analysis are presented in Section 4..

3.3.4 Verification of Integrations

Each day during sample analysis, the senior chemist downloaded all the accumulated analysis data onto another computer for peak verification. The senior chemist and one trained technician checked each integration performed, to verify that the Baseline™ system properly identified and integrated each of the four perfluorocarbon peaks. Once verified, the analysis data was downloaded for merging with the Tracer Technologies data-base program.

3.4 Data Processing

3.4.1 Tracer Release Data

During the study, the tracer release data was documented in two ways. Every five minutes the flow meter reading was entered into the tracer release log book. In addition, every half hour during a release, a digital scale was used to measure the bulk weight loss of the tracer in the storage tank, and this value was entered in the Tracer release log. The data was then reviewed for completeness and accuracy by the tracer release manager. A computer data file was generated and stored on floppy disks documenting the following:

- Name of release locations.
- Latitude and longitude coordinates of release sites.
- The Julian day of the actual releases.
- The start and end time of the release (PDT).
- The amount of tracer released.
- The type of tracer released.

The release rate data was processed in the following steps:

1) A computer data file of pertinent release data was created by referring to the tracer release log sheets and tracer release log books.

2) A correction factor was used to modify the calibration-based release rates such that the integration of these release rates over an entire release period equalled the total weight loss in the storage tank.

The tracer release rates for each of the three perfluorocarbon tracers during each intensive are plotted as a function of time in Section 3.1.3 (Figures 3-2 and 3-3).

3.4.2 Tracer Data

During sample log-in by the sample custodian, the bag number, site location, and period number were entered into a computer data-base. This data-base, specifically designed by Tracer Technologies for tracer experiments, records all bag numbers, locations and period numbers. Numerous flags are written into the software to provide warning if samples have conflicting locations, periods, or bag numbers. This permits quick recognition of problem bags and allows for immediate correction. In addition, all entries are entered by bar-code to eliminate data-entry errors.

Upon analysis, the bag number is entered into the Baseline™ data acquisition system whereupon the analysis results are stored into a data-base file designated by lot number. As backup, the chromatograms are also recorded on a strip chart recorder. Once the lot is analyzed, the data-base file is reviewed by a senior chemist and a technician for proper identification and integration of peaks.

When the review process is completed, the GC data-base file is merged with the sample log data-base. This step integrates the bag number and concentration with the sample information. The data is then ready to be viewed with the computer display program or generated into hard copy.

3.4.3 Data Reporting

Three categories of raw data were generated in this program: tracer release data, ground sampler data, and airborne tracer data. Tracer release data are reported by location with regard to tracer type, release time, duration, and hourly averaged release rate. Ground sampler data consisted of a listing of measured tracer concentration, location of sample, and time interval of sample. Airborne data are reported in a format that provides sample identification number, sample time interval, aircraft position, altitude of the aircraft, and the average concentration of each tracer measured. Hard copies of the raw data can be found in the Appendix A, and all data are provided on magnetic media in ASCII format.

Also provided is a computerized data software package for easy display of the tracer measurement results on an IBM PC or compatible computer system. This system allows the user to display either the time history at one of the sampling locations or a spatial map for a given time period. A description of the different formats is presented below.

1) Computer Text files

The computer text files are ASCII files containing all pertinent release and tracer data. The record formats of the ASCII files are detailed in Table 3-4.

2) Tracer Technologies Tracer Display Program

An executable program file and several data files were created to provide graphic displays for all tracer results. The primary display is a map of the study area which marks each sampling location by site number. For any given sampling period, tracer concentrations of analyzed samples are shown on four vertical bar indicators adjacent to each site number. Selected sampling periods may be viewed in chronological sequence or at random.

Separately, the program also provides a bar graph display of all tracer results from a given sampling location during any single intensive test. Sampling locations are selected individually by site number. The display program is menu-driven and very easy to use. The program was designed to be used on an IBM PC with color monitor.

The program is started by typing **Sdisp** in the program directory. The program will then prompt for the intensive test number. Once an intensive number is entered, a menu will appear which offers the following 4 options:

A) Time Display - Once this option is chosen you will be prompted for a start hour. Two time series maps, each representing two tracers, depict the tracer concentrations from the time selected until the end of the intensive. Tracer PDCH is represented by the color blue, and Tracers PMCH and PTCH are represented by the color red. "Return" will return you to the main menu.

B) Spatial Display - Once this option is chosen you will be prompted for a specific start hour. A map of the study area then will be displayed, including horizontal lines representing each site. If a sample exists for that hour there will be four colors on that line. Yellow represents PMCH, magenta represents PDCH, and green represents PTCH. The height of the color bar indicates the relative level of concentration at the site in units of (fl/l). If a red horizontal line appears at the site, there is no sample available at the site for that hour. Collocated sites are side by side on the display. Release locations for each tracer are designated by an asterisk with the appropriate tracer color. You can scroll forward by pressing the return key. The '-' key is used to scroll backwards. Control N

TABLE 3-4. Data File Structures

File: SSS.GND		File: SSS.AIR		File: SSS.REL	
Field	Parameter	Field	Parameter	Field	Parameter
1-18	Site Name	1-5	Test #	1-5	Test #
20-22	Julian Day	8-30	Site Name	8-19	Site Name
25-32	Latitude	33-37	Latitude	22-31	Latitude
35-43	Longitude	42-47	Longitude	35-45	Longitude
46-49	Time (PDT)	52-54	Julian Day	51-53	Julian Day
52-55	PMCH (fl/l)	59-62	Start Time (PDT)	61-64	Start Time (PDT)
58-61	PDCH (fl/l)	67-70	Altitude (AGL)	74-77	Stop Time (PDT)
64-67	PTCH (fl/l)	73-76	PMCH (fl/l)	87-90	Tracer(kg) Amount
		79-82	PDCH (fl/l)	98-101	Tracer
		85-88	PTCH (fl/l)		

shows the site number for each site on the screen. Control A is toggled to display the aircraft samples. Control Q exits out of the spatial display and back into the main menu.

C) Number of SSS Test - changes the intensive number.

D) Exit - Exits program to DOS.

3) Tracer concentrations are presented by test in Appendix A.

4.0 QUALITY ASSURANCE

4.1 Internal Performance Audits

Internal performance and systems audits for all field and laboratory operations were conducted by the project Quality Assurance (QA) Manager. During the tests, the QA Manager audited several tracer releases and over 20 sampling sites. The tracer releases were audited to insure that proper procedures were followed and documented by the release technician. During test periods the QA manager also visited sampling sites on a random basis to ensure that proper procedures were being carried out. During sample analysis the QA Manager also was responsible for checking laboratory analysis.

4.2 Reference and Blank Analysis

The analysis section is concerned primarily with GC performance and the analytical method. Included in this section are discussions on the references and blanks which were analyzed. Discussions of the collocated data and release data are presented in Section 4.6.

To provide a check on the gas chromatograph performance, references and blanks were run on a regular basis. Prior to the analysis of each lot (24 samples), a reference and nitrogen blank were analyzed with the gas chromatograph. The reference analysis verified that the gas chromatograph was operating within the 15% control limits. The nitrogen blank was analyzed to assure that the GC was clear of any perfluorocarbon carry over, and also to assure that the nitrogen was void of PFCs since it also was used to prepare the references. The references were prepared at the laboratory in Escondido using standards prepared gravimetrically by Scott-Marrin and analyzed by Brookhaven National Laboratories. The references consisted of 200 femtoliters of tracer per liter of air (fl/l) of each of the three tracers.

4.2.1 References

Prior to the analysis of each lot of samples, a 200 fl/l reference sample was analyzed to verify the gas chromatograph performance. These references are plotted by test number in Figures 4-1 and 4-2. The concentrations of each tracer are plotted against the analysis sequence. The means and standard deviations of each tracer are presented in Table 4-2.

TABLE 4-1. Summary of Reference Statistics

Test #	PMCH (fl/l)	PDCH (fl/l)	PTCH (fl/l)	
SSS-1	208.0	204.8	201.6	Mean
	14.9	8.9	13.1	Std. Dev. (±)
SSS-2	211.7	205.2	200.6	Mean
	12.5	9.7	10.6	Std. Dev. (±)

4.2.2 Blanks

Nitrogen blanks also were analyzed prior to the analysis of every lot of air samples. The results of these blanks are plotted by test number in Figure 4-3. Means and standard deviations for each tracer are presented in Table 4-2.

TABLE 4-2. Summary of Blank Statistics

Test #	PMCH (fl/l)	PDCH (fl/l)	PTCH (fl/l)	
SSS-1	4.8	0.0	0.0	Mean
	11.2	0.0	0.0	Std. Dev. (±)
SSS-2	0.3	0.0	1.2	Mean
	1.8	0.0	5.0	Std. Dev. (±)

