

ACROSS NORTH AMERICA TRACER EXPERIMENT (ANATEX)

VOLUME I: DESCRIPTION, GROUND-LEVEL SAMPLING AT PRIMARY SITES,

AND METEOROLOGY

R. R. Draxler
J. L. Heffter
(Editors)

Air Resources Laboratory Silver Spring, Maryland January 1989





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NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION

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ACROSS NORTH AMERICA TRACER EXPERIMENT (ANATEX)

VOLUME I: DESCRIPTION, GROUND-LEVEL SAMPLING AT PRIMARY SITES, AND METEOROLOGY

ABSTRACT. ANATEX was conducted during the first 3 months of 1987 with routine emissions of tracers, regardless of the synoptic conditions, from two sources separated by about 1000 km. Groundlevel tracer measurements were made at "primary" sites up to 3000 km from the sources and at "remote" sites for hemispheric coverage. Tracer measurements were also made from aircraft flying within about 500 km of the sources and on towers located along a ground-level sampling arc (Volumes II and III). Three months of sampling data provide a comprehensive data base for evaluating the accuracy and reliability of the transport and dispersion aspects of long-range models. Since a different and unique tracer was released from each source site, the sampling data can be used to demonstrate the ability of models to separate the effects of local and distant sources. Further, because these data are on the regional scale, covering the entire eastern United States and Canada, it is possible to characterize the meteorological influences on regional transport.

ANATEX was conducted between January 5, 1987, and March 29, 1987. Three different tracers totaling about 7500 kg were released during this period. There were 33 releases of the different tracers from each of two sites: Glasgow, Montana (GGW) and St. Cloud, Minnesota (STC). Tracer was routinely released every 2.5 days, alternating between 0500-0800 GMT and 1700-2000 GMT. Thus, a unique feature of ANATEX is that it was conducted during a wide variety of meteorological conditions with both daytime and nighttime tracer releases. Supplemental rawinsondes were taken at 0600 and 1800 GMT during the entire ANATEX period, near both tracer sources and at four additional sites within about 500 km. Ground-level air samples of 24-h duration were taken at 77 sites for 84 days starting January 5. Most of the sites were located near rawinsonde stations east of 105°W and between 26°N and 55°N and along two arcs at 1000 and 1600 km from GGW. Additional longterm weekly samples were taken at 12 remote sites between San Diego, California and Pt. Barrow, Alaska and between Norway and the Canary Islands. Short-term 6-h samples were collected at ground-level and 200 m along an arc of five towers between Tulsa, Oklahoma and Green Bay, Wisconsin. Aircraft sampling near GGW and STC was used to establish the initial tracer path, as the ground-level sampling network was non-existent or too widely spaced near the source locations.

1. INTRODUCTION

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The adverse effects of air pollutants on humans and the environment during long-range transport and dispersion of the pollutants continues to be of major concern (e.g., acid rain, Arctic haze, accidental pollutant releases). Air pollution models have been developed to simulate atmospheric and chemical processes out to distances of several thousand kilometers from pollutant sources. Evaluation and verification of the meteorological and chemical aspects of these model calculations is essential in our efforts to establish the uncertainty associated with them. Improvement in model calculations can be achieved through the development of better parameterizations of the processes important to the long-range transport of pollutants.

One of the more traditional methods for the evaluation and verification of model-simulated meteorological processes is field experiments, in which a known amount of an inert tracer is released from a source, or several sources, and concurrent measurements of its air concentration are made at various downwind distances and locations.

In ANATEX, routine tracer releases and air sampling were conducted over a wide network as far as 3000 km from the source. Because the tracers were released on a routine basis, the experiment was conducted in a variety of meteorological conditions. One of the limitations of many past experiments has been the need to conduct them during homogeneous synoptic situations for transport into a narrow sampling sector. However, the long-range transport flow in large synoptic systems and near-frontal zones in ANATEX is an inevitable part of assessment modeling.

The objectives of ANATEX are given below; several of these objectives are the direct results of further studies suggested from previous data analyses and model evaluations:

- 1. Differentiation between sources contributing to air concentrations at receptor sites located at various distances and alignments from those sources.
- 2. Determination of the growth rate of the tracer due to horizontal diffusion as it extends to distances beyond 1000-1500 km.
- 3. Investigation of the changes in the vertical distribution of tracer with time or distance.
- 4. Investigation of the vertical wind shear effects on horizontal and vertical tracer distributions.
- 5. Verification of model calculations with respect to time or distance from the source.
- 6. Determination of how model accuracy improves as calculations are averaged in time or space.

The ANATEX experimental design addressed each of these issues. (1) Tracers were released simultaneously from two sources separated by 1000 km. Tracers were unique and identifiable in each sample and hence can be used to examine questions of source attribution. (2) Samples were taken over the entire eastern half of the United States and southern Canada, permitting evaluation of plume growth rates. (3,4) Routine aircraft sampling was conducted at several downwind distances to measure vertical tracer profiles and provide data on the initial transport. (5,6) Additional meteorological data were collected for use in model simulations and sensitivity studies.

ANATEX was initiated and primarily funded by Headquarters, Air Force Technical Applications Center (AFTAC). The National Oceanic and Atmospheric Administration/Air Resources Laboratory (NOAA/ARL) was selected as the lead agency in planning this effort, in conjunction with the AFTAC Meteorology Working Group consisting of scientists from Savannah River Laboratory, Lawrence Livermore National Laboratory, Los Alamos National Laboratory, and Pacific Northwest Laboratory. The Department of Energy's Office of Health and Environmental Research (DOE/OHER) also provided guidance and funding.

In this report we summarize the experimental design, the ground-level sampling data from primary sites, and available meteorological data. Subsequent reports will contain the aircraft sampling results (Vol. II) and the tall tower and remote site sampling results (Vol. III).

2. EXPERIMENTAL DESIGN

2.1 Summary

The following is a summary of the experiment:

Release Sites: Glasgow, Montana (GGW) and St. Cloud, Minnesota (STC)

Experiment Period: January 5, 1987 through March 29, 1987 (84 days)

Tracer: 3 perfluorocarbons (PTCH, oPDCH, and PMCH)

Releases: Simultaneous releases of about 84 kg of PTCH for 3 h from GGW, and about 47 kg of oPDCH for 3 h from STC every 2½ days, which resulted in an alternate day-night release cycle. In addition, there was a simultaneous release of about 50 kg of PMCH for 3 h with the oPDCH from STC, every 5 days (day cycle only).

Ground-level sampling: 77 "primary" sites east of 105°W, mostly near rawinsonde stations and along two arcs (1000 km and 1600 km from GGW), taking 24-h samples; and 12 "remote" sites, for hemispheric coverage, taking weekly samples.

Upper-air sampling: aircraft flights within 500 km of the sources, and samplers near the tops of five tall (≥ 200 m) towers.

Meteorology: 2 additional soundings per day (0600 and 1800 GMT) at the sources and four other stations within about 500 km from the sources, hourly surface observations, and 2-h gridded (90 km) meteorological data fields.

2.2 Tracer Release

All perfluorocarbon tracers used in this experiment were manufactured by ISC Chemicals, Ltd. (United Kingdom). All are liquid (evaporated on release) fully fluorinated hydrocarbons, and therefore they are inert, nondepositing, and nontoxic. Some physical properties of the tracers are given in Table 2-1.

PMCH was used in previous experiments such as the Cross Appalachian Tracer Experiment (CAPTEX, Ferber et al., 1986), while the new tracers, oPDCH and PTCH, as well as improvements to the chromatographic analysis system have been developed for ANATEX by Brookhaven National Laboratory (BNL) (section 4). The required technology was transferred to the Environmental Measurements Laboratory (EML) and the Air Resources Laboratory Field Research Division (ARLFRD). These three labs are responsible for the tracer analysis of the samples. With multiple laboratories it is essential to maintain laboratory intercalibration. Several standards for these tracers were made and distributed to each laboratory for periodic intercomparisons.

The tracers were released at an industrial park about 20 km north of Glasgow, Montana (GGW), and at the Technical High School in St. Cloud, Minnesota (STC). The terrain near both sites is very flat. The Glasgow release area is devoid of any tall vegetation, and is located on a gently rising bluff about 20 km north of and about 132 m higher than the rawinsonde station near the town of Glasgow. The St. Cloud release is near the center of the urban area, but is more suburban in character, and having trees 10-20 m in height. The site is about 1.5 km west of the Mississippi River, which cuts a deep channel through the town. The rawinsonde station is at the airport, about 7.6 km east, and across the river from the release site. Specific site information is given in Table 2-2.

At each location the tracer was evaporated into a heated airstream such that as the tracer/air mixture entered and cooled to the temperature of the ambient environment, its mixing ratio was less than the saturation mixing ratio of the tracer in air. We used the same release device used in previous perfluorocarbon experiments (Fig. 2-1). Both release sites were located in small one-story buildings. The tracer was vented through a standard stove-pipe exit about 2 m above the roof and the releases were coordinated by ARLFRD. Tracer was shipped to each release site directly from the manufacturer.

The tracers were released from both sites every $2\frac{1}{2}$ days, thereby providing 33 alternate day and night releases. We released the different tracers simultaneously from each site, the equivalent of about 84 kg of 100% pure PTCH for 3 h from GGW and about 47 kg of 100% pure oPDCH for 3 h from STC. In addition during each daytime release at STC, we also released about 50 kg of PMCH. Although we expected to detect PMCH only to about 1000 km because of its high background, it provided additional temporal resolution in the sampling data. The release schedule and 3-h tracer release totals are summarized in Table 2-3.

2.3 Primary Sampling Network

The daily ground-level sampling program for ANATEX was conducted for 84 days (12 weeks) from January 5, 1987, to March 30, 1987. Seventy-seven primary ground-level sampling sites (Fig. 2-2) took 24-h-duration (starting at 1400 GMT) air samples. The sampling network density and sampling frequency were limited

Table 2-1. Perfluorocarbon tracer technical data

	Perfluoro- methyl- cyclohexane	Perfluoro- ortho- dimethyl- cyclohexane	Perfluoro- trimethyl- cyclohexane
Abbreviation	PMCH	оРДСН	РТСН
Boiling (°C)	76	103	125
Freezing (°C)	-30	-26	<-33
Vapor pressure (mb)	141	46	
Molecular weight (g/mol)	350	400	450
Background (fL/L)*	3.5	0.1**	<0.03**
Purity (% by weight)	99.9	44.4, 40.9***	98.2
Conversion g/m ³ to fL/L	$6.4x10^{10}$	5.6x10 ¹⁰	5.0×10^{10}
PMCH contamination (%)		0.032, 2.54***	0.003
oPDCH contamination (%)			0.063

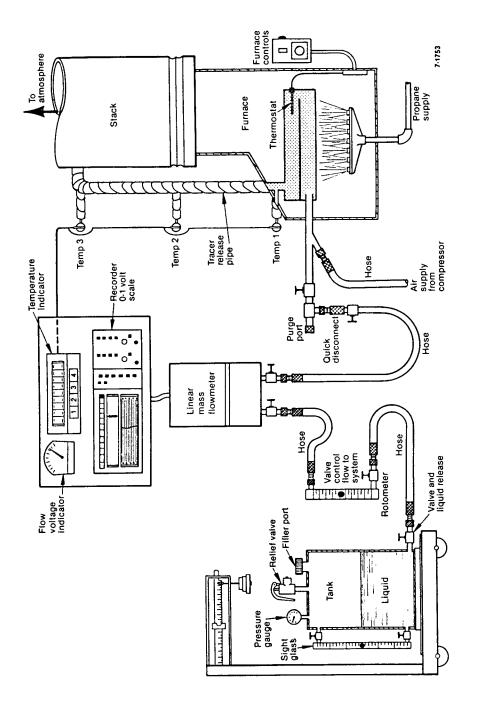
^{*}Femoliters per liter $(10^{-15} L/L)$.

Table 2-2. Tracer source data

Site	Elevation	Latitude	Longitude	Tracer
GGW	831 m	48.40°N	106.51°W	РТСН
STC	311 m	45.56°N	94.17°W	PMCH, oPDCH

^{**}Below current analytic sensitivity.

^{***} oPDCH was manufactured in two lots with different purities.



Schematic of the tracer release mechanism used at both GGW and STC. Figure 2-1.

Table 2-3. Purity corrected tracer release totals (kg) by release number, date, and hours (GMT)

Release	Date	Time	oPDCH	PMCH	PTCH
1	Jan 5	17	50.7	49.5	76.6
2	Jan 8	5	48.8	0.0	88.8
3	Jan 10	17	50.8	49.7	83.5
4	Jan 13	5	50.6	0.0	83.9
5	Jan 15	17	51.1	50.2	83.4
6	Jan 18	5	51.5	0.0	83.9
7	Jan 20	17	50.0	48.6	83.5
8	Jan 23	5	51.1	0.0	83.7
9	Jan 25	17	50.5	49.3	83.6
10	Jan 28	5	51.0	0.0	83.6
11	Jan 30	17	50.8	49.6	83.7
12	Feb 2	5	51.0	0.0	83.6
13	Feb 4	17	50.7	49.6	83.7
14	Feb 7	5	47.2	2.9	83.7
15	Feb 9	17	46.8	52.4	83.7
16	Feb 12	5	47.0	2.9	83.7
17	Feb 14	17	46.8	52.5	83.7
18	Feb 17	5	47.0	2.9	83.7
19	Feb 19	17	47.1	53.0	84.1
20	Feb 22	5	47.4	2.9	83.7
21	Feb 24	17	47.1	53.0	83.7
22	Feb 27	5	47.6	3.0	83.7
23	Mar l	17	46.9	52.6	83.7
24	Mar 4	5	47.2	2.9	83.7
25	Mar 6	17	47.1	53.0	83.7
26	Mar 9	5	51.3	0.0	83.6
27	Mar 11	17	47.1	53.0	83.8
28	Mar 14	5	51.4	0.0	83.6
29	Mar 16	17	47.0	52.7	83.6
30	Mar 19	5	49.9	.1	83.7
31	Mar 21	17	46.8	52.4	83.7
32	Mar 24	5	47.2	2.9	83.6
33	Mar 26	17	44.6	49.0	75.1

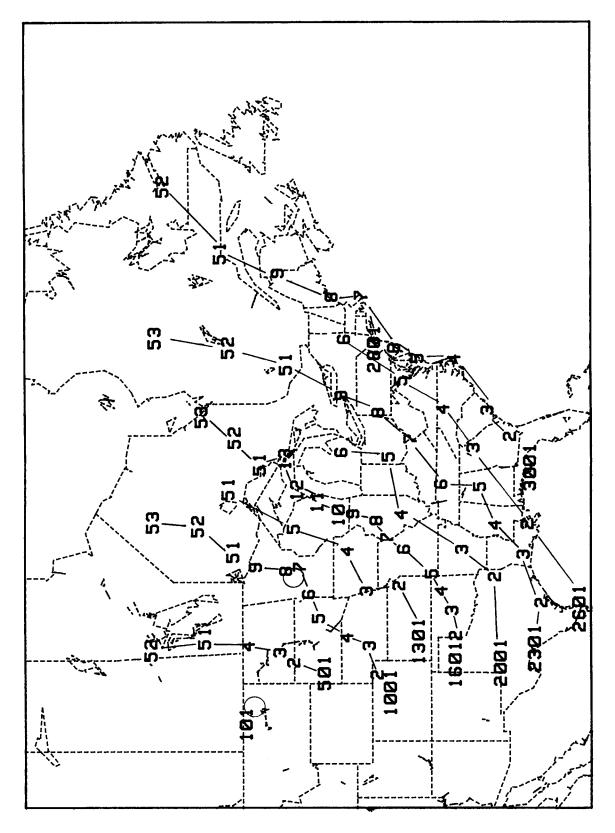


Figure 2-2. Primary ground-level sampling network. Station locations are at the center of each site number. Circles indicate locations of tracer release.

by sampler availability and analysis capacity. Fifty-four sites were located near the regular (0000 GMT and 1200 GMT) upper-air rawinsonde stations in the United States and Canada for general spatial coverage. These sites were all within 3000 km of GGW, and between 25° and 55°N latitude and 60° and 108°W longitude. An additional fifteen sites were located between the rawinsonde stations along two arcs at about 1000 km and 1600 km from GGW for a more comprehensive analysis of horizontal tracer distributions. Another eight sites were located to fill gaps in the overall network. All together, the sites formed eight arcs. The sampling sites were selected in cooperation with the National Weather Service (NWS) for sampling in the United States, and in cooperation with the Atmospheric Environment Service (AES) for operations in Canada. Sites were numbered by approximate arc distance from GGW, and from south to north, starting with 01 in the United States and 51 in Canada (e.g., the fifth site from the south in the United States at about 1300 km from GGW is site 1305; the first site from the south in Canada at that distance is 1351). The arc distance is shown on the location of the southernmost sampler on Fig. 2-2. The numbers are centered on the sampler location. The GGW release site is southeast of 101, and the STC release site is between 1007 and 1008. Samplers in the United States were operated by NWS personnel, NWS cooperative observers, and DOE National Laboratory personnel. Samplers in Canada were managed by the AES.

Table 2-4 provides a detailed summary of the 77 primary ground-level sampling sites for ANATEX. The first column of the table gives the ANATEX site number, and the second column gives the six-digit World Meteorological Organization (WMO) ID number. The sites without WMO ID numbers are NWS cooperative observer sites. The third and fourth columns give the station name and the two-letter state or province abbreviation, where MB is Manitoba; ON, Ontario; QB, Quebec; and NF, Newfoundland. The fifth and sixth columns give the latitude and longitude, respectively, in degrees and hundredths (i.e., 4877 = 48.77°), followed by the sampling site elevation in meters.

