

also show nearly constant mixing ratios above 60 mb at concentrations of approximately 2.5 parts per million by mass (ppmm). The differences below 70 mb are probably associated with shorter term (less than a month) variability within the atmosphere. The results obtained from this comparison suggest that Boulder is a suitable location to continue the stratospheric water vapor measurement series begun in Washington, D.C.

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 (NWR), Colorado. Sampling and chromatographic analysis procedures remained virtually identical to those established in mid-1977 (Komhyr et al., 1980), except that during late October and November a second chromatograph (Perkin Elmer model 3920) was used to analyze air samples collected mainly at South Pole.

Additional work was performed in 1980 to assess the validity of water vapor corrections derived theoretically and used in converting halocarbon and N₂O trace gas ambient (moist) air concentrations to concentrations in dry air. It was found, using a newly acquired General Eastern Corporation dewpoint hygrometer, that measured and theoretically derived amounts of water vapor differed by no more than about 5%. Such an error translates to a 0.15% error in trace gas concentrations expressed in terms of dry air, and is inconsequential.

The GMCC F-11, F-12, and N₂O calibration gases are periodically calibrated by R. A. Rasmussen of the Oregon Graduate Center, Beaverton, Oregon. A question has existed about the validity of the absolute calibration values originally assigned by Rasmussen to his N₂O standards since, for example, the N₂O calibration scale associated with gas standards prepared by R. F. Weiss of the Scripps Institution of Oceanography (personal communication, 1980) was approximately 10% lower than that of Rasmussen. To resolve the discrepancy, a new technique was developed in our laboratory (Komhyr et al., 1982) for preparing N₂O and other calibration gas standards. As applied to N₂O, the method involves preparation by gravimetric means of an N₂O/CO₂ gas mixture of highly accurately known mass ratio, and subsequent dilution of this mixture with N₂O- and CO₂-free air to approximately ambient air concentrations of these trace gases. From a determination of the absolute CO₂ concentration in this dilution gas mixture, using highly accurately calibrated CO₂ gas standards and an infrared measurement technique, the N₂O concentration in the dilution mixture is readily inferred.

Application of this calibration method to our N₂O calibration gas in tank 3072 yielded an N₂O mole fraction of $297.7 \pm 2\%$ ppbv compared with the originally assigned Rasmussen value of $331.4 \pm 5\%$ ppbv. (The 2% error for our value is an estimate based on possible systematic errors associated with the performance of this preliminary calibration.) This new result agrees with N₂O calibration values of R. F. Weiss, as well as of Connell et al. (1981) who employed a tunable diode laser to measure N₂O in air. More recently, Goldan et al. (1981) obtained similar results following recalibration of their N₂O primary standards prepared in 1975 by static and dynamic dilution techniques.

Table 12.--Summary of CCl₃F and CCl₂F₂ measurement results derived from linear regression analyses from 3 years of data centered around 7 September 1978

Station	No. obs.	Growth rate (pptv yr ⁻¹)	95% s.e. growth rate	Mixing ratio (pptv)	95% s.e. mixing ratio
<u>CCl₃F</u>					
BRW	133	12.10	±0.62	172.9	±0.51
NWR	130	10.78	±0.72	168.6	±0.65
MLO	128	12.84	±0.64	163.8	±0.52
SMO	136	12.35	±0.57	155.3	±0.49
SPO	42	11.17	±2.77	157.0	±2.54
<u>CCl₂F₂</u>					
BRW	112	15.10	±1.39	298.6	±1.09
NWR	58	18.24	±1.46	295.9	±1.26
MLO	112	18.97	±1.54	295.0	±1.16
SMO	118	17.48	±0.81	273.1	±0.68
SPO	32	17.93	±1.96	264.7	±1.72

3.6.2 Data and Data Analysis

F-11, F-12, and N₂O data obtained at the GMCC baseline stations and NWR are shown plotted in figs. 10, 11, and 12, respectively. Outliers have been removed from the data, using data selection criteria described elsewhere (Komhyr et al., 1981e).