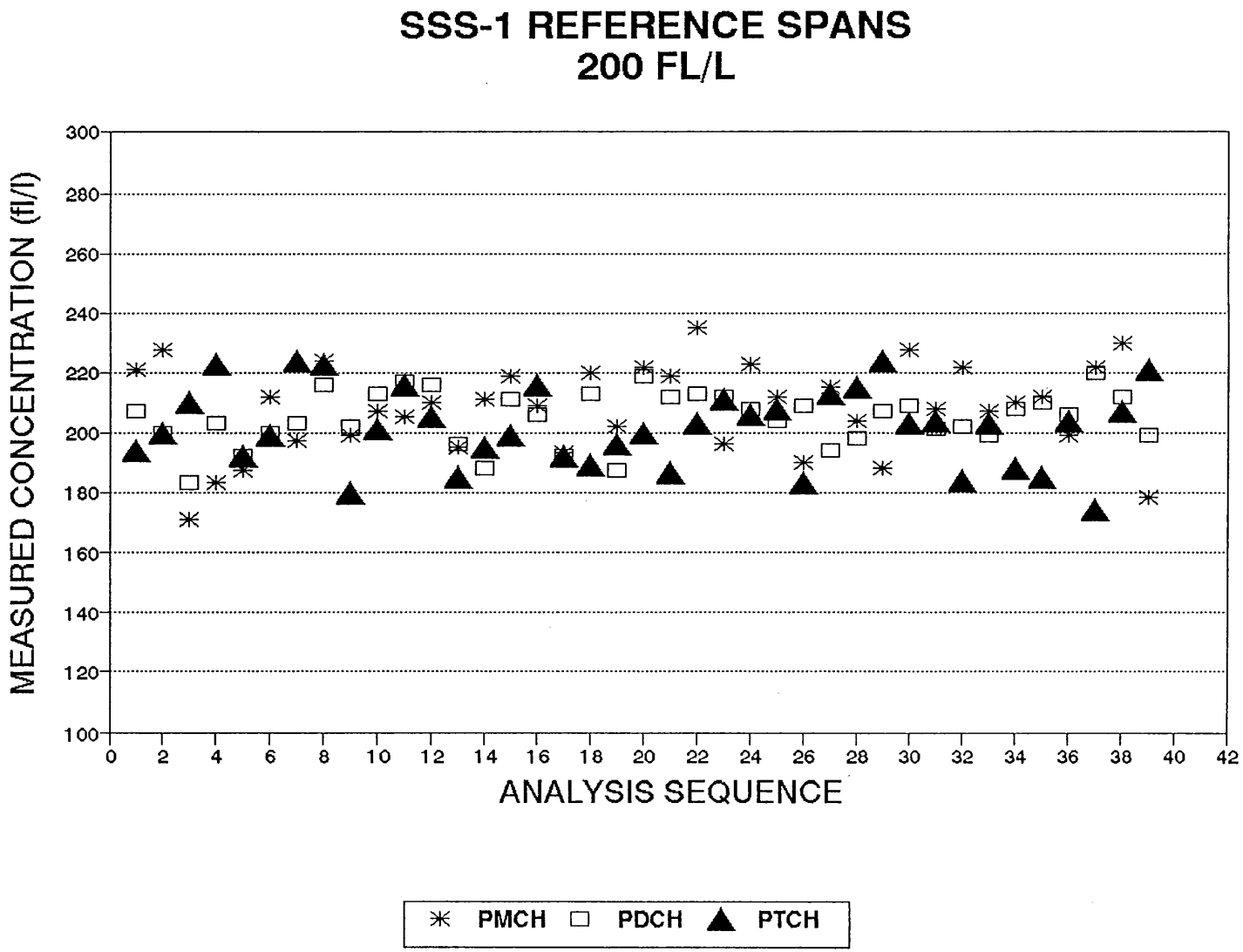


FIGURE 4-1 - GAS CHROMATOGRAPHY REFERENCES: TEST 1

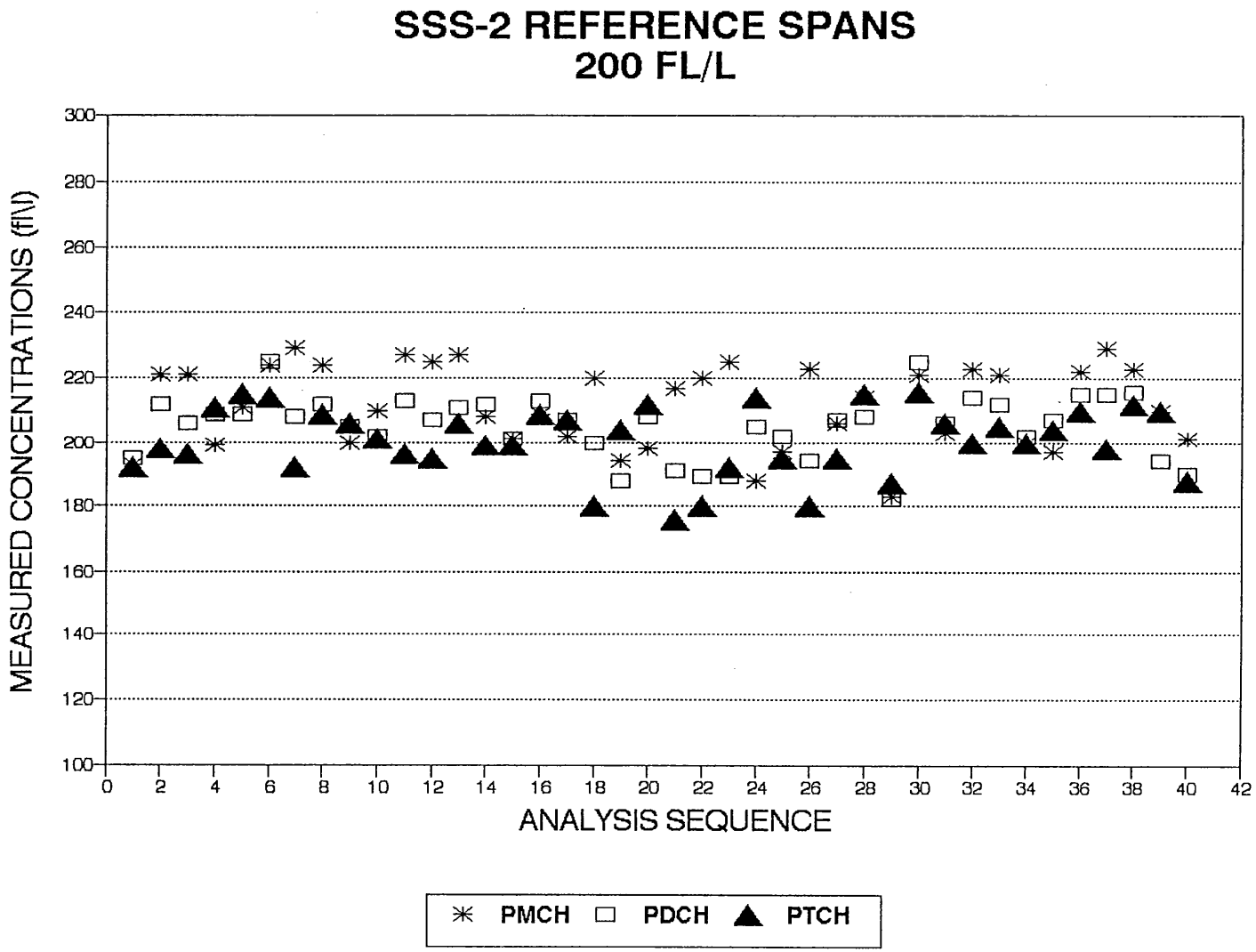
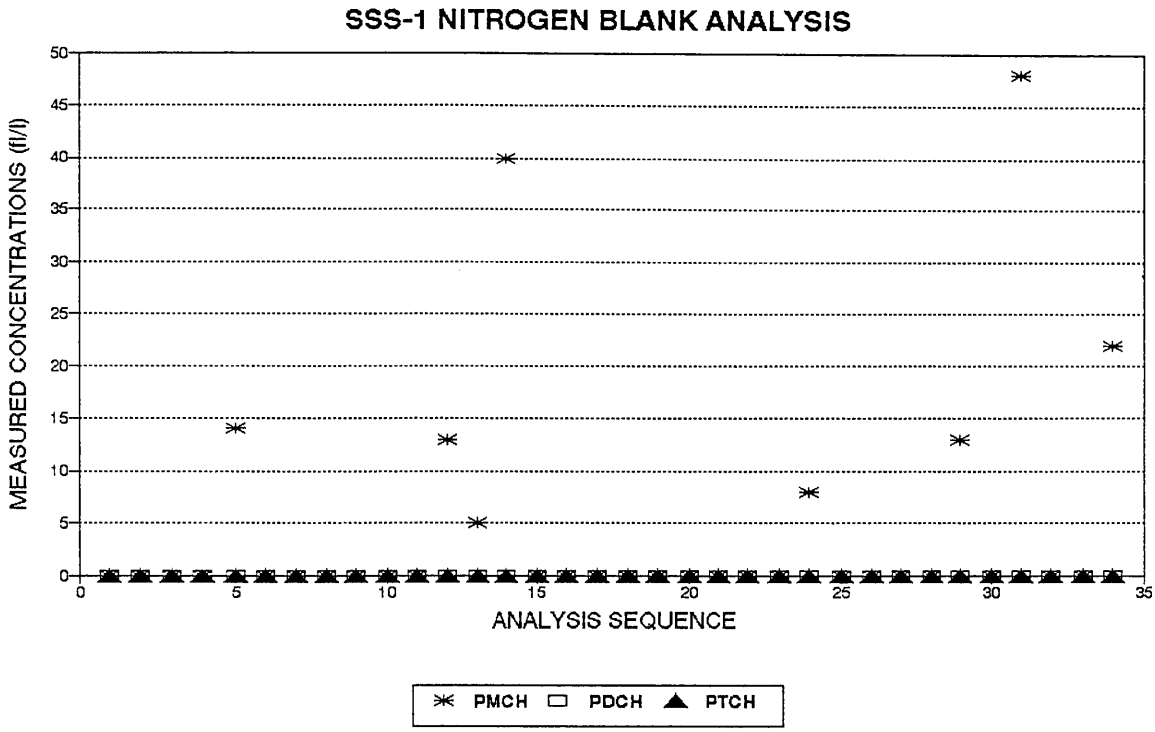
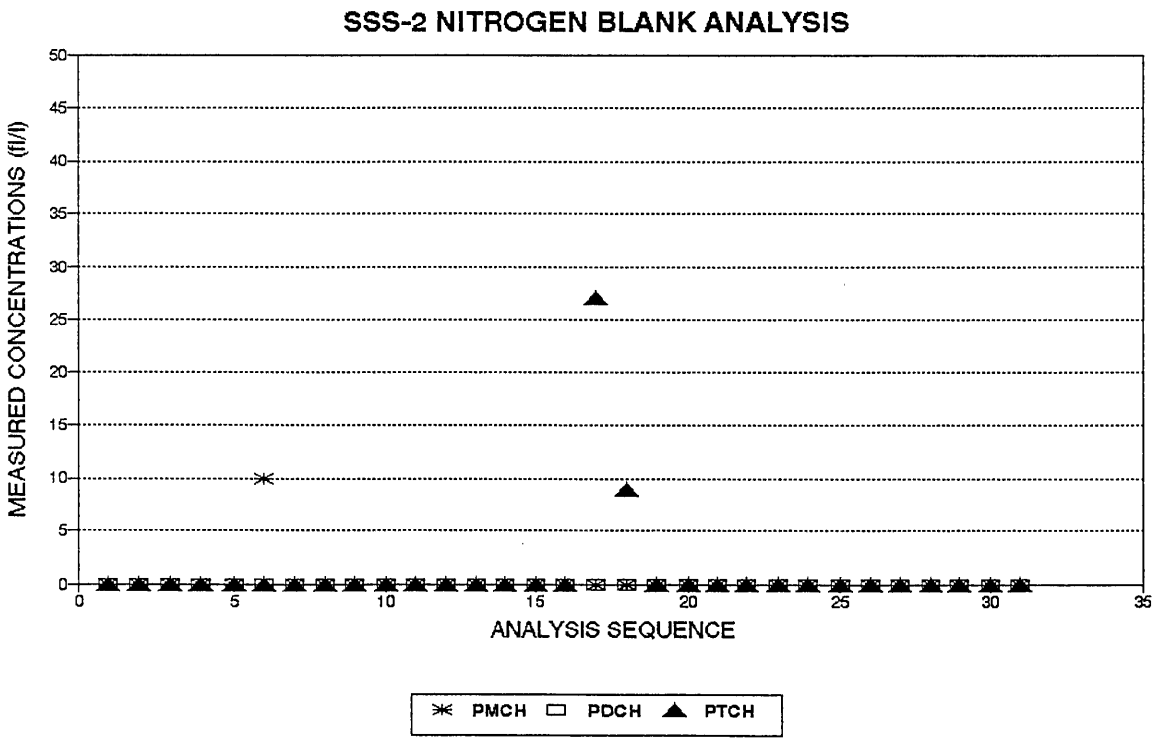


FIGURE 4-2 - GAS CHROMATOGRAPHY REFERENCES: TEST 2

FIGURE 4-3
NITROGEN BLANK ANALYSIS - TESTS 1 & 2





4.3 Quality Assurance Field Visits

Approximately 20 sampling sites were visited by the QA manager throughout the tracer program. The QA manager visited the sites during intensive sampling to verify that samples were labeled properly and that the sampler was operating correctly. The QA manager also visited the different release locations to ensure that procedures were being followed. The role of the AQ manager's visits were to verify that all procedures were correctly followed. Since the Taaps test were performed by the same people who performed SJVAQS, all procedural errors had been previously identified by the QA manager in tests prior to TAAPS experiments. During TAAPS, the QA manager did not discover any transgressions of standard operating procedures.

4.4 Tracer Purity

Twelve samples of tracer used in the study were shipped to Brookhaven National Laboratory for absolute purity analysis. Three different samples of each type of the four tracers were shipped. The samples were analyzed on a HP-5890a GC with a thermal conductivity detector. The separation was performed on a 12' x 1/8" column of Carbopack B/SP-1000 at 190 degrees C and a helium carrier gas flow of 200 cc/min. Each sample was analyzed three times for percent composition, then an average of the three runs was calculated. The results of the analysis are summarized in Table 4-3. The values listed in Table 2-1 represent the average percent tracer compositions shown in Table 4-3. No tracer contained more than 3% of one of the other tracers used.

Tracers PMCH, PDCH, and PTCH contained cross-contamination. The PMCH samples were primarily 98% pure with approximately 0.1% PMCP contamination. The PDCH samples' combined average percent compositions were approximately 98% pure with contamination of PMCH ranging from 0.6 to 2.28%. The PTCH samples' combined percent composition was primarily 97%, with PDCH contamination ranging from 1.5 to 2.15%. Due to the low contamination levels present in each of the above tracer chemicals, negligible effect was incurred on the field study results.

4.5 Data Recovery

Data recovery rates were calculated for each test and are presented for each site in Table 4-5 and are summarized for the test in Table 4-4. Percent data recoveries were calculated for ground samples and for aircraft samples separately. In addition an overall percent data recovery for the entire study was calculated for ground samples and aircraft samples separately. The data recovery rates were calculated using the following formulas:

$$\text{Percent Data Recovery (Test Based)} = \frac{NSPT}{NSAT} * 100 \qquad (1)$$

TABLE 4-3. Summary of Tracer Purity Analysis

Sample	Percent Composition		
	PMCH	PDCH	PTCH
PMCH, Batch1	98.12	----	----
PMCH, Batch2	98.28	----	----
PMCH, Batch3	97.90	----	----
PDCH, Batch1	2.28	97.17*	----
PDCH, Batch1	0.918	97.01*	1.78*
PDCH, Batch1	0.602	99.25*	----
PTCH, Batch1	-----	2.15	97.71*
PTCH, Batch1	-----	2.11	97.32*
PTCH, Batch1	-----	1.54	97.36*

* Note: The average percent composition for this data is calculated by summing together the individual average percent composition of each tracer isomer. And since each average calculation contains an uncertainty value, the uncertainty of the summation of these averages is increased; thus the accuracy of this number is decreased.

Where NSPT = Number of Samples Possible for a Test
NSAT = Number of Samples Analyzed for that Test

$$\text{Percent Data Recovery (Overall Study)} = \frac{NSPS}{NSAS} * 100 \qquad (2)$$

Where NSPS = Number of Samples Possible for entire study
NSAS = Number of Samples Analyzed for entire study

TABLE 4-4. Summary of Data Recovery Rates

Test #	Ground Air Samples % Data Recovery	Aircraft Samples % Data Recovery
SSS-1	86.6%	90.0%
SSS-2	76.8%	97.5%
Overall Data Recovery =	81.7%	93.8%

4.6 Precision and Uncertainty of Measurements

4.6.1 Tracer Release

Table 4-6 lists the maximum uncertainty of each of the tracer releases for both tests. In each case the amount of tracer released was within 10% of the target amount. The primary contribution to the uncertainty of the release lies with the accuracy of the digital scales used to measure the bulk weight loss of tracer in the tracer reservoir. The digital scales were accurate to within plus or minus 2 lbs. or .9 kg.

TABLE 4-5. Data Recovery Rates

Site	Data Recovery Test 1	Data Recovery Test 2
Academy	100.0%	95.8%
Angel's Camp	100.0%	75.0%
Corcoran	95.8%	100.0%
Delano	62.5%	100.0%
El Nido	95.8%	95.8%
Giant Forest	83.3%	100.0%
Mariposa Reservoir	100.0%	79.2%
Modesto	100.0%	95.8%
North Fork King's River	95.8%	0.0%
Raisin City	100.0%	58.3%
Tehachapi	100.0%	58.3%
Terra Bella	95.8%	91.7%
Visalia	91.6%	8.3%
Woodward Reservoir	100.0%	95.8%
Yosemite	100.0%	75.0%
Ash Mountain	50.0%	100.0%
Auberry	95.8%	100.0%
Cedar Grove	95.8%	100.0%
Cherry Lake	91.6%	54.1%
Democrat Station	95.8%	100.0%
Dinkey Creek	95.8%	95.8%
Kaiser Diggings	75.0%	95.8%
Lebec	95.8%	95.8%
Mammoth Mountain	95.8%	87.5%
Onyx	62.5%	100.0%
Road's End	0.0%	88.9%
Strawberry	100.0%	100.0%
Tuolomne Meadows	79.1%	95.8%
Westfall Station	95.8%	95.8%
Edwards	0.0%	0.0%
China Lake	95.8%	0.0%
Bishop	100.0%	0.0%
Auberry (collocated)	100.0%	91.2%
Academy (collocated)	100.0%	0.0%

TABLE 4-6. Uncertainty of Tracer Releases

Test #	Location	Tracer	Maximum Uncertainty (±)
SSS-1	Stockton	PMCH	4.3 %
SSS-1	Fresno	PDCH	4.7 %
SSS-1	Bakersfield	PTCH	9.4 %
SSS-2	Stockton	PMCH	4.5 %
SSS-2	Fresno	PDCH	5.5 %
SSS-2	Bakersfield	PTCH	4.8 %

4.6.2 Tracer Concentrations

The primary data used to determine the uncertainty in air sample tracer measurements were the collocated samples. During the study there were two collocated samplers at Auberry. There was also a collocated sampler at Academy during the first test only. Discussions of the gas chromatograph analysis error are presented in Section 4.2 and Section 4.4.

