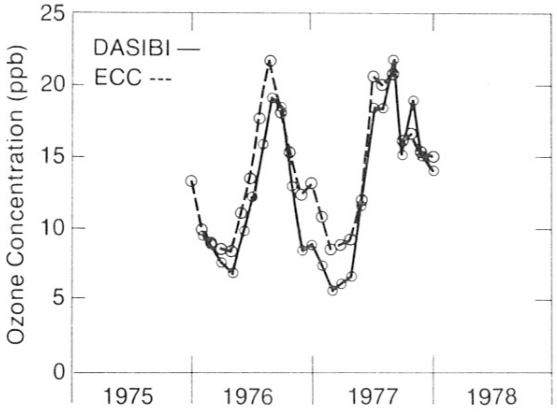

Figure 13. Adjusted monthly mean surface ozone concentrations at Samoa measured with ECC and with Dasibi meters for 1975-1978.

The measured ozone amount for the ECC meter was found to vary with sensing solution concentration. During 1977, ECC measurements have been made using a 1.5% solution of potassium iodide (KI); such a solution gives readings that are about 8% too high compared to the NBS standard. A 1.0% solution of KI gives results within 0.1 percent of the NBS value. The linear regression relationships based on the comparisons using the two solutions are given as follows:

(1) For a 1.5% solution, NBS standard = 2.4 + (0.921 ± 0.013) ECC;

(2) For a 1.0% solution, NBS standard = 1.73 + (0.999 ± 0.012) ECC.

Using these comparisons and comparison of the ECC sensors with other operating instruments in the GMCC program, the data through 1977 are being adjusted to the scale represented by the NBS standard. This reprocessing has been completed for the Samoa ECC and Dasibi meter observations, and the monthly means are shown in Fig. 13.

3.4 Halocarbons

3.4.1 Operations

1977 changes in the halocarbon program include the following: (1) conversion from evacuated flasks to pressurized flasks, (2) continued measurement of trichlorofluoromethane (F-11) with the addition of dichlorodifluoromethane (F-12) and nitrous oxide (N_2O) measurements, and (3) use of reference gases for daily gas chromatograph calibrations. This section describes these changes more fully and presents the 1977 data.

Station Sampling

In January 1977, a dual-cylinder pump-up system was installed at the South Pole. The system consists of a 7-μ filter, a metal bellows

pump, a pressure relief valve, and a tee dividing the air flow between two cylinders. A short section of stainless steel tubing connects the pump to one port of the station's gas sampling manifold and stack. Four pairs of flasks were pressurized in late January and early February 1977, and then shipped to Boulder for analysis before the winter station closing. One pair of flasks was then exposed each month through November; they were returned to Boulder in December. Two pairs of flasks were pumped in December.

Similar pump-up systems were installed at the other baseline stations in July 1977. Sample pairs were pumped each week along with the normal exposure of an evacuated flask through November when the evacuated flask sampling program was discontinued. Niwot Ridge, Colo., samples consisted of evacuated cylinder pairs exposed each week throughout the year.

New Chemical Measurements

When a 10' x 3/16" Porasil B column was installed in late April, gas chromatographic measurements of F-12 could be taken in addition to those for F-11. In late June, a 3' x ¼" Porasil A column was installed in the gas chromatograph. Then N_2O, as well as F-12, could be separated, but resolution between the air peak and N_2O was not very good. Finally in late July, a 4' x 1/8" Porasil A column was installed that gave good separation of F-12 and N_2O from the air peak. This column was used during the rest of the year with periodic reconditioning.

Gas Chromatograph Calibrations

Until March 1977, calibration of the Boulder chromatograph was based on a limited number of gas sample intercomparisons with the ARL/NOAA Idaho Falls Field Research Office chromatograph.

When the Idaho Falls chromatograph was first set up, detector efficiency factors were assigned to it based on operating condition research by J. Lovelock. These efficiency factors were considered constant because of equipment long-term stability. Gas samples were analyzed before and after a change in the gas chromatograph operating conditions. New efficiency factors were then determined and transferred to the Boulder equipment by sample comparison.

As experience with the chromatograph increased, equipment instabilities were discovered, and a static dilution system was built for routine calibration. Initial work with the apparatus showed that concentrations on the order of parts per trillion could not be reproduced.