In addition to elevation, land features were extracted from the 7.5-min-series topographic maps for each site throughout the United States and Canada. Columns eight and nine show the maximum and minimum elevations, respectively, in meters on the topographical map that has the sampler. Column ten is composed of three-digit numbers (third digit sometimes omitted) representing three variables. The first digit represents the population density, where four classifications are given depending upon the population surrounding the sampler location: (1) city (>100,000 persons), (2) town (10,000-100,000), (3) village (1,000-10,000), and (4) rural (<1,000). The second digit represents the land use surrounding the sampling site. Five land use categories are given: (1) commercial, (2) residential, (3) industrial, (4) farming, and (5) airport. The final digit, if included, represents a special category that includes any local surface features around the outlying area. These categories include (1) coastal/lake, (2) river valley, (3) prairie, (4) forested, and (5) marsh.

Column eleven represents the station affiliations given as follows:

- 2 NWS cooperative observer site;
- 3 NWS site;
- 4 Canadian site managed by AES;
- 5 Federal Aviation Administration;
- 6 EML.

The last column gives the time zone in hours from Greenwich Mean Time (GMT).

Table 2-4. Primary ground-level sampling sites*

Time Zone	-7	7	1	999995	9999
Affil.	7	w 01 m 01 4 4	м с м с м с с с с с с с с с с с с с с с	0 0 m m 0 4	m a m m a
Site Desc.	42	253 253 423 353 353	00000000000000000000000000000000000000	322 321 15 252 324 354	15 32 15 22 214
Elev. Min.	701	890 747 497 282 259	104071055656	786 256 314 259 439 312	1070 585 360 177 311
Elev. Max.	844	1045 814 588 460 488	7 4 8 0 8 7 0 7 0 8 8	838 341 402 302 491	1109 649 399 280 402
Elev.	718	964 791 503 305 273	1046の2177172	821 3993 469 348	1098 605 392 207 311
Lon.	10763	10307 10217 10075 10073 10005	00000000000000000000000000000000000000	10035 9542 9602 9240 9043 8693	10170 9980 9760 9580 9437
Lat.	4877	4405 4593 4677 4862 5110	348 348 348 348 348 348	3780 3912 4137 4255 4593	3523 3520 3540 3630
State or Province	MT	S S S O N O N O N O N O N O N O N O N O	CC CO WWW WC CO ON WWW WOO ON WWW WW WOO ON WWW WW W	KS KS NE IA WI ON	TX OK OK MO
Site Name	WHITE WATER	RAPID CITY LEMMON BISMARCK UPHAM DAUPHIN THE PAS	DENVER STERLING NORTH PLATTE AINSWORTH HURON MADISON SANTIAGO BRAINERD BIG FALLS DRYDEN PICKLE LAKE	CIMARRON PERRY OMAHA WATERLOO PARK FALLS GERALDTON	AMARILLO ERICK OKLAHOMA CITY TULSA NEOSHO
WMO #	1	726620 726695 727640 718550	2	725530 725480 727410 718340	723630 723530 723560
Site #	101	501 502 503 551 552	1001 1002 1003 1004 1005 1007 1009 1051	1301 1302 1303 1304 1305 1351	1601 1602 1603 1604 1605

Table 2-4. (cont.)

Time		0 0 0 0 0 0 0 0	1	
Affil.	w rv w w w w w w w w w w w w w w w w w w	m m m n m m	м м м м м м м м м м м м м м м м м м м	4
Site Desc.	25 25 15 15 12 21 251 251 315	15 441 25 31 12 15	25 22 22 152 121 223 324 354	
Elev. Min.	180 195 134 210 259 183 177 198 198	841 85 76 139 238	262 12 2 79 134 162 213 271 170	4
Elev. Max.	22222222222222222222222222222222222222	895 152 192 198 311 283	344 143 143 378 317 317 433 488 538	
Elev.	270 234 299 220 220 230 230	873 124 172 162 297 238	314 33 101 141 180 246 351 276 170	\vdash
Lon.	9222 9118 8968 8910 8925 8703 8437 8247	10218 9465 9227 8908 8412 8375	10092 9692 9267 9008 8672 8657 8255 8022 7817 7597	36
Lat.	3882 3993 4067 4220 44448 4575 4797 5127	3195 3235 3483 3898 3987 4297	9 6293 20183 9 69 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9	5375
ate or ovince	M H H H H H H O O N	TX TX AR IL OH MI	TX LLA LLA MS AL TN WV WV NY OB	QB
Site Name Star	COLUMBIA QUINCY PEORIA ROCKFORD MADISON GREEN BAY ESCANABA SAULT STE MARIE WAWA KAPUSKASING	MIDLAND LONGVIEW LITTLE ROCK VANDALIA DAYTON FLINT	DEL RIO VICTORIA JENNINGS JACKSON CAHABA PUMPING STATION NASHVILLE HUNTINGTON PITTSBURGH BUFFALO MANIWAKI CHIBOUGAMAU- CHAPAIS	
WMO #	724450 724396 725320 725430 726410 726482 727340 717380 717380	722650 722470 723400 724337 724290	722610 722550 722350 723270 724250 725200 717220	718230
Site #	1606 1607 1608 1610 1611 1612 1652 1653	2001 2002 2003 2004 2005 2006	2301 2302 2303 2304 2304 2304 2307 2307 2308 2351 2351	2353

Table 2-4. (cont.)

Time Zone	111111	1.5	1
Affil.	m 01 m m m m	9	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
Site Desc.	15 111 254 244 254 15	224	351 251 451 251 251 251 351 351
Elev. Min.	2 -1 165 213 73	110	27 27 0 0 0 0 0 116 0
Elev. Max.	250 250 311 146	369	50 17 15 22 22 235 366 366
Elev.	246 270 85 84	289	44 12 12 32 190 190 35
Lon.	9743 9005 8332 8003 7747 7380	7467	8503 8240 7998 7555 7547 7457 7075 6802 6627
Lat.	2590 2990 3395 3615 3898 4275	4078	2973 3125 3125 3527 3795 4167 4365 5022
State or Province	TX LA GA NC VA NY	ŊΩ	FL SC NC VA MA MA ME ME NF NF
Site Name	BROWNSVILLE GRETNA ATHENS GREENSBORO DULLES ALBANY	CHESTER	APALACHICOLA WAYCROSS CHARLESTON CAPE HATTERAS WALLOPS ISLAND ATLANTIC CITY CHATHAM PORTLAND CARIBOU SEPT-ISLES GOOSEBAY
ww #	722500 723110 723170 724030	! 1 !	722200 722130 722080 723040 724020 724070 725055 726060 727120 718110
Site #	2601 2602 2603 2604 2605 2606	2801	3001 3002 3003 3004 3005 3005 3007 3009 3051

*See text for units, destinations, and explanations.

Eight of the primary sampling sites were enhanced with an additional sampling unit for sample comparison. These sites provided duplicate data essential for developing quality assurance statistics. Sites 503, 1005, 1304, 1606, 1611, 2006, 2306, and 2605 provide duplicate samples, representing about 10% of all the ground-level data collected.

Each of the 77 primary sampling sites was provided with a sequential sampler (a programmable atmospheric tracer sampler, PATS) (two at duplicate sites). Controls in the sampler provided for automatic start at a preselected day and time for a preselected number of samples and duration of sampling (24 hour per tube in this experiment). Further description of the sampler is given in section 3. After 21 samples were collected, the lid containing the sampling tubes was removed for sample analysis (sent to the laboratory), and a fresh lid was attached in its place to continue the sampling program. Lids were changed on January 26, February 16, and March 9.

For ANATEX, 272 sampling lids were available. Each lid was baked out and tested for leaks before the start of the experiment by EML. Since about 340 lids were required for the experiment, lids that were removed during the first lid change on January 26 were sent directly to BNL for analysis, and returned to the sites for the March 9 lid change. ARLFRD trained sampler operators either by telephone or through correspondence, and was responsible for maintaining records on each unit. Lids were returned from each site to ARLFRD after each cycle for record-keeping quality assurance. Details of the sampler logistics are given in section 5.

Several months before the experiment, samples were taken at all sampling sites to determine contamination from spurious sources and tracer background values. The sampler location was moved at several sampling sites when analysis indicated possible interference to the perfluorocarbon analyses.

THE GROUND-LEVEL AIR SAMPLING SYSTEM

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New York, NY 10014-3621

The Environmental Measurements Laboratory's (EML) contribution to the ANATEX program consisted of the following:

- 1. Modifying the sampler units to improve performance, and eliminating the frequent causes of malfunctions experienced during previous tracer experiments (Lagomarsino et al., 1987).
- 2. Testing, preparing, decontaminating, and calibrating samplers for all primary surface sampling stations.
- Providing consultation to field operators in case of sampler malfunction(s), supplying parts for field repair, and if necessary, replacing units.
- 4. Sharing in the sample analyses with other laboratories (BNL and ARLFRD) because of the large number (7560) of surface samples.

3.1 The PATS Samplers

The programmable atmospheric tracer sampler (PATS) was the primary sampler of the perfluorocarbon tracers for all ANATEX surface stations. The sampler was initially developed by Russell Dietz of BNL, and was commercially manufactured for NOAA by the Gilian Instrument Corporation (Wayne, New Jersey). Funding was provided by the U.S. DOE. The unit, shown in Fig. 3-1, consists of two sections: the lid, air flow module (AFM), and the base, power control module (PCM). The entire unit is housed in a weatherproof 36 cm x 25 cm x 20 cm container and weighs approximately 7 kg. The lid holds 23 stainless steel sampling tubes, each packed with approximately 150 mg of Ambersorb adsorbent (Rohm and Haas Company, Philadelphia, Pennsylvania). The Ambersorb adsorbs the tracers from the sample air flowing through the tube. The sample air flow may be directed through any desired tube by means of a multiple port switching valve (Scanivalve, Scanivalve Corp., San Diego, California) that is controlled by the PCM.

The base of the PATS contains a constant mass flow pumping system that draws sample air through each tube. The flow rate is selected by an internal switch to draw either 10, 20, 30, 40, or 50 cc min⁻¹ of air. Programmable controls may be set for the number of samples, sample duration, and for single and multiple start and stop times over a 7-day period. The base controls are also used to assist in automated analyses when the lid is coupled to a gas chromatograph (GC). Power is supplied by an internal rechargeable 9-V battery for operation at remote locations, or by a charger where 110 V AC is available. A digital printer and integrated circuit memory module record the start time, the day of the week, and the tube number for each sample. Two liquid crystal displays (LCDs) show the clock time, day of the week, and current tube number.

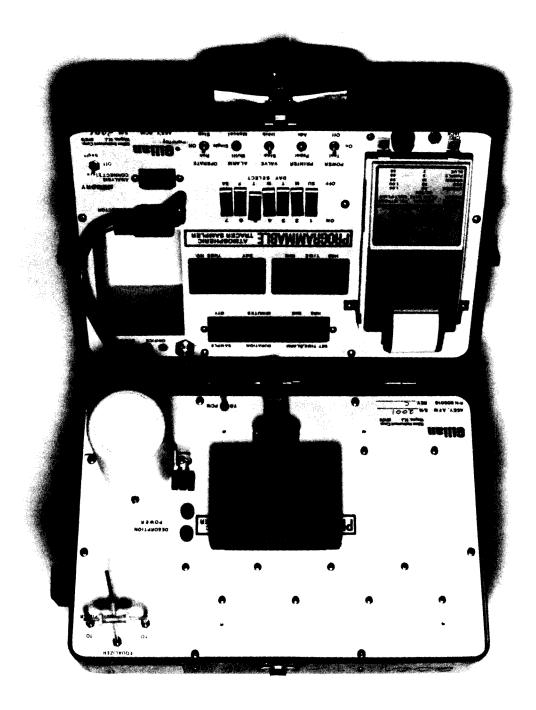


Figure 3-1. The ground-level air sampler for primary sites.

All lids are interchangeable with any base, so that when 23 samples have been collected, a new lid may be substituted to continue sampling.

3.2 ANATEX Ground-level Sampler Requirements

The ANATEX ground-level sampling plan called for 85 bases and 340 lids at 77 stations (eight units were colocated). The 85 bases could be easily supplied; however, the total lid inventory consisted of only 272 units. As a result, the ANATEX 84-day sampling period was divided into four sampling cycles, each cycle consisting of 21 days. The sample frequency was one air sample per day per tube at a rate of 50 cc min⁻¹ or 72 L day⁻¹. EML prepared and supplied all the required bases and lids for the first three cycles. On completion of the first sampling cycle, the sample lids were shipped to BNL, where they were analyzed and returned to the sampling sites for the fourth sampling period.

3.3 Sampler Modifications

The ANATEX program required continuous, reliable sampler performance over a 3-mo sampling period. The PATS field and laboratory performance records from previous experiments showed persistent sampler malfunctions in 3 areas:

- 1. Printer failures or jamming of the printer paper.
- 2. Sampling pump failures.
- 3. Internal battery failures.

To improve performance in these areas, EML's Instrumentation Division undertook the responsibility of designing improvements and modifications, fabricating the necessary hardware, and retrofitting all units.

3.3.1 Memory modules

The PATS printer paper tape output reflects sampler performance during the experimental period. Questions often arise concerning the date and time of sample collection, sample duration, whether multiple samples were collected on a single tube, and sample tube number. During past experiments, this information was on occasion lost because of printer failure or overwriting on the printer tape. The log sheets maintained by the sampler operator were sometimes unclear or incomplete, and therefore the information could not be recovered. Additionally, replacement printers are no longer manufactured, and currently available models require extensive modifications of the printer and base printer circuit board.

As a potential future replacement for the printer, a memory module was designed by EML to store the same information as would be transmitted to the printer (Polito, 1987). A memory device was affixed to each lid, and a related control circuit board was installed in each base. The memory module was connected to the base, by the operator, through its own special connector, and activated by a toggle switch located on the base face plate. Printer data from up to 96 samples may be stored before overwriting the memory. The information was retrieved with a portable printer or by a EML computer data acquisition system during GC analyses of the lids.

3.3.2 Variable-duty-cycle pumps

To determine tracer concentrations from the tracer collected, the accurate measurement of the total volume of sampled air for each tube is required. During past experiments, the manufacturer-installed Accuhaler pump failed excessively because of three major drawbacks in its design. First, the reproducibility of the volume of the sampling stroke (cc/stroke) was often in question. Second, the bellows was activated by a shaft that is very susceptible to wear. Third, the drive motor sometimes stripped its gears. The Accuhaler pumps were replaced by an EML-designed variable-duty-cycle pump that is physically and electrically interchangeable with the Accuhaler system. The pump is a further development of the battery-powered, tethered air pump system (TAPS) (Latner, 1986) used to collect samples at various altitudes with tethered balloons. The constant flow is regulated by a pressure sensor at the outlet side of the pump. The pressure is held constant by a pressure switch that controls the flow circuit, essentially an integrator that supplies to the pump motor a voltage ramp, rising or falling as the contacts open or close. The flow rate, set at 50 cc min⁻¹, may be lowered by setting switches that control the on-off cycling of the pump over a l-min period. A flashing light-emitting-diode (LED), mounted on the base, gives a visual indication that the pumping system is operating properly.

3.3.3 Battery low-voltage indicators

Power for the PATS unit is drawn from an internal 9-V battery that may be recharged with a portable AC charger. For ANATEX, the charger was connected at all times, since all samplers were at indoor locations where AC power was available. The sampler will not operate unless the battery voltage is greater than 6 V, even though connected to a charger. To monitor low battery voltage, a battery indicator circuit was designed and installed in each base. An LED, mounted on the base, activates when the battery voltage is below 6 V.

3.4 Preparation of the PATS Units

Since the PATS units were to be operated by inexperienced and nontechnical field personnel, it was desirable to furnish samplers that would maintain a high degree of reliable performance over the 3 month sampling period. Extensive preoperational testing procedures were implemented to minimize downtime.

In addition to the previously discussed modifications, the electronic functions of each base were checked for proper performance. The sampling pumps were calibrated and the batteries fully charged. Details of the test procedures and calibration methods will be described in a separate publication.

During ANATEX all samplers were placed at indoor locations because of the adverse environmental conditions expected during the winter months. The PATS sampling pumps operate from the inlet side so that sample air was drawn through each adsorbent tube. Outdoor air was drawn through a 6-ft (1.8 m) length of polyurethane tubing that had been connected to the lid sample inlet port. Any leak from the inlet port, filter, Scanivalve, or polyurethane tubing connections to the adsorbent tubes would allow indoor air to mix with the outdoor sample air stream, yielding a nonrepresentative sample. Indoor air may contaminate the samples with halogenated degreasers, solvents, etc. The indoor contaminants may be of such magnitude that they cannot be quantitatively removed during gas

chromatographic analyses and consequently could obscure the chromatographic peaks.

Each lid was tested for leaks by the pressurization procedure developed for CAPTEX (Lagomarsino et al., 1987). Faulty Scanivalves and adsorbent tube connections were repaired by the PATS manufacturer. Defective sample inlet ports and filters were either repaired or replaced at EML. Pressurization tests were repeated to verify that the deficiency had been corrected. Pressure leak tests were also performed after the 6-ft (1.8 m) of polyurethane tubing had been attached to the sample inlet port.

