

3.5 Stratospheric Water Vapor

Establishing a program for routine stratospheric water vapor profile measurements was much slower than anticipated. Problems developed in two crucial areas: the balloon system used to carry the frost point instrument in the stratosphere, and the production of the frost point instrument by the manufacturer.

For many years a 7,000-gm neoprene balloon was used to carry the instrument aloft. This specially produced balloon was no longer satisfactory because a number of balloons burst before reaching the desired altitude. It thus became necessary to develop a new balloon system. Working with J. Mastenbrook of the Naval Research Laboratory, we designed and tested a 700-m³ plastic balloon with a controlled rip patch. This balloon, which ascends at a rate of about 275 m min⁻¹ and descends at a rate of about 450 m min⁻¹, has proved moderately reliable but is more cumbersome to launch than the neoprene balloon. Further work is being carried out to make the balloon system more reliable and simpler to launch.

The other major problem experienced during the year was delay in transferring the technology for producing the frost point hygrometer to a commercial manufacturer. Several design changes were made by J. Mastenbrook to simplify the manufacture and improve performance. In earlier versions of the frost point instrument (see GMCC Summary Report 1978) the mirror temperature was kept at the frost point temperature by maintaining the size of the condensate on the mirror essentially constant. A recent improvement to the instrument maintains uniform density (thickness) of the condensate deposit and uses a more sensitive optical detection system to maintain the mirror temperature at the frost point temperature.

3.6 Halocarbons and N₂O

3.6.1 Operations

Collection of air samples for CCl₃F (Freon-11), CCl₂F₂ (Freon-12), and N₂O (nitrous oxide) analyses was continued during 1979 at the four GMCC stations and Niwot Ridge, Colo. Sampling and chromatographic analysis procedures remained virtually identical to those established in mid-1977 (Komhyr et al., 1980). During 1979 sampling frequency was increased at SPO. Beginning with the 1979-1980 austral summer, the sampling rate at SPO one pair sample per week during summer and two pair samples per month during winter. At Niwot Ridge the evacuated flask sampling was replaced with pressurized air sampling, the method of sample collection used at all other GMCC stations. During an overlap period, 7 December 1979 to 30 April 1980, air samples at Niwot Ridge were collected by both methods.

Several problem areas were studied during the year. The scatter in the SPO data for all three constituents was relatively high compared with the data scatter at other stations. In most cases, questionable trace gas concentrations were probably too high because of contamination, but some unreasonably low concentrations were also noted. It is unlikely that such low values are representative of the Antarctic atmosphere. They probably result from adsorption of the trace gases onto walls of the sample cylinders because of prolonged sample storage. An attempt is being made to reduce the magnitude of this problem by selecting and using sample cylinders that have given reliable data in the past. The difficulties experienced point to the desirability of having an on-site gas chromatograph at SPO for halocarbons and N₂O measurements.

We determine halocarbon and N₂O concentrations relative to moist air and use theoretically deduced conversion factors, including relative humidity data, to express results in terms of dry air. Experiments were conducted during 1979 to assess the validity of the theoretical conversion factors in use.

Investigations were also conducted into the stability of trace gas concentrations stored in sample cylinders. It was possible to show that halocarbon and N₂O concentrations did not change by more than 1% in air samples stored for 2 to 3 weeks. This is a normal cylinder residence time for air samples collected at all GMCC stations except SPO.

An important aspect of halocarbon and N₂O monitoring is the procurement and maintenance of stable calibration gases. Uncertainties among various laboratories that prepare calibration gases range from ±5% for F-11 to ±10% for F-12 and N₂O. Instead of preparing calibration gases, we used a high pressure tank of air as a standard. The stability of the halocarbon and N₂O concentrations in this primary standard tank (no. 3072) is being monitored by comparison with similar trace gas concentrations in several other tanks, as well as by interlaboratory comparisons. To date, we have no evidence of any change in F-11 and N₂O in this primary standard. F-12, however, has been drifting at a rate of about 1% per year. F-11, F-12, and N₂O concentrations within our primary standard tank no. 3072 have been calibrated by several laboratories. Results are summarized in table 13.

In table 14 results of four multilaboratory F-11, F-12, and N₂O intercomparisons are listed. GMCC concentrations for specific air samples are compared with

Table 13.--Concentration in GMCC F-11, F-12, N₂O primary reference standard tank no. 3072 as determined by various laboratories

Date	Calibrating laboratory	Type of calibration	N ₂ O(ppbr)	Concentration F-12(pptv)	F-11(pptv)
Dec 1977	OGC	D*	331.4	353.4	149.1
Oct 1978	OGC	D	331.3	355.3	147.3
Nov 1978	OGC	D	331.5	357.2	149.4
Apr 1979	NCAR	D	317.7	253.7	140.3
Apr 1979	AL/NOAA	D	-	-	139.0
Aug 1979	OGC	I+	328.0	243.2	148.9
Oct 1978	NCAR	I	325.3	255.6	139.0
Oct 1978	AL/NOAA	I	325.3	244	141
Oct 1979	AL/NOAA	I	360.6	251	151

*Direct; +Indirect.