Until a mixing gas standard system could be developed for low concentrations, high pressure cylinders, specially cleaned and prepared, were pumped with local air to serve as working reference tanks. In late February, the first tanks were filled at Niwot Ridge, Colo., and ana-

lyzed. One tank, 3072, was chosen to be the daily working gas; a second tank, 3078, was later chosen to be a long-term reference. In the sample analysis scheme using reference gases, tank 3072 reference gas is analyzed daily before and after every two chromatographic analyses of an unknown sample. On a 3- to 6-mo basis, tank 3078 is analyzed by comparing it to tank 3072.

In December 1977, tanks 3072 and 3078 were compared to R. Rasmussen's Standard 006 at the Oregon Graduate Center in Beaverton, Ore. Tank concentrations for N_2O, F-12, and F-11 were determined (see Section 6.9 for discussion of this intercomparison). Station sample concentrations of these constituents determined by comparison to tank 3072 have been adjusted to the Oregon Graduate Center scale.

3.4.2 Data

1977 provisional F-11, F-12, and N_2O data are presented in Table 14 for the four observatories and Niwot Ridge near Boulder. 1977 F-11 data for evacuated flask and pressurized flask sampling are shown in Fig. 14. All available GMCC F-11 measurements from evacuated flask sampling are compared in Fig. 15. Figures 16 and 17 show F-12 and N_2O data plots, respectively, for 1977. Although similar data exist for the Barrow, MLO, and Samoa stations from evacuated flask sample collections and analyses, they are not included because a high degree of data variability resulted from sampling problems.

Data in this report should be regarded as provisonal since they may contain errors resulting from sample collection problems, analyzer malfunctions, and possibly reference gas calibration drifts. Furthermore, the data have not been referenced to dry air. Data quality nevertheless has improved significantly since implementation of the use of calibration gases in sample analyses. Because of variability in the 1977 and early 1978 (not shown) F-12 data, a longer record is needed for definitive information about growth rates and latitudinal gradients. However, as of December 31, 1977, the annual growth rate of F-11 appears to be about 8% per year, computed from measurements in 1977 and early 1978. This rate is approximately one-half the growth rate measured earlier in the 1970's, probably reflecting the lower rates of F-11 input into the atmosphere compared with the exponential rate of input increase before 1974. The data also suggest that the latitudinal gradient in F-11 is significantly smaller than reported earlier. This result implies that the lifetime of F-11 in the atmosphere is probably more than 50 yr and that the potential threat of destruction of stratospheric ozone by F-11 is probably real.

N_2O data show considerably less scatter than the F-11 measurements and indicate that atmospheric N_2O concentrations are remaining essentially constant. The biological sources of N_2O are probably sufficiently large to mask increases in atmospheric N_2O concentrations arising from human activities such as increased use of fertiliziers.

Table 14. 1977 Provisional Halocarbon Data From Baseline Stations

Station	Date	F-11 Evac. Conc.	F-11 Evac. Cyl. S.D.	F-11 Pres. Conc.	F-11 Pres. Cyl. S.D.	F-12 Evac. Conc.	F-12 Evac. Cyl. S.D.	F-12 Pres. Conc.	F-12 Pres. Cyl. S.D.	N_2O Evac. Conc.	N_2O Evac. Cyl. S.D.	N_2O Pres. Conc.	N_2O Pres. Cyl. S.D.
Barrow													
	Jan 6	177	1										
	12	198	1										
	26	166	-										
	Feb 15	166	-										
	22	172	1										
	Mar 11	163	-										
	19	164	1										
	24	164	0										
	Apr 8	165	4										
	13	167	2										
	20	L	-										
	May 2	172	3			551	6						
	10	L	-			L	-						
	24	182	1			2630	13						
	Jun 2	160	2			311	1						
	9	L	-			L	-						
	16	166	1			367	-						
	Jul												
	Aug 3	182	1	156	4	3172	10	278	12	393	3	344	7
	8	174	6	158	2	426	1	343	17	381	11	334	8
	17	178	4	154	2	377	14	290	9	408	8	327	8
	Sep 4	174	4	157	4	1008	11	291	11	373	6	338	4
	11	L	-	157	4	L	-	285	7	L	-	332	13
	17	168	2	163	3	434	3	294	12	331	14	334	11
	28	L	-	158	5	L	-	303	10	L	-	328	5
	Oct 8	178	5	163	5	365	3	295	10	344	1	336	4
	11	169	5	167	3	527	41	305	15	327	8	329	4
	20	202	2	166	3	684	35	321	15	321	14	338	4
	Nov 2	173	3	164	2	463	2	317	8	331	5	335	4
	9	172	4	169	4	641	8	307	9	337	5	334	5
	14	L	-	166	3	L	-	321	4	L	-	332	3
	26	184	5	167	2	1167	23	379	14	330	-	339	10
	Dec 11			171	1			329	6			335	9
	17			170	4			345	2			338	2
	29			168	5			325	6			340	3
Mauna Loa													
	Jan 6	156	2										
	11	158	1										
	19	163	2										
	24	165	1										
	Feb 4	158	1										
	14	156	1										
	23	161	-										
	28	178	0										
	Mar 9	159	2										
	16	151	-										
	21	164	0										
	Apr 4	150	2										
	13	148	2										
	19	154	3										
	26	171	2										