During analysis, the perfluorocarbon tracers retained on the Ambersorb absorbent from the sample air are desorbed by resistance heating of the stainless steel tubes to 400°C. Current (14.5 A DC) is supplied from a constant-current power supply through the Scanivalve solenoid assembly. The assembly consists of a 24-position rotary solenoid having two power decks capable of handling 20 A. Twenty-three leads are wired to the power deck, each connected to an adsorbent tube clamp. Two set screws, one located on the tube clamp and the other on an insulated rail, secure and provide the electrical connection to each adsorbent tube. The manufacturer specifies that the screws be torqued to maintain good electrical contact and to secure the adsorbent tube without piercing its thin stainless steel wall. During the preparation of the PATS units, lid inspections indicated that a number of set screws had either become loose or were completely dislodged. In the thermal desorption of the tracers for gas chromatographic analyses, poor contact from loose screws would probably result in incomplete desorption of the tracers because of low desorption temperature. This was not critical at EML because we had replaced the gas chromatograph AC desorption power source with a constant-current power supply. Regardless, all missing screws were replaced and all screws were torqued to the manufacturer's specifications prior to shipment to the field.

An essential requirement of the pre-experiment preparation was the quantitative decontamination of the adsorbent tubes so that residual compounds from previous use would not contribute to or interfere with the ANATEX analytical results. To assure that all tubes of each lid were purged of all contaminants, each tube was thermally desorbed by a bake-out process with nitrogen gas flow. The bake-out system consisted of 10 bases with lids. Each base controlled the sequence of tubes within the associated lid. The lids were electrically connected in series to a constant current power supply for desorption heating. High-purity nitrogen was used as the purge gas. By setting the current at 16 A DC, the desorption temperature exceeded that used for the gas chromatographic analyses. Bake-out time was 15 min per tube with the nitrogen purge gas flow rate set at 40 cc min-1. On completion of the bake-out, 2 lids from each bakeout batch of 10 lids were randomly selected and 4 tubes also randomly selected from each lid were analyzed for contaminants. A total of 31 bake-out batches were required for the entire lid inventory (the last several batches contained less than 10 lids). The results of analyses of adsorbent tubes from 6 of the 31 bake-out batches exhibited chromatographic peaks above the expected GC background. The bake-out procedure was repeated for each contaminated batch and the adsorbent tubes were reanalyzed. No additional decontamination was required after the second bake-out run.

3.5 Sample Analysis

A total of 133 ANATEX lids, representing 2940 samples, were analyzed by EML. The analyses were performed by the gas chromatography-electron capture system developed at BNL (section 4). Quantitative results for the three ANATEX tracers, PMCH, oPDCH, and PTCH were obtained. Sample concentrations of four additional perfluorocarbon compounds present in ambient air but not deliberately released for ANATEX, PMCP, mcPDCH, mpPDCH, and ptPDCH were also obtained. This additional information was provided to assist in quality assurance evaluations. A total of 20,580 individual tracer determinations were made. All information pertaining to both sample collection and analysis were incorporated into the EML ANATEX data base. Appropriate flags identifying specific problems with either sampling or analysis were affixed to each sample.

4. DESCRIPTION AND DESIGN OF PERFLUOROCARBON TRACER (PFT) ANALYSIS SYSTEM

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The PFT system was first proposed to NOAA more than a decade ago by James Lovelock (1974). Its practice has been implemented by the U.S. DOE at its BNL and EML facilities and by NOAA in terms of quantitatively and, more or less, routinely releasing, collecting, and automatically analyzing PFT air samples.

Before describing the PFT technology in detail, it will be useful to look at a simplified picture of how the tracers are analyzed, in order to understand the advantages of the PFTs over other types of gaseous tracers. The PFTs are analyzed by gas chromatography, shown in a simplified schematic in Fig. 4-l. The constituents in an air sample are thermally desorbed from the sample tube and are injected into the carrier gas stream via the sample valve. Before entering the chromatographic column, all the components will be present as a "slug" (see the square wave in Fig. 4-la). After passing through the column, the constituents will be physically separated to an extent that depends on the nature and conditions of the column. However, the atmosphere contains many compounds whose concentrations exceed those of the PFTs and that are detectable in the electron capture detector (ECD) used to measure the PFTs. Included are 0_2 , nitrogen oxides, chlorofluorocarbons (CFCs), SF6, and others, each of which could interfere with the early-eluting PFTs (Fig. 4-1b). As is described later, physical means (e.g., sampling onto an adsorbent with subsequent purging) removes most of the oxygen and some of the CFCs, but a catalyst bed operating at about 200°C (Fig. 4-2) is needed to destroy many of the remaining intefering compounds so that the surviving PFTs can be detected (Fig. 4-1c). The importance of the catalyst bed should not be underestimated in the successful determination of PFTs.

It is the physical and chemical inertness of the PFTs that not only prevents their loss in the atmosphere but also helps in their separation and analysis from less stable interfering compounds and makes them biologically inactive; thus they are perfectly safe to use (Dabberdt and Dietz, 1986). Because of their low solubility in H₂O and moderate vapor pressure, they are not readily scavenged or deposited in the atmosphere, but, unlike SF₆, their vapor pressures are low enough to allow them to be readily sampled onto solid adsorbents. Their limited industrial use not only results in a low ambient background concentration, but also precludes the possibility of numerous higher local concentrations that might confuse atmospheric tracer experimental results.

The high affinity of PFTs for reaction with electrons makes them some of the most sensitive compounds for detection on the ECD, which is a small (0.1 to 0.2 mL) reaction chamber containing an electron source. The cloud of electrons in the chamber is periodically collected, producing a current. When tracer molecules enter the cell, the reacted electrons cannot be collected; this resulting reduction in current is a measure of the PFT concentration.

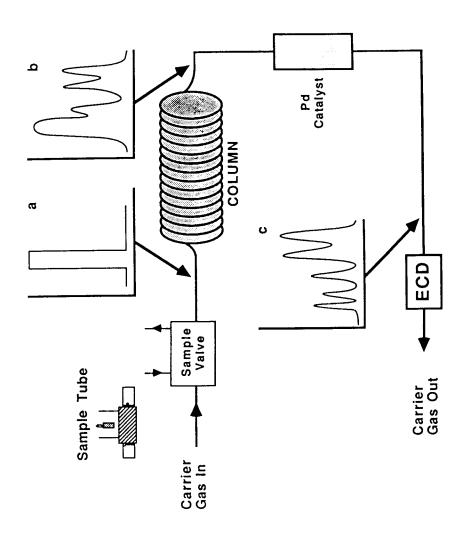


Figure 4-1. Simplified schematic of a gas chromatograph (GC) system showing the function of the sample valve, the GC column, and the palladium (Pd) catalyst bed prior to electron capture detection (ECD). (a) Sample; (b) Interfering compounds and PFTs; and (c) PFTs alone.

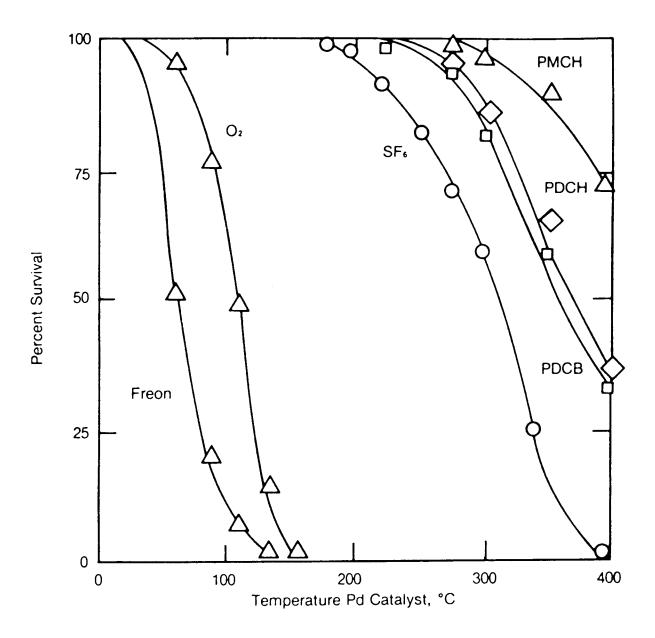


Figure 4-2. Effect of catalyst bed temperature on destruction of PFTs and interfering compounds such as $\rm O_2$ and CFCs (chlorofluorocarbons).

4.1 Previously Used PFTs

Two example chromatograms of the analysis of 14.5- and 3.8-L ambient air samples are shown in Fig. 4-3. Specific details of the sampling and analysis technique are described later. Briefly, it consisted of pulling the air through tubes packed with a solid charcoal-like adsorbent (Ambersorb) which was then thermally desorbed into the gas chromatograph. The identification of the PDCB, PMCP, and PMCH peaks as well as the group of peaks representing the PDCH isomers had been previously determined (Dietz and Senum, 1984). The definitions of the symbols for each of the named peaks are given in Table 4-1. By collecting and analyzing ambient air samples of about 0.5 to 14.5 L in volume and plotting tracer quantity versus air sample volume, as shown in Fig. 4-4, it was possible to determine the ambient air concentrations of each of the PFTs, as listed in Table 4-1. The standard deviations on the concentrations do not reflect the uncertainty in the calibration gas standards, which is another +5%.

Table 4-1.	Identification	οf	current	and	potential	PFT	components
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			Elution*	Ambient air
No.	Symbol	Name (perfluoro-)	time,min	conc., fL/L
1	PDCB	dimethylcyclobutane	1.26	0.34 + 0.01
2	PMCP	methylcyclopentane	1.32	3.22 + 0.03
3	PMCH	methylcyclohexane	2.08	3.5 + 0.2
4	ocPDCH	ortho(cis)DCH**	3.43	0.3 + 0.1
5	mtPDCH	meta(trans)-DCH	3.97	8.0 + 0.8
6	pcPDCH	para(cis)-DCH	4.04	3.1 + 0.5
7	PECH	ethylcyclohexane	4.12	<2 -
8	otPDCH	ortho(trans)-DCH	4.16	0.1 + 0.05
9	mcPDCH	meta(cis)-DCH	4.24	6.7 + 0.3
10	ptPDCH	para(trans)-DCH	4.62	4.7 + 0.4
11	i PI	l-indane	4.53	? –
12	2 PI	2-indane	5.99	?
13	1 PTCH	1-trimethylcyclohexane	8.98	<0.07
14	2 PTCH	2-trimethylcyclohexane	9.50	<0.03

^{*}Mid-point of tracer peak in gas chromatogram at conditions given in Fig. 4-3, but with column at 160°C.

The actual determination of which isomers of PDCH were represented by the peaks in Fig. 4-3 at retention times of about 6 to 8 min (the numbers at the top of the figure) was only recently resolved. The elution order for the isomers of the hydrocarbon dimethylcyclohexane (DCH) was previously determined by gas chromatography on a graphitized carbon support (Engewald et al., 1977). The seven isomers of DCH (the cis and trans of each of the ortho, meta, and paraisomers plus the 1,1-isomer) were available as relatively pure hydrocarbons. These were analyzed on the same support used in our PFT gas chromatograph, confirming the elution order found by Engewald et al. (1977).

^{**}ortho, meta, and para mean the 1,2-, 1,3-, and 1,4-isomers; cis and trans mean the alkyl groups (e.g., methyl) are on the same or opposite sides, respectively, of the molecular plane; DCH represents dimethylcyclohexane.

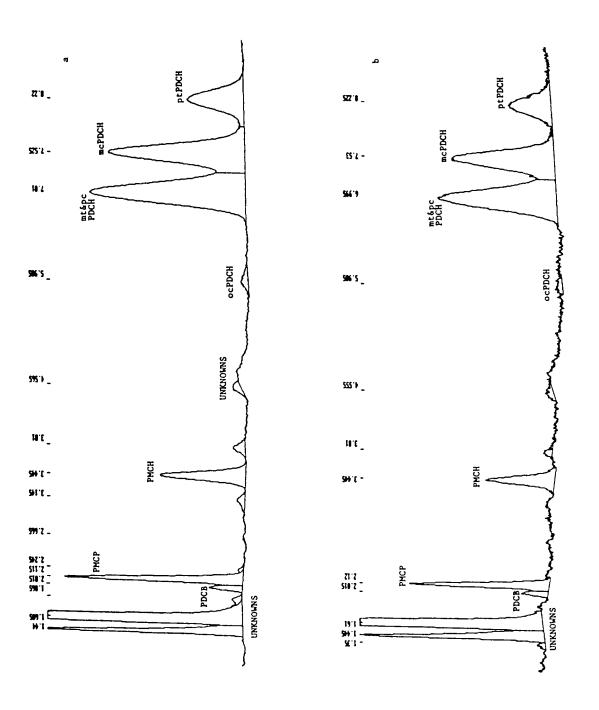
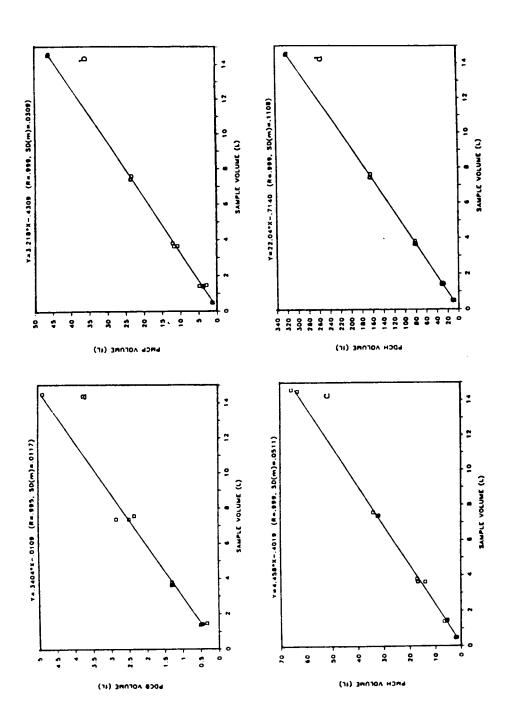


Figure 4-3. Chromatograms of adsorbent-collected ambient air samples analyzed on a 6-ft (1.8-m) by 0.093-inch (2.36-mm) ID, 0.1% SP 1000 on Carbopack C (Supelco) column at 140°C with 22 mL/min of 5% H₂ in N₂. The numbers at the tops of the chromatograms are retention times (min). (a) 14.5-L air sample; (b) 3.8-L air sample.



Quantity of four PFTs found in the ambient air for samples ranging from 0.5 to 14.5 L. The slope of the line representing PFT quantity (fL) versus air sample volume (L) is the back-ground ambient air concentration (fL/L). See Table 4-1 for tracer names. (a) PDCB; (b) PMCP; (c) PMCH; (d) PDCH (the total of all isomers). Figure 4-4.

Starting with pure quantities of the ortho-, meta-, and para-xylenes as well as ethyl benzene, the catalytic (cobalt trifluoride) fluorination by the PFT manufacturer (ISC Chemicals Limited, Avonmouth, Bristol, Great Britain) yielded the perfluorinated versions. Subsequent analysis by thermal conductivity gas chromatography gave the chromatograms shown in Fig. 4-5 and the PDCH compositions shown in Table 4-2. Thus, starting with pure ortho-xylene, the resultant product is only 84.4% ortho-PDCH, 46.4% as the cis isomer and 38.0% as the trans isomer. The purities of the resultant meta- and para-PDCH, which were only 83.1 and 91.8%, respectively, as shown in Table 4-2, were computed by an interative procedure since not all of the isomers are separately resolved. In fact, as shown in Fig. 4-5, only ocPDCH (the first peak) and ptPDCH (the last peak) are clearly resolved. The mtPDCHs and pcPDCHs are nearly coincident as are the otPDCHs and mcPDCHs. In addition, the PECH is right between the two meta-PDCH peaks.

Referring back to the ambient air chromatograms of Fig. 4-3, it was possible to identify the PDCH isomers in the last four peaks, which have been appropriately labeled. The ambient-air concentration of each of the six PDCH isomers listed in Table 4-1 was computed as follows. The ocPDCH concentration was determined directly because it was separately resolved. Then the otPDCH was computed assuming the same ratio as in the manufactured ortho-PDCH (Table 4-2), which was then subtracted from the next-to-the-last peak to leave the ambient concentration of the mcPDCH. Note that the peak in Fig. 4-3 was only labeled as mcPDCH because the otPDCH was trivial (compare the ocPDCH peak). Similarly, the ptPDCH was directly determined (it stands alone), and the computed pcPDCH was then subtracted from the combined mtPDCH and pcPDCH to yield the mtPDCH.

Table 4-2.	Composition*	of PDCH	isomers,	percent	(mol))
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	Ortho-	Meta-	Para-
Component	PDCH	PDCH	PDCH
PMCH	2.4	1.0	
oc PDCH	46.4	3.1	0.1
mtPDCH	6.6	38.7	3.8
pc PDCH	0.3	4.1	36.7
otPDCH	38.0	2.6	0.1
mcPDCH	5.6	44.4	4.2
ptPDCH	0.4	6.1	55.1
Totals	99.5	100.0	100.0
Primary			
cis and tran	s: 84.4	83.1	91.8

^{*}Analyzed by thermal conductivity (TC)GC which, unlike the ECD, gives the same response for each isomer.