Analysis Methodology

The statistical methodology utilized was to determine the standard deviation associated with the data set, and then to set the precision such that there is a 95% confidence that the actual data is within the resulting limits. The analysis follows the development in "Statistical Analysis of Measurement Errors", Jaech J.L. 1985.

It is assumed that for each of the data sets there is a random measurement error resulting in a difference from the true data. The standard deviation of the set is determined as:

$$S^2 = 1/(2(n-1)) * \sum_{k=1}^{n}(d_k - \bar{d})^2 \qquad (3)$$

where

n = number of samples in the set

d_k = difference between paired values in each set

$\bar{d}$ = mean difference between sets

S = standard deviation of measurements

The resulting precision should be ± 1.96 S. This is the value that would be added to the data to account for data uncertainties. This methodology can be applied to any paired data set.

Analysis

Since the collocated data varied over such a wide range of concentrations (0 - 1000 fl/l), we decided to stratify the data by concentration and determine the standard deviations as a function of concentration level. We used three levels with concentration ranges of:

(1) $0 < x \leq 50$

(2) $50 < x \leq 200$

(3) $200 < x < 1000$

The disadvantage of this stratification is that there are fewer samples in some concentration bins and, therefore, significant scatter might be expected in the results. All tracers were lumped together for analysis because there were not enough collocated measurements to analyze each tracer separately.

The associated statistics for the three concentration levels are presented in Table 4-6. Figure 4-4, on the following page, shows the resulting standard deviations for all of the tracers at the midpoint of each concentration range for all collocated samples. The line plotted through the points is a least-squares regression line for the three concentration levels. A summary of the precision data is presented in Table 4-7.

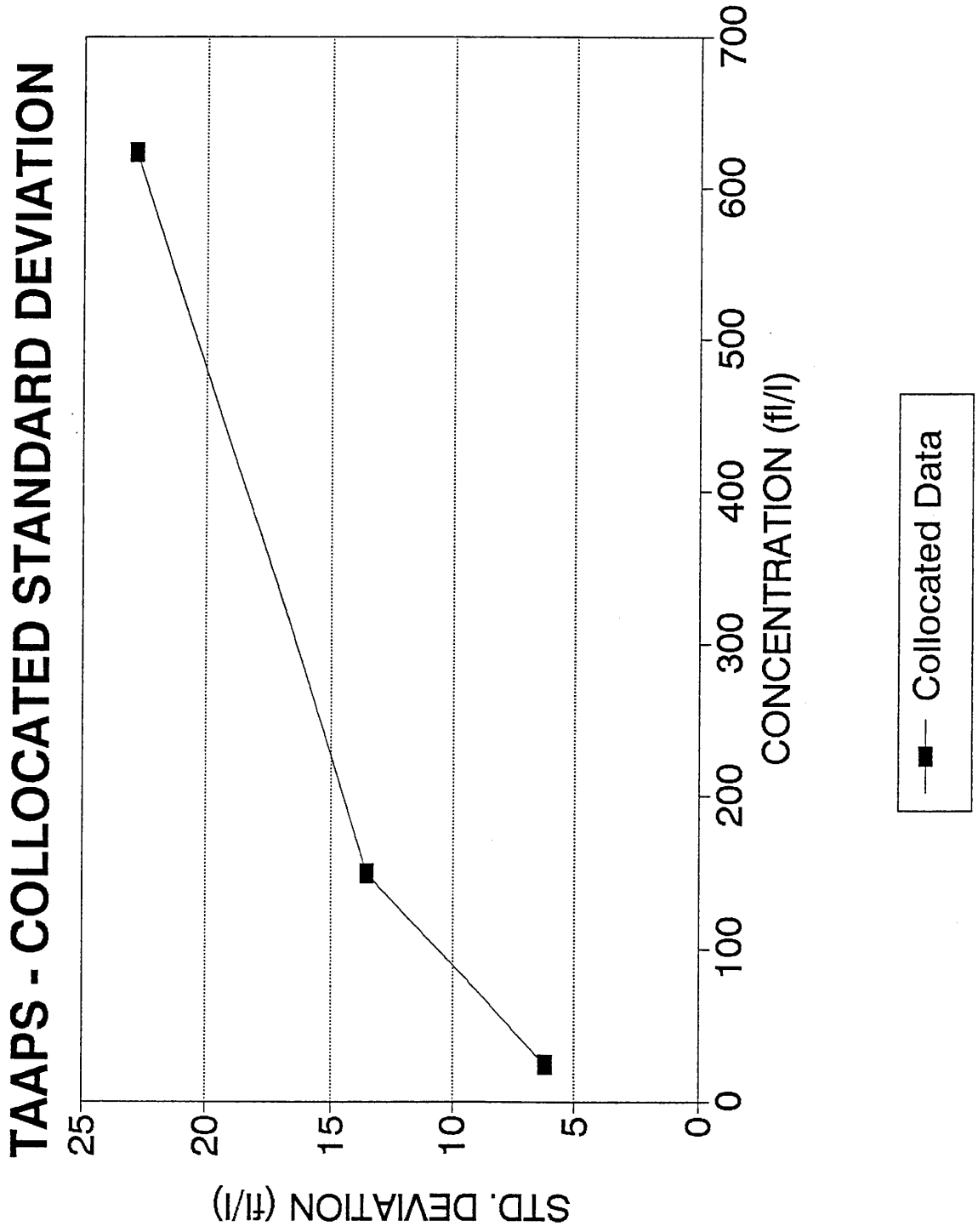


FIGURE 4-4 - Tracer Concentration Versus Standard Deviation: Collocated Samples

TABLE 4-7. Difference Averages and Standard Deviations: Collocated Samples (fl/l)

Concentration Range	$0 \leq x \leq 50$	$50 < x \leq 200$	$200 < x \leq 500$
Average Difference	-4.14	-10.73	27.63
Standard Deviation	6.16	13.52	26.67

TABLE 4-8. Collocated Precision Analysis (fl/l)

Concentration Range	$0 \leq x \leq 50$	$50 < x \leq 200$	$200 < x < 1000$
Upper 95% Probability Limit	7.93	15.77	79.90
Lower 95% Probability Limit	-16.21	-37.23	-24.64

5.0 METEOROLOGICAL SUMMARY

This section describes the meteorological conditions associated with each of the tests. This includes the conditions in the days preceding the tests as well as conditions during the tests. The synoptic conditions are examined for each case using weather maps and data produced by the National Weather Service while local conditions in the valley are assessed using meteorological data collected in support of the study.

5.1 August 12-14

5.1.1 Synoptic Conditions

In the days preceding this test, the western United States was under the influence of a strong high pressure ridge at the 500 mb level. On August 8 and 9, this ridge was centered over the Great Basin and produced extremely warm temperatures throughout the western United States. Among the areas experiencing temperature extremes was the central valley. Temperatures reached as high as 44°C (111°F) in the valley during this period. The only prominent surface feature in California consisted of a low pressure area extending from northern Baja California to the northern end of the central valley. This thermal low was a result of the extreme heat found inland from the coastal areas.

The high pressure ridge aloft acted to stifle the flow of marine air that generally enters the central valley from the San Francisco Bay Area and provides some measure of cooling. Additionally, the flow of marine air into the valley creates a circulation that flows throughout the valley.

The ridge, owing to the subsidence it produced, acted to lower the mixing height. The morning mixing height (as determined by the upper air sounding at Oakland) on August 9 was ~ 300 m. On August 10, the morning mixing height was ~ 350 m and on August 11, it had increased to 400 m. All of these heights indicate a very shallow mixed layer where vertical dispersion of accumulated pollutants is confined to a smaller volume.

This extended period of high pressure aloft, the resulting low mixing heights and the choking off of the sea breeze created stagnant conditions in the valley. This situation is ideal for the development of an ozone episode. Maximum hourly ozone values in Fresno reached 13 pphm on August 10 and 11 (the state one hour standard is 9 pphm while the federal primary one hour standard is 12 pphm). These conditions would persist for several days until an approaching low pressure system and cold front would weaken the ridge and allow some degree of relief from the conditions.

By August 11, the ridge had begun to flatten slightly and the surface thermal low had retreated to the southern deserts. However, the extreme heat and stagnant conditions persisted in the central valley.

On the morning of August 12, the ridge had flattened and the breakdown of the heat wave and ozone episode had begun. Temperatures in the valley cooled slightly as an influx of marine air entered the valley through the Bay Area. The morning mixing height in Oakland had increased to ~ 500 m. By the next morning (August 13), a cold front from the Gulf of Alaska had advanced to just off the Washington, Oregon and northern California coast.

The cold front, in addition to cooling temperatures, also raised the height of the mixing layer (the morning mixing height at Oakland was up near 600 m) and helped disperse pollutants that had accumulated in the valley during the episode. On August 13, peak ozone readings in Fresno were down to 8 pphm.

By August 14, the mixing height had increased further (~ 700 m), temperatures cooled further and ozone readings were down further (7 pphm).

5.1.2 Local Conditions

Local conditions in the San Joaquin Valley mirror the conditions seen on the synoptic scale. Prior to the test, relatively stagnant conditions are seen. During and after the test, local dispersion conditions improved dramatically. To illustrate this, we have chosen to look at wind data taken at Travis Air Force Base. This location is ideal for assessing the dispersion potential of the valley since it is located near one of the two entry points for marine air into the valley. By examining afternoon winds at this site, conclusions can be drawn concerning the magnitude of the flow of marine air into the valley.

During the period of the episode (August 8 - 11), afternoon wind speeds at Travis AFB were relatively light. On the afternoon of August 8 (at the beginning of the stagnation period), the wind was ~ 8 knots. Afternoon winds remained in this range for the next three days until they jumped to 18 knots on August 12. This corresponded with the breakdown of the ridge and the beginning of the test. Strong afternoon winds persisted throughout the next several days indicating that the breakdown of the episode was complete. It should be pointed out that all of the reported afternoon winds were southwesterly indicating that they were associated with the sea breeze regime.

Elsewhere within the valley, the effects on winds from the stagnant conditions were more subtle. At Fresno, for instance, the normal northwesterly winds seen during periods of moderate to strong marine air inflow into the valley was replaced by a scattered wind pattern most likely produced by local thermal effects. Not until August 12 did the persistent northwest wind return.

5.2 October 24-27

5.2.1 Synoptic Conditions

Prior to the test, the central valley was experiencing unseasonably warm temperatures. This was a result of two synoptic scale features. The dominant feature affecting weather in California was a surface high pressure system located over Washington and Idaho. The location of this high resulted in an offshore flow gradient (higher pressure inland than along the coast). From October 20 through the end of the test, the gradient (as measured by the pressure difference between San Francisco and Las Vegas) remained weak or slightly offshore. When the gradient is weak or slightly offshore, neither onshore nor offshore winds are allowed to develop to a significant degree. This leads to periods of stagnation.

In addition to the aforementioned surface feature, there was a ridge at the 500 mb level that was centered over the western United States. This ridge developed on October 20 and would contribute to elevated 500 mb heights for more than a week. As in the previous case, this combination of features would serve to decrease the height of the mixed layer as well as contribute to the warm temperatures. Mixing heights taken from the morning soundings at Oakland were consistently in the 300 to 400 meter range.

On October 24, the ridge intensified over California. Unseasonably warm temperatures would be recorded throughout the state as the strong ridge combined with the surface pressure gradient. The morning mixing height at Oakland was less than 300 m. These conditions would also contribute to elevated ozone levels in the central valley. The maximum hourly ozone reading at Fresno on October 24 was 10 pphm.

Forecasts called for the ridge to weaken on October 25 as a trough and cold front approached the northern California coast. On the morning of October 25, the center of the ridge had moved eastward and was centered over western Wyoming. However, California still remained under the influence of the ridge as 500 mb heights remained high (~ 5,850 m). The surface cold front remained to the north and west of California.

At this point, previous forecasts were being revised concerning the arrival of the trough and cold front. High pressure over California would keep this system to the north where it would not be able to bring relief from the stagnant conditions. 500 mb heights recorded at Oakland remained in excess of 5,800 m throughout the end of the test. Mixing heights would remain in the 300 meter range until after the test was completed.

As one might expect, ozone levels remained high (10 pphm at Fresno and Bakersfield on October 26; 11 pphm on October 27). In sum, no breakdown of the episode occurred until after the completion of the test. Conditions during the test were the same as conditions prior to the test. The breakdown of this episode did not begin to occur until October 28.

5.2.2 Local Conditions

As in the August episode, local conditions reflect those of the larger scale. Winds at Travis AFB were relatively light. This was especially true on October 24 when the sea breeze did not develop. Afternoon winds were light and easterly rather than southwesterly. The easterly winds coincided with the weakest San Francisco-Las Vegas pressure gradient seen during the test (-3.9 mb). On October 25, the sea breeze returned when moderate southwesterly winds were recorded during the afternoon. However, through the rest of the test, afternoon southwesterly winds were very light and were indicative of a weak inflow of marine air into the valley.

Elsewhere in the valley, winds remained light throughout the testing period as a result of the stagnant conditions. As was the case at Travis AFB, the strongest winds were seen on the afternoon of October 25. Coincidentally, October 25 saw the lowest ozone readings of the entire episode throughout the valley.