Table 14.--Interlaboratory trace gas concentration comparisons

Comparison organizer	GMCC value (Rasmussen calibration)	No. participating labs	Consensus value	σ
Rasmussen 1976	F-11 145	15	140.2	16
NBS 1976	F-11 194	15	171	23
Fraser 1978	F-11 143.6	7	146.7	3.0
	156.0	8	156.0	5.5
	F-12 250.4	5	255.8	12.3
	258	5	254	7.3
	N ₂ O 335.4	5	325.6	16
	332.0	5	323	14
Rasmussen 1979	F-11 71	19	62	8
	174		162	23
	F-12 123	19	110	13
	294		279	16
	N ₂ O 233	19	207	25
	337		321	13

average concentrations for the samples obtained by several other laboratories. Rasmussen (OGC) calibration values were used for GMCC standards in these comparisons. Although most laboratories report a measurement precision of $\pm 1\%$, the absolute calibrations vary by as much as $\pm 10\%$, as shown by the standard deviations of the consensus values in table 14. Preliminary tests conducted in the Boulder laboratory indicate that the GMCC N₂O data, reported in the OGC calibration scale, should be adjusted by the factor 0.898.

3.6.2 The Data

F-11, F-12, and N₂O sample data for 1979 are plotted in figs. 13 to 15. All collected data are included in the plots except several (<10) values that fell off scale. The gap in the South Pole record resulted from concentrating sampling there during the austral summer months. More sampling cylinders have since been procured, which will allow enhanced sampling frequency during summer months and sampling during winter.

The gas chromatograph used for sample analyses was inoperative during much of August 1979, resulting in a 1 week or more data loss at all stations, followed by a several week period of questionable results. A small gap in the data record, followed by a number of scattered values, is evident in the August data plots.

The data in figs. 13 to 15 have not been screened for background atmospheric conditions. One unexplained event indicated in fig. 14 is the significant increase

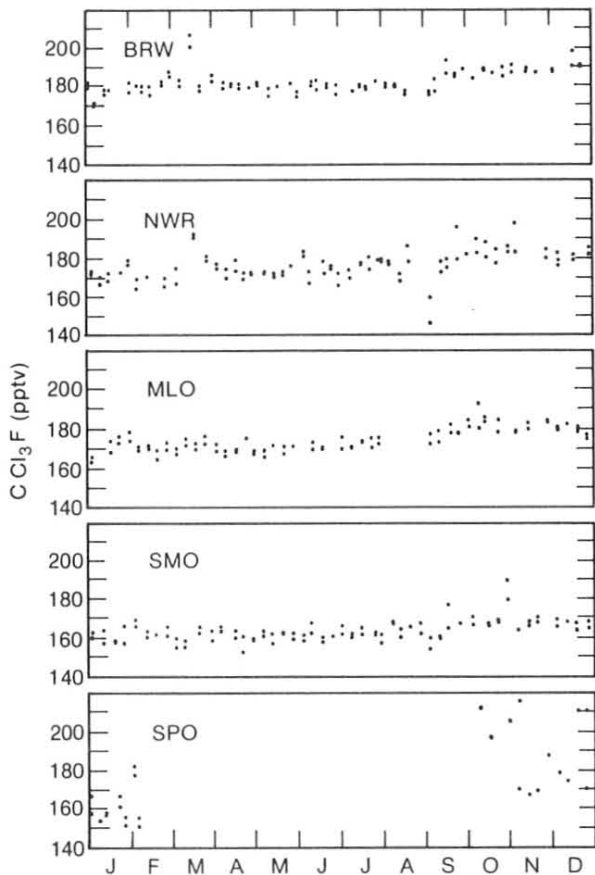


Figure 13.-- CCl_3F sample data obtained during 1979 at BRW, Niwot Ridge, MLO, SMO, and SPO.