The resultant ambient air concentrations for each of the PDCH isomers are only good estimates because the relative response of the ECD to each of the isomers is not the same. The ECD was originally calibrated with the meta-PDCH, which is the predominant isomer in the ambient air at 15.9 of the 22.0 fL/L total (see the slope from Fig. 4-4d) or 72%; thus the meta-PDCH concentrations

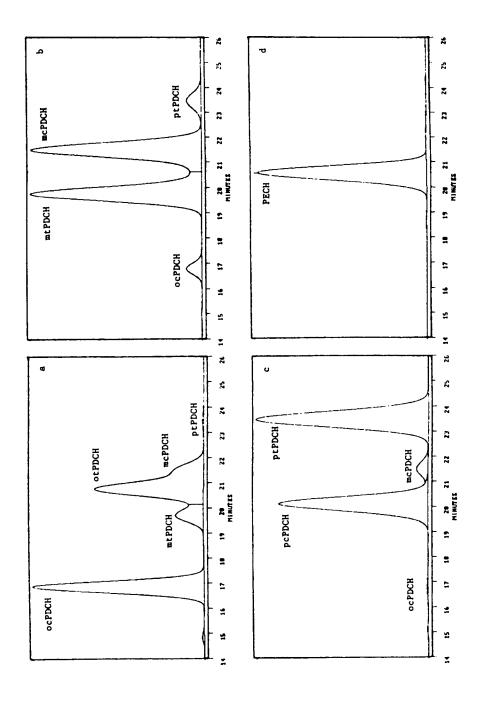


Figure 4-5. Identification of the relative elution order of the isomers of PDCH as well as the location of PECH (see Table 4-1 for tracer names). (a) ortho-PDCH; (b) meta-PDCH; (c) para-PDCH; (d) PECH.

should be reasonably accurate. A preliminary evaluation of their ECD response showed that only the ptPDCH, the last peak, has a significantly lower response, indicating that its ambient concentration might be higher. Further laboratory studies will be conducted to accurately determine this important variable of ECD response.

From the ambient chromatograms in Fig. 4-3 and the known concentrations of each PFT (Table 4-1), it is possible to see that the limits of chromatographic detection for tracer volumes range from 0.2 fL for PDCB and PMCP, and 1 fL for PMCH and ocPDCH, to about $1.5\,$ fL for ptPDCH.

4.2 ANATEX PFTs

There are two basic processes that have been used commercially for the production of PFTs, here restricted to the family of perfluoroalkylcycloalkanes because they have the maximum response to the ECD. Other perfluoroalkanes and other perfluorocarbons are 2 or more orders of magnitude poorer in detection capability (Dabberdt and Dietz, 1986). The one process, cobalt trifluoride catalyzed fluorination, is available from ISC Chemicals Limited in England. The purity of ISC's tracers has been from 85% to 99%, and a limited amount of the other existing and identified PFTs as impurities, generally less than 1%. This can be important in a tracer experiment if the PFT being released has a 1% impurity of another also being released. Of course, a correction can be made based on the analyses of the impurities in the released PFTs, but that correction becomes more significant as the number of tracers used in any one experiment increases. Fortunately, ISC has been able to keep the purity of the PFTs it supplies quite high for these applications. All of the PFTs in Table 4-1 with the exception of No. 1, PDCB, are supplied by ISC.

The other process for making PFTs is the dimerization of perfluoroalkenes at high pressures (up to 3000 atmospheres) and moderate temperatures (400°C). Originally patented by E.I. duPont in Wilmington, Delaware, more than 19 years ago, the technique was used at one time to make PDCB. DuPont abandoned the technology more than 5 years ago; other companies can now produce a number of the dimerization products, generally perfluorodialkylcyclobutanes, but at costs up to 10 times or more than those of the PFTs from ISC. However, PDCB is a potential continental-scale tracer because it has the highest ECD response of any of the PFTs and has a low ambient concentration. Unfortunately, at the scale of the quantities used in long range tracer experiments, no single manufacturer is willing to set up the specialized equipment necessary to work with the reactive starting materials.

A number of compounds were suggested to ISC, one being perfluorotrimethylcyclohexane (PTCH) and another, perfluoroindane (PI). A mixture of these two new tracers plus four of the earlier PFTs was analyzed as shown by the chromatogram in Fig. 4-6a, the figure shows the elution of the 1 at 4.5 min and of the seven isomers of PTCH at 6.3 to 11.2 min. The two major isomers of PTCH were arbitrarily named. Ultimately they will be identified to locate potential future tracer types. The retention or elution times of all the PFTs at the 160°C column temperature are shown in Table 4-1.

A 50 L ambient air sample was analyzed under the same GC conditions. The normal PDCH isomer distribution was attained as shown in Fig. 4-6b. Note that the 1 PI in the standard had the same elution time as the ptPDCH in the air

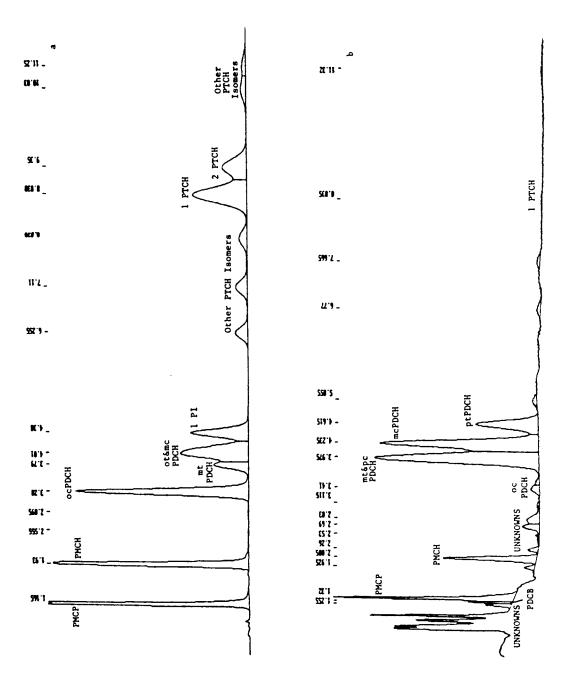


Figure 4-6. Chromatograms of (a) about equimolar standard of PMCP, PMCH, ortho-PDCH, meta-PDCH, PI and PTCH; and (b) about 50-L of ambient air, but with the column of Fig. 4-3 at 160°C. The numbers at the tops are retention times (min).

sample. This alone would preclude PI as a continental-scale tracer because the background ptPDCH would interfere. But it was also determined that PI was sensitive to catalyst destruction, depending upon the catalyst's operating condition and cleanliness. Thus PI was temporarily abandoned as a tracer pending further research on alternative catalysts.

In Fig. 4-6b, it is difficult to see if any PTCH exists in the ambient air. It certainly would appear to be less than the ocPDCH level. Figure 4-7 shows an expansion of that chromatogram in two regions. The early region shows that the PDCB is still separated from the PMCP. The late region shows that at the l PTCH elution time, the very small peak would correspond to an ambient air concentration of about $0.07~\rm fL/L$, which would make it a viable continental-scale tracer.

It was shown that the family of PFTs can be uniquely detected on a single analysis of an air sample by a special gas chromatograph to be described in detail later. Table 4-3 lists the currently usable PFTs, their limits of detection, and the principal supplier. There is a good likelihood that additional research into fluorination of alkylcycloalkenes and the dimerization of perfluoroalkylcyclobutanes will lead to a much larger family of useful PFTs.

No.	Limit of	
	Tracer	detection, fL
1	PDCB	0.2
2	PMCP	0.2
3	PMCH	0.9
4	ocPDCH	1.0
5	mtPDCH	4**
6	ptPDCH	1.5
7	PTCH	3.5

Table 4-3. Currently usable PFTs*

4.3 Laboratory Gas Chromatograph System

The system is composed of the gas chromatograph (GC), the data handling devices, gas standards, and the PFT adsorbent samplers. The use of the system requires a temperature-controlled room and an uninterruptable power supply capable of supporting the data handling system during brief power failures. The GC has internal battery backup for its microprocessor.

The operation of the GC can first be given in a simple overview. Whether from programmable or passive samplers, the sample is automatically thermally desorbed and passed through a precut column and a Pd catalyst bed before being reconcentrated in an in situ trap. The trap prevents the collection of unwanted low-molecular-weight constituents as well as the temperature-programmed precut

^{*}All PFTs supplied by ISC Chemicals Ltd. (England) except PDCB, which is available in small quantities elsewhere.

^{**}Determined by difference.

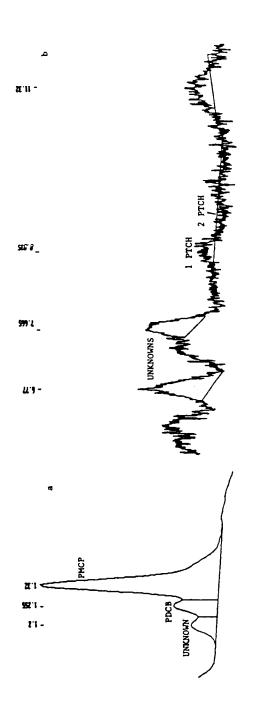


Figure 4-7. Expansion of Fig. 4-6b. (a) Early region showing resolution of PDCB and PMCP; (b) late region indicating the detection of negligible quantity of PTCH in ambient air.

column, which further prevents the passage of unwanted high-molecular-weight constituents. After thermally desorbing the trap, the PFTs are passed through another Pd catalyst bed followed by a permeation dryer and then separation in the main column and detection in the ECD.

The current configuration of the GC system (Fig. 4-8) was used to produce the chromatograms shown in Fig. 4-6. Two processes occur during a single cycle: analysis of a previously collected sample and loading of a new sample onto the trap. At the start of the cycle, the FD valve and the Florasil trap valve (FS) turns on. Note that all the valves are shown in their off position; on means the FS valve rotor turns 90° and the others, 60°. Thus, when heat is applied to the FS trap, the adsorbed PFTs are flushed out through catalyst bed A, catalyst bed B, the dryer, the main column, and the detector (ECD). As shown by the chromatogram in Fig. 4-6, the entire time for the last PTCH isomer to elute is under 12 min; therefore the cycle time was set for 12 min.

However, during this time, another sample tube is desorbed, processed, and collected on the trap. For the first 3 min, the sample tube is purged of oxygen by the carrier gas (5% $\rm H_2$ in $\rm N_2$). Then both the PC and SV are turned on and heat is applied to the sample tube to sweep the PFTs into the precut column, a 22-in (56 cm) by 0.113-in (2.9 mm) thin-walled stainless steel column packed with Unibeads 25 (Alltech) at 85°C. The unknown, early-eluting interfering compounds will flow out of purge vent #2. Just before the first PFT elutes from the precut column, the FD valve is turned off and the FS trap is opened. This allows the PFTs to be collected in the Florasil trap as they leave the precut column, which is ohmically heated to a higher temperature. When the last PFT component has entered the trap, all the valves return to their off position (at 9.6 min), which allows the precut column to be backflushed at the higher temperature for more than 2 min to eliminate any heavy components.

The precut column system prevents components lighter than the first PFT from entering the catalyst bed A or the trap. Components heavier than the last PFT selected for analysis are also precluded. By tailoring the precut column temperatures, the PFT "window" can be increased or decreased at either the beginning or the end.

As mentioned earlier, the catalyst is important in removing interfering compounds. With this system, the PFT sample passes once through catalyst bed A on its way into the trap, once again upon recovery from the trap, and once through catalyst bed B. This assures a good cleanup of the sample.

The data-handling system is a basic Nelson Analytical 3000 Chromatography system with an IBM PC/AT, an ink-jet printer, A/D converters, and the Nelson 2600 Chromatography Software, set up in the laboratory as shown in Fig. 4-9. Other appropriate software and hardware complete the system, which currently handles three GCs for the analysis of PFTs. Once a data collection method has been stored in the A/D box, the computer can be used for other operations, such as checking previous data for proper peak integration, while the A/D box stores the current analysis output. The system data storage is sized such that chromatograms for up to 25 to 35 analyses can be stored on one floppy disk, thus accommodating an entire PATS lid or capillory adsorption tube sampler (CATS) rack.

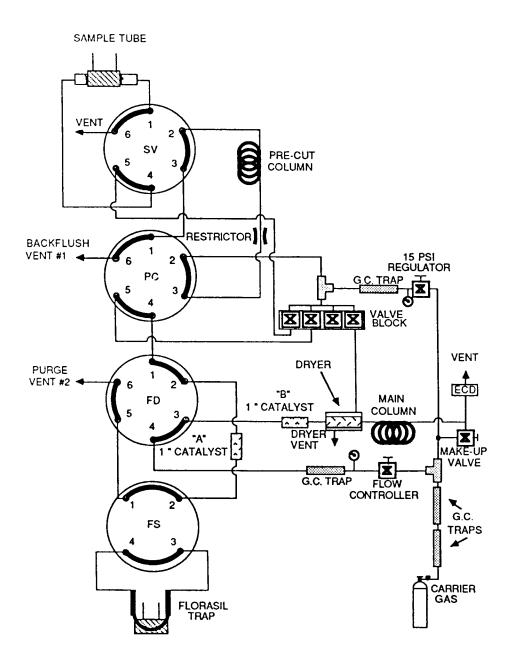


Figure 4-8. Schematic of the laboratory GC plumbing. SV, Sample valve; PC, precut column backflush valve; FD, flow direction valve to isolate the chromatography occurring in the main column from the loading of the next sample; FS, Florasil trap valve. All valves are shown in their off position.

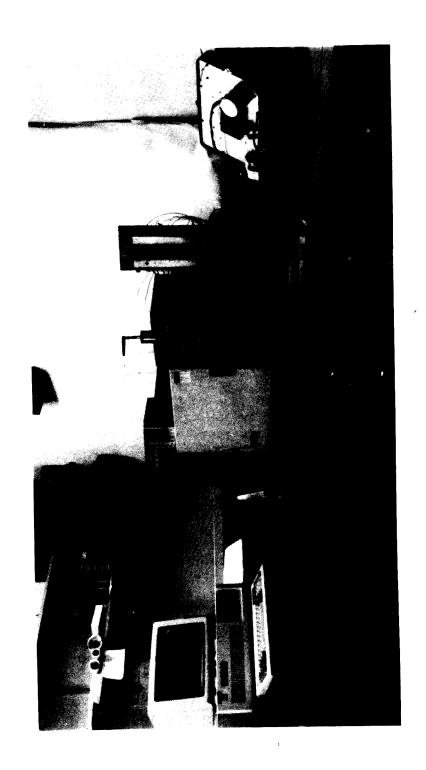


Figure 4-9. Gas chromatograph laboratory system. The IBM PC/AT is on the left followed by the printer, the Nelson A/D converter, the GC with recorder on top, the CATS desorption rack, and a BATS.

Gas standards for calibrating the GC have been prepared in-house as well as commercially (Airco Industrial Gases, Riverton, New Jersey, in their Spectro Seal aluminum cylinders) in the working range of 1 part per 10^8 , 1 part per 10^{10} , and 1 part per 10^{12} . BNL prepared primary standards in the range of 100 to 1000 part per 10^6 in He using pressure-volume techniques, which were corroborated by analyzing on a thermal conductivity detector (TCD) GC. The working-range cylinders were then prepared by pressure-dilution in 100-fold steps, using ultrapure air (BNL standards) or nitrogen (Airco standards). Airco has prepared the cylinder standards on a very large manifold accommodating up to 24 cylinders. Thus Airco can make one large batch of a PFT standard to be distributed in cylinders to many users of the PFT technology such that every one has the same working standards.

BNL has prepared working standards containing different mixtures of PFTs, one containing PDCB, PMCH, and mPDCH, and another containing PMCH and mPDCH. Airco had previously prepared one set of standards containing PMCP, PMCH, and mPDCH. It also prepared a large batch for ANATEX containing PMCP, PMCH, oPDCH, pPDCH, and PTCH.

The working standards are corroborated by comparing them with dynamically prepared PFT mixtures by passing nitrogen at a measured flow rate over temperature-controlled, gravimetrically calibrated PFT sources.

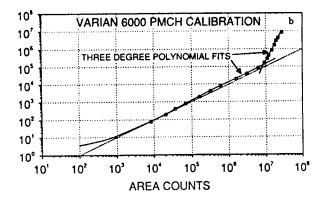
Sampling of either of the standards, working or dynamic, is accomplished by passing a set flow rate of the PFT standard through a BATS tube or CATS for a known period of time and then analyzing on the GC system. If preset flow restrictors are used to deliver 50 cc/min of the gas standard at tank pressure, a 1-min sample of the 1 part per 10^{12} standard would contain just 50 fL of each tracer. By increasing the standard loading time automatically, using a BATS base to increment the time, and by switching to the higher working standards once a 30- to 50-min sample of two decades lower is loaded, it is easy to prepare sample tubes containing PFTs from 50 to 10^7 fL (the latter is 20 min of 1 part per 10^8 at 50 cc/min). Since the standards can readily be loaded onto CATS tubes, boxes of such samplers are routinely stored and used in the laboratory for calibrations about two to three times daily.