Table 14. 1977 Provisional Halocarbon Data From Baseline Stations (continued)

Station	Date	F-11 Evac. Conc.	F-11 Evac. Cyl. S.D.	F-11 Pres. Conc.	F-11 Pres. Cyl. S.D.	F-12 Evac. Conc.	F-12 Evac. Cyl. S.D.	F-12 Pres. Conc.	F-12 Pres. Cyl. S.D.	N_2O Evac. Conc.	N_2O Evac. Cyl. S.D.	N_2O Pres. Conc.	N_2O Pres. Cyl. S.D.
Mauna Loa (continued)													
	May 2	154	2			281	9						
	11	148	5			258	6						
	16	178	4			358	2						
	24	154	1			293	3						
	31	153	2			262	2						
	Jun 6	168	2			310	7						
	16	150	2			343	5						
	22	155	2			267	7			342	8		
	30	167	1			299	17			368	3		
	Jul 6	165	4			317	5			349	8		
	13	156	-			275	3			361	8		
	19	154	4			307	7			347	7		
	27	157	1			283	3			358	2		
	Aug 3	160	2			977	14			353	2		
	11	160	5			310	7			338	16		
	25			152	4			305	11			352	9
	30	169	1			293	2			366	6		
	Sep 6	158	2			273	2			344	2		
	15	166	7	153	5	329	4	265	6	363	11	334	3
	20	170	3	154	4	317	4	277	14	422	18	337	10
	28	161	3	157	6	272	2	269	5	337	3	332	2
	Oct 6	165	1	155	5	335	3	287	9	346	6	328	5
	13	158	9	147	2	300	3	300	25	382	7	333	3
	19	160	5	155	2	829	-	275	3	319	16	327	5
	Nov 4	161	4	158	4	349	5	282	4	359	3	337	11
	10	158	5	152	3	309	7	274	3	352	4	329	9
	17	164	7	155	5	281	3	281	10	338	3	330	2
	24	156	3	153	1	333	4	269	3	336	6	329	6
	Dec 8			157	4			288	4			328	10
	15			154	6			288	2			331	4
	22			157	3			284	10			336	2
	29			156	3			278	3			334	6
Samoa													
	Jan 6	147	1										
	13	156	1										
	23	143	2										
	27	150	0										
	Feb 3	157	2										
	12	146	1										
	18	153	0										
	26	192	2										
	Mar 8	136	1										
	11	140	-										
	17	154	2										
	Apr 1	135	2										
	8	142	3										
	19	150	2										
	30	152	2			280	4						
	May 5	151	4			293	6						
	14	141	2			250	6						
	19	142	5			266	7						
	26	145	4			299	8						

Table 14. 1977 Provisional Halocarbon Data From Baseline Stations (continued)