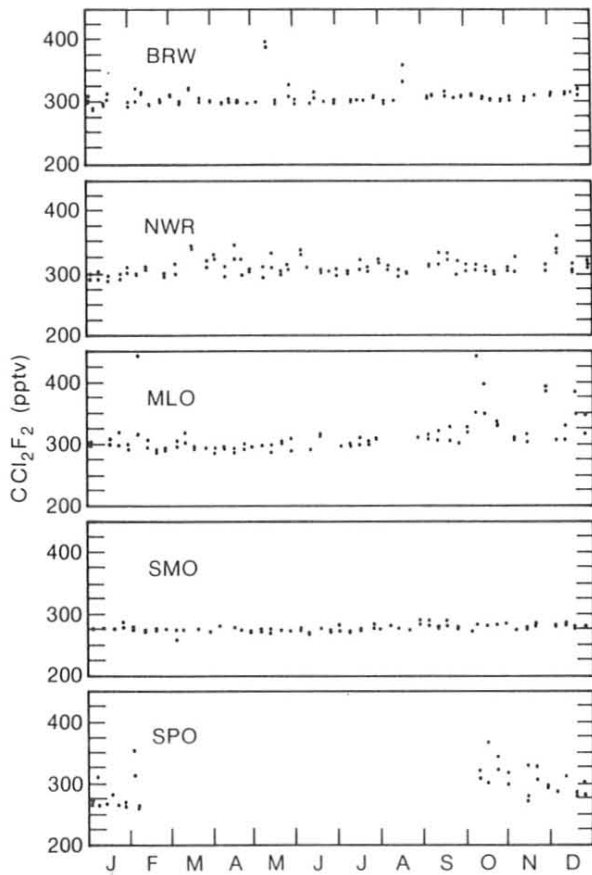


Figure 14.-- CCl_2F_2 sample data obtained during 1979 at BRW, Niwot Ridge, MLO, SMO, and SPO.

in scatter of the Mauna Loa F-12 data toward the end of the year. Another perplexing feature is the relatively high N_2O growth rate ($\sim 1\% \text{ yr}^{-1}$) observed at SMO compared to that measured at all other stations. Whether this growth rate is real or an artifact of sample collection and analyses is not known.

3.6.3 Data Analysis

The 1979 data support the conclusions concerning F-11, F-12, and N_2O global abundances, latitudinal distributions, global growth rates, interhemispheric exchange rates, and atmospheric lifetimes reported in the GMCC Summary Report 1978. A decrease in the rate of increase of F-11 and F-12 in the global background atmosphere is indicated, however, reflecting the decrease in production and release of these chemicals into the atmosphere. The global growth rate of N_2O is still not well established by the data that nevertheless suggest a small interhemispheric gradient with larger values in the north.

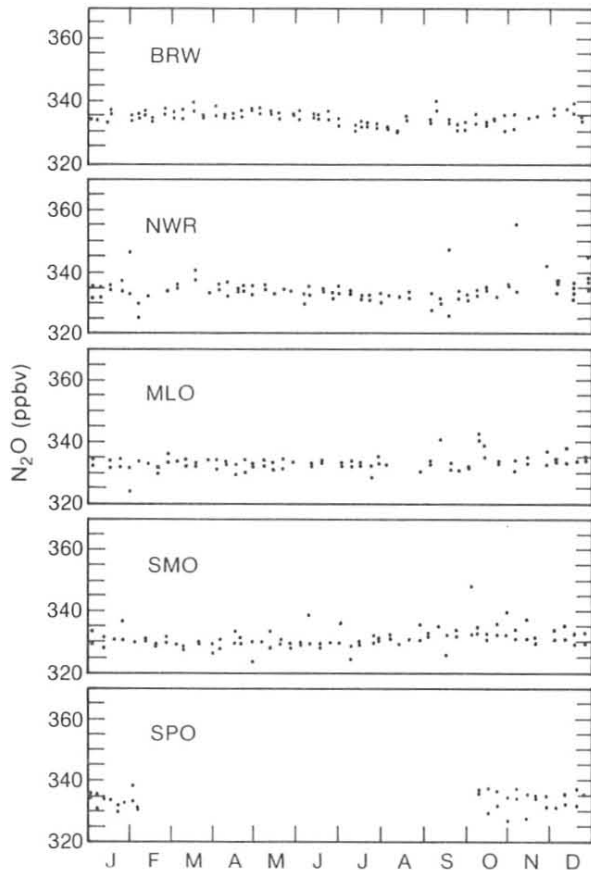


Figure 15.--N₂O sample data obtained during 1979 at BRW, Niwot Ridge, MLO, SMO, and SPO.

3.7 Surface Aerosols

The routine GMCC surface aerosol program for 1979 included the measurement of condensation nuclei concentration and volumetric light scattering at BRW, MLO, SMO, and SPO. Condensation nuclei concentration is measured continuously with a modified version of the G.E. condensation nuclei counter at all four sites. A Pollak (manually operated) condensation nuclei counter is located at each site to serve as a secondary standard and provide calibration points for the automatic nuclei counter. A four-wavelength nephelometer was operating at each site during 1979. This report will present the first light scattering data acquired at SPO.

The calibration of the automatic nuclei counter is checked daily by comparison with the Pollak nuclei counter. If necessary, the automatic nuclei counter is forced to agree with the Pollak counter. The complete calibration procedure and scaling of the data are described by Bodhaine and Murphy (1980). The four-wavelength nephelometers are calibrated by filling them with carbon dioxide gas at 2-mo intervals. The output of the instrument can then be adjusted to give the known volumetric scattering coefficients of carbon dioxide. Bodhaine (1979) gives details of the theory and practice of nephelometer calibration and the latest recommended values of the scattering coefficients of air, argon, carbon dioxide, and Freon-12.