6.0 TRACER EXPERIMENT RESULTS

6.1 Analysis Methodology

This section presents surface concentration contour analysis of the tracer data to identify the position of the specific tracer plumes during each two-hour averaged sampling period for each test. Ground surface concentration contour values of 100, 50, and 10 femtoliters of tracer per liter of air (fl/l) were constructed to identify the outer boundaries of each tracer plume. Much higher concentrations levels occurred and were observed within each tracer plume, however, characterization of plume structure was not within the scope of this study. The following analysis compares the relative positions of the tracer plumes, at ground level, from sample period to sample period, thereby gaining a visual depiction of the subject air mass movement. While it is recognized that the tracer sampling network was not dense enough to support a very detailed depiction of the specific tracer plumes, the sampling grid was adequate to identify the position of the tracer cloud and its movement from the point of release. Some additional data was used to support the analysis of the tracer data. These include local wind measurements, air quality observations, and airborne samples of the tracer plumes in areas above the Sierra Nevada Range. In section 6.4 a theory is presented to explain how pollutants are transported from the SJV into the upper Sierra Nevada.

6.2 Tracer Experiment #1 -- August 12-14, 1990

The first tracer experiment occurred on 12 through 14 August 1990 and was conducted in anticipation of a normal mid-summer air quality scenario in the SJV. During the release period, ambient hourly ozone concentrations averaged 8.2 pphm at Fresno, 5.7 pphm at Stockton and 4.3 pphm at Bakersfield area stations. The tracer sampling network was operational at 1000 PDT on 12 August 1990 and proceeded to collect two-hour averaged sequential samples during the next 48 hours. Some instantaneous "grab" samples were collected from a fixed wing aircraft along the Sierra Nevada Range approximately 24 hours after the completion of the tracer release.

6.2.1 Fresno Tracer Release

Approximately 29 kilograms of perfluoro 1,2 Dimethylcyclohexane (PDCH) was released in the Fresno area between 1000 and 1400 PDT on 12 August 1990. The exact area configuration of the release was described in Section 2.0 of this report.

Figures 6-1 through 6-9 illustrate key steps in the atmospheric transport process which occurred to the tracer plume released from the Fresno area. Figure 6-1 depicts the interpreted position of the tracer plume just following the completion of the release. At this time the plume was generally east and north of Fresno showing no signs of impact in the Sierra Nevada regions. Within 4 hours, as seen during the period defined by 1600 and 1800 PDT (see Figure 6-2), the tracer plume had significantly migrated to the south. During this transition, the plume seemed to "hug" the foothill regions rather than transport along the center axis of the SJV. Between 2000 and 2200 PDT the plume was positioned firmly against the Sierra foothill regions between Fresno and Bakersfield. Figure 6-3 illustrates the plume position during this period and also denotes plume migration up the Kaweah River Valley and King Canyon. Sampling stations at Cedar Grove and Giant Forest indicated considerable tracer concentrations during this period. Figure 6-4 depicts the tracer plume during the very next monitoring period, 2200 to 2400 PDT. At this time, the plume began to migrate further south with significant impacts being registered in the Tehachapis and Tejon Pass. During the next eight hour segment, as seen in Figures 6-5 through 6-9, the tracer plume settled east of Bakersfield with limited impact in the mountain regions. During this final phase of observation, the data suggest that the plume mass declined considerably, evidenced by a steady decrease in overall maximum concentration. It is believed that the plume mass is lost mostly through vertical venting into the upper atmosphere. This is supported by the observance of a mild surface convergence zone in the vicinity of the plume position at this time. A surface convergence zone is an area in which opposing winds meet with a resultant motion in the vertical direction. Dispersion will increase as pollutants are drawn vertically into higher velocity upper level winds. As a result, concentrations of the Fresno released tracer were either too small to be detected in the leeward positions of the Sierra Nevada Range or the plume was carried eastward by way of upper level winds.

Aircraft based tracer observations for this test were conducted too late to see any portion of the tracer plume which resided in the Tehachapi mountain region. By 1200 PDT on 13 August, 1990, surface plume concentrations were at undetectable levels in this region and evidence of the plume is seen aloft. On the other hand, for portions of the plume which were entrained into the more northern mountain valleys and canyons (i.e. Kaweah River Valley and King's Canyon), much slower dispersion occurred. In these regions the airborne data was useful in confirming the upper extent of the tracer plume (see Figure 6-10). Since considerable trapping of eastward moving air occurred in these extreme regions, the air parcels were dispersed more slowly.

Between 1200 and 1400 PDT on 13 August 1990, (24-26 hours after the initial tracer release) PDCH concentrations on the order of 32 fl/l were detected in the Mariposa area. Samples were collected at an altitude of about 2000 ft above mean ground level. This data indicates that the tracer plume in these regions is probably well dispersed throughout the mixing layer. Figure 6-10 provides the airborne sample data for the Fresno tracer for this period. The bold numbers on the map indicate the tracer concentrations in fl/l. The non-bold numbers represent the airborne site numbers. All

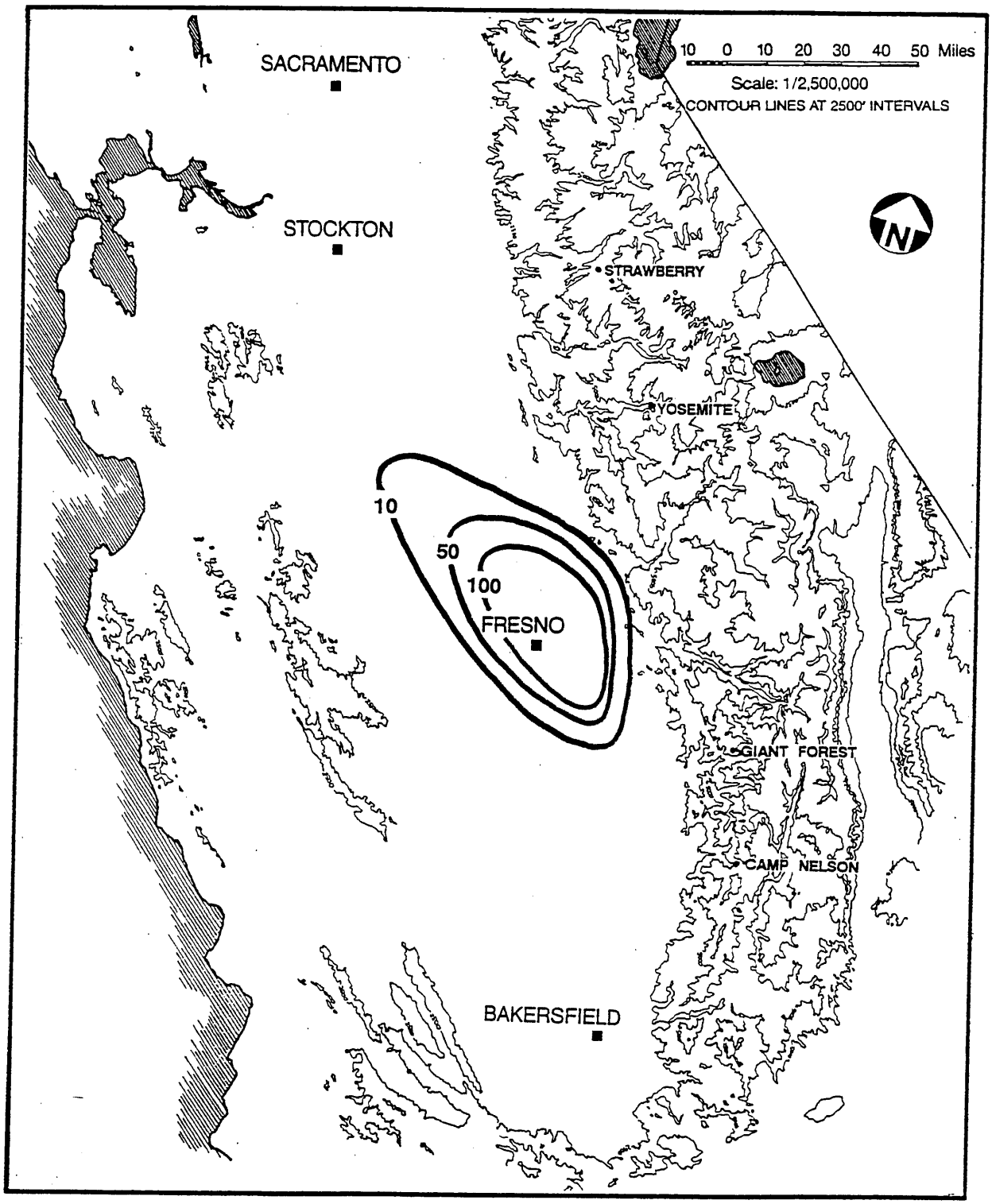


FIGURE 6-1 - Fresno Tracer Isopleths
August 12, 1990: 1400-1600 PDT
(Concentrations are in fl/l)

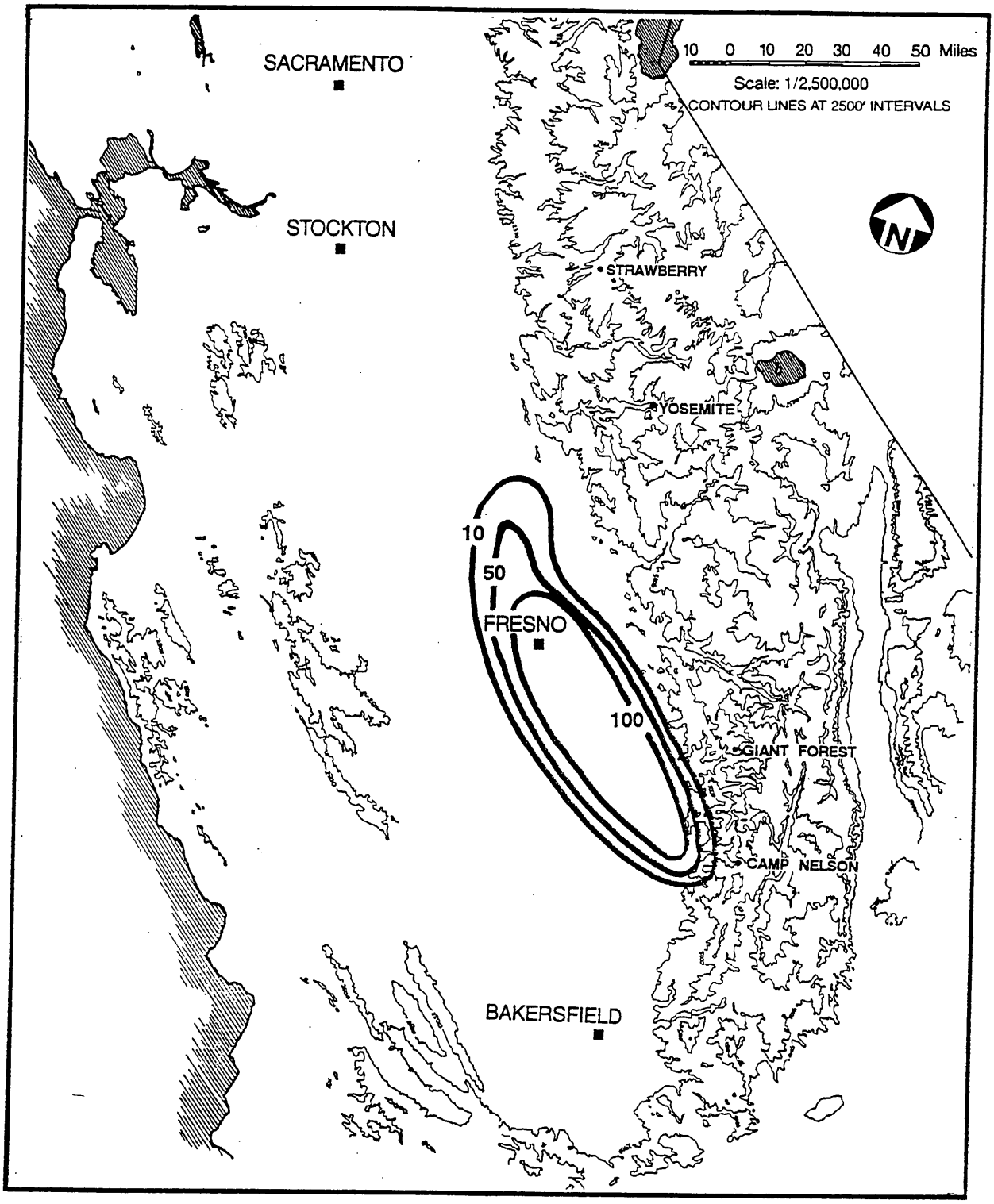


FIGURE 6-2 - Fresno Tracer Isopleths
August 12, 1990: 1600-1800 PDT
(Concentrations are in fl/l)

