3.6 Halocarbons and Nitrous Oxide

3.6.1 Operations

Air was collected weekly in paired stainless steel flasks at BRW, NWR, MLO, and SMO during 1982. Weekly flask pairs were collected only during January, November, and December at SPO. Flasks were shipped to and from the stations in small wooden boxes until April when the boxes were replaced by high-strength cardboard shipping containers. Also in April, an extra pair of flasks was shipped to BRW, MLO, and SMO to be added to the three pairs already being used at each station. This ensured that samples would be taken even if shipping time to and from Boulder increased.

When flask samples reached the Boulder chromatographic laboratory, they were analyzed for CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), and nitrous oxide (N_2O). A new programmable integrating recorder that provides direct peak-height measurements and control of the analysis by a timetable was purchased in April. Computer programs were revised for speedy entry, reduction, and plotting of the data.

At the Boulder laboratory, room-temperature fluctuations had been large and had degraded chromatographic performance, until September when an air conditioner was installed. The stabilized room temperature has resulted in more consistent results from the gas chromatograph.

Only one change was made to equipment at the field stations: a PV array was installed at NWR to charge the batteries that run the sampling pump.

Sample flasks normally used at SPO during the February-October winter-over period were kept in Boulder for special tests in 1982. Fifty flasks were purged and pressurized with high-purity nitrogen. After a few weeks, the flasks were analyzed on the gas chromatograph for pressure loss and contamination. After the problem flasks were made free of leaks, all flasks were taken to NWR and filled with air over a 4-h period. Again, after sitting for a few weeks, the flasks were analyzed. Inconsistent and contaminated flasks were baked at 180°C while being evacuated. This procedure eliminated flask problems.

The sampling instructions and background articles given to new station personnel for use in training were revised and upgraded this year.

3.6.2 Calibration

The calibration gas standard, tank 3072, was taken to OGC in January for its routine stability check. CFC-11 and N_2O have not significantly changed since 1977 whereas CFC-12 has increased by 2.5 pptv yr^{-1}. However, continued quarterly comparisons of tank 3072 with two other gas standards, tanks 3079 and 3088, show no significant relative concentration changes in any of the three constituents.

Two absolute calibration systems, one for N_2O/CO_2 gas mixtures and the other for CFC-11/CFC-12/N_2O mixtures, were built in February. Calibration data confirmed previous results that the correct N_2O concentrations for tank 3072 are 10% less than OGC originally reported.

When attempts were made to prepare CFC-11 and CFC-12 calibration mixtures using N_2O as the internal standard, no GC response to N_2O was seen. The electron capture detector's response to N_2O increased as the CO_2 concentration increased. This anomalous behavior was confirmed by other laboratories. Tests are under way to ascertain the effect of CO_2 secular trends and annual cycles on the N_2O flask data.

3.6.3 Data Analyses

Halocarbon and N_2O selected data for 1982 have been combined with 5 years of previous data for statistical analyses and plotting. Figures 17, 18, and 19 are plots of CFC-11, CFC-12, and N_2O data respectively. BRW halocarbon data exhibit an annual cycle with highest concentrations during December and lowest values in June. No other station shows a statistically significant periodicity. SPO data continue to be the most variable. N_2O data at BRW also have an annual cycle, but this could be due to variations in CO_2 that affect the measurements and will be corrected later. SMO N_2O data show an unexplained increase in concentration all through 1982.

Tentative mean concentrations for 1982 and first- and second-order least-squares regression analyses on the 6-yr halocarbon and N_2O data sets are summarized in table 13. Only MLO continues to show a statistically significant

Table 13.--Mean mixing ratios for 1982, and results of first- and second-order regression analyses of CFC-11, CFC-12, and N_2O data for 1977-1982*