A complete calibration curve can be run using the prepared standards, but in two modes, as shown in Fig. 4-10. Normally, as the quantity of tracer analyzed increases, the electrometer gain is reduced an order of magnitude when its output nears 1 V, the Nelson system voltage input limit. If the range 10 areas are multiplied by 10, the tracer volume versus peak area data continue on a smooth curve above the range-1 overload point, which, for PMCH, occurs at about 10^5 fL. It is apparent from Fig. 4-10a that the data in the region up to about 10^3 fL (1 pL) fall on the unity slope line. But from 10^3 to 10^4 fL, the curve displaces to a new unity slope line before starting to curve again at the overload of the PFT-electron reaction in the ECD, which occurs at about 5 x 10^5 fL. These data are best fitted by a sixth-order polynomial with a usual tracer quantity prediction of about $\pm 4\%$ or better. Below 50 fL (the limit of the usual low end of the calibration), the polynomial deviated markedly from the unity line which is what is used in that region. Five femtoliter standards (1 min of 1 part per 10^{12} at 50 cc/min) confirmed the linearity.

The alternative approach, which was used for the ANATEX analyses, is shown in Fig. 4-10b. The electrometer range is not changed at the range-l overload. Although the peak heights do not increase above l V (the Nelson A/D cutoff), the

areas increase, because the peaks are broadening, but at a higher quantity-per-unit area rate. A third-order polynomial was fitted to the data below the 1 V overload (clearly evident at about 10^5 fL of PMCH), and another above that level. The precision of this approach appears to be as good as the former, but here there is no concern for guessing which electrometer range should be used when analyzing unknown samples, and, for ANATEX, the range-1 setting provided the maximum sensitivity for analyzing the ambient levels found in most ground-level samples.

Remembering that the limit of detection for PMCH was about 1 fL, the dynamic range would appear to be about 7 orders of magnitude. However, the GC has a memory of about 0.01% of the previous sample when analyzing the next, which then decreases at a slower rate upon subsequent analyses of lower concentration samples.



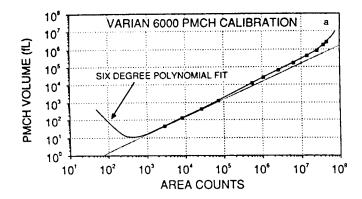


Figure 4-10. PMCH calibration data obtained and correlated in two ways.

- (a) The electrometer gain was reduced by one-tenth above 10° fL.
- (b) The gain was not reduced and the overload region was separately fitted.

4.4 Aircraft Dual-Trap Analyzer

The peak PFT concentrations typically encountered in long-range tracer experiments range from 1000 to 5000 fL/L at 100 km downwind to about 100 to 400 fL/L at 800 km downwind. These concentrations can easily be measured with BATS located both on the ground and in aircraft. The expense of an aircraft platform, however, mandates that the sampling occur where the plume is actually located. Thus, the need exists for a real-time PFT analyzer.

In the late 1970s, Lovelock, under a contract to NOAA, built a prototype instrument that was subsequently modified at BNL. The unit consisted of two adsorbent traps, packed with the same material used in the BATS and CATS, and an $\frac{10}{10}$ ECD chromatograph. While one trap was sampling at 1 L/min for 5 min, the other was heated to recover and analyze the collected PFTs. Since the traps reversed position every 5 min, no tracer was lost.

A new version of this real-time analyzer was built in 1983 for the fall CAPTEX experiment. Improvements allowed the separation of 3 PFTs in a 4-min chromatogram of a 4-min air sample collected at the rate of 1 L/min. The unit was able to see down to the ambient levels of PMCP and PMCH, indicative of the limit of detection of about 10 fL (D'Ottavio et al., 1986).

5. PFT SAMPLER DATA MANAGEMENT

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The conduct and management of the ANATEX field sampling program was a sizable logistics operation. A key function in the management of the operation was the need to unambiguously document each and every sample collected during the 3-mon period. The cooperation of each participating laboratory, of subcontractors, and especially of the large number of cooperative sample servicing personnel at each site was vital. The success of the sampling program was due in part to their extra efforts and conscientious attention to details.

The ground-level sampling sites were identified by a unique site identification number (site ID, see Table 2-4). That site ID was used to tag every item of correspondence, material shipment, etc. related to that location. In order to physically identify items by site, bar code stickers for each of the site numbers were printed and mailed to the respective sites prior to the beginning of the field sampling on January 5. An initial startup form was included, so that the observer could provide special requested information about the location. At the same time the observer attached one of the several site barcode ID stickers to the startup form. In that manner the site became tagged with the barcode ID number that would be attached to all samples returned from that location. Barcode labels were provided only with that initial mailing. Since the sets of numbers were unique to a single location, the location paperwork and samples could always be identified.

During early December, samplers were shipped to the field sampling sites from EML and from ARLFRD offices. Those samplers included the base pumping and control module, and a lid configured to collect samples during the first 21 days of ANATEX. Later in December, a second lid containing sampling tubes for 21 additional days (termed cycle 2) was shipped to the U.S. sites. (Lids for the full set of 4 cycles were sent simultaneously to the Canadian sites to avoid additional delays and potential problems while passing through U.S. and Canadian Customs.)

Each operator was provided an ANATEX observation form (Fig. 5-1) to be completed during the operation of each cycle of sampling (21 days for each individual lid). That form provided for entries on a daily basis concerning the status of the sampler, external sampler conditional indications, what sample tube was being collected, etc., and was returned with each lid when it was shipped from the remote location.

Although relatively clear and complete instructions were provided with the initial shipments of samplers, some operators had questions and difficulties. Telephone contacts were made with each operator during the first few days of the startup of sampling. Those calls confirmed the status of sampling at the remote sites. In nearly every case, the operator was able to be talked through problems in the startup of sampling, and a minimum of lost data was achieved.

place site barcode here

ANATEX 1987 OBSERVATION FORM

---INITIAL SETUP---

SI	TE I.D.	NO			OPERA	ATOR		
LI	D AFM S	/n			BASE	PCM S/N _		
ST	ART DAT	E			STAR	T TIME		
			TIME ZO	NE	MST, CST	, EST or AS	ST	
			DOC	UMENTAT I	ON OF OPE	RATION		
	LOC	CAL	I	NSTRUMEN	ΙΤ	STATUS C	łecks	OBSERVER
	DATE	TIME	TIME	DAY #	TUBE #	BATTERY	PUMP	INITIALS
START								
								
								
								
END								
END								
	COMMEN	NTS:						
						-		

PUMPING LED is flashing.

3. The status checks are "OK" if the LOW BATTERY LED is off and the

2. Complete this form as time permits but no more than one observation

per day. Observations on the start and end day are especially useful.

NOTES: 1. The time you selected from the Standard Operating Procedure.

Figure 5-1. Example form to be completed by operators at each PFT tracer sampling site during ANATEX field measurements.

Prior to the end of sampling during the first cycle, special instructions were mailed to the field sites concerning the removal of the cycle l lids and their replacement with cycle-2 lids. Telephone contacts were made with each operator at the time of the lid changes to assist in the changeover to the next cycle. Those calls confirmed the successful change of lids at the sites, or allowed assistance in the change when problems occurred. Corresponding telephone assistance was provided for each subsequent changing of sampling lids.

At the conclusion of each cycle of sampling, lids were packed in shipping cartons at the field sites and returned to ARLFRD in Idaho Falls for inspection and check-in. The memory module records of sampler pumping operations were extracted for each lid. The backup printer tapes of sampler pump operation for each lid were reviewed and filed. The sampler pump tape logs were filed and compared with the dumps of memory module records of sampler pumping operation. Differences were noted and reconciled if possible.

The records of sampler operation and details of abnormalities in sampling were entered into a computerized data base. That data base contained the cross referencing of sample lid ID, site ID, dates and times of sampling for each tube in the given lid, and a code value or "flag" describing the known exceptions in its use or performance. Those descriptors were retained in the ANATEX data archive files.

Following the inspection, check-in, and documentation of lid usage, the sampler lids were distributed among the three laboratories (BNL, EML, and ARLFRD) for gas chromatographic analyses. Printed copies of sample lid usage and performance were prepared for use by the laboratories during gas chromatographic analyses. Cycle-l lids were sent to BNL for rapid analysis and preparation for use during cycle-4 sampling. Upon completion of the chromatographic analyses and preparations of the lids for reuse, they were returned to ARLFRD for final inspection and shipment to the field sites. Following completion of laboratory analyses of lids from the other cycles, all lids were returned to EML for inventory, storage, and repairs as needed.

The results of laboratory gas chromatographic analyses were written on magnetic tapes and disks. The summary results were sent to ARLFRD and combined into the comprehensive data archive. That archive represents one form of the ANATEX data base. Magnetic tapes and listings were prepared from that archive for follow-on analyses and quality assurance assessments.

6. PFT DATA QUALITY ASSURANCE

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The perfluorocarbons used as tracers in ANATEX are extremely stable non-toxic compounds, measurable at very low concentrations by gas chromatography and electron capture detection. The tracer is recovered from the sampling tube by thermal desorption before chromatographic separation and electron capture counting. Air concentration is calculated from this recovered tracer.

ANATEX measurements are archived differently from the way perfluorocarbon data have been archived in the past. Each excess concentration is given with an objective uncertainty, a subjective flag, and additional quality assurance values.

6.1 Excess Concentration

The excess concentration (X) reported for each sample in deci-femtoliters per liter, dfL/L (10 dfL = fL), is determined from the calculated concentration C and the background concentration B by

$$X = C - B + U . (1)$$

In Eq. (1) the calculated concentration is the ratio of the measured tracer volume from the laboratory analyses to the calculated air volume; B is based on the cumulative calculated concentration distribution profile for the entire sampling lid containing that particular sample; the uncertainty U is determined from the background uncertainty and the analysis uncertainty. The various terms in Eq. (1) are discussed in detail in sections 6.2-6.4. Excess concentrations are listed in the Appendix in tabular form for quick reference by date and sampling site.

6.2 Calculated Air Volume

The pumps on each instrument were calibrated before the instruments were sent out to the field and when they were returned to the laboratory. During ANATEX, 95% of all ground-level samplers showed the pre- and post-experiment calibration to be within +15%. However, we determined that there was a considerable variation in the flow rate between sampling tubes within a lid. Ten percent of the lids showed sampling tube flow rate variations of as much as 50%. Although the pump was very likely pumping at the "calibrated" rate, air was not necessarily drawn through the sampling tube at that rate. This result is not surprising because there are a number of tubing connections, absorbent material packing from tube to tube may differ, and there is the potential for kinks or other constrictions to the tubing.

Flow rate variations were accounted for by using a reference PFT, ptPDCH. It was not deliberately released and was not present as a significant contaminant in any of the other tracers. Therefore it could be used as an

excellent standard since its atmospheric background concentration is very stable at 4.5 fL/L. The actual air volume (V_a) can be computed for each sample by

$$V_a = V_{ptPDCH}/4.5 \tag{2}$$

where V_{ptPDCH} is the measured ptPDCH volume. It should be noted that the ptPDCH present at the 0.5% level in the STC tracer was sufficiently small to have little effect on the computations in Eq. (2).

The cumulative frequency distributions of ptPDCH are shown, by analysis laboratory, in Fig. 6-1. Ideally, the slopes should be near zero. Differences from the zero slope must be attributed to air flow variations, measurement problems, and analyses uncertainties. Relatively small slopes with little distinction between laboratories can be seen above the 20th percentile.

6.3 Background

When we examine a cumulative frequency distribution for all measured samples, we find that a plume is present about 30% of the time. This is illustrated on Fig. 6-2 for PMCH, oPDCH, and PTCH using BNL data. If the ambient background concentration were constant, the distribution would be flat and then slope rapidly upward, indicating excess above background or plume. However, analysis uncertainty of about 10% as well as real variation in background could easily account for the slight increase in background slopes shown in the figure. Note that the PMCH distribution is nearly flat until the 75th percentile. The slopes in the backgound region for oPDCH and PTCH are progressively steeper, indicating a greater analysis uncertainty at these lower concentrations. However, the rapid slope increase above which a plume is indicated is still evident for both tracers.

In our analysis of the data, we proceeded under the assumption that the ambient concentration distribution on any one sampling lid (21 days) would be similar to the distribution over the entire experimental period. Therefore, the 40th percentile concentration on each lid for each tracer was chosen to best represent the ambient background for that lid--40% being the "plateau" frequency well below possible plume frequencies and well above occasional steep slopes at low frequencies due to analysis uncertainty. It was necessary to consider each lid individually because differences in laboratory conditions led to larger variations in background results.

The quality of the concentration and background calculations is based, to a large extent, on the assumption that the ptPDCH can be used as an ambient reference tracer [the air volume in each sampling tube is derived from the reported ptPDCH tracer volume — see Eq. (2)]. This is supported by the results in Table 6-1, which summarizes the 40th percentile cumulative concentration for all tracers reported by the laboratories. The values were determined by assuming a 72 L sample was collected. The variation between the assumed ptPDCH ambient background of 4.5 fL/L and the reported values was the smallest of all nonreleased tracers; even at ARLFRD, the difference was only 15%. The other aspect of this table that should be noted is the consistency of released tracer background levels between laboratories. For the tracers oPDCH and PMCH, the maximum variation in background is 14% and 3%, respectively. PTCH background values are much more variable due to a contaminant interference that depended

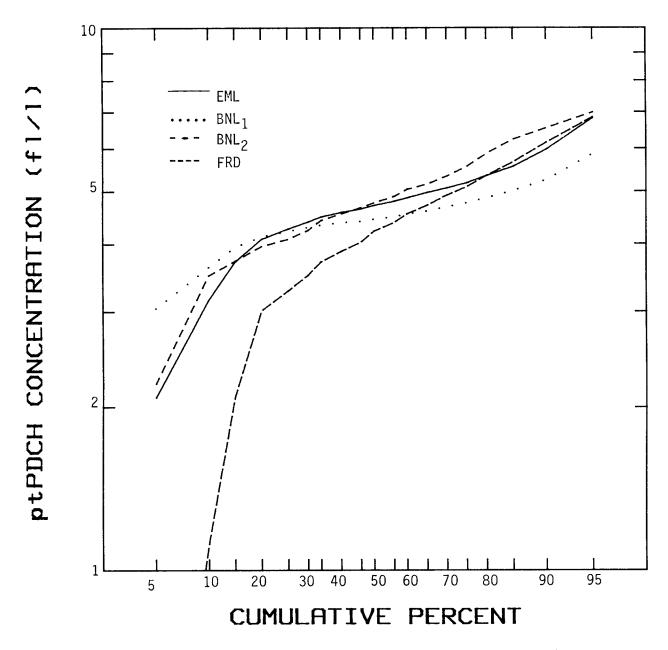


Figure 6-1. Cumulative concentration distribution of ptPDCH for all ground-level samples determined by each laboratory, assuming a constant flow of 72 L of air per sample.

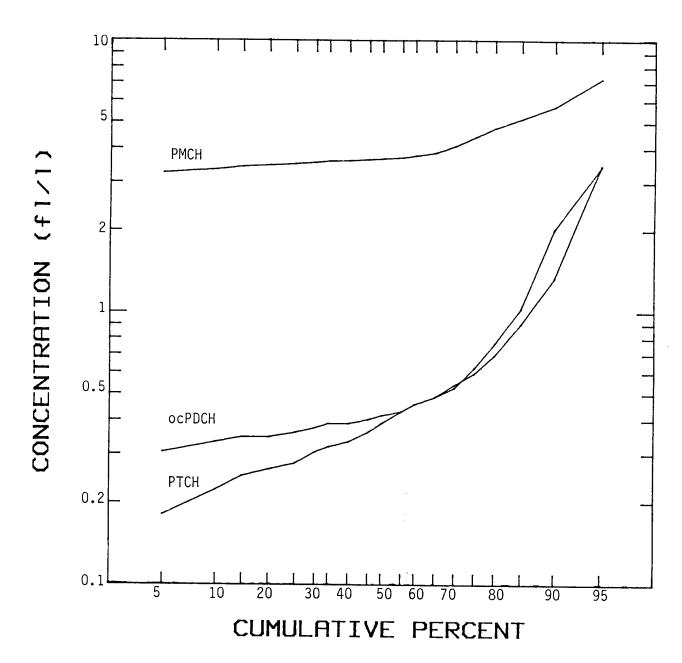


Figure 6-2. Cumulative concentration distributions of the three primary tracers after flow rate normalization by ptPDCH. Results are from BNL analysis of ground-level samples.

primarily upon the instrument used for analysis. This is reflected in the uncertainties associated with reported tracer concentrations.

Table 6-1. EML, BNL, and ARLFRD analyses of ambient tracer background concentrations (fL/L), i.e., the 40th percentile concentrations of all ground-level samples

Perfluorocarbon	EML	BNL1	BNL2	FRD
PMCP	2.69	2.07	1.88	1.71
PMCH	3.61*	3.61	3.53	3.64
oPDCH**	0.38*	0.39	0.44	0.39
mtPDCH	8.33	11.14	14.13	13.18
ptPDCH	4.57	4.38	4.54	3.88
PTCH***	0.09	0.41	0.76	0.55

^{*} used 30th percentile only for results shown in this table.

6.4 Uncertainty

The uncertainty associated with each reported air concentration depends on two factors: (1) the uncertainty in the background level and (2) the precision and accuracy of analytic methods used to determine tracer volumes. The uncertainty in background was determined by calculating the variance of background concentrations (concentrations below the 40th cumulative percentile value) for a sampling lid (21 individual samples). The precision of the laboratory analysis was determined by passing a known sample (laboratory standards) through the analyzer several times at regular intervals to establish a correction factor to apply to all subsequent tracer analyses. The correction may vary as a result of day-to-day variations in flow rate through the analyzer as well as differences in the chromatographic column temperature. When this factor exceeded 10%, the analyzer was cleaned and recalibrated. The precision of the analyses depend upon the tracer volume sampled. In general, deviations are 10% for tracer volumes less than 400 fL and 5% for greater volumes. The uncertainty given with each reported air concentration is therefore the square-root of the sum of the background plus analysis variances.