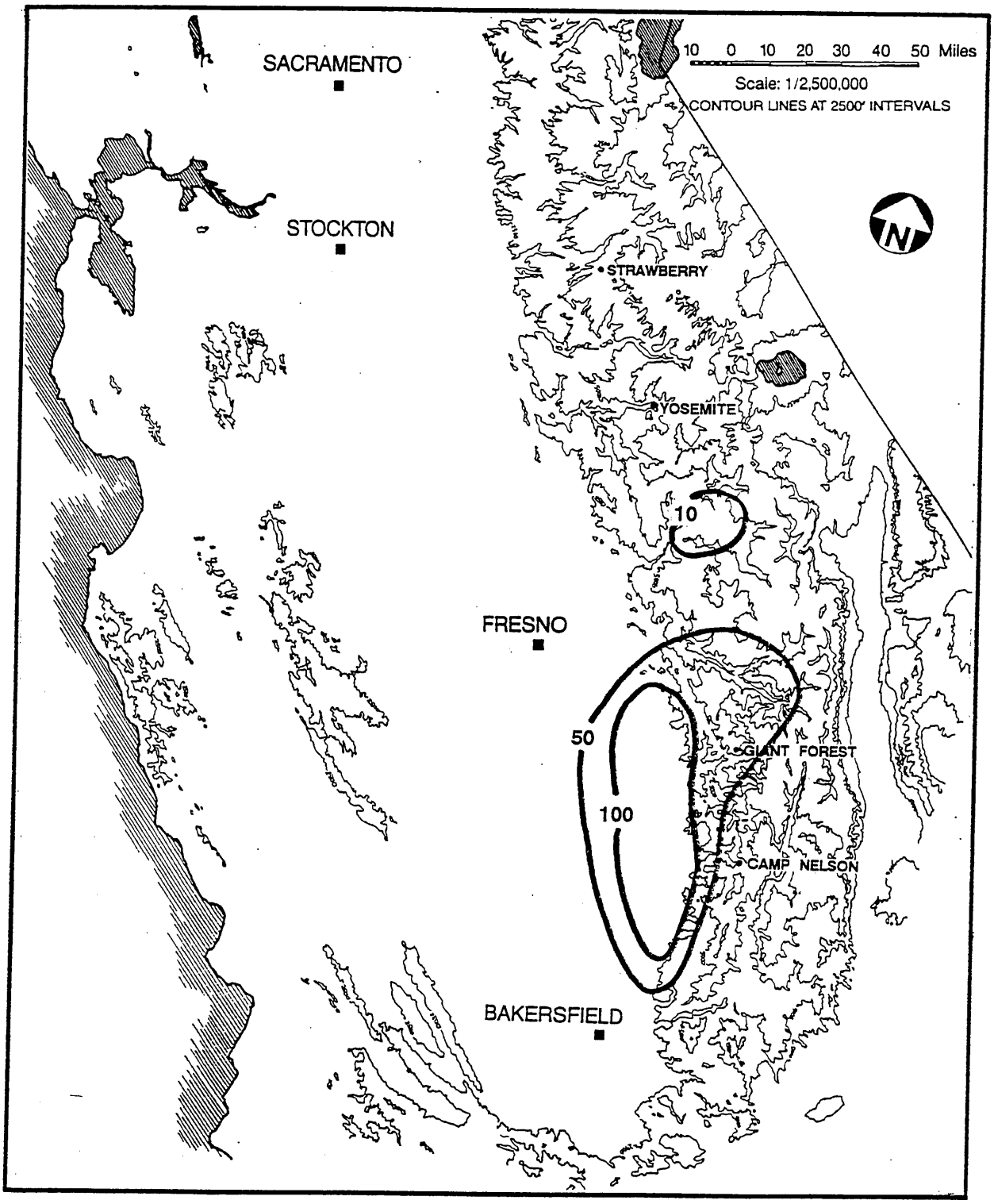


FIGURE 6-3 - Fresno Tracer Isopleths
August 12, 1990: 2000-2200 PDT
(Concentrations are in fl/l)

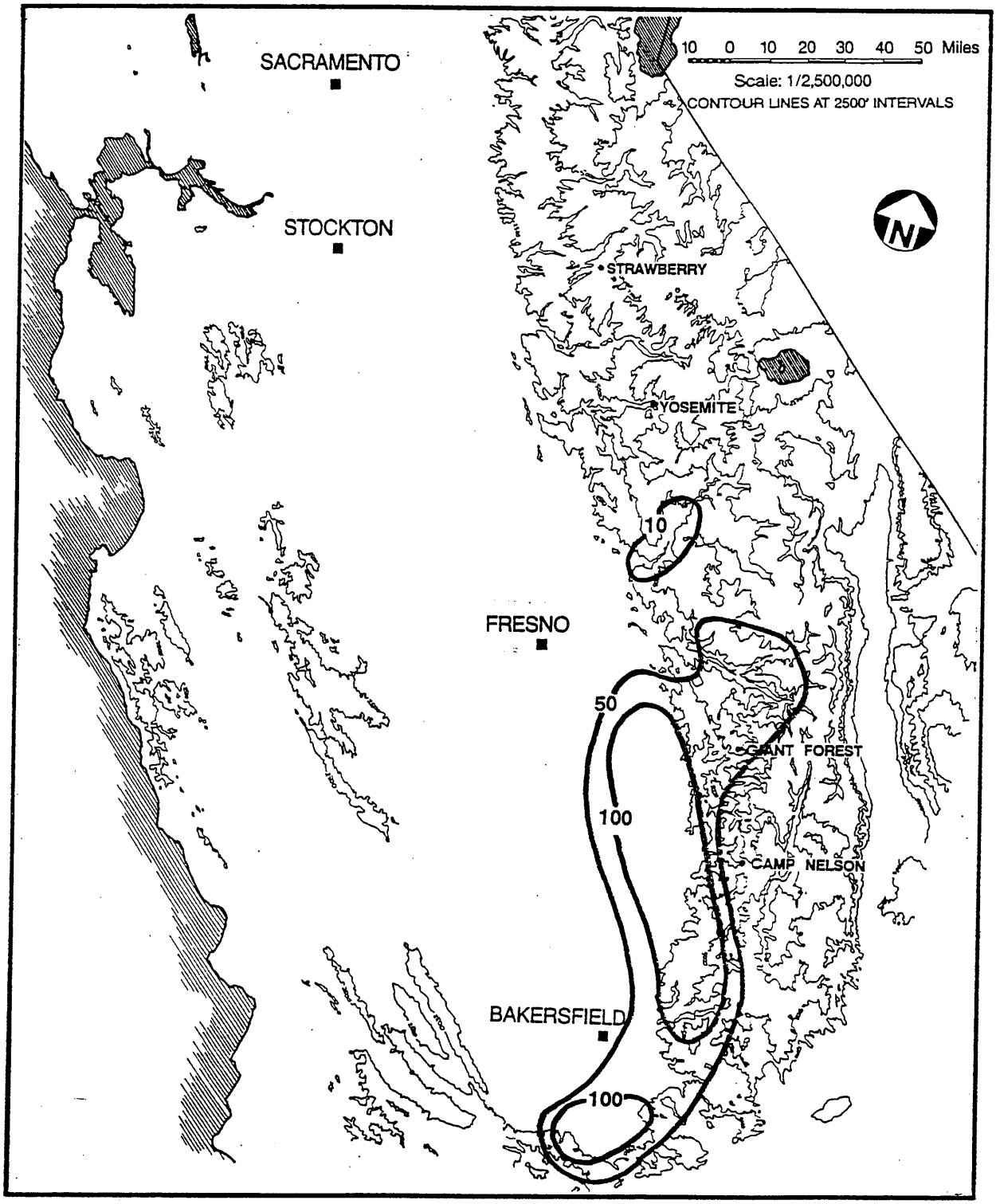


FIGURE 6-4 - Fresno Tracer Isopleths
August 12, 1990: 2200-2400 PDT
(Concentrations are in fl/l)

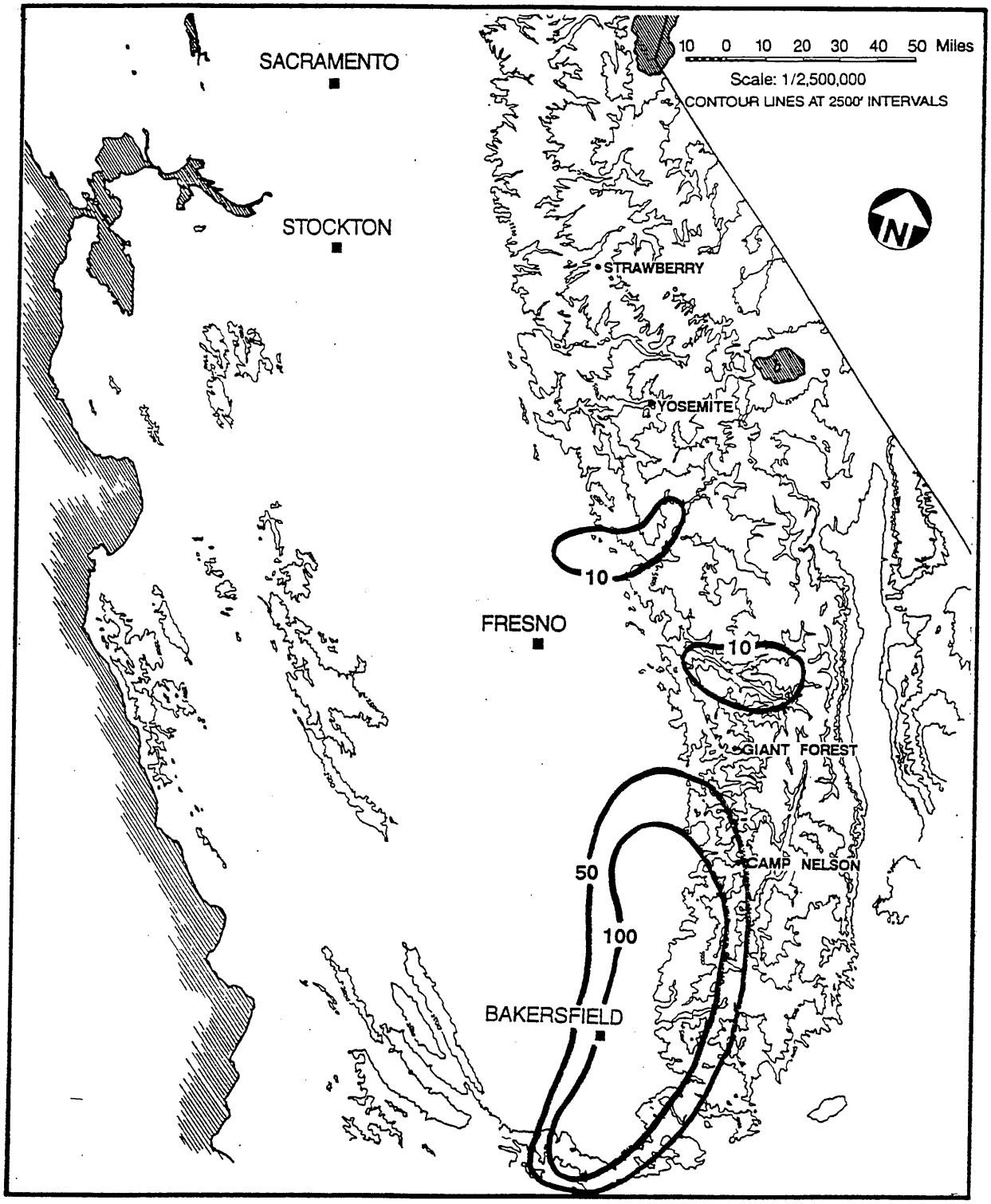


FIGURE 6-5 - Fresno Tracer Isopleths
August 13, 1990: 0000-0200 PDT
(Concentrations are in fl/l)

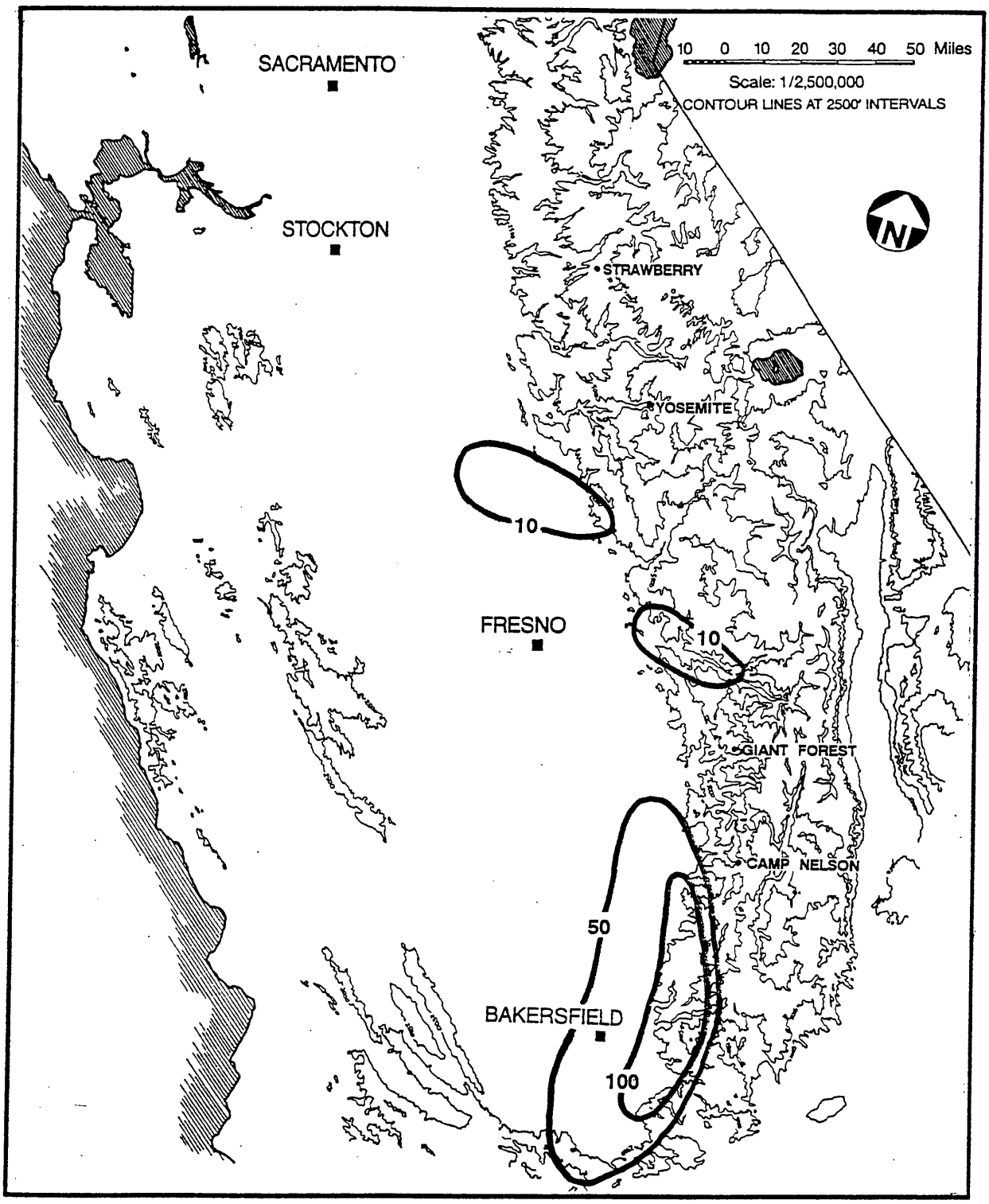


FIGURE 6-6 - Fresno Tracer Isopleths
August 13, 1990: 0200-0400 PDT
(Concentrations are in fl/l)

