

3.6 Halocarbons and Nitrous Oxide

3.6.1 Operations

Air samples in paired stainless steel flasks were collected weekly during 1983 at BRW, NWR, MLO, and SMO for CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), and nitrous oxide (N_2O) analyses. At SPO, samples in paired flasks were collected weekly only during January and December; at other times, they were collected once per month.

The samples were analyzed on a gas chromatograph at GMCC, Boulder. A Hewlett-Packard 87XM computer was procured in September and interfaced with the laboratory integrating recorders so that chromatographic peak-height data could be processed and stored on disk at the end of each analysis.

In September, a Shimadzu mini-2E gas chromatograph was procured for use at SPO. The chromatograph was modified by removing the injection port and installing a gas sampling valve, and by removing carrier gas inlet controls and installing a metal diaphragm flow controller. Operating and servicing instructions for the chromatograph were prepared for use by SPO personnel. After testing, the chromatograph, an HP 3390A integrating recorder, calibration gas (tank 3081), and accessories were shipped to SPO in early November. The apparatus was installed and became operational at SPO in late December.

3.6.2 Calibration

In early September, three 48.7-L steel gas cylinders (tanks 3077, 3081, and 3093) were filled with clean mountain air to serve as CFC-11, CFC-12, and N_2O gas standards. The tanks were filled at Climax, CO, at an elevation of 3.8 km. Pumping equipment consisted of a 15- μm inlet air filter, a -70°C water vapor cold trap, a metal bellows forepump, and a RIX high-pressure three-stage air compressor. The pumps were powered by a gas-powered generator. Tanks 3077, 3081, and 3093 were pressurized to 1800, 2050, and 2050 psi, respectively.

The NOAA/GMCC halocarbons and N_2O calibration gas standard (tank 3072), as well as tanks 3081 and 3093, were transported for calibration to OGC (Beaverton, OR) in late September. Calibrations of the standard indicated that CFC-11 and N_2O concentrations have remained stable since 1977. The CFC-12 concentration has been increasing in the past, but appears to have stabilized during the last 2 years.

3.6.3 Data Analysis

CFC-11, CFC-12, and N_2O selected data are shown in figs. 21-23, respectively, for 1977-1983. The BRW halocarbon data exhibit an annual cycle with highest concentrations during November-December and lowest values during June-July. Similar periodicity in the data is not evident at the other stations. SPO data continue to exhibit the most variability due to sampling problems. The N_2O data have not been corrected for CO_2 interference during chromatographic gas analyses.

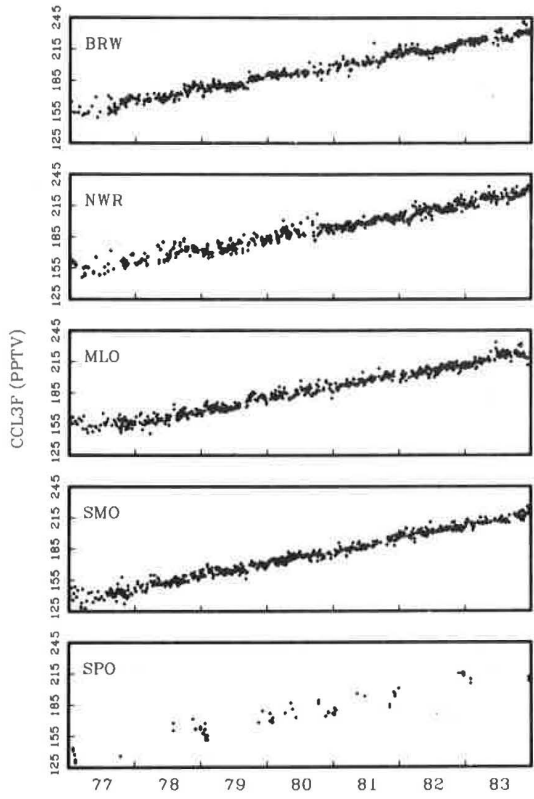


Figure 21.--CFC-11 data record.

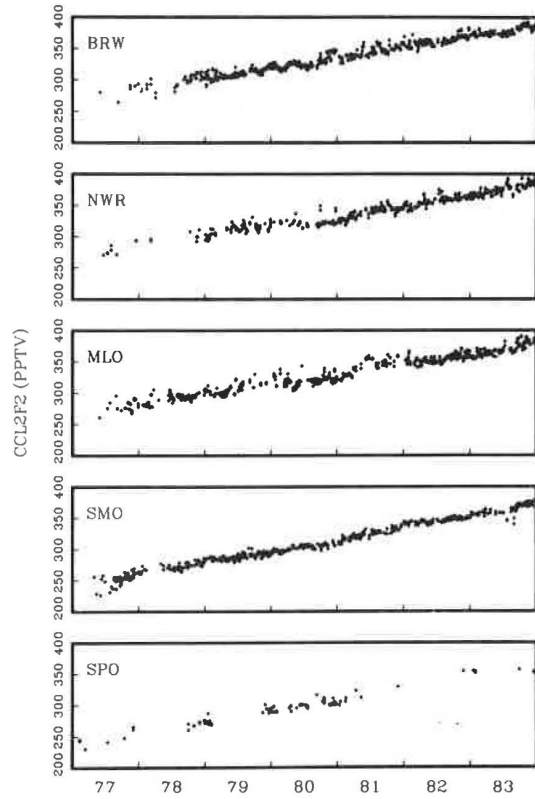


Figure 22.--CFC-12 data record.