Station	Date	F-11 Evac. Cyl. Conc.	F-11 Evac. Cyl. S.D.	F-11 Pres. Cyl. Conc.	F-11 Pres. Cyl. S.D.	F-12 Evac. Cyl. Conc.	F-12 Evac. Cyl. S.D.	F-12 Pres. Cyl. Conc.	F-12 Pres. Cyl. S.D.	N_2O Evac. Cyl. Conc.	N_2O Evac. Cyl. S.D.	N_2O Pres. Cyl. Conc.	N_2O Pres. Cyl. S.D.
Samoa (continued)													
	Jun 5	144	2			247	1						
	10	152	1			275	3						
	18	144	2			282	1			366	-		
	23	151	8			261	6			367	14		
	29	147	3			271	5			371	2		
	Jul 14	143	-			255	7			365	11		
	27	151	1			252	1			338	3		
	Aug 4	148	2			262	3			350	12		
	12	154	6	140	3	259	3	253	7	350	8	324	11
	19	160	5	144	0	340	10	249	5	364	5	345	13
	25	150	1	142	0	272	1	250	6	350	17	380	26
	31	150	3	137	0	257	3	247	4	342	1	326	5
	Sep 14	147	4	141	5	300	1	246	3	343	8	343	9
	21	142	3	141	0	263	5	249	3	350	4	328	12
	28	160	1	143	2	266	4	247	4	344	5	334	6
	Oct 7	147	5	145	9	298	4	254	14	336	4	337	7
	16	149	3	142	4	287	4	251	6	347	2	326	6
	20	167	3	144	5	278	3	250	4	251	2	331	6
	29	147	2	140	7	311	4	256	10	334	3	314	8
	Nov 3	139	0	140	4	279	2	256	2	247	2	328	6
	10	171	3	139	4	276	3	247	3	354	14	330	8
	17	145	2	143	6	297	3	248	3	376	6	326	2
	24	146	1	146	5	291	1	248	1	354	7	324	5
	Dec 3			141	5			252	5			327	7
	7			139	5			260	6			336	12
	15			139	3			258	5			323	12
	30			145	3			258	4			324	8
Niwot Ridge													
	Jan 7	161	1										
	17	165	3										
	27	160	1										
	Feb 3	159	2										
	9	208	1										
	23	184	4										
	Mar 7	248	9										
	9	147	-										
	18	156	2										
	25	150	2										
	30	157	-										
	Apr 7	L	-										
	13	156	2										
	22	216	0										
	27	155	2										
	May 5	184	5			332	16						
	10			152	2								
	12	151	2			264	4						
	17			169	2								
	19	150	-	157	1	267	3						
	24			151	1								
	26	166	3			302	12						
	31	150	5			266	3						

Table 14. 1977 Provisional Halocarbon Data From Baseline Stations (continued)

Station	Date	F-11 Evac. Cyl. Conc.	F-11 Evac. Cyl. S.D.	F-11 Pres. Cyl. Conc.	F-11 Pres. Cyl. S.D.	F-12 Evac. Cyl. Conc.	F-12 Evac. Cyl. S.D.	F-12 Pres. Cyl. Conc.	F-12 Pres. Cyl. S.D.	N_2O Evac. Cyl. Conc.	N_2O Evac. Cyl. S.D.	N_2O Pres. Cyl. Conc.	N_2O Pres. Cyl. S.D.
Niwot Ridge (continued)													
	Jun 1			155	2								
	8	152	1			324	0						
	15	149	0			285	22			332	8		
	21	163	5			270	4			325	2		
	28	L	-			L	-			L	-		
	Jul 13	152	5			271	3			323	7		
	19	151	3			281	-			335	10		
	27	L	-			L	-			L	-		
	Aug 2	156	4			281	5			330	10		
	10	156	3			270	5			333	3		
	17	L	-			L	-			L	-		
	25	156	5			295	20			327	9		
	Sep 1	154	2			271	2			328	2		
	15	156	6			290	10			330	5		
	22	154	0			309	3			333	6		
	29	155	7			290	16			329	6		
	Oct 8	160	6			319	15			332	9		
	13	161	4			319	23			331	3		
	23	160	3			332	26			332	4		
	27	164	4			302	10			360	8		
	Nov 3	157	4			307	17			333	3		
	11	160	5			292	17			331	9		
	21	159	5			297	10			333	3		
	29	155	8			303	11			331	6		
	Dec 7	168	8			383	21			344	9		
	17	168	3			291	4			343	5		
	31	160	0			308	1			340	5		
South Pole													
	Jan 26			145	3			251	5			346	7
	Feb 4			141	7			240	1			346	4
	7			135	5			245	14			344	3
	10			131	-			244	2			342	9
	Mar 14			73	4			229	0			326	8
	Apr 14			79	3			235	1			343	8
	May 13			L	-			L	-			L	-
	Jun 13			ND	-			241	2			317	5
	Jul 13			124	-			240	-			336	-
	Aug 15			L	-			L	-			L	-
	Sep 13			L	-			L	-			L	-
	Oct 12			130	8			246	-			326	-
	Nov 14			L	-			L	-			L	-
	Dec 1			154	4			263	0			337	1
	18			L	-			L	-			L	-

Note: L = sample leaked.