Station	No. of obs.	Mean mixing ratio for 1982	Mixing ratio on 1 Jan 1977†	Growth rate†	Growth rate change†
CFC-11		(pptv)	(pptv)	(pptv yr^{-1})	(pptv yr^{-2})
BRW	258	214.9	154.1 ± 0.40	11.12 ± 0.11	--
NWR	268	210.5	150.1 ± 0.43	10.93 ± 0.12	--
MLO	261	206.3	142.9 ± 0.68	13.38 ± 0.50	-0.32 ± 0.08
SMO	269	202.2	134.7 ± 0.37	12.10 ± 0.11	--
SPO	85	214.9	134.6 ± 1.96	12.70 ± 0.57	--
CFC-12		(pptv)	(pptv)	(pptv yr^{-1})	(pptv yr^{-2})
BRW	244	362.9	273.4 ± 1.89	14.15 ± 1.26	0.38 ± 0.18
NWR	228	356.8	280.7 ± 2.23	11.12 ± 1.44	0.45 ± 0.21
MLO	243	353.8	268.5 ± 1.03	15.67 ± 0.28	--
SMO	258	345.8	245.3 ± 1.28	15.30 ± 0.92	0.49 ± 0.14
SPO	83	364.5	242.8 ± 4.10	9.03 ± 2.70	2.09 ± 0.41
N_2O		(ppbv)	(ppbv)	(ppbv yr^{-1})	(ppbv yr^{-2})
BRW	250	303.8	300.1 ± 0.20	0.61 ± 0.05	--
NWR	243	304.8	299.1 ± 0.23	0.99 ± 0.06	--
MLO	250	304.0	298.3 ± 0.25	0.99 ± 0.07	--
SMO	239	309.3	299.1 ± 0.31	1.59 ± 0.09	--
SPO	105	302.2	297.5 ± 0.32	0.81 ± 0.09	--

*Coefficients are followed by their standard deviations. If a second-order coefficient was not significant, a first-order analysis was performed.
†95% confidence interval.

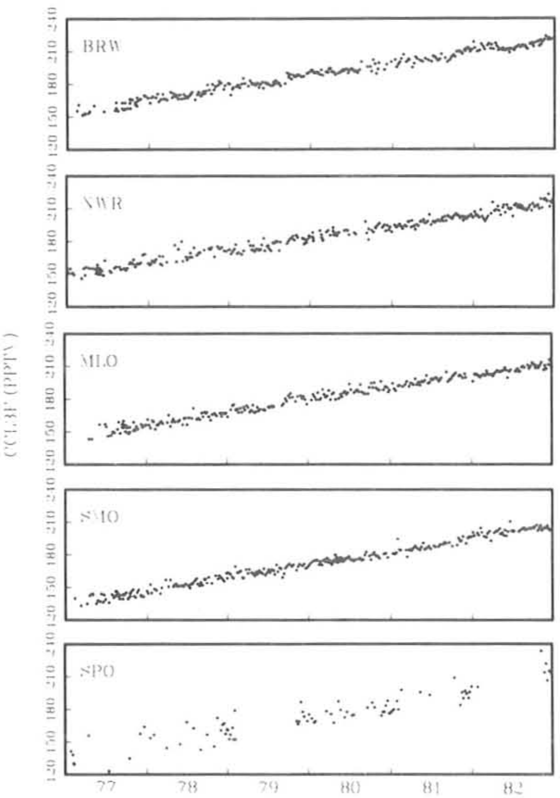

Figure 17.--CFC-11 data record.

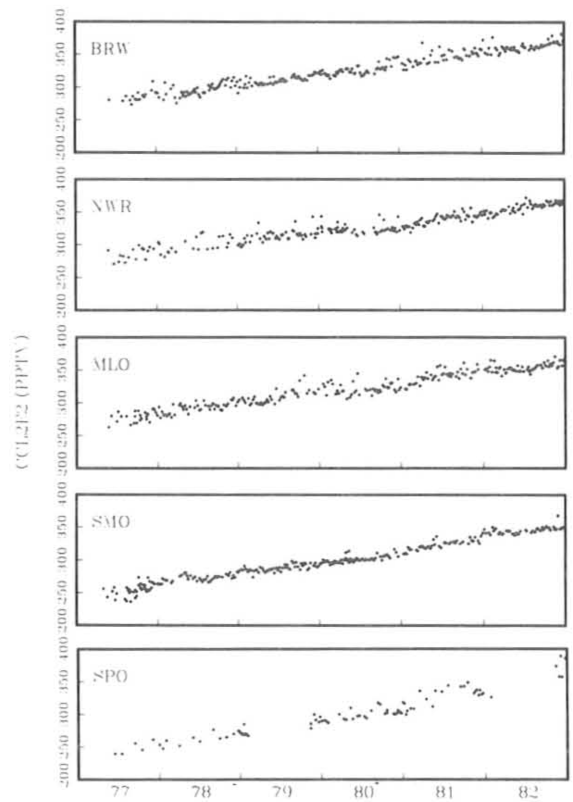

Figure 18.--CFC-12 data record.

