4.1.4 Halocarbon Studies

A number of activities in this field have involved several components of the Air Resources Laboratories in addition to GMCC. However, only GMCC activities will be reported here.

Freon-11 (CCl_3F)

Program. The major change of the Freon-11 program has been the relocation of the preparation and analysis phases from Idaho Falls to the Techniques and Standards Group in Boulder, Colorado. The flask program initiated in September 1973 was continued through 1974. Evacuated stainless steel flasks were used to sample surface ambient air at Barrow, Alaska, Mauna Loa, Hawaii, and Cape Matatula, American Samoa. The flasks were prepared at the Air Resources Laboratory Field Research Office at Idaho Falls, Idaho, and airmailed to the sampling stations. Station personnel exposed the flasks and returned them to Idaho Falls for Freon-11 analysis. The analysis setup using an Electron Capture Gas Chromatograph was presented in the GMCC Summary Report No. 2, 1973.

Some special short-term sampling, in which pairs of flasks were exposed simultaneously for observation of coincidence in the sampling techniques, was performed at Cape Matatula, Mauna Loa, and South Pole.

Equipment. A new chromatographic system is to be installed at Boulder, Colorado. Major equipment orders for the following were placed in late 1974 and will be installed in 1975:

(1) Hewlett-Packard 5713A Electron Capture Gas Chromatograph

(2) Hewlett-Packard 3380A Reporting Integrator

(3) Tylan Corp. Mass Flow Controller FC-200

Because the Electron Capture Chromatograph's detector contains the radionuclide Ni-63, it was necessary to procure a nuclear license covering the quantity of radiation that would be handled. An amendment to the current NOAA-ERL license has been submitted to the Nuclear Regulatory Commission for approval.

Because of the high risk of leaks contaminating evacuated flasks during transport, it seems advisable to pressurize the flasks prior to shipping them to the stations and to flush and repressurize them with sampled air for return and analysis. A prototype flask pressurizing unit has been designed and is under construction and testing.

Data. Freon data for 1974 are tabulated in tables 9-12. Proper data interpretation must include a decision that a sample is truly "background air" or that it contains local or transient contamination. The usual method of data selection is based on meteorological information. If the wind direction is within a chosen "clean air" quadrant, the sample is assumed to be contamination free. If, however, the wind is coming from a direction outside the quadrant, the sample is considered contaminated and is eliminated from the data record. The use of wind direction is a direct although incomplete method of determining the representativeness of a Freon sample. Trajectories provide a

Table 9. Barrow Halocarbon Data, 1974.

Date	Freon-11 Concentration pptV	σ	CCl_4 Concentration pptV	σ
Jan 3	160.5	5.9	157.8	5.0
16	94.5	6.2	47.9	5.1
Feb 1	95.2	3.1	38.4	1.4
Mar 21	95.1	1.3	90.3	1.2
30	91.5	5.4	21.7	2.7
Apr 25	112.4	4.1	141.7	12.3
May 8	167.5	4.8	135.0	32.2
Jun 15	5986.0	72.0	15.3	0.7
Jul 2	111.1	13.2	61.5	3.6
9	381.3	15.2	60.9	3.1
31	133.3	8.2	75.1	2.0
Aug 20	114.1	7.9	77.3	4.3
Sep 10	122.0	4.0	101.5	3.3
17	103.2	3.4	96.1	2.3
24	MF		45.5	3.2
Oct 1	MF		42.2	2.6
11	MF		34.6	2.9
22	195.8	11.1	13.6	1.8
Nov 11	159.7	9.3	98.1	4.5
20	141.4	10.7	24.2	1.1
Dec 3	132.2	4.2	ND	
18	150.3	7.8	102.1	7.8
28	142.3	6.2	24.0	1.7
31	147.2	2.0	ND	

MF = equipment malfunction
ND = not detected

more reliable basis for judgment, but these are not yet available. Low wind speed is also an indication of variable wind flow and possible contamination.