The ground-level concentration uncertainties were sorted by excess concentration. The results are shown as boxplots of uncertainty U versus excess X in Fig. 6-3 for the three released tracers. Boxplot cumulative frequency divisions are indicated at 10, 25, 50, 75, and 90 percentiles in this and all subsequent boxplot figures. It is evident that the uncertainties associated with all tracers is relatively high for low excess concentration values. Therefore, data interpretation for concentration values less than about 20 dfL/L for PMCH, about 8 dfL/L for oPDCH, and about 4 dfL/L for PTCH should take into consideration these uncertainties.

^{**}all oPDCH abbreviations refer to the ocPDCH isomer rather than the otPDCH.

^{***} normalized to a release of 100% PTCH.

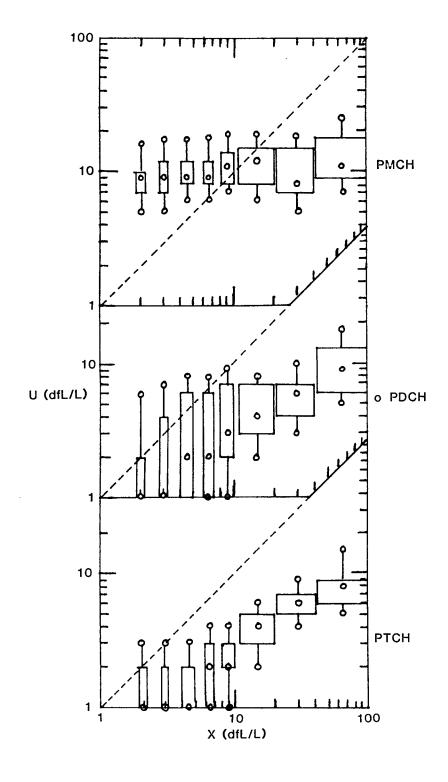


Figure 6-3. Boxplots of cumulative frequency distribution of uncertainty U versus excess concentration X for PMCH, oPDCH, and PTCH. The box indicates the 25th and 75th percentile values, while the circles show the 10th, 50th and 80th percentile values.

Some comments related to the PMCH uncertainties follow. In general, the absolute value of the uncertainties is much higher for PMCH--the tracer used in most previous experiments. PMCH has an ambient background 10 times higher than the other two tracers used in ANATEX. Although only one-fourth of that released during each CAPTEX trial was released during each ANATEX run, even with uncertainties larger than the other two tracers, on many occasions the PMCH pattern can be followed 1000-2000 km, 3 to 4 times the distance of the farthest sampler during CAPTEX. The purpose of using the PMCH was primarily to identify the oddnumbered releases (daytime) from STC. Recall that PMCH and oPDCH were released in an approximately 1:1 mixture during daytime releases and oPDCH alone was released during nightime (even-numbered) releases. For this purpose the PMCH works well. Two complications arose. First, the oPDCH came from the manufacturer in two batches, unknown to us at the time. The latter batch was 2-3% PMCH while the first batch was only 0.03% PMCH. This is evident from Table 2-3. second complication was due to mixing the tracers before odd-numbered releases. We have determined that the mixing procedure was not adequate to ensure a uniform mix. Although during the 3-h release period all the PMCH and oPDCH would have been released in the amounts indicated in the release table, the ratio between the two could have varied considerably during the release. We suspect that more oPDCH was released during the initial period, followed by greater amounts of PMCH.

6.5 Error Flags

In addition to objective measures of uncertainty, each sample was identified by a subjective flag, derived from a variety of sources to indicate the following:

Flag 0 - A good sample.

Flag l - An alternate method to calculate the flow rate. As discussed in section 6.2, flow rates were usually calculated using ptPDCH, a perfluorocarbon that was not deliberately released during the experiment. When flow rates could not be calculated in this manner, we used a constant pump value based on the average flow for the lid, as determined by air pump calibrations before and after the experiment.

Flag 3 - Unreliable tracer volumes. These were flagged by the laboratories during GC processing. This could be due to problems during integration of the chromatogram.

Flag 5 - Suspect excess concentrations. From ARL analyses of concentration maps, excesses were examined based on our own interpretation of spatial and temporal patterns near each sampling site. When inconsistencies were noted at a site, regardless of whether any other flags were turned on, the samples were flagged with the number 5. We recommend you do not use these values; however, the concentrations are available for your own interpretation.

Flag 7 - Unknown chemicals interfered with the tracer analysis. EML used this flag; other laboratories may have had similar problems, but they were not always recorded.

Flag 9 - Sample results not available because of such things as timing errors in collection, broken tubes, or fatal problems during analysis.

6.6 Volume Deviations and Tracer Ratios

Also reported with each sample was the ratio of the sample air volume for that tube to the standard deviation of air volumes for all tubes on that lid. The sample air volumes are computed using ptPDCH. We can never be sure if volume deviations were due solely to air flow variations or if they were due to problems with the ptPDCH analysis. Therefore, we also examined the ptPDCH with respect to another reference tracer. The theoretical ratio of mtPDCH to ptPDCH is known. The measured ratio of these reference tracers from the analysis sample was then compared with the theoretical ratio by laboratory from Table 6-1. The resulting comparison (ratio) is called the mtpt ratio. An mtpt ratio that differs significantly from unity is an indication of potential analysis problems. To determine the ratio's significance for application to the validity of air flow variations, the distribution of ratios was calculated only for samples with volume deviations exceeding 2 sigma (Fig. 6-4a). When ratios were within the range of 0.8 to 1.1 (corresponding conservatively, for data acceptance, to the 25 and 75% cumulative frequency distribution values), the sample should be used with the assumption that a legitimate flow deviation occurred. The sample should be disregarded for ratios outside the above range, indicating a possible analysis problem. Less than 1% of the total number of samples collected were affected.

One measurement of laboratory performance would be the distribution of mtpt ratios for all samples. The smaller the departure from unity, the better the overall analysis. We would expect the flow deviations to be evenly distributed among laboratories. Figure 6-4b shows the distribution of ratios for each GC. EML, BNLl, and BNL2 ratio distributions and ranges differ only slightly. The ratio range of FRD is similar but the distribution covers considerably smaller ratios. This is due to a significantly lower theoretical ptPDCH background, as determined from FRD analyses (Table 6-1).

6.7 Duplicate Sites

Eight stations had two colocated sampling units to collect data for statistical analysis of concentration uncertainties. This represents about 10% of all ground-level concentration data. With two exceptions, all duplicate pairs were analyzed by the same laboratory. The results, in terms of excess concentration, are shown by laboratory in Figs. 6-5, 6-6, and 6-7. In general, when concentrations are greater than 1.0 fL/L, the uncertainty is very small. At lower concentrations the uncertainty (scatter) can be substantial, due primarily to the error in determining background that is subtracted to obtain the excess concentration. This was shown earlier in the discussion of the independently determined uncertainty, where uncertainties approached 100% (Fig. 6-3) at the lower concentrations. Overall, if we include 0-0 pairs, 70% of all duplicate samples are within a factor of 2.

At this point we can relate the scatter in the duplicates to the uncertainty value determined independently for each sample. First we sorted the pairs by mean concentration, computed the RMS (root mean square) difference of the pairs in each concentration interval, and computed the mean uncertainty in the interval from the maximum uncertainty of the two samples in each pair. These results are summarized in Table 6-2. With the exception of one interval of oPDCH that had only three cases, the uncertainties were comparable with the scatter in the duplicates as expressed by the RMS difference. As a percent of

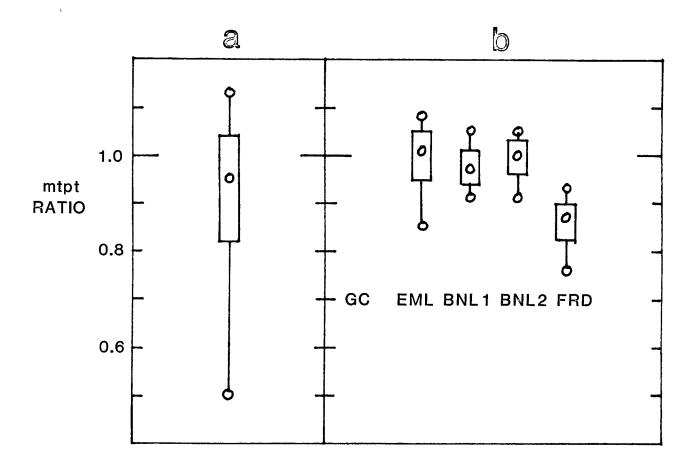


Figure 6-4. (a) The mtpt ratio boxplot for samples with volume deviations exceeding 2 sigma. (b) The mtpt ratio boxplot for all samples by GC.

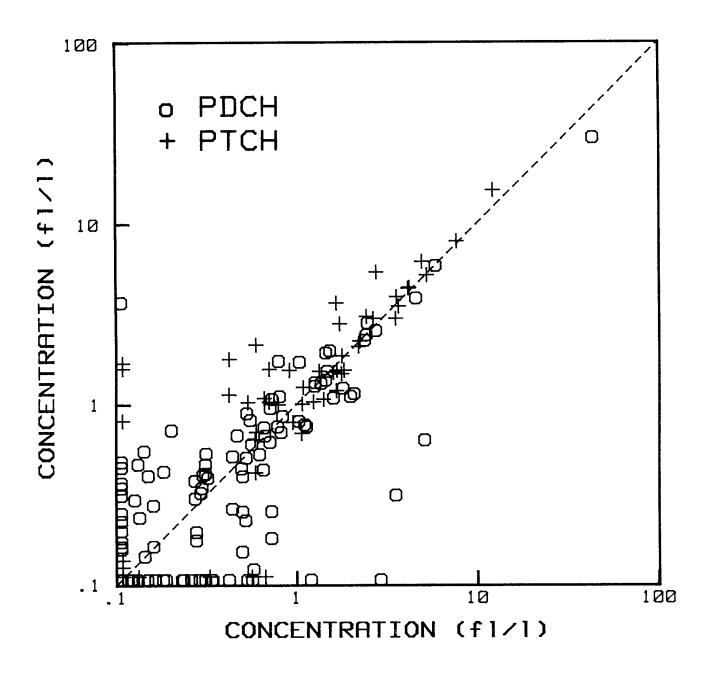


Figure 6-5. Scatter diagram of duplicate sample pairs for samples analyzed at EML.

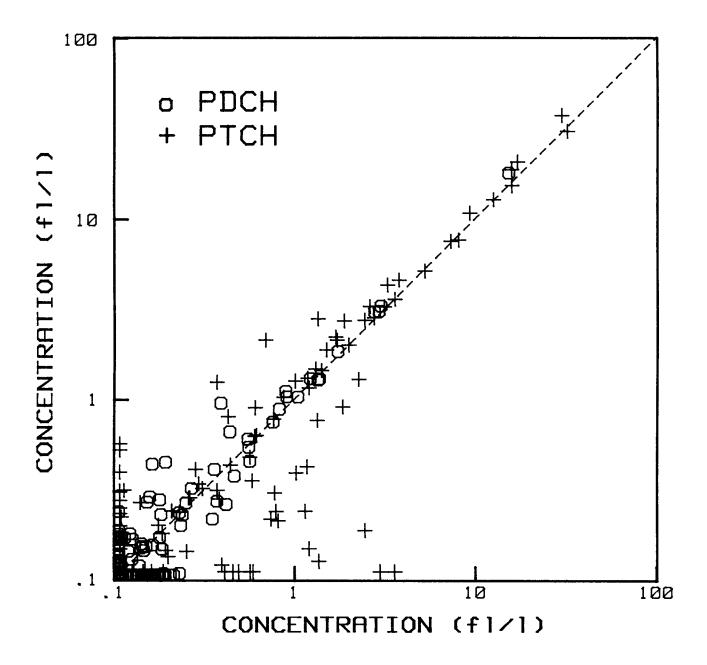


Figure 6-6. Scatter diagram of duplicate sample pairs for samples analyzed at BNL.

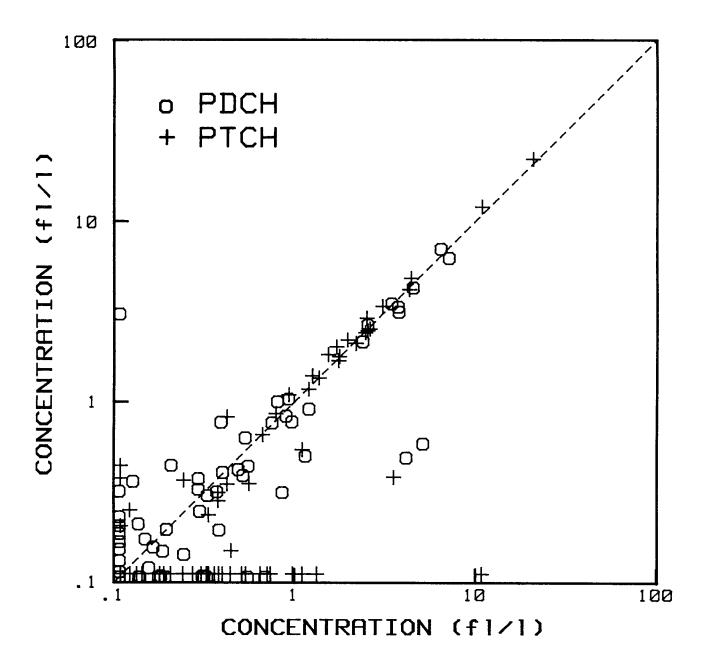


Figure 6-7. Scatter diagram of duplicate sample pairs for samples analyzed at FRD.

concentration, the errors range from 100% or more at the lower values to about 20% of the highest concentrations, a result consistent with previous analyses.

Table 6-2.	Comparison o	f deviations	and mean	uncertainties of
the du	plicate pairs	at various	concentrat	cions (fL/L)

Tracer	Statistic	0.1	0.2	0.5	1.0	2.0	5.0
oPDCH	RMS dev.	0.1	0.2	0.2	0.8	1.0	0.5
	Uncertainty	0.3	0.4	0.4	0.7	0.8	0.9
	Cases	54	60	36	24	17	3
PTCH	RMS dev.	0.2	0.3	0.5	0.7	0.5	1.8
	Uncertainty	0.3	0.3	0.4	0.6	0.8	1.1
	Cases	20	41	35	38	30	8

Since the duplicates were generally analyzed by the same laboratory, a question remains regarding bias between laboratories. This was not considered to be a large problem because all laboratories used the same tracer gas standard to develop their own calibration curves. However, four duplicate lids were accidentally switched and sent to different laboratories providing an inadvertent opportunity for interlaboratory comparison. This comparison is shown on Fig. 6-8, with FRD values along the abscissa. Clearly evident is the lack of bias. However, consistent with our previous findings, low-level analyses of PTCH were more difficult because of differences in GC response and integration methods.

As a test of comparability between laboratory analyses, triplicate 24-h air samples were collected at site 2801 for 21 days during January 1988, 1 year after ANATEX. This was done to provide a lid to each analysis laboratory for comparison of results at near-background levels of each tracer. The time series of the oPDCH concentration without subtraction of background is shown in Fig. 6-9. At the ambient background level of about 0.35 fL/L, the variation between laboratories is about 15% (0.05 fL/L), consistent with the reported uncertainties in the GC analyses. No bias between laboratories is evident. However, this 21-day period showed several small peaks, and one large one about 3 times the background level. These peaks were not attributed to oPDCH tracer, but to the presence of other unknown compounds that interfered with the GC analysis because they had the same elution time as oPDCH. Figure 6-9 clearly illustrates that greater uncertainty exists at low concentrations, and why on occasion, spurious results may also occur in the ANATEX data at these low levels.

6.8 Sampler Contamination

Significant quantities of oPDCH were found on all tubes of some sampling lids assembled at ARLFRD for shipment to the analysis laboratory after the completion of the experiment. These included many cycle-4 lids as well as some Canadian lids from all cycles. The Canadian lids, unlike the others, were not shipped from the sampling sites until the completion of the ground-sampling at the end of cycle 4.

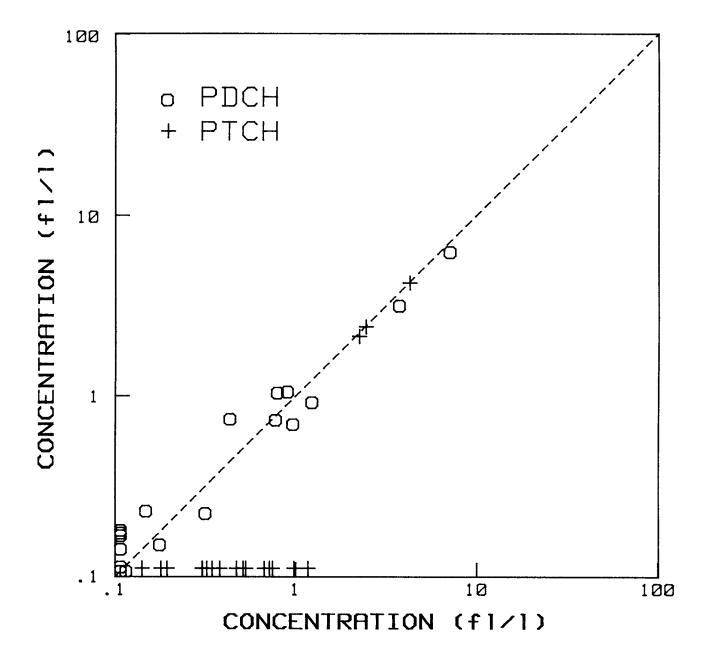


Figure 6-8. Scatter diagram of duplicate sample pairs (42 sample pairs) analyzed at two different laboratories: EML (ordinate) and FRD (abscissa).