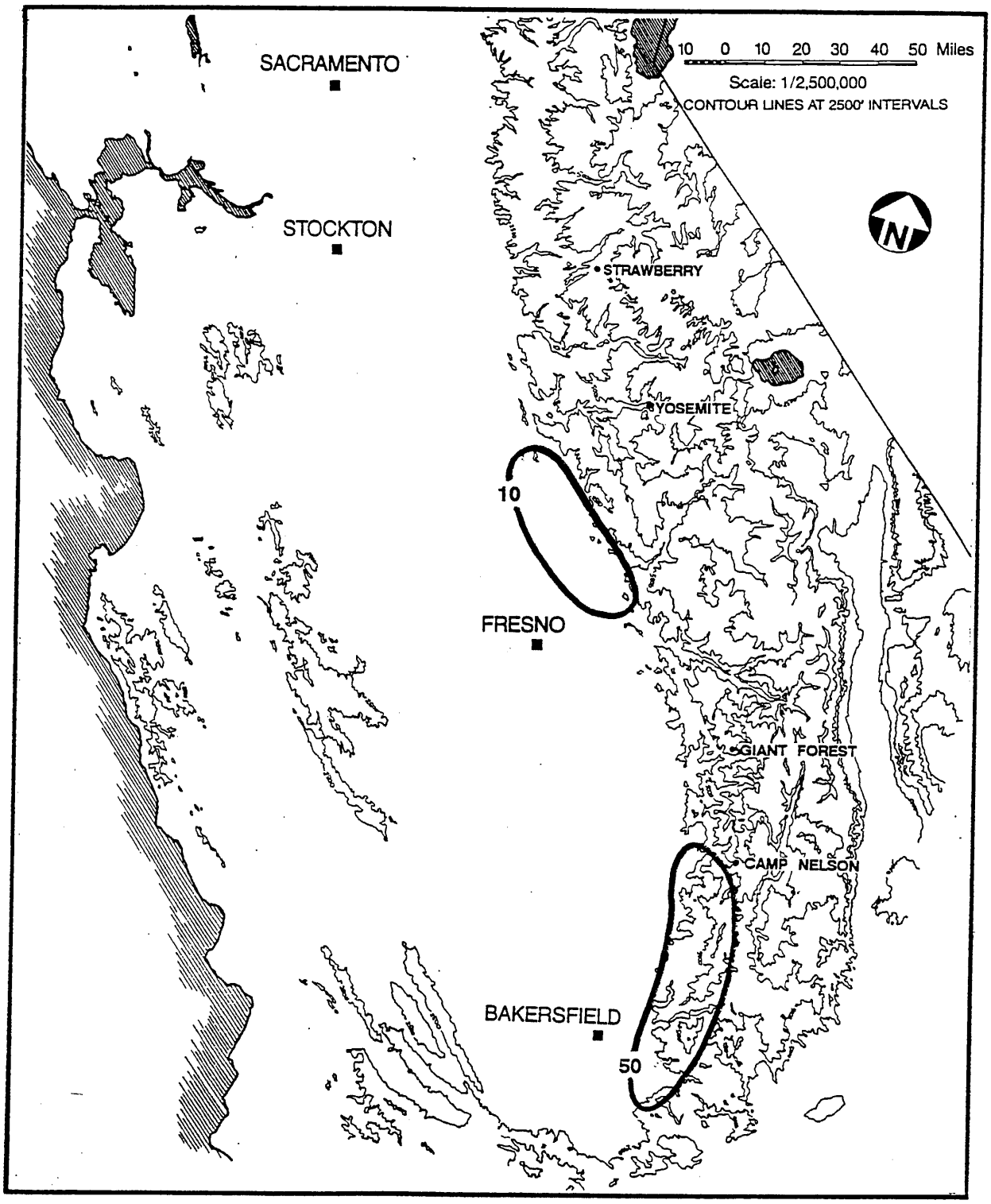


FIGURE 6-7 - Fresno Tracer Isopleths
August 13, 1990: 0400-0600 PDT
(Concentrations are in fl/l)

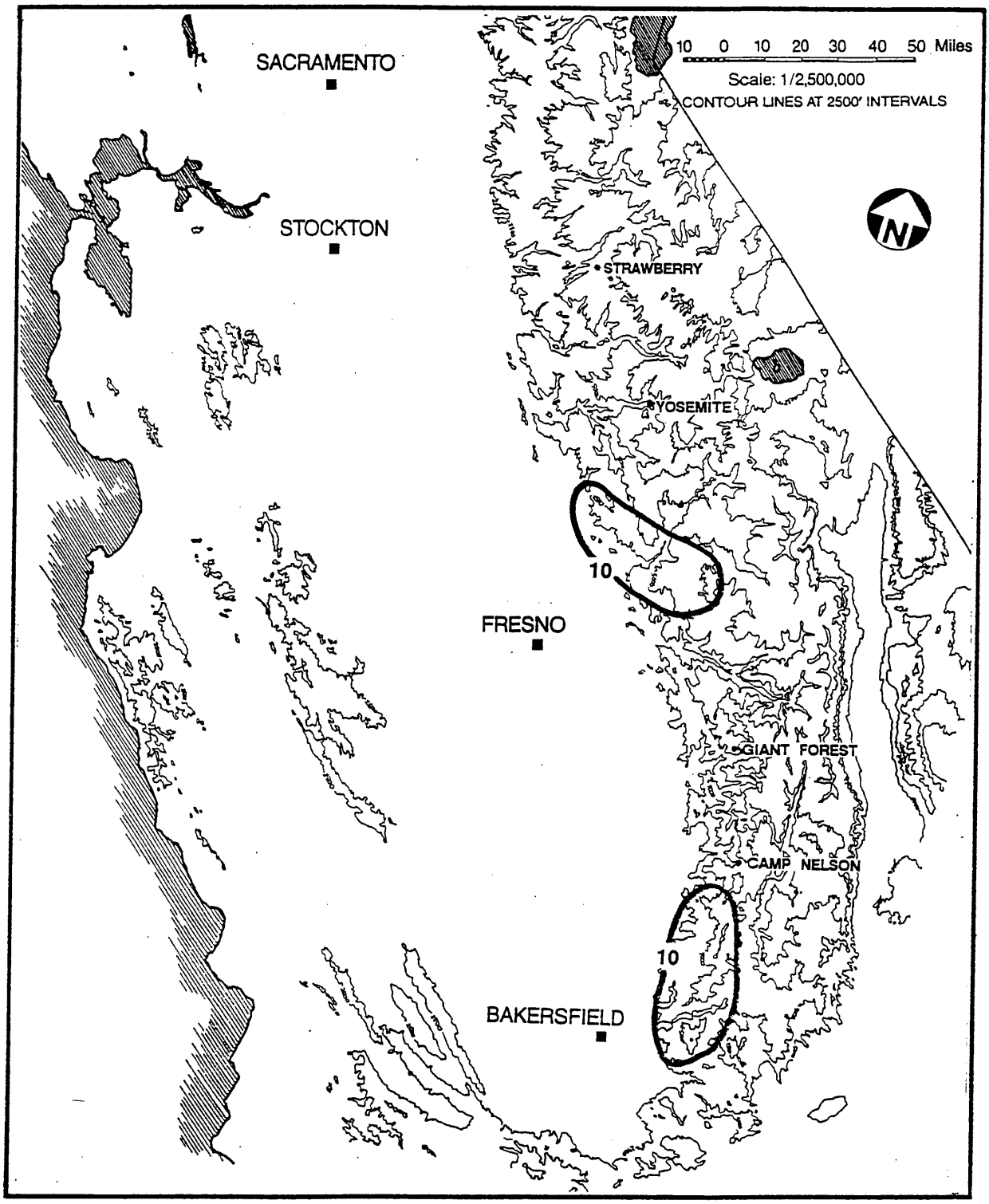


FIGURE 6-8 - Fresno Tracer Isopleths
August 13, 1990: 0800-1000 PDT
(Concentrations are in fl/l)

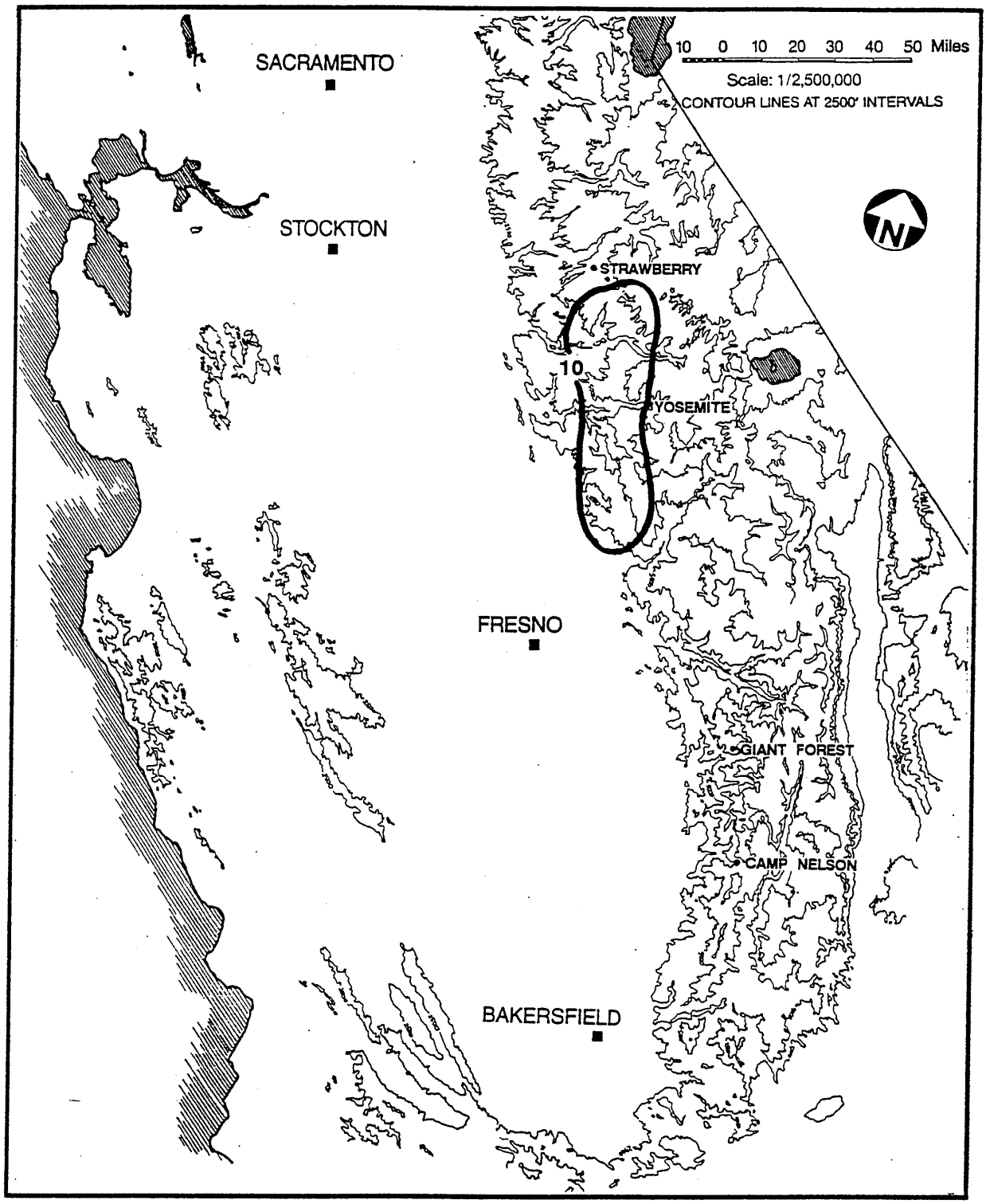


FIGURE 6-9 - Fresno Tracer Isopleths
August 13, 1990: 1000-1200 PDT
(Concentrations are in fl/l)

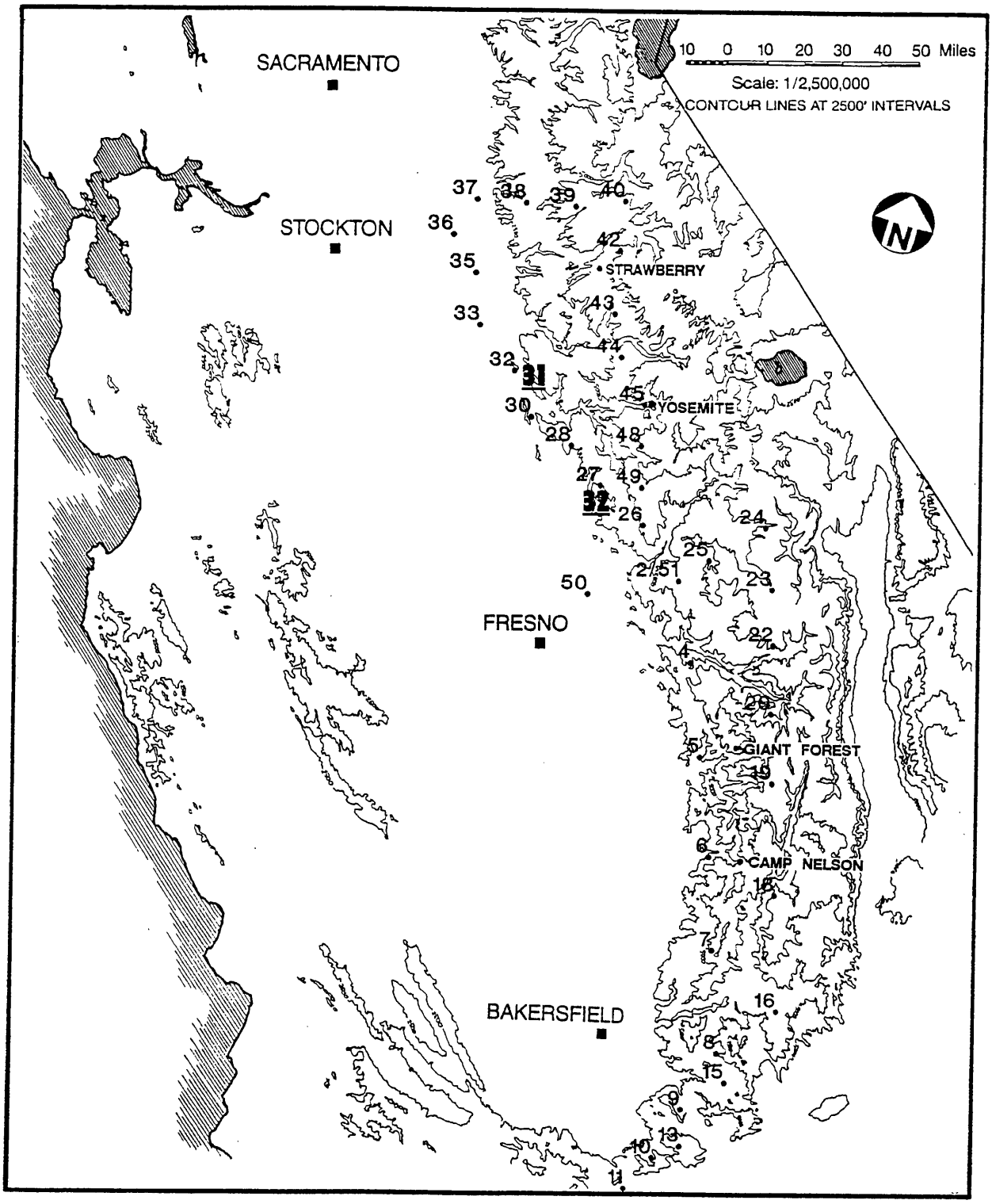


FIGURE 6-10 - Fresno Tracer Concentrations (PDCH)
Airborne - August 13, 1990: 1200-1400 PDT
(Concentrations are in boldface, fl/l)