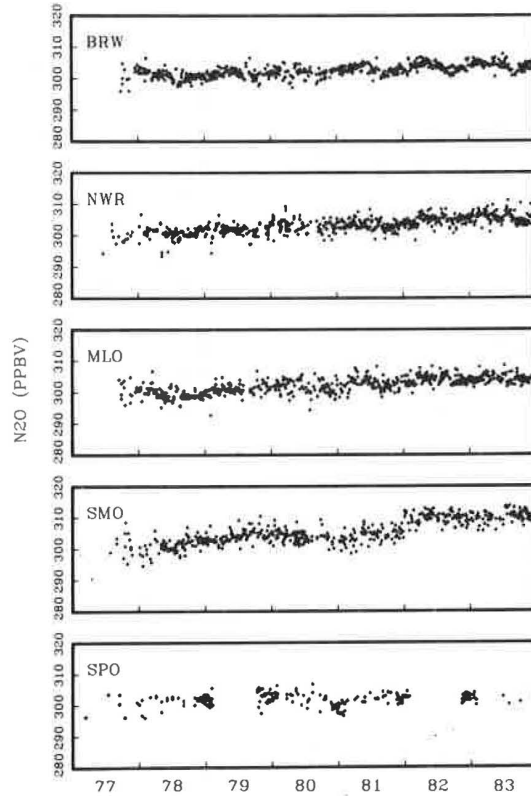


Figure 23.--N₂O data record.

Table 16.--Mean mixing ratios for 1983, and results of second-order regression analyses of CFC-11, CFC-12, and N₂O data for 1977-1983*

Station	No. of obs.	Mean mixing ratio for 1983	Mixing ratio on 1 Jan 1977	Growth rate	Growth rate change
<u>CFC-11</u>		(pptv)	(pptv)	(pptv yr ⁻¹)	(pptv yr ⁻²)
BRW	524	227.3	154.2 ± 0.58	11.09 ± 0.36	0.01 ± 0.05
NWR	555	223.2	154.0 ± 0.71	8.93 ± 0.42	0.26 ± 0.05
MLO	517	218.7	148.2 ± 0.62	10.02 ± 0.39	0.13 ± 0.05
SMO	541	213.7	135.4 ± 0.51	11.81 ± 0.32	0.03 ± 0.04
SPO	66	208.6	135.5 ± 1.97	12.10 ± 1.33	-0.03 ± 0.20
<u>CFC-12</u>		(pptv)	(pptv)	(pptv yr ⁻¹)	(pptv yr ⁻²)
BRW	436	378.3	269.7 ± 1.77	16.11 ± 0.92	0.10 ± 0.11
NWR	347	374.6	279.6 ± 2.25	9.72 ± 1.10	0.77 ± 0.13
MLO	414	368.9	268.3 ± 1.66	15.00 ± 0.95	0.10 ± 0.12
SMO	473	362.9	241.0 ± 0.92	18.02 ± 0.55	0.10 ± 0.07
SPO	80	353.3	238.2 ± 2.38	17.02 ± 1.38	0.10 ± 0.19
<u>N₂O</u>		(ppbv)	(ppbv)	(ppbv yr ⁻¹)	(ppbv yr ⁻²)
BRW	539	304.1	300.2 ± 0.34	0.48 ± 0.19	0.01 ± 0.02
NWR	544	305.6	299.1 ± 0.42	1.07 ± 0.23	-0.01 ± 0.03
MLO	538	304.1	298.4 ± 0.41	1.10 ± 0.23	-0.03 ± 0.03
SMO	470	310.1	300.2 ± 0.54	0.84 ± 0.31	0.11 ± 0.04
SPO	190	302.0	300.3 ± 0.61	0.69 ± 0.36	-0.07 ± 0.05

*Coefficients are followed by their standard deviations.

Mean concentrations for 1983 and results of second-order least-squares regression analyses of the 7-yr halocarbon and N₂O data sets are summarized in table 16. Indicated growth rates are all highly significant. Significance (95% confidence interval) of the growth rate changes appears to be highly dependent from year to year on the last year's data. For the full 7-yr record, only the MLO and NWR CFC-11 and the NWR CFC-12 second-order terms are statistically significant.