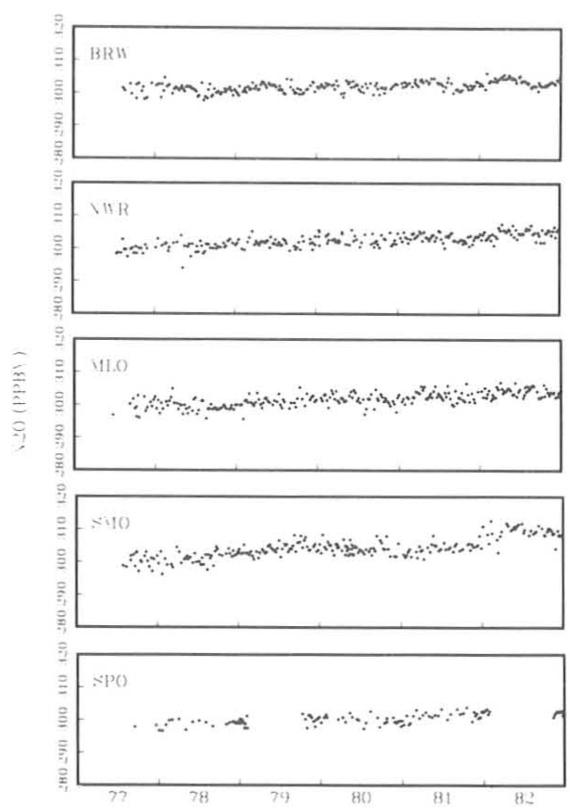

Figure 19.--N_2O data record.

decrease in CFC-11 growth rate, whereas it is the only station not showing an increasing growth rate in CFC-12.

3.7 Stratospheric Aerosols--Lidar

GMCC lidar activity at MLO came into national prominence on 28 January 1982 when the Mystery Cloud was first detected and reported by T. DeFoor and K. Coulson. The commercial news media publicized the discovery and some commotion was raised because of the unknown origin of the cloud. The cloud spread northward rapidly and was detected by lidars located at higher latitudes. Interest in the cloud faded rapidly, as did the cloud. However, at the end of March and in early April, Mexico's El Chichon volcano erupted and produced a tremendous stratospheric dust cloud that persisted the entire summer as an annulus in an equatorial band between about 10°S and 30°N.

Information on the El Chichon cloud was quickly relayed to the scientific community as a highly significant meteorological event. The El Chichon stratospheric cloud mass was about the same order of magnitude as the Agung stratospheric cloud in 1963. MLO lidar operators increased the observation rate from once to twice per week to obtain finer time resolution of changes in cloud-profile structure, and more than 50 observations were made. GMCC received numerous requests for MLO lidar data. Among applications of the data are investigations of satellite remote sensing errors, Umkehr remote-sensing errors, climate modeling, ozone photochemistry modeling, and stratospheric dynamics. In the annals of historical meteorology, the MLO lidar data will occupy an important position. A summary of the MLO lidar data is given in sec. 4.8.

3.8 Surface Aerosols

The GMCC surface aerosol monitoring program during 1982 included continuous measurement of CN concentration and integrated light scatterring at BRW, MLO, SMO, and SPO. All data were recorded as 1-min and 1-h means on magnetic tape and also on backup chart recorders. CN concentrations were measured using G.E. CNC's (catalog no. 112L428) with modifications suggested by N. Ahlquist of the University of Washington. Calibration points for the automatic CNC's were provided by daily Pollak CNC observations. Light scattering was measured using four-wavelength nephelometers that measure the scattering portion of aerosol extinction simultaneously at wavelengths of 450, 550, 700, and 850 nm. Calibrations of the nephelometers are performed at 2-mo intervals by filling them with CO_2 gas and adjusting the instrument outputs to the known scattering coefficients of CO_2.

3.8.1 Barrow

The BRW Pollak CNC operated properly throughout 1982 and provided daily observations for routine calibration checks of the G.E. automatic CNC. The G.E. CNC produced acceptable data for about 47% of the year. Other than downtime for routine maintenance and calibration, the major periods of downtime were DOY 1-12, 23-47, 49-53, 61-77, 124-140, 142-173, 251-265, 282-284, and 314-316.

The nephelometer produced acceptable data for about 76% of the year, with the only significant periods of downtime occurring during DOY 137-141, 219,