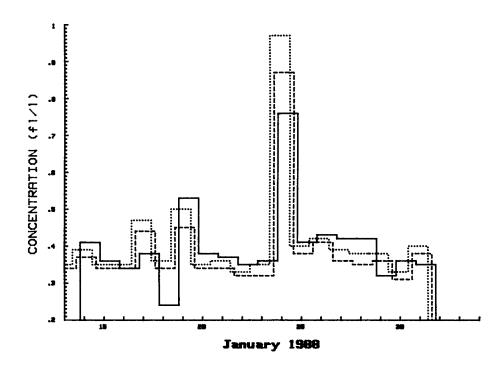


Figure 6-9. Time series of oPDCH concentrations (including background) at site 2801 during January 1988. Analysis by laboratory: BNL (solid), FRD (dashed), EML (dotted).

These lids were suspect because the ratio of oPDCH to PMCH was far in excess of what the experimental plan dictated. However, the ratio was similiar to that in the tracer aliquots that were collected during the course of the experiment to monitor the tracer release. These aliquots were not shipped for analysis until after completion of most field measurements and we suspect the shipments of lids and pure tracer must have come in contact at some point during their transfer. An examination of tube 23 on all sampling lids, a tube that should never have been used for sampling, showed about 70 lids with non-zero oPDCH amounts. A cumulative frequency distribution of tube 23 tracer volumes with ambient background indicated by a horizontal line is shown in Fig. 6-10. If we assume that contamination levels below about 50% of the ambient background are within the range of analysis error, then little contamination (10-20%) can be seen for PMCH and PTCH but about 80% of the oPDCH samples may be contaminated.

These contamination levels have of course been subtracted out of the final data by subtraction of the lid's 40th percentile concentration from all tubes, a value that will reflect the contamination level on that lid. Although the contamination has been removed, concentrations on these lids will have a higher level of uncertainty.

6.9 PFT Data

6.9.1 Overview

About 5950 samples were processed out of a total of 6468 planned samples (77 sampling sites times 84 daily sampling periods, excluding duplicates). Approximately 9% of the processed samples were flagged "bad" (code 9), which left about 5420 usable excess concentrations for model evaluation and validation. This is about 84% of the planned number, which met our original expectations for an experiment of this magnitude and complexity.

The concentration boxplots of the remaining samples are given in Fig. 6-11 for each of the three tracers and for all sites in the primary network (sampling arcs 1 through 8). Plume (excess values \geq 4 dfL/L) boxplots are also shown in the figure at arc intervals and for all arcs.

As expected, the distributions for all samples are dominated by either no plume (0) or values that are most likely in the noise level (1 to 2 dfL/L). The threshold indicating a plume (\geq 4 dfL/L) is somewhat arbitrary since low values (4-6 dfL/L) may still be in the noise level during many episodes.

In general, the distributions for each tracer are similar and tend toward lower values as you move outward over the sampling arcs. Of note is the similarity of PTCH and PMCH distributions over the outer arcs and a large shift in a distribution for PTCH going over the inner arcs.

6.9.2 ANATEX PFT data tape description

The excess concentrations and related quality assurance features as determined using Eq. (1) in section 6.1 have been archived on magnetic tape for the 77 primary sampling sites for 84 sampling periods of 24-h duration starting January 5, 1987. The following is a description of the archive data tape characteristics, data organization, and record format:

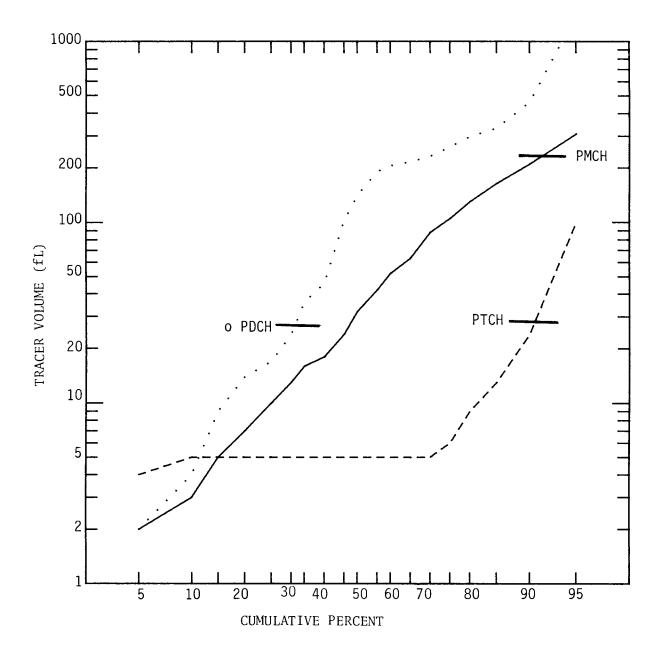


Figure 6-10. Cumulative tracer volume distributions of tube 23 of lids with suspected tracer contamination. Horizontal lines indicate approximate tracer volume level of ambient background.

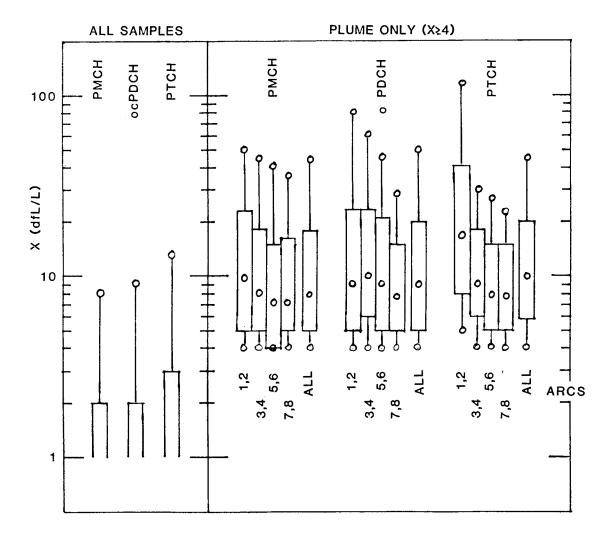


Figure 6-11. Excess concentration X boxplots for PMCH, oPDCH, and PTCH for all samples, and for plume only (X \geq 4 dfL/L) by arc interval.

TAPE CHARACTERISTICS

1600 BPI, ASCII, NO LABEL RECORD FORMAT = FIXED BLOCK RECORD LENGTH = 60 BLOCK S1ZE = 3000

TAPE ORGANIZATION

2 FILES

DATA ORGANIZATION

77 SAMPLING SITES 84 SAMPLING PERIODS RECORD = ONE SAMPLING SITE FOR ONE SAMPLING PERIOD

FILE 1 (84 SAMPLING PERIODS FOR EACH SAMPLE SITE)

FILE 2 (77 SAMPLING SITES FOR EACH SAMPLE PERIOD)

RECORD FORMAT

START COLUMN	FIELD LENGTH	FIELD DESCRIPTION	COMMENTS

1	14	Site #	See Table 2-4
5	1 X		
6	12	Month	Start of daily sample
8	12	Day	beart of daily sample
10	1 X		
11	13	Laboratory	1=EML $2=BNL1$ $3=BNL2$ $4=FRD$
14	1X		
15	14	PMCH Excess Concentration	dfL/L
19	1X		157 /7
20	13	PMCH Uncertainty	dfL/L; see note 2
23	1X	PMGW 71	a
24	13	PMCH Flag	See note 3
27	1X	DDGH E	151 /1
28	14	oPDCH Excess Concentration	dfL/L
32	1X	-DDCII Ile conte inter	dfL/L; see note 2
33	13 1x	oPDCH Uncertainty	dil/L; see note 2
36 37	13	oPDCH Flag	See note 3
40	13 1X	OrDCh Flag	see note s
41	14	PTCH Excess Concentration	dfL/L
45	1X	Tion Execus Concentration	4.13/ 13
46	13	PTCH Uncertainty	dfL/L; see note 2
49	1X	1 1 0 11 0 11 0 1 0 1 0 1 0 1 0 1 0 1 0	,
50	13	PTCH Flag	See note 3
53	1 X	3	
54	13	Air Volume Deviation	See notes 4 and 6
57	1X		
58	13	mtpt Ratio	See notes 5 and 6
	-99	Missing	

NOTES

Note 1: For field length, I2 means two integers; I3, three integers; etc. 1X means one space.

Note 2: The uncertainty (standard deviation) of the excess concentration is determined from two terms: (1) The uncertainty in the GC background or noise level; the variance of concentrations on a sampling lid that are less than the 40th percentile cumulative concentration (considered a reasonable cutoff for background). (2) The uncertainty in the concentration from the analytic precision of measuring reference standard tracer volumes; variances determined by each laboratory for a GC.

Note 3: FLAG DESCRIPTION

OK for EML. OK for other laboratories; however, no information on analysis interference was available from them (see flag 7).

- Sample air volume based on average flow for the lid as determined by air pump calibrations before and after the experiment rather than by using the ptPDCH volume for the sample.
- 3 Suspect from GC processing.
- 5 Suspect from ARL map analyses.
- Analysis interference of known or unknown originreported by laboratory 1 and 4 only.
- 9 Bad

Note 4: Deviation of air volume for a sample from the mean air volume of all samples on the lid, in standard deviation units (e.g., 3 = deviation of 3 sigma above the mean air volume, -1 = 1 sigma below the mean). The air volume deviation by itself is not a measure of excess concentration reliability since air flow variations from sample to sample occur legitimately.

Note 5: The ratio of mtPDCH to ptPDCH as measured in a sample is compared with the theoretical ratio determined for ambient air and in the presence of plume. The mtpt ratio is the measured to theoretical ratio (times 100 in the archive). A mtpt ratio that differs significantly from unity is an indication of analyses problems.

Note 6: An excess concentration with an air volume deviation within about 2 sigma may be considered reliable (no significant air flow variation), regardless of the mtpt ratio. A concentration with a deviation beyond 2 sigma and a mtpt ratio between 0.8 and 1.1. may also be considered reliable (a legitimate air flow variation). Any concentration with a deviation beyond 2 sigma and a mtpt ratio outside the 0.8 to 1.1 range should be disregarded or used with extreme caution.

7. METEOROLOGY

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7.1 Upper-Air Rawinsonde Data

7.1.1 Overview

Supplemental upper-air soundings (0600 GMT and 1800 GMT) were made at the two source sites (GGW and STC) and four other rawinsonde stations: Bismarck, North Dakota; Rapid City, South Dakota; Green Bay, Wisconsin; and Peoria, Illinois. The stations were chosen to best define the initial transport and mixing and to give better temporal definition along the 1600 km sampling arc. The supplemental rawinsondes are summarized in Table 7-1 by giving the missing soundings. Out of a total of 732 scheduled, only 17 were missing during the ANATEX period.

Considerable effort was required to achieve a quality-assured data set of upper-air observations for ANATEX. During the field experiment, the observations were copied from NOAA/National Meteorological Center (NMC) 10-day rotating disk files on a day-to-day basis and archived at ARL for real-time operational use (ANATEX-OPERATIONS). The observations were also obtained from the USAF/Environmental Technical Applications Center for the normal archiving procedures followed at ARL during the past 13 years, providing upper-air observations in North America (NAMER-WINDTEMP) to air pollution researchers.

A combined data set was then created by merging ANATEX-OPERATIONS and NAMER-WINDTEMP, giving the maximum number of reporting stations. Included in this data set were the special 0600 GMT and 1800 GMT soundings taken during ANATEX at the six designated upper-air stations. Special soundings whose transmissions were missed were obtained directly from the upper-air stations, decoded from World Meteorological Organization (WMO) format to WINDTEMP format, and added to this combined data set.

The data were then run through a special quality-assurance program written at ARL to flag data errors and inconsistencies including the following:

- (1) Data level below station elevation.
- (2) Data level out of sequence.
- (3) Wind direction out of range 0 to 360°.
- (4) Wind speed out of range 0 to 80 m/s.
- (5) Excessive wind shear (>.1/s for Δ speed >10 m/s) or (> 10 m/s in two successive layers).
- (6) Temperature or dewpoint out of range -100 to 50°C.
- (7) Excessive temperature lapse-rate ($<-3^{\circ}/100 \text{ m}$, $>3^{\circ}/100 \text{ m}$ for a \triangle temp $>3^{\circ}$ C).

Corrections were made on an individual basis, and if necessary, an observation was deleted. The final data set, ANATEX-WINDTEMP was thus created and archived.

Table 7-1. Missing ANATEX supplemental rawinsonde soundings, by station*

2.5-Day Release Sequence	MDD	BIS	RAP	STC	GRB	PIA	
January							
RLSE +00 hours	(7) 21/06	1	1 1		(5) 15/18 (5) 16/06	1 1	
+24	(6) 19/06	i	(7) 21/18	(10) 29/06			
+36	NS	NS	NS	!		(6) 27/06	
+48	SN	SN	SN	ļ	(9) 2//18 $(10) 30/06$	<u> </u>	
February							
RLSE +00 hours	1	1	1		¦	(19) 19/18	
+12	1	}	1		(22) 27/18	!	
+54	;	}	!		<u> </u>	(12) 03/06	
+36	NS	NS	NS		!	01/67 (17)	
+48	NS	NS	NS		!	1	
March							
RLSE +00 hours	(26) 09/06	!	(31) 20/06		(32) 24/06	NS	
+12	!	!	<u> </u>		ţ	1	
+24	}	1	;		!	SN	
+36	NS	NS	SN		!	NS	
+48	NS	NS	NS		(28) 16/06	NS	
Total Missing	3	0	2	1	7	4	17
	66	66	66	163	163		732

Note: Entries give release number in parentheses and day/hour GMT of missing sounding;

NS = not scheduled.

*GGW = Glasgow, MT; BIS = Bismarck, ND; RAP = Rapid City, SD; STC = St. Cloud, MN; GRB = Green Bay, WI;

PIA = Peoria, IL.

7.1.2 ANATEX-WINDTEMP data tape description

The ANATEX-WINDTEMP data tape contains rawinsonde and pibal observations for North America (excluding Alaska) from the surface to 500 mb for January 4, 1987, to March 31, 1987. Its statistics are as follows:

TAPE CHARACTERISTICS

```
TYPE 9 track, 6250 bpi, EBCDIC
LABEL None
RECORD FORMAT FB
RECORD LENGTH 25
BLOCK SIZE 10000
```

TAPE ORGANIZATION

```
4 observation times per day 1 file per month FILE 1 = JAN (04-31), FILE 2 = FEB (01-28), FILE 3 = MAR (01-31)
```

DATA ORGANIZATION FOR EACH OBSERVATION TIME

```
TIME REC (FOR WINDS):
     STA REC (STATION 1)
            WIND REC (HEIGHT 1)
            WIND REC (HEIGHT 2)
     STA REC (STATION 2)
            WIND REC (HEIGHT 1)
            WIND REC (HEIGHT 2)
            ETC.
     ETC.
TIME REC (FOR TEMPERATURES):
     STA REC (STATION 1)
            TEMP REC (HEIGHT 1)
            TEMP REC (HEIGHT 2)
            ETC.
     STA REC (STATION 2)
            TEMP REC (HEIGHT 1)
            TEMP REC (HEIGHT 2)
            ETC.
```

DATA FORMAT

ETC.

TIME REC:	YEAR	MONTH	DAY	120021	NUMBER OF REPORTS	NUMBER OF RECORDS	MET	FIELDS
	12	12	12	12	14	15	12	1 = WINDS
								2 = TEMPS
STA REC:	BLOCK STATION 15	LATITU (DEG*1		LONGITUDE (DEG*100) 16			MBER OI EVELS I3	र

WIND REC:	WIND HGT (M, MSL) I4	WIND DIRECTION (DEG) 14	WIND SPEED (M/S*10) 15	
TEMP REC:	TEMPERATURE	PRESSURE	TEMPERATURE	DEWPOINT
	HGT (M, MSL)	(MB)	(DEG K*10)	(DEG K*10)
	I4	14	I5	I5

(9999=MSG)

NOTES

In the data format, the field length is given under the field description. I2 means two integers; I3, three integers; etc.

7.2 Nested Grid Model Results

(9999 = MSG)

7.2.1 Overview

NMC's Nested Grid Model (NGM) has been rerun for the ANATEX period (January-March 1987) for the purpose of creating an archive of the model output meteorological fields. The available fields and their corresponding levels are listed in Table 7-2 in the order they appear on the magnetic tape. Fields that have corresponding levels denoted with sig** are three-dimensional fields available at the 10 sigma levels listed at the bottom of the table. Note that the three-dimensional fields are not available at the surface. Fields that have corresponding levels denoted with "sfc" are two-dimensional fields at surface level. The fields are available at the initial time (0000 and 1200 GMT) and every 2 h out to 12 h as forecast by the NGM. Occasionally the initialized data required for running the NGM were not available, in which case the NGM was rerun with the previous 12-h initialized fields and run out to 24 h or longer, if needed, to fill in the missing data. However, for the period from February 23 to March 3 all intialized data were missing; hence the data are omitted for this 7-day period. All missing periods are shown in Table 7-3.