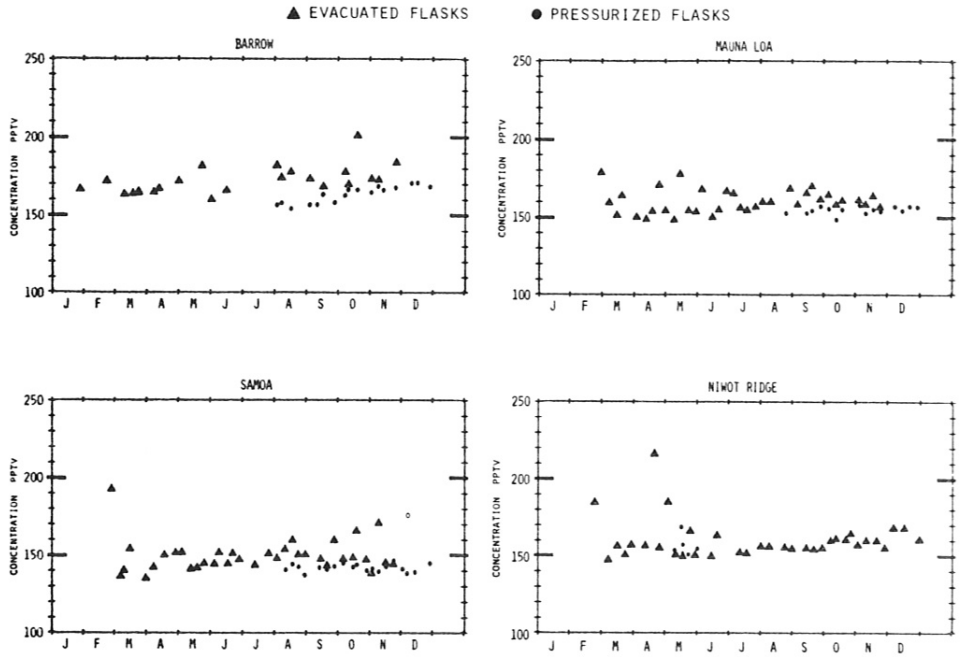

Figure 14. 1977 provisional F-11 data from evacuated and pressurized flask sampling for Barrow, Mauna Loa, and Samoa Observatories and for Niwot Ridge, Colo.

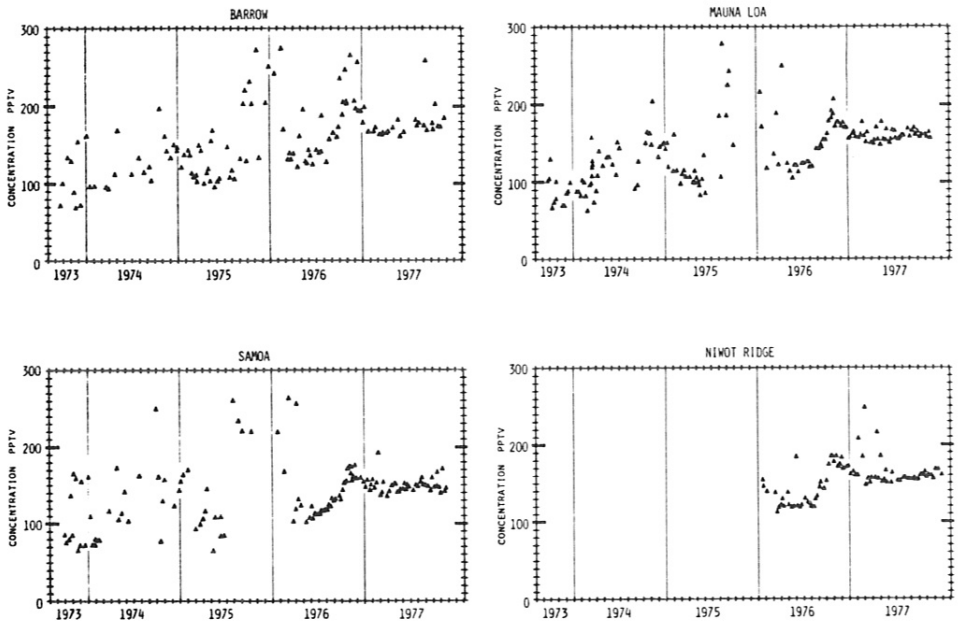

Figure 15. All GMCC F-11 measurements from evacuated flask sampling for Barrow, Mauna Loa, and Samoa Observatories and Niwot Ridge, Colo.