A selection criterion was determined for the samples based on local conditions at each station. For all the stations, if the Freon-11 value exceeded 200 ppt, it was excluded as being contaminated. Also, if the wind velocity was below 2.2 m/sec (5 mph), the value was deleted. The "clean air" quadrant for Barrow, Alaska was chosen to be 320-360, 0-170 degrees; for Samoa, 300-360, 0-130 degrees. Mauna Loa, Hawaii, presents a unique problem since the observatory is in the center of the island with cities on the coast

Table 10. Cape Matatula Halocarbon Data, 1974.

Date	Freon-11 Concentration pptV	σ	CCl_4 Concentration pptV	σ
Jan 2	159.9	4.8	84.4	1.9
11	108.4	4.5	75.7	5.6
19	71.8	2.0	66.8	2.0
26	72.8	4.3	83.4	10.0
30	80.3	2.6	115.8	3.3
Feb 9	78.0	2.6	65.4	4.4
Mar 25	115.9	4.7	68.8	5.8
Apr 4	2640.1	196.1	91.9	3.5
4	1053.9	84.5	78.7	2.1
13	6546.1	414.4	101.5	2.5
13	3034.5	117.9	78.8	4.6
24	1463.7	359.4	422.2	211.6
24	4933.0	664.1	411.9	320.4
27	171.9	4.9	111.6	10.4
May 4	103.6	13.1	164.5	89.2
15	112.8	29.7	91.7	4.7
28	140.7	3.7	92.7	7.1
Jun 12	101.7	4.4	89.9	2.2
Jul 24	161.8	13.5	99.7	8.4
Sep 14	MF		60.8	4.2
25	MF		51.8	7.2
Oct. 2	248.7	20.2	90.3	4.3
10	159.8	9.7	100.3	6.6
19	76.8	3.3	92.2	2.2
26	129.0	8.9	97.6	5.2
Nov 3	157.1	16.4	99.2	11.1
Dec 10	121.8	6.0	100.1	4.8
20	1579.0	110.0	104.9	6.3
30	143.2	7.6	94.2	3.2

MF = equipment malfunction

on all sides. The samples were taken during the daytime generally at the time of upslope winds and so no selection was made based on a "clean air" quadrant. Aitken nucleus readings were taken concurrent with the flask sampling and these showed normal levels for most conditions.

After data were selected, both linear and semi-log least squares regression fit were determined. The 1974 semi-log regressions are graphically

Table 11. Mauna Loa Halocarbon Data, 1974.

Date	Freon-11 Concentration pptV	σ	CCl_4 Concentration pptV	σ
Jan 16	86.5	6.5	75.6	3.0
25	87.5	5.1	192.1	17.6
Feb 2	82.4	5.2	ND	
8	101.9	2.6	47.6	6.0
15	98.6	2.3	ND	
22	80.8	1.3	83.4	2.1
Mar 1	61.7	2.7	49.7	0.8
11	96.3	5.3	78.8	7.3
15	97.5	2.2	19.6	3.3
19	5792.7	183.3	11.8	0.6
19	156.9	4.0	ND	
19	5244.0	110.2	4.5	0.8
19	117.8	10.4	ND	
19	121.8	7.6	ND	
19	107.2	2.5	ND	
21	126.9	14.5	ND	
21	126.7	9.8	ND	
29	73.3	1.6	54.2	1.5
Apr 5	88.0	9.9	49.3	5.8
12	107.8	2.5	ND	
19	139.5	2.5	166.6	10.7
May 3	120.3	12.0	273.1	269.6
17	131.9	15.2	111.7	35.8
23	131.1	9.8	121.1	17.0
Jun 7	122.0	14.7	142.3	27.0
21	108.9	10.0	ND	
28	150.9	25.4	97.6	2.8
Jul 5	143.2	4.5	ND	
Sep 6	89.8	4.3	ND	
13	95.2	3.0	ND	
20	125.9	2.9	108.9	3.4
30	MF		ND	
Oct 4	MF		54.2	3.9
11	MF		ND	
18	149.5	13.1	ND	
25	164.3	9.1	ND	
Nov 1	161.9	5.0	103.8	2.7
9	147.3	6.9	65.5	3.8
15	204.1	15.0	ND	
Dec 6	131.3	3.4	ND	
13	145.3	3.1	62.5	3.0
20	147.8	6.3	113.5	2.8
27	150.0	1.3	58.0	5.5

MF = equipment malfunction; ND = not detected < 5 ppt

Table 12. South Pole Halocarbon Data, 1974.