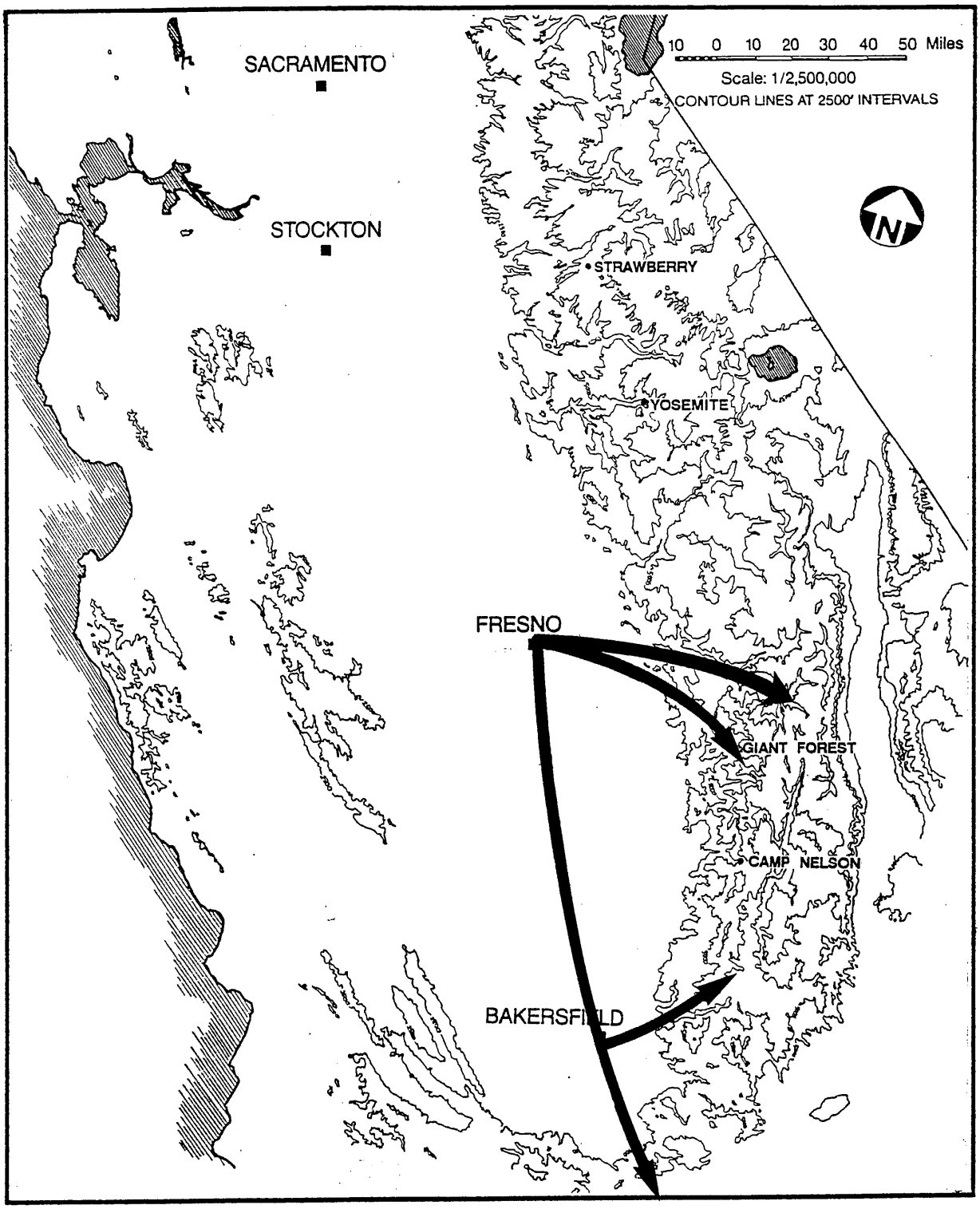


FIGURE 6-11 - Fresno Pathways into the Sierra Nevada: August Test

other airborne data indicated zero concentration levels of PDCH.

There appear to be two major pathways for transport of the Fresno tracer into the Sierra for this test. The two pathways are depicted in Figure 6-11. One pathway is King's Canyon which is located east of Fresno. Tracer appears to funnel up this canyon towards Cedar Grove and Giant Forest. The other pathway is the Kern River canyon, located just east of Bakersfield, where tracer appears to have transported from the Bakersfield area to Democrat Station in the Sierra.

6.2.2 Stockton Tracer Release

Between 1000 and 1400 PDT on 12 August 1990, approximately 29 kilograms of the tracer compound, perfluoromethylcyclohexane (PMCH), was released from the Stockton area. Figures 6-12 through 6-22 depict the progression of the Stockton tracer plume. The interpretive position of the Stockton tracer plume, based upon measurements collected between 1600 and 1800 PDT (2 hours after the completion of tracer release), is illustrated in Figure 6-12. During this sampling period the plume was positioned south and east of Stockton with a basic trajectory toward the Sierra Nevada foothills. Figure 6-13 shows the Stockton tracer plume during the sampling period 6 hours after release. At this time the plume began to split, such that one portion directly impacted the Sierra Nevada Range by migrating up the Yosemite Valley and the other segment continued to move in a general south direction along the foothill areas. Figure 6-15 further demonstrates the segmentation of the original Stockton plume as the one part stalled in the Yosemite Valley and the other portion continued to migrate along the foothills, up the SJV. At 12 hours after the release, the Stockton plume resided due east of Fresno.

Figures 6-15 through 6-17 illustrate the movement of the plume during the nocturnal period, about 12 to 18 hours after release occurred. In this sequence the plume retrogrades slightly, as very calm wind conditions persist in the SJV. As a result, the plume segment situated in the SJV drifts northward and the portion which was earlier situated in the Yosemite Valley, has moved sightly west, carried by light drainage flow seen in the mountain valleys. This is further evidenced by the decline in concentration in some of the mountain sites and positive, non-zero readings seen at stations situated due east of Fresno. During the later morning hours, as air flow became better defined in the SJV, impacts of the Stockton plume suddenly were seen in the Tehachapis south and east of Bakersfield. Figures 6-18 through 6-20 illustrate these impacts and also show a general tendency of the plume to again migrate into the western portions of the Sierra Nevada Range. A close look at the air flow pattern in the SJV during this period indicates the presence of a very mild convergence zone in the Sierra foothills region between Fresno and Bakersfield. This convergence zone is partly due to mild drainage winds from the Sierra regions of Giant Forest and Camp Nelson meeting circulation winds within the SJV. This zone prohibited the surface plume of the Stockton tracer

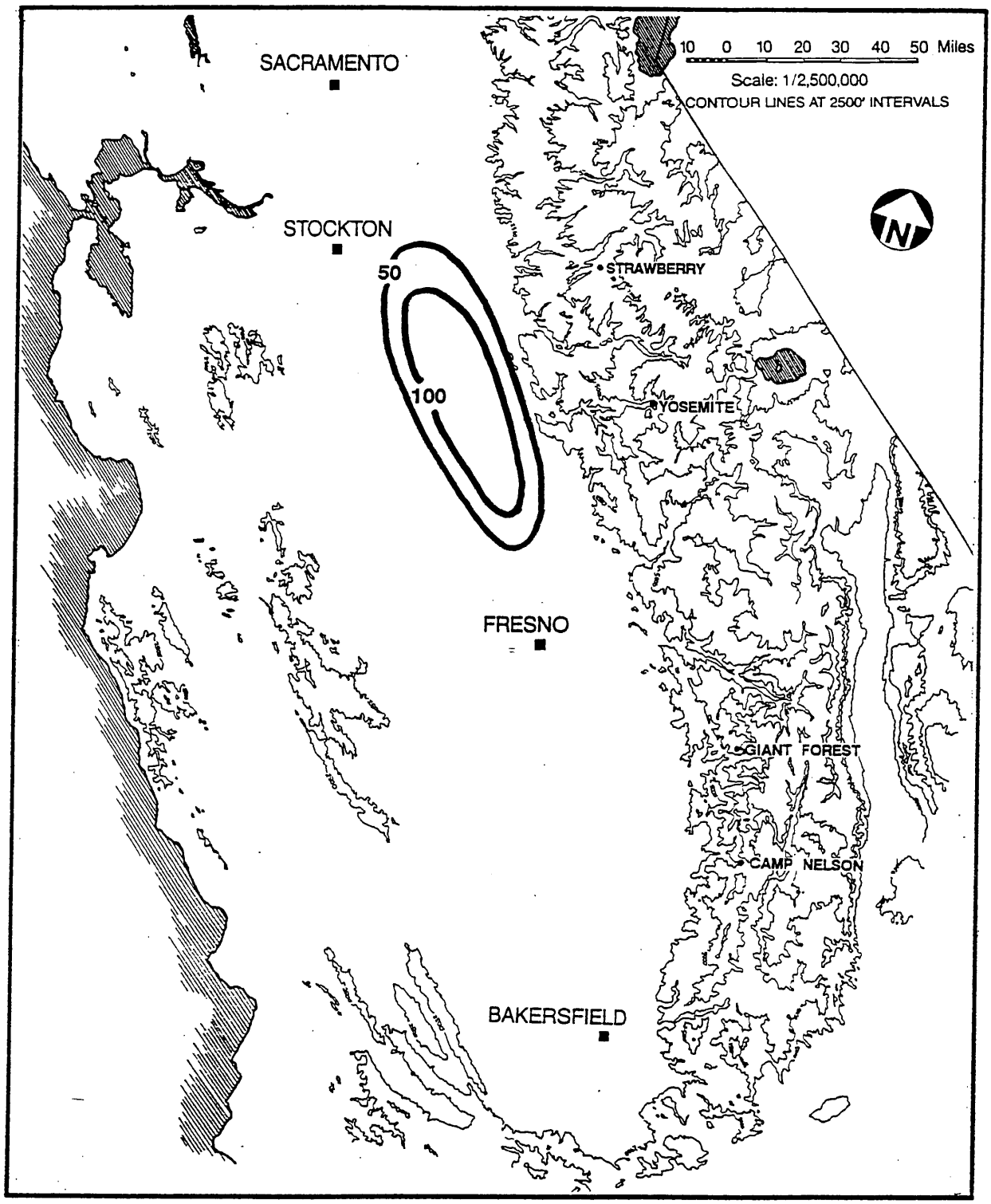


FIGURE 6-12 - Stockton Tracer Isopleths
August 12, 1990: 1600-1800 PDT
(Concentrations are in fl/l)

