3.6 Halocarbons and Nitrous Oxide

3.6.1 Operations

Routine collection of air in stainless steel flask pairs continued during 1981 at the four GMCC stations and at NWR. Samples were collected weekly at all stations except SPO where biweekly sampling prevailed. Sample quality was generally high, except at SPO where long storage time and extreme temperatures degraded the samples. Analysis of the air samples for CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), and nitrous oxide (N_2O) continued at the Boulder chromatographic laboratory with few instrument problems and no procedural changes.

A used Perkin Elmer 3920 gas chromatograph, obtained in 1980, was totally reconditioned in 1981. Detectors were sent to Nuclear Sources and Services, Inc., for cleaning and testing. The electrometer circuit board was exchanged for a new one, all new carrier gas lines and controls were installed, temperature circuits were calibrated, oven insulation was improved, and a sampling valve was modified to provide on-column sample injection. After reassembly of the chromatograph, tests indicated that the detector response was high but sensitive to environmental temperature changes.

The chromatographic laboratory was reconfigured in December by installing all ancillary equipment in a rack between the two gas chromatographs. This has greatly facilitated sample analyses. Additions to the laboratory in 1981 were a spare pressure manometer system and flow controller system.

3.6.2 Calibration

The GMCC CFC-11, CFC-12, and N_2O secondary standard calibration gas tank (no. 3072) was sent to R. Rasmussen of OGC in April for its routine stability check. Results showed a decrease in CFC-11 and a continuing increase in CFC-12.

A question has been raised concerning the stability of the GMCC CFC-12 calibration secondary standard since no drift of this standard has been detected during calibration intercomparisons performed in Boulder relative to two other CFC-12 calibration gases. Tank no. 3072 gas has been intercompared quarterly with tank no. 3079 gas for 3 years and with tank no. 3088 gas for 4 years. This problem points to the neccessity of maintaining an independent calibration facility in Boulder for the halocarbon and N_2O monitoring programs.

An absolute calibration system for trace gases such as CFC-11, CFC-12, and N_2O was devised by W. Komhyr in 1979 (GMCC Summary Report for 1980, DeLuisi, 1981). As applied (e.g., to N_2O), the method involves preparation by gravimetric means of an N_2O/CO_2 gas mixture of accurately known mass ratio, and subsequent dilution of this mixture with N_2O- and CO_2-free air to approximately ambient air concentrations of these trace gases. From a determination of the absolute CO_2 concentration in this dilution mixture using accurately calibrated CO_2 gas standards and an NDIR analyzer, the N_2O concentration in the dilution mixture is readily inferred. CFC-11 and CFC-12 trace gases are calibrated by a similar method.

Preliminary work in implementing the calibration technology described above has already been accomplished. Calibration data obtained for N_2O indicate concentration values 10% lower than those obtained at OGC, but in agreement with those obtained by other researchers. These differences will be resolved in the near future.

3.6.3 Data Analyses

Selected 1981 data for CFC-11, CFC-12, and N_2O have been added to 4 years of previous data and are plotted in figs. 15, 16, and 17, respectively. Mean concentrations for 1981 and results of least-squares quadratic regression analyses of the 5-yr data sets for CFC-11 and CFC-12 are summarized in table 9. CFC-11 mean mixing ratios for 1981 are in the range of 188-205 pptv, with the highest concentration found at BRW. Regression analyses predict mixing ratios in the range of 135-154 pptv on 1 January 1977 and growth rates in the range of 11-14 pptv yr^{-1}. CFC-11 data for MLO show a slight but statistically significant decrease in growth rate. CFC-12 mean mixing ratios for 1981 are in the range of 321-345 pptv, with the highest concentration again found at BRW. Regression analyses predict mixing ratios in the range of 239-276 pptv on 1 January 1977 and growth rates in the range of 12-18 pptv yr^{-1}. CFC-12 data for BRW and SPO show statistically significant increases in growth rates. The CFC-12 data incorporate corrections for calibration gas drift as indicated by calibrations performed at OGC. It is likely that results for CFC-12 will change significantly following resolution of the gas calibration problem referred to in sec. 3.6.2.