Date	Freon-11 Concentration pptV	σ	CCl_4 Concentration pptV	σ
Jan 14	61.9	3.1	ND	
14	182.9	7.7	ND	
20	142.0	4.4	53.7	1.4
20	89.3	2.9	28.0	1.6
Feb 5	99.7	4.2	ND	
5	149.9	3.4	50.4	4.2

ND = not detected < 5 ppt

presented in figures 23-25. The regression results for the entire period for both procedures are shown in table 13. We prefer the linear regression results until we have ore data to indicate the best approach.

Coincidence sampling at Mauna Loa on March 19 and 21 shows large deviations in some cases and good agreement in others. Samoan coincidence samples obtained on April 4, 13, and 24 were all highly contaminated. Antarctica coincidence samples had large deviations. This has raised the question of the appropriateness of the sampling technique.

Instrument Performance. There is wide scatter in the data for the past year. This can be attributed to three causes:

(1) Variations in actual atmospheric Freon concentration at the time of sampling.

(2) Imperfect sampling because of absorption, chemical reaction, vacuum flask leaks, sampling hookup leaks, inadequate cleaning, etc.

(3) Subtle changes in the detector response of the analytic equipment (gas chromatograph) due to temperature variations, carrier flow rate changes, carrier gas contamination, inadequate calibration, etc.

Many things affect the operation of the gas chromatograph. Good documentation of their effect has not been possible because of the lack of standard gases with which comparisons of response to controlled variations could be made. With a new chromatographic system, a pressurizing sample system, and renewed efforts in standard gas production, many variables will be eliminated and higher quality data produced.

Cooperative Program — Adrigole, Ireland

The cooperative program with Dr. J. E. Lovelock for measurement-analysis of CCl_3F and CCl_4 continued with 1974 at Adrigole, Ireland. Beginning in November 1973 the observation frequency was increased to 4 per day at 0000,

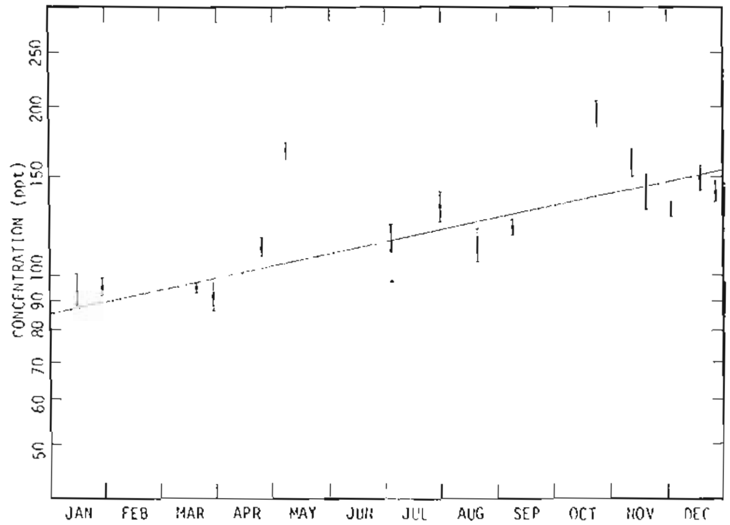

Figure 23. Semi-log regressions of selected Freon-11 data from Barrow, Alaska, 1974.

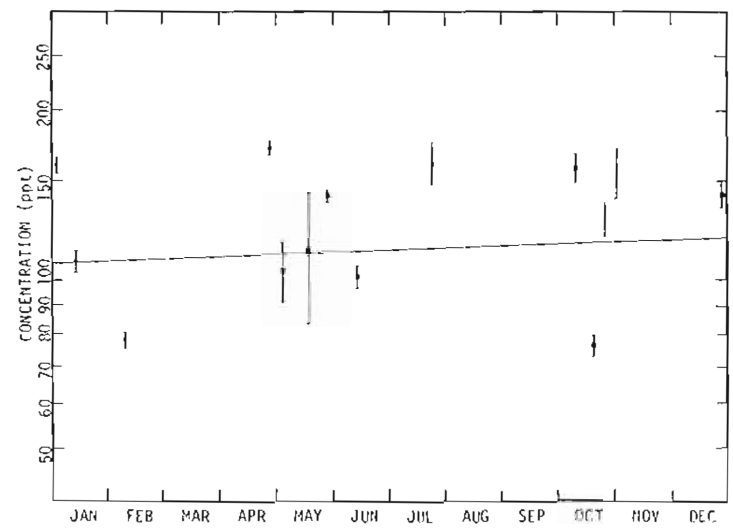

Figure 24. Semi-log regressions of selected Freon-11 data from Cape Matatula, Samoa, 1974.