Positive F-11 and F-12 growth rates are indicated in the plots of figs. 10 and 11. Actual growth rates at the five stations, derived from linear regression analyses for a 3-yr period of record centered at 7 September 1978, are shown in table 12. From the data, provisional minimum atmospheric lifetimes of 41 and 65 years have been computed for F-11 and F-12, respectively. In performing the lifetime calculations, random measurement errors were taken into account as well as assumed ±5% systematic errors in year-to-year F-11 and F-12 release rates and in reference gas calibrations.

N₂O growth rates shown in table 13, derived from linear regression analyses from 3 years of data centered around 1 July 1979, are also positive and

Table 13.--Summary of N₂O measurement results derived from linear regression analyses from 3 years of data centered around 1 July 1979

Station	No. obs.	Growth rate* (ppbv yr ⁻¹)	95% s.e. growth rate	Mixing ratio† (ppbv)	95% s.e. mixing ratio
BRW	143	0.43	±0.25	301.50	±0.21
NWR	121	0.90	±0.30	301.78	±0.25
MLO	136	0.88	±0.32	300.66	±0.28
SMO	144	1.44	±0.36	303.17	±0.29
SPO	63	0.44	±0.36	299.44	±0.33

*Mean growth rate: 0.82 ppbv yr⁻¹.

†Northern Hemisphere concentration minus Southern Hemisphere concentration (excluding SMO): 301.1 - 299.4 = 1.9 ppbv.

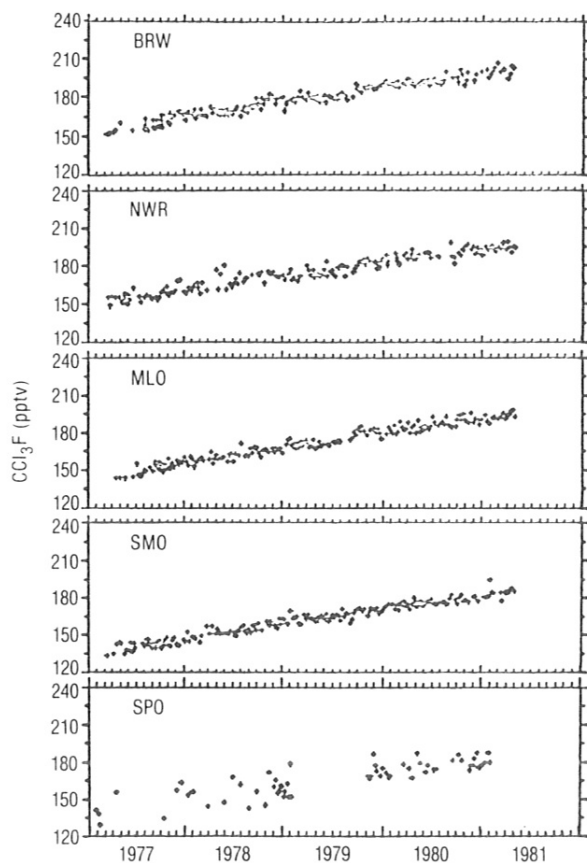


Figure 10.--NOAA Air Resources Laboratories' CCl_3F data record.

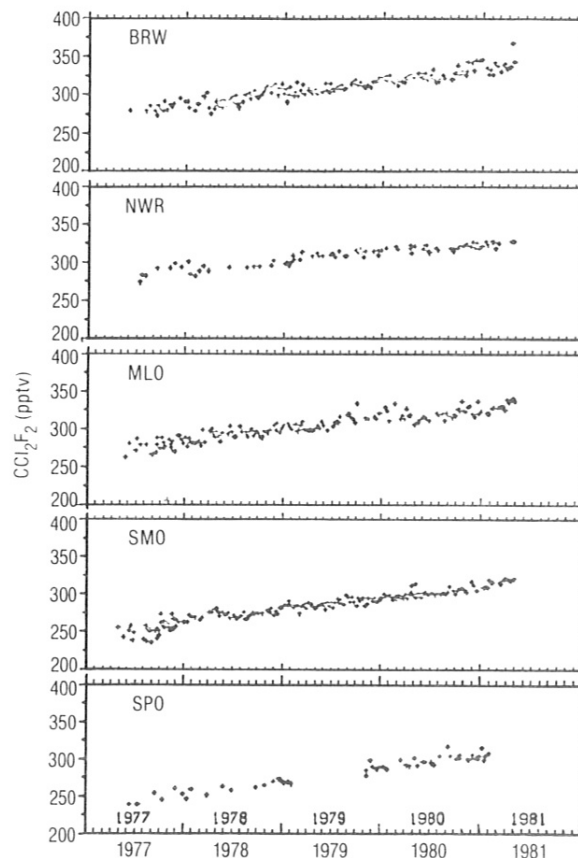


Figure 11.--NOAA Air Resources Laboratories' CCl_2F_2 data record.