Table 9.--Mean mixing ratios for 1981 and results of least-squares quadratic regression analyses of GMCC CFC-11 and CFC-12 data for 1977-1981*

Station	No. of obs.	Mean mixing ratio for 1981 (pptv)	Mixing ratio on 1 Jan 1977 (pptv)	Growth rate (pptv yr^{-1})	Growth rate change (pptv yr^{-2})†
CFC-11					
BRW	209	204.7	153.7 ± 0.45	11.33 ± 0.16	-
NWR	216	199.0	150.5 ± 0.47	10.78 ± 0.16	-
MLO	210	196.7	141.2 ± 0.80	14.36 ± 0.70	-0.45 ± 0.13
SMO	221	188.3	135.4 ± 0.40	11.76 ± 0.14	-
SPO	75	188.0	138.4 ± 1.89	11.02 ± 0.61	-
CFC-12					
BRW	190	345.4	274.4 ± 2.11	12.63 ± 1.64	0.70 ± 0.28
NWR	143	337.5	275.5 ± 1.42	13.78 ± 0.40	-
MLO	190	339.7	267.4 ± 1.22	16.08 ± 0.41	-
SMO	216	322.3	243.4 ± 0.83	17.53 ± 0.29	-
SPO	70	321.3	239.4 ± 3.30	12.09 ± 2.53	1.36 ± 0.44

*Coefficients are followed by their standard deviations.
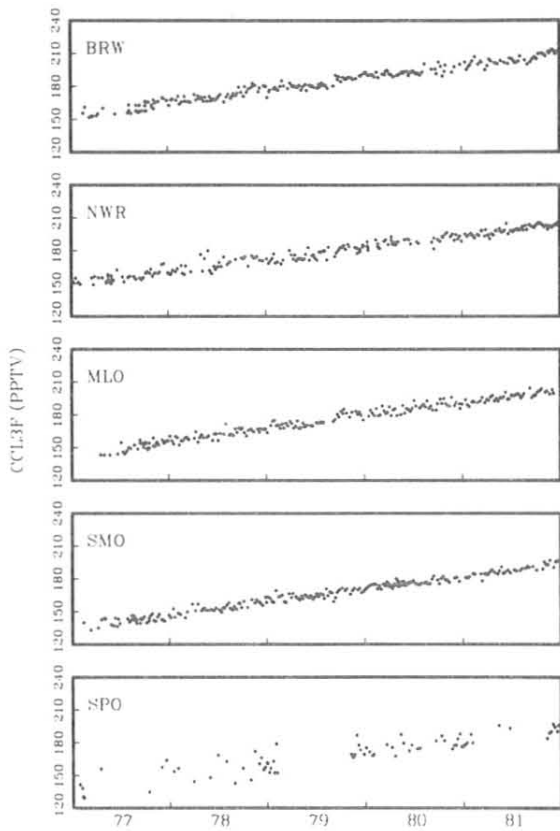†98% confidence interval.
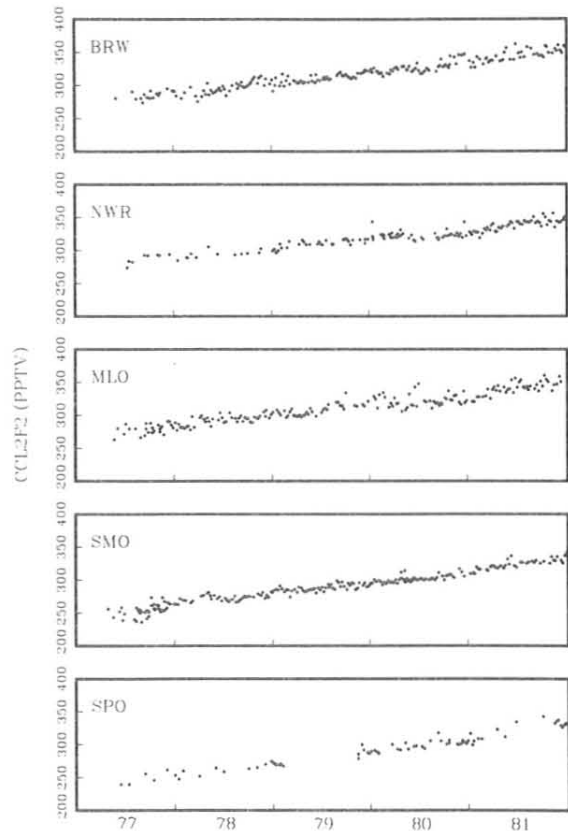
Figure 15.--GMCC's CFC-11 data record.
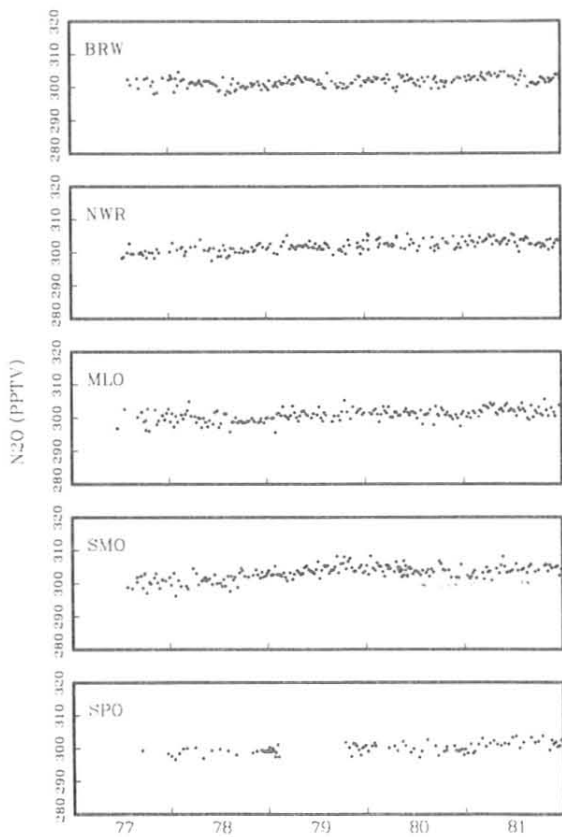