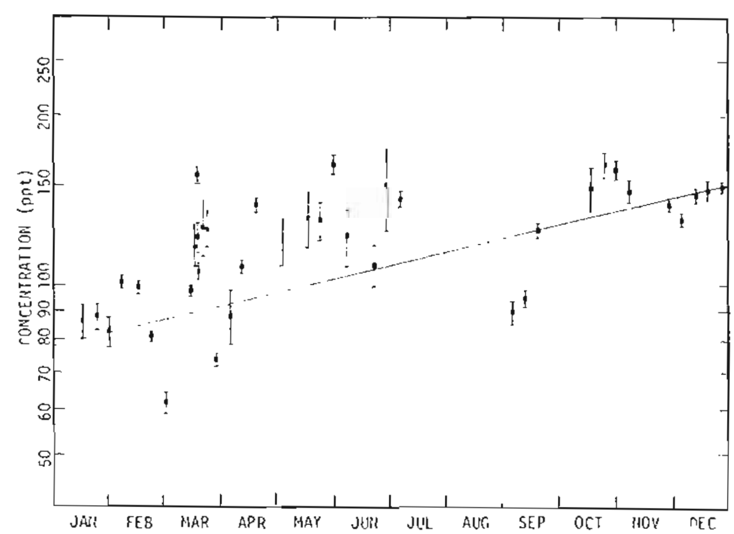

Figure 25. Semi-log regressions of selected Freon-11 data from Mauna Loa, Hawaii, 1974.

Table 13. Concentrations and Growth Rates of Freon-11 Derived From Regression Analyses of Selected Data, September 1973-December 1974.

Linear Regression	1 January 1974	31 December 1974	Change
Barrow, Alaska	89.9 pptv	144.4 pptv	+54.5 pptv
Cape Matatula, Samoa	98.0 pptv	121.1 pptv	+23.1 pptv
Mauna Loa, Hawaii	87.3 pptv	143.9 pptv	+56.6 pptv
Average	91.7 pptv	136.5 pptv	+44.7 pptv
Semi-log Regression	**1 January 1974**	**31 December 1974**	**Change**
Barrow, Alaska	86.5 pptv	151.6 pptv	+65.1 pptv
Cape Matatula, Samoa	96.5 pptv	126.6 pptv	+30.1 pptv
Mauna Loa, Hawaii	83.8 pptv	146.3 pptv	+62.5 pptv
Average	88.9 pptv	141.5 pptv	+52.6 pptv

0600, 1200, and 1800 Greenwich Meridian Time. These essentially continuous data were obtained for 9 months. (Data are not available for March, April, and May 1974).

Meteorological trajectories extending backwards in time and space for 10 days are being calculated for each observation. These data are being used to identify source regions and trends in the halocarbons. A sample of a complex trajectory set for June 26, 1974 is shown in figure 26. In addition, statistical correlations were prepared to reveal any diurnal trends. None was found. Hence the entire body of data can be pooled to form daily and monthly averages.

Unstratified data indicate an increase in CCl_3F concentrations of more than 30% to near 110×10^{-12} parts per part of air. A similar or even larger increase in CCl_4 may have occurred but the data for this compound require further study.

4.2 Measurement of Aerosols

4.2.1 Mauna Loa Ruby Laser Radar (Lidar) System

The lidar system measures atmospheric scattering properties in the upper atmosphere that have climatic importance. These lidar data supplemented with other measurements such as solar aureole, skylight, and spectral transmission form an integral system that can be used to monitor cirrus clouds, changes in the Junge layer strength, and injection of particles by volcanic activity that could lead to changes in the stratospheric albedo.