significant. Note from fig. 12 that the N_2O mixing ratio appears to have peaked at Samoa in late 1979. The data indicate, furthermore, that an excess N_2O mixing ratio of 1.9 ppbv exists in the Northern Hemisphere.

3.7 Surface Aerosols

The GMCC surface aerosol monitoring program during 1980 included the measurement of condensation nuclei at BRW, MLO, SMO, and SPO, and light scattering at BRW and MLO. Condensation nuclei were measured continuously using the G.E. automatic condensation nucleus (CN) counter (catalog no. 112L428) with modifications to the electronics suggested by N. Ahlquist of the University of Washington. These modifications have been discussed in GMCC Summary Report No. 5 (Hanson, 1977) and have resulted in improved sensitivity and reliability of the instrument. A Pollak CN counter (model P, BGI, Inc., Waltham, Mass.) is located at each site to act as a secondary standard and provide routine calibration for the other nucleus counters onsite.

Light scattering was measured at the GMCC stations using specially constructed four-wavelength integrating nephelometers manufactured by MRI, Inc.,

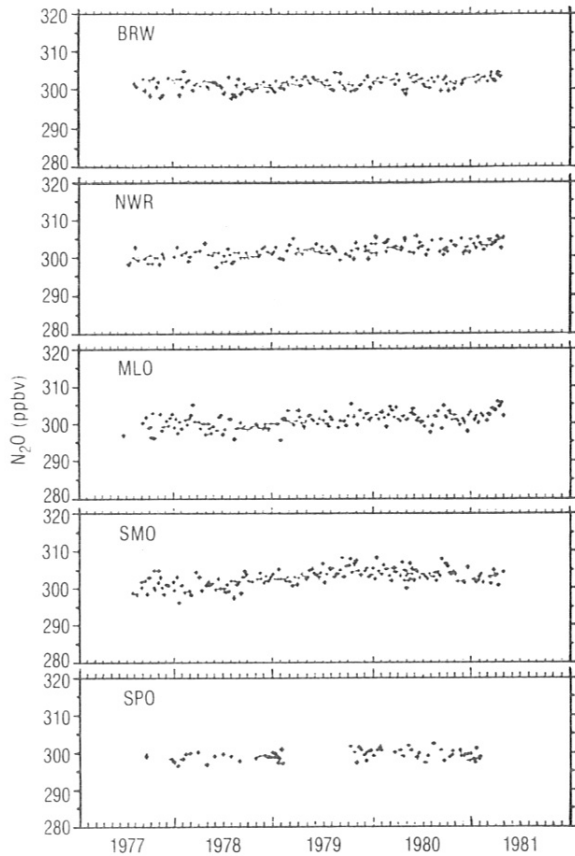


Figure 12.--NOAA Air Resources Laboratories' N₂O data record.

Altadena, Calif. The details of this instrument were discussed in GMCC Summary Report No. 5 (Hanson, 1977). These instruments were calibrated by filling them with CO₂ at 2-mo intervals and adjusting their outputs to agree with the known scattering coefficients of CO₂. In addition to the absolute calibrations performed at 2-mo intervals, weekly relative calibrations were made using the internal calibration objects built into the instruments.

3.7.1 Barrow

The BRW Pollak CN counter (SN 16) operated routinely throughout 1980 without problems. Daily observations provided routine checks for the G.E. automatic CN counter, and a more extensive calibration was performed if necessary on a weekly basis.

The G.E. counter produced acceptable data for 77% of the year. Although there were minor periods of downtime, the main period was from day-of-year (DOY) 152 to 179, accounting for most of the month of June.

The nephelometer produced acceptable data for 86% of the year. The majority of the downtime occurred during the months of May and June for unknown reasons. All data were recorded on magnetic tape and a backup chart recorder.