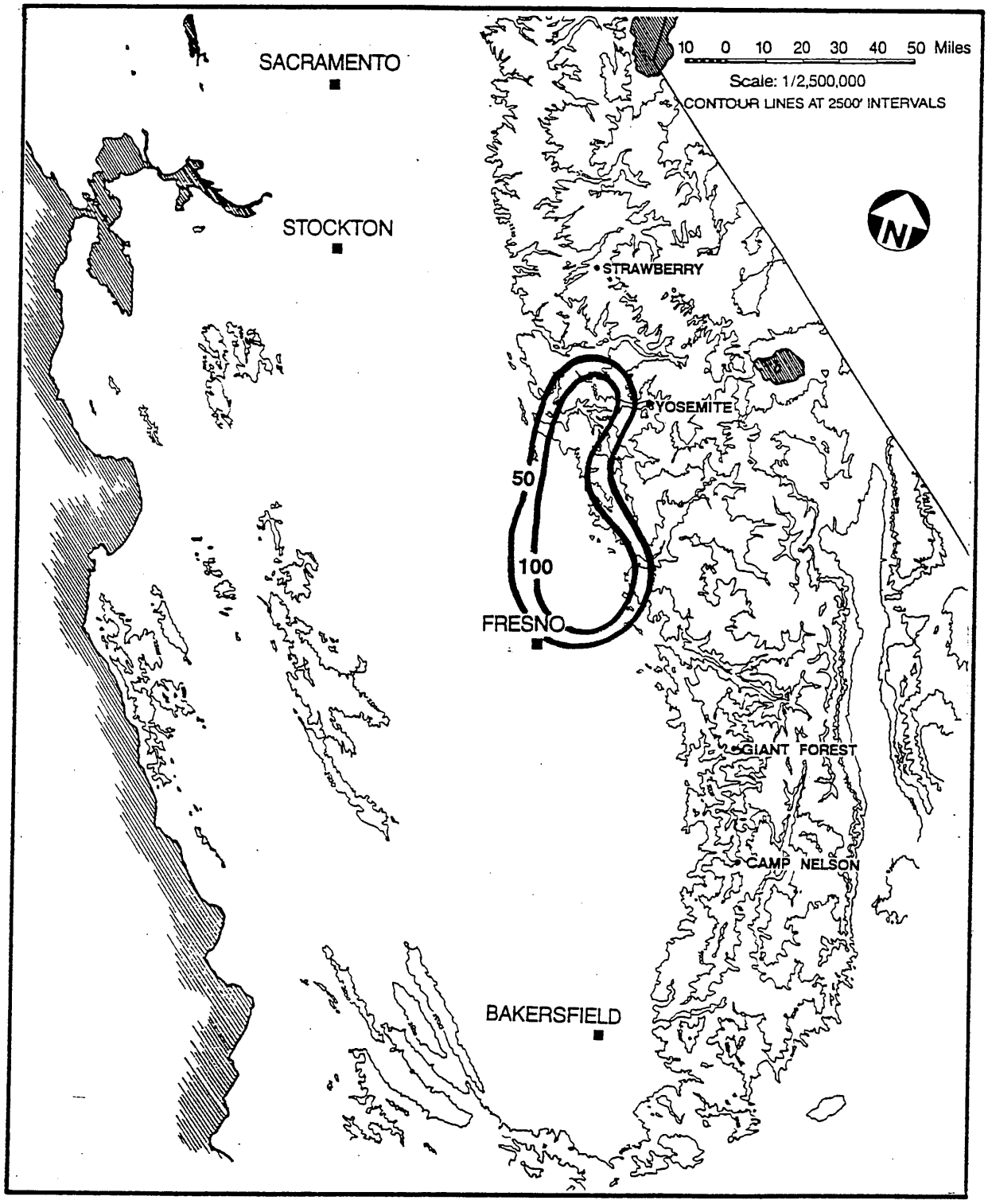


FIGURE 6-13 - Stockton Tracer Isopleths
August 12, 1990: 2000-2200 PDT
(Concentrations are in fl/l)

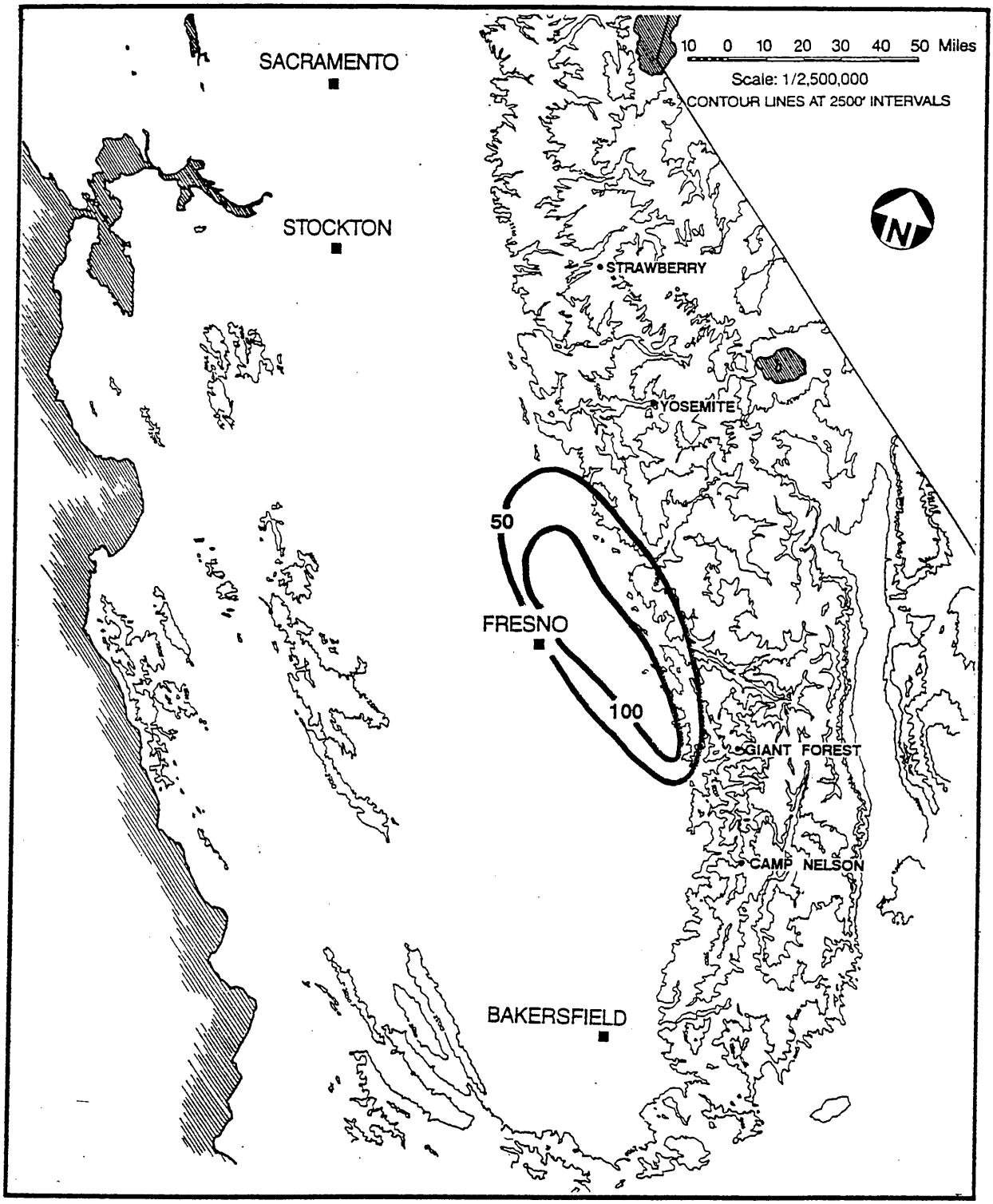


FIGURE 6-14 - Stockton Tracer Isopleths
August 13, 1990: 0000-0200 PDT
(Concentrations are in fl/l)

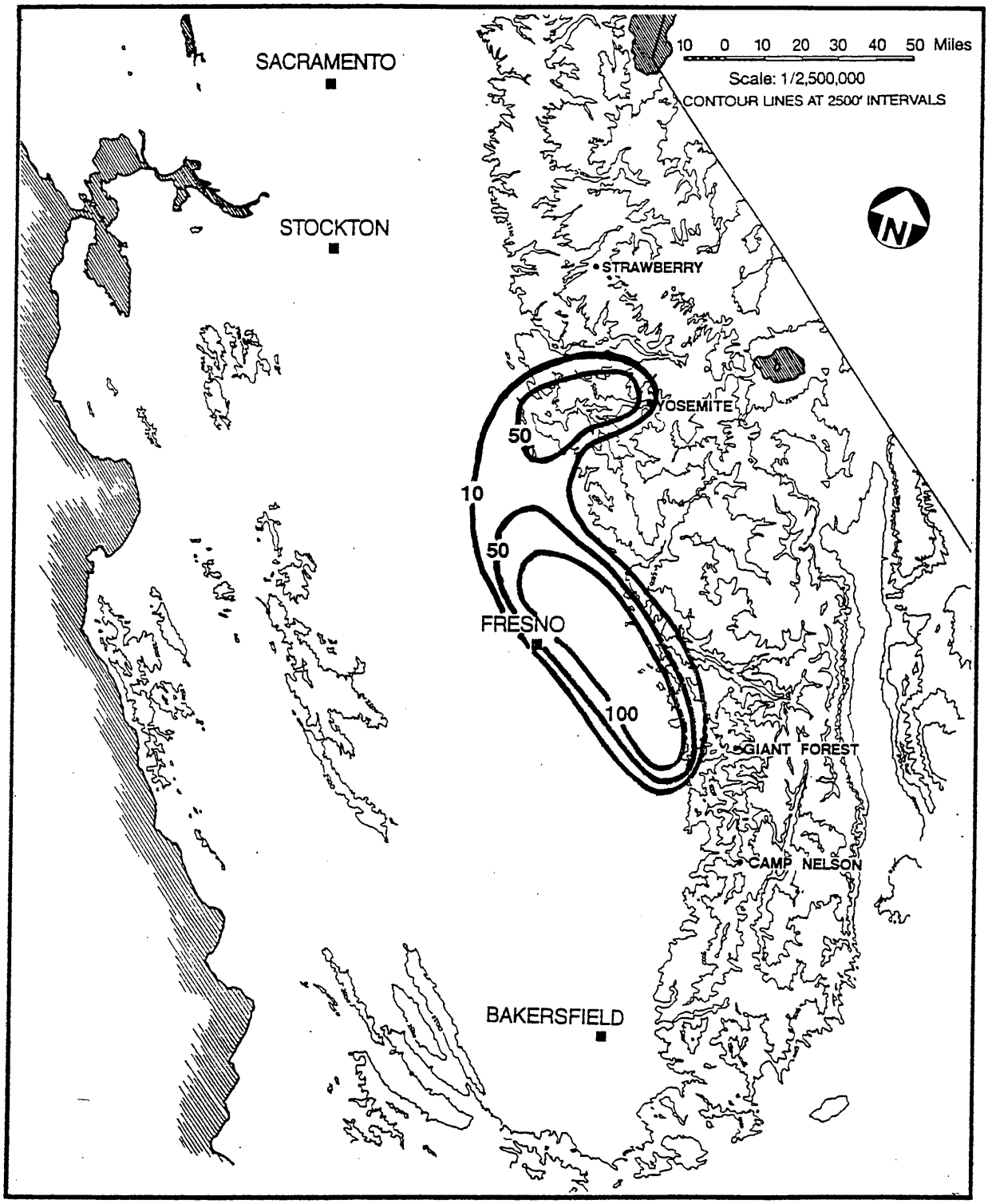


FIGURE 6-15 - Stockton Tracer Isopleths
August 13, 1990: 0200-0400 PDT
(Concentrations are in fl/l)

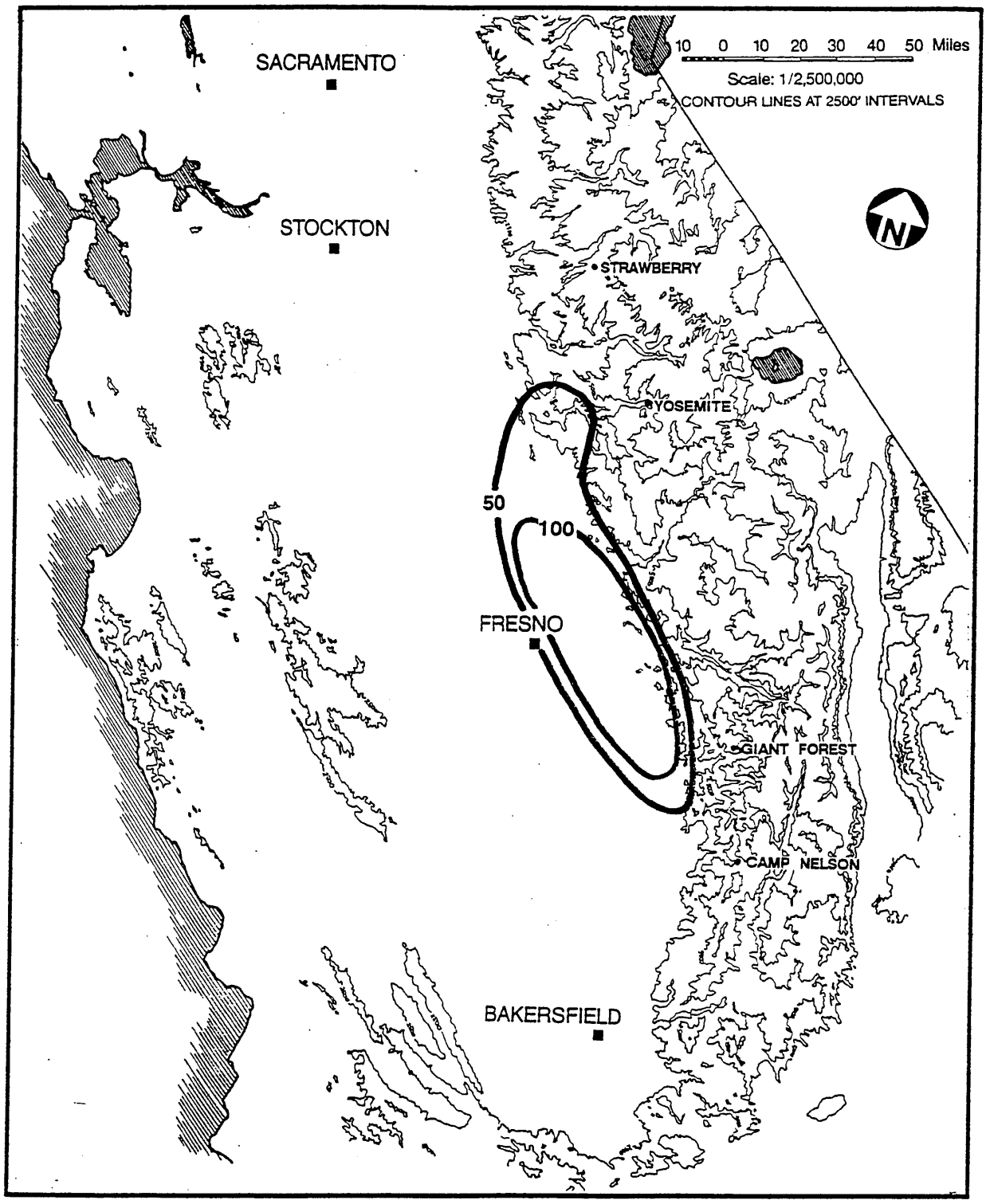


FIGURE 6-16 - Stockton Tracer Isopleths
August 13, 1990: 0400-0600 PDT
(Concentrations are in fl/l)