Figure 16.--GMCC's CFC-12 data record.

Figure 17.--GMCC's N_2O data record.

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Table 10.--Mean mixing ratios for 1981 and results of least-squares
quadratic regression analyses of GMCC N_2O data
for 1977-1981*

Station	No. of obs.	Mean mixing ratio for 1981 (pptv)	Mixing ratio on 1 Jan 1977 (pptv)	Growth rate (pptv yr^{-1})	Growth rate change (pptv yr^{-2})†
BRW	199	302.5	300.4 ± 0.23	0.47 ± 0.08	-
NWR	187	303.2	298.5 ± 0.47	1.76 ± 0.37	-0.16 ± 0.06
MLO	199	302.0	298.9 ± 0.28	0.70 ± 0.09	-
SMO	197	304.1	297.4 ± 0.58	3.67 ± 0.45	-0.48 ± 0.08
SPO	94	301.1	297.6 ± 0.39	0.78 ± 0.11	-

*Coefficients are followed by their standard deviations.
†98% confidence interval.

Mean concentrations and summary results for similar regression analyses
of the N_2O data are presented in table 10. N_2O mean mixing ratios for 1981
are in the range of 301-304 pptv, indicating that the gas is well mixed glob-
ally. Regression analyses predict mixing ratios in the range of 297-300 pptv
on 1 January 1977. Growth rates are in the range of 0.5-1.8 pptv yr^{-1}, except
for SMO, which shows the much larger growth rate of 3.67 pptv yr^{-1} that is not
yet explained. N_2O data for NWR and SMO show small but statistically signifi-
cant decreases in growth rates.

3.7 Stratospheric Aerosols--Lidar

3.7.1 Operations

Twenty-four successful lidar observations of the stratosphere were made
during the second half of 1980, and 22 successful observations were made
through 1981. The operational plan for lidar observations calls for an aver-
age rate of one observation every 2 weeks during unperturbed stratospheric
conditions and an increase in the frequency of measurements where significant
enhancements in stratospheric dust are detected.

3.7.2 Data Analysis

Lidar data for 1980 and 1981 have been processed and will be published,
along with a summary, in a NOAA Technical Memorandum. A brief summary of the
1980-1981 observations is given here in terms of stratospheric dust optical
depth integrated between approximately 13-15 to 28-30 km, which is the upper
limit of the sounding.

Figure 18 shows a plot of stratospheric dust optical depth (λ = 694.3 nm)
vs. time using the present data set. No range of uncertainty is given with
these data; however, a comparison between these values and values of strato-
spheric dust optical depth for 1980 deduced from the MLO apparent transmission