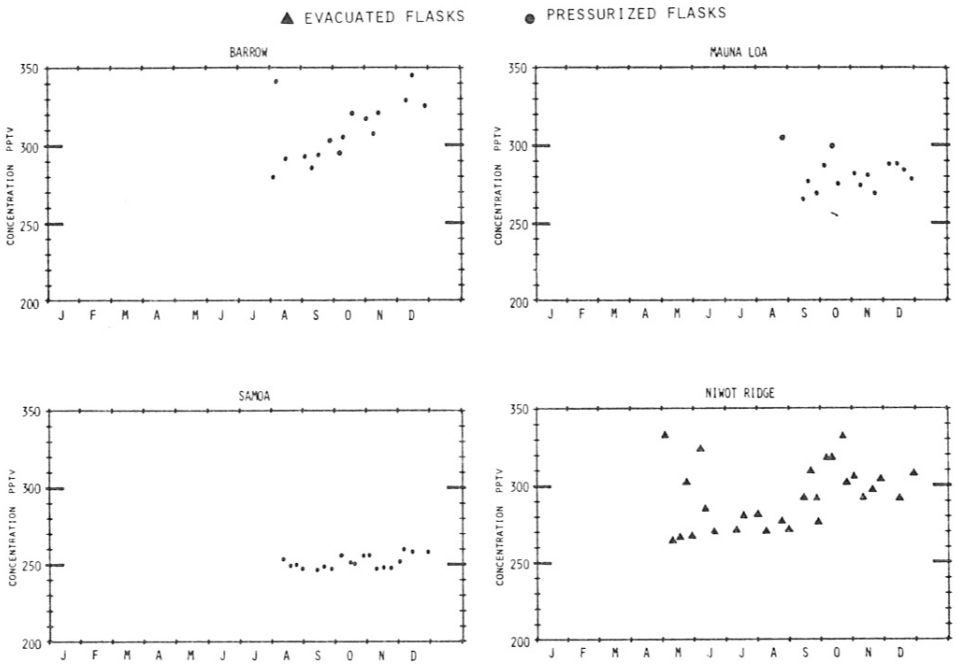

Figure 16. 1977 provisional F-12 data from evacuated and pressurized flask sampling for Barrow, Mauna Loa, and Samoa Observatories and Niwot Ridge, Colo.

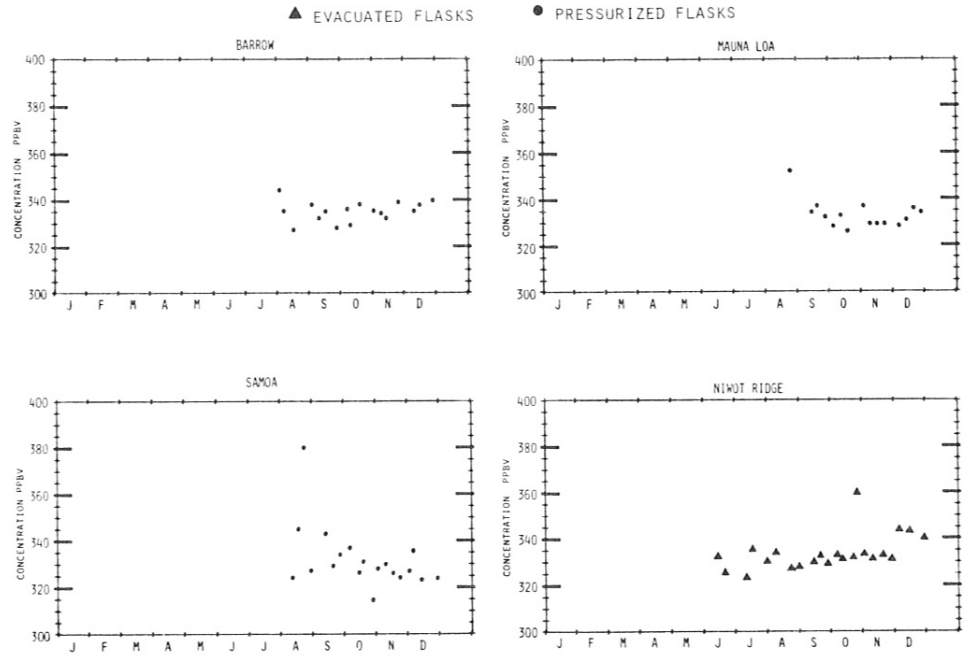

Figure 17. 1977 provisional N_2O data from evacuated and pressurized flask sampling for Barrow, Mauna Loa, and Samoa Observatories and Niwot Ridge, Colo.