The domain of the fields is depicted in Fig. 7-1. The 65 x 56 grid, which is on a polar-stereographic projection oriented $105^{\circ}W$, has a resolution of 91.452 km at $60^{\circ}N$ and is actually a subset of the 83 x 83 NGM operational output grid. (The North Pole is located at 25.5, 84.5).

7.2.2 ANATEX nested grid model data tape description

The data tapes contain one file per week (Monday through Sunday) except for the first and last file of the set. Table 7-4 shows which days are contained in each unlabeled file. Each record contains a field of data at a specific level. The records repeat for each available level and each forecast hour out to 12 h, in the order presented in Table 7-2. The format of the data on tape is given below. Each data element is packed into one byte. An unpacking routine is provided with the data tape. All files are ASCII. Do not attempt conversion to EBCDIC as packed binary data will be changed. You can obtain an EBCDIC version directly from ARL.

Table 7-2. Meteorological fields available from the Nested Grid Model during the ANATEX experimental period

Field	Designator	Units	Level
Height	HGT1	m	1000 mb
Height	HGT5	m	500 mb
Absolute Vorticity	ABSV	s-1	11
Mean Relative Humidity	RELH	%	1.0 to .47191 sig
Accumulated Total Precipitation	TPPT	m	sfc
Accumulated Convective Precipitation	CPPT	m	11
Snow Depth	SNOW	m	11
Ice Free Water Surface	ICEC	%	11
Surface Exchange Coefficient	EXCO	$(kg/m^3)_m/s$	11
Upward Turbulent Flux of Sensible Heat	HFLX	W/m^2	11
Upward Turbulent Flux of Water Vapor	WFLX	(kg/m ²)/s	11
Soil Temperature	TGRD	K	11
Surface Pressure	PRSS	mb	11
No. of Mixed Layers Next to Surface	MXLR	(unitless)	11
Surface Height	HGTS	m	11
Mean Sea Level Pressure	MSLP	mb	11
U Wind Component	UWND	m/s	sig*
V Wind Component	VWND	m/s	11
Vertical Velocity	WWND	mb/s	11
Specific Humidity	SPHU	kg/kg	11
Temperature	TEMP	K	11

^{* .98230, .94317, .89671, .84367, .78483, .72101, .65307, .58196,}

^{.50864,} and .28591 sigma.

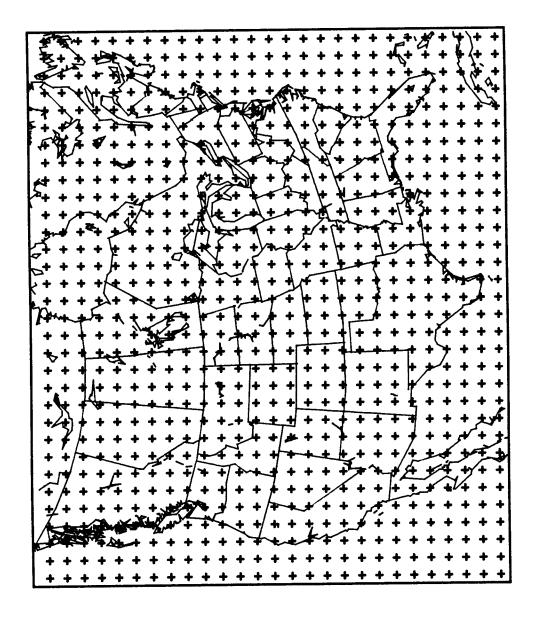
Table 7-3. Dates when the NGM was run with a forecast of more than $12\ \text{hours}$

issing Initialization Period	Available Initialization Period	Forecast Hours Saved on Tape
87/01/05 1200 GMT	87/01/05 0000 GMT	12-24
87/01/10 0000 GMT	87/01/09 1200 GMT	12-24
87/01/12 1200 GMT	87/01/12 0000 GMT	12-24
87/02/19 0000 GMT	87/02/18 1200 GMT	12-24
87/02/19 1200 GMT	87/02/18 1200 GMT	24-36
87/02/22 0000 GMT	87/02/21 1200 GMT	12-24
87/02/22 1200 GMT	87/02/21 1200 GMT	24-36
87/02/23 - 87/03/01	missing initialization of forecasts made for this	•

Table 7-4. Days contained in each unlabeled file on tape

Tape Number	File Number	Period Contained in File
1	1	January l - January 4
	2	January 5 - January 11
	3	January 12 - January 18
	4	January 19 - January 25
	5	January 26 - February 1
2	1	February 2 - February 8
	2	February 9 - February 15
	3	February 16 - February 22
	4	March 2 - March 8
3	1	March 9 - March 15
	2	March 16 - March 22
	3	March 23 - March 29
	4	March 30 - March 31
	5*	Unpacking Program

^{*}This last file contains the listing of an example program you can use to dump and unpack the gridded meteorological data. Format: LRECL-80 BLKSIZE-800 RECFM-FB.



Every other grid point is shown Figure 7-1. NGM output grid for the ANATEX period. starting at 2,2 in the lower left corner at "+."

TAPE CHARACTERISTICS

TYPE	6250 bpi
LABEL	none
RECORD FORMAT	FB
RECORD LENGTH	3695 bytes
BLOCK SIZE	14780 byte

DATA ORGANIZATION

- 4 two-dimensional fields
- 12 two-dimensional surface fields
- 5 three-dimensional fields

DATA FORMAT

YEAR (87)	MONTH (1 to 3)	DAY HOUR (00 o 12 G		*	FIELD DESIGNATOR (Table 7-2)	HORIZONTAL GRIDSIZE (65)	VERTICAL GRIDSIZE (56)
Ι2	12	12 12	12	12	A4	12	12
UNPACE PRECIS	KED DATA SION	SCALING EXPONENT	FIRST UNPACKE DATA VALUE (at grid point		PACKED DATA VALUE (65×56 one	S byte values)
E16	• 9	13	E16.9		3640A	1	
*LEVE	6 = 0.	0 mb 0 mb	$ \begin{array}{rcl} 9 & = & 0 \\ 10 & = & 0 \\ 11 & = & 0 \\ a & & 12 & = & 0 \\ a & & 13 & = & 0 \end{array} $	0.84367 0.78483 0.72101 0.65307 0.58196 0.50864 0.28591	sigma sigma sigma sigma sigma		

7.3 Surface Meteorological Data

7.3.1 Overview

Surface data were archived at ARL by the following process. The NMC hourly surface observations (first order, military, and FAA stations) were archived on a daily basis. The NMC 3-h surface observations (first-order stations only) were archived weekly. The hourly and 3-h data were then merged to create a 3-h interval data tape.

The data tape contains 3 files (File l = JAN 87, File 2 = FEB 87, File 3 = MAR 87). Each record contains an hourly station report; there is one report every 3 h. Because of a simplified merging process, a station may be repeated as many as three times since the station may have been reported once in the hourly reports and twice in the 3-h reports.

7.3.2 ANATEX surface data tape description

The ANATEX surface data tape contains hourly surface observations every 3 h for the area $20^\circ N$ to $60^\circ N$ and $+50^\circ W$ to $+125^\circ W$. A description of the data tape follows:

TAPE CHARACTERISTICS

TYPE 9 track, 6250 bpi, EBCDIC

LABEL None
RECORD FORMAT FB
RECORD LENGTH 85
BLOCK SIZE 8500

TAPE ORGANIZATION

3 files - (FILE 1 = JAN 87, FILE 2 = FEB 87, FILE 3 = MAR 87) Observation times per day - every 3 hours

DATA ORGANIZATION

RECORD = HOURLY STATION REPORT (ONE REPORT EVERY 3 HOURS)

A station may be repeated as many as 3 times because of the merging process.

RECORD	FORMAT							_	ND CEDUATE AN	
YEAR	MONTH	DAY	HOUR	STATION ID		TITUDE G * 100)	LONGITUDE (DEG * 10	:	DBSERVATION TIME (GMT) OOTH OF AN	
I 2	12	12	12	A8		15	15		14	
STAT: ELEVA	I I ON	SEA LI PRESSI (MB *	URE	STATION PRESSUR (MB * 1	E	WIND DIRECTIO (DEG)	WIND N SPEE (M/S *	D	AIR TEMP	
I	5	15		15		13	13	,	14	
DEPR	POINT ESSION E * 10)	WEA'	SENT THER CODE)	CLOUD CO (FRACTI (WMO CO	ON)	LOW CLOUD (WMO CO	s CLOU	GHT OF ID BASE O CODE)	PRESSUR TENDENC (WMO COD	Υ
I	3	1	3	12		12		12	12	
PRESSU	ITUDE OF RE TENDE B * 10)	•	PRECIP A PAST 6 (MM *	HRS	SNOW DEPTH (CM)	PAST	P AMOUNT 24 HRS * 10)	(NO.	IP DURATION OF 6-HR LODS)	i
	13		I	4	13		14		12	

NOTES

Missing data are denoted by -1. In the record format, the field length is given under the field description. I2 means two integers; I3, three integers; etc. A8 means an 8-digit character. WMO codes can be obtained from NWS sources.

7.4 Source Meteorological Data

Small towers (10 m) were located near each tracer release site; at GGW the tower and release location were coincident, at STC, they were about 100 m apart. Wind speed, wind direction, and temperature were recorded continuously. For a general evaluation of conditions during each tracer release, a summary of the 3-h averages during the release and three subsequent 3-h periods is given in Tables 7-5 and 7-6 for GGW and STC, respectively.

Table 7-5. Glasgow release site 3-h vector average wind directions (°) and speeds (m/s)

Midnight Releases						
	Release Time (0500-0800 GMT)	Release + 3 h (0800-1100 GMT)	Release + 6 h (1100-1400 GMT)	Release + 9 h (1400-1700 GMT) Dir/Speed		
Date	Dir/Speed	Dir/Speed	Dir/Speed	D11/Speed		
1-08-87 1-13-87 1-18-87 1-23-87 1-28-87 2-02-87 2-07-87 2-12-87 2-17-87 2-22-87 2-27-87 3-04-87 3-09-87 3-14-87 3-19-87	242 / 1.0 288 / 4.6 197 / 3.0 146 / 1.7 108 / 3.5 282 /11.2 238 / 5.5 106 / 3.4 158 / 3.8 261 / 2.5 - / - 215 / 3.2 101 / 7.0 73 / 8.1 53 / 3.2	239 / 1.2 287 / 5.3 216 / 3.6 165 / 2.7 99 / 4.1 304 / 9.0 258 / 5.5 116 / 3.8 154 / 3.1 134 / 2.8 - / - 231 / 2.1 93 / 7.6 93 / 6.2 40 / 2.1	270 / 1.7 288 / 7.1 219 / 3.1 150 / 2.8 92 / 3.8 302 / 6.7 290 / 5.9 105 / 3.0 176 / 4.0 125 / 2.4 - / - 237 / 3.2 92 / 7.2 99 / 5.4 102 / 2.8 327 / 3.7	254 / 3.1 286 / 5.9 275 / 4.6 148 / 3.4 119 / 4.0 302 / 4.8 295 / 4.1 155 / 2.5 175 / 3.0 105 / 3.2 - / - 234 / 2.9 104 / 7.4 98 / 5.1 103 / 2.7 293 / 3.6		

Midday Releases

Date	Release Time (1700-2000 GMT) Dir/Speed	Release + 3 h (2000-2300 GMT) Dir/Speed	Release + 6 h (2300-0200 GMT) Dir/Speed	Release + 9 h (0200-0500 GMT) Dir/Speed
1-05-87 1-10-87 1-15-87 1-20-87 1-25-87 1-30-87 2-04-87 2-09-87 2-14-87 2-19-87 2-24-87 3-01-87 3-06-87 3-11-87 3-16-87	- / - 246 / 3.1 267 / 2.3 209 / 4.7 266 / 6.0 175 / 2.7 214 / 2.5 156 / 1.0 160 / 2.5 231 / 3.1 92 / 3.3 274 / 2.9 247 / 3.9 92 / 4.7 62 / 4.2 335 /10.7	- / - 259 / 3.8 257 / 2.4 242 / 6.4 281 / 4.8 162 / 1.1 232 / 2.5 154 / 2.2 246 / 1.6 292 / 3.9 73 / 4.5 317 / 3.9 256 / 3.4 - / - 58 / 4.2 348 /11.7	- / - 267 / 4.5 191 / 1.3 269 / 6.7 287 / 4.7 165 / 1.5 188 / 1.3 103 / 2.6 228 / 1.3 315 / 2.3 79 / 4.4 335 / 3.3 204 / 1.5 - / - 64 / 4.1 358 /10.7	- / - 290 / 7.2 217 / 1.9 290 / 8.0 272 / 4.0 189 / 2.6 201 / 3.0 115 / 3.7 358 / 1.0 265 / 2.2 91 / 4.3 19 / 3.8 30 / 0.9 - / - 56 / 3.4 4 / 9.2
3-26-87	181 / 5.6	172 / 5.5	155 / 3.8	159 / 3.9

An Aero-Vane system mounted at 10 m was used to make these meteorological measurements.

Table 7-6. St. Cloud release site 3-h vector average wind directions (°) and speeds (m/s)

Midnight Releases							
Date	Release Time (0500-0800 GMT) Dir/Speed	Release + 3 h (0800-1100 GMT) Dir/Speed	Release + 6 h (1100-1400 GMT) Dir/Speed	Release + 9 h (1400-1700 GMT) Dir/Speed			
1-08-87 1-13-87 1-18-87 1-23-87 1-28-87 2-02-87 2-07-87 2-12-87 2-17-87 2-22-87 2-27-87 3-04-87 3-09-87	- / / / / / / / / / / - 149 / 3.4 182 / 4.7 49 / 3.0 97 / 2.0	- / / / / / / / / / / - 138 / 2.8 - / - 54 / 3.0 98 / 1.7	- / / / / / / / / / / / / - 124 / 3.0 - / - 50 / 1.4	- / / / / / / / / / / / - 122 / 3.3 - / - 58 / 2.3 98 / 2.1 159 / 1.4			
3-19-87 3-24-87	131 / 1.4	141 / 1.2	157 / 1.9	- / -			
Midday Releases							
	Release Time (1700-2000 GMT)	Release + 3 h (2000-2300 GMT)	Release + 6 h (2300-0200 GMT)	Release + 9 h (0200-0500 GMT)			

Date	Release Time	Release + 3 h	Release + 6 h	Release + 9 h
	(1700-2000 GMT)	(2000-2300 GMT)	(2300-0200 GMT)	(0200-0500 GMT)
	Dir/Speed	Dir/Speed	Dir/Speed	Dir/Speed
1-05-87 1-10-87 1-15-87 1-20-87 1-25-87 1-30-87 2-04-87 2-09-87 2-14-87 2-19-87 2-24-87 3-01-87 3-06-87	- / / / / / / / / / / / / / / - 350 / 7.1 212 / 5.2 250 / 0.8	- / / / / / / / / / / / / / - 337 / 6.5 223 / 5.7 264 / 1.1	- / / / / / / / / / / / / / - 214 / 3.1 260 / 0.5	- / / / / / / / / / / / / / - 213 / 3.1 10 / 0.9
3-16-87	152 / 2.4	152 / 2.0	132 / 1.0	111 / 1.2
3-21-87	- / -	- / -	- / -	- / -
3-26-87	- / -	- / -	- / -	- / -

An Aero-Vane system mounted at 10 m was used to make these meteorological measurements.

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We wish to thank the release site operators at GGW and STC whose care and dedication, both day and night, enabled us to achieve a high degree of precision for source term determination. We especially wish to acknowledge all the sample site operators for running the ground-level samplers with enthusiasm and competence, and for dedicated participation, which greatly helped make ANATEX a success.

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APPENDIX: PFT Sampling Data Tables

For a quick reference to the measured concentration data, excess concentrations (in dfL/L) are listed in tabular form by date and sampling site. Tables A-1, A-2, and A-3 are for PMCH, oPDCH, and PTCH respectively. Missing values are given as -99. It should be emphasized that values are accompanied by uncertainties, flags, and quality assurances, as mentioned in the text, so data interpretation directly from these tables should be done with caution.

Table A-1. Excess PMCH concentration (dfL/L).

January 1987

Table A-l (con't.)

February 1987

Table A-1 (con't.)

March 1987

Table A-2. Excess oPDCH concentration (dfL/L).

January 1987

Table A-2 (con't.)

February 1987

Table A-2 (con't.)

March 1987

7 8 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 DAY 1 $\begin{smallmatrix} 9 & 0 & 0 & 1 & 9 & 3 & 8 & 9 & 1 & 0 & 0 & 9 & 9 & 3 & 1 & 2 & 0 & 1 & 0 & 2 & 1 & 1 & 2 & 0 & 1 & 2 & 1 & 2 & 0 & 1 & 2 & 1 & 2 & 0 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 & 1$ 903~9609090853914450703039004203925382900932173012990235001002311000100540719 501 502 503 504 551 552 1001 1002 1003 1004 911929 91929 91929

Table A-3. Excess PTCH concentration (dfL/L).

January 1987

9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 5 6 $\begin{smallmatrix} 24 \\ 053 \\ 23 \\ 09 \\ 400 \\ 865 \\ 960 \\ 000 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\ 200 \\$ -99 -9**9** -99 -99 -99

Table A-3 (con't.)

February 1987

Table A-3 (con't.)

March 1987