Table 17 contains CFC-11 monthly average data for each station during the period 1977-1983. SPO data should be used cautiously since they are quite scattered and sparse (see fig. 21). This SPO variability problem is caused, we believe, by air samples having to be stored many months before analysis.

CFC-12 and N₂O data are not tabulated because calibration gas instability and CO₂ interference corrections have not been ascertained completely.

3.7 Stratospheric Aerosols--Lidar

Lidar measurements acquired since 1974 by GMCC at MLO have been uniformly processed for vertical profiles of aerosol backscattering ratio, ratio of total backscatter to Rayleigh backscatter, and cumulative optical depth. For 1974-1981, 173 profiles were analyzed. A NOAA Data Report, soon to be printed, will provide details of the processing procedure and results. Lidar measurements from 1982 to the present were also processed in the same fashion as the

Table 17.--Monthly average CFC-11 concentrations (pptv)
using pressurized flask pairs

Month	BRW	NWR	MLO	SMO	SPO	Month	BRW	NWR	MLO	SMO	SPO
<u>1977</u>						<u>1980 (cont.)</u>					
Jan	--	--	--	--	141.4	Jul	191.7	187.2	189.3	177.9	--
Feb	--	--	--	--	130.1	Aug	193.0	--	187.0	176.6	--
Mar	--	--	--	--	--	Sep	193.6	184.6	186.6	181.1	--
Apr	--	--	--	--	--	Oct	193.8	190.0	194.5	179.3	185.9
May	--	--	--	--	--	Nov	193.0	195.1	192.4	178.7	--
Jun	--	--	--	--	--	Dec	199.0	190.9	190.9	179.3	176.9
Jul	--	--	--	--	--	<u>1981</u>					
Aug	156.8	--	--	144.1	--	Jan	198.6	194.1	188.4	181.2	178.4
Sep	156.9	--	--	144.2	--	Feb	203.5	194.0	192.2	187.8	--
Oct	165.7	--	152.4	144.3	--	Mar	200.0	198.7	193.5	182.8	--
Nov	164.7	--	154.3	144.7	--	Apr	202.2	193.7	195.1	186.0	--
Dec	169.6	--	156.3	141.3	--	May	200.6	198.3	194.3	186.8	--
<u>1978</u>						Jun	202.5	199.0	197.8	186.3	--
Jan	168.1	--	160.2	148.5	--	Jul	202.2	199.0	198.6	188.1	--
Feb	164.9	--	154.3	146.7	--	Aug	203.7	201.2	197.8	189.4	--
Mar	166.3	--	158.4	153.2	--	Sep	203.4	202.3	200.2	191.1	--
Apr	168.9	--	158.8	152.8	--	Oct	208.1	203.9	202.3	192.1	--
May	167.6	--	160.1	151.8	--	Nov	210.4	201.7	200.7	194.1	183.7
Jun	168.4	--	160.5	152.0	--	Dec	213.0	202.8	203.1	194.7	194.1
Jul	169.6	--	159.6	152.0	162.4	<u>1982</u>					
Aug	169.7	--	164.1	154.7	--	Jan	211.1	204.3	200.8	198.5	--
Sep	179.3	--	166.5	154.4	--	Feb	214.3	202.4	205.5	200.7	--
Oct	175.5	--	164.0	156.6	--	Mar	214.9	208.4	202.8	197.5	--
Nov	180.8	--	166.6	159.8	171.9	Apr	213.4	208.6	203.6	201.3	--
Dec	179.6	--	166.1	158.7	160.8	May	211.5	208.9	206.1	199.9	--
<u>1979</u>						Jun	210.5	209.4	204.4	202.8	--
Jan	175.1	--	169.3	161.6	157.1	Jul	213.8	213.0	205.7	201.6	--
Feb	178.2	--	170.9	165.4	165.4	Aug	214.0	210.6	207.7	203.5	--
Mar	181.2	--	171.0	162.7	--	Sep	216.2	212.9	209.6	204.0	--
Apr	180.8	--	170.6	163.5	--	Oct	217.5	212.0	210.3	204.9	--
May	179.8	--	169.6	163.8	--	Nov	221.0	217.0	210.4	204.7	233.4
Jun	179.3	--	170.0	162.5	--	Dec	221.2	217.5	209.6	204.5	214.5
Jul	180.7	--	172.8	164.8	--	<u>1983</u>					
Aug	180.0	--	--	167.7	--	Jan	223.1	215.1	211.6	210.2	207.4
Sep	186.5	--	177.0	163.9	--	Feb	222.4	218.8	212.9	206.9	--
Oct	186.6	--	183.2	170.6	--	Mar	223.5	219.7	214.6	211.7	--
Nov	188.1	--	180.5	168.8	--	Apr	224.8	223.2	215.5	211.1	--
Dec	188.6	182.8	179.4	169.4	--	May	--	220.8	217.6	210.7	--
<u>1980</u>						Jun	226.3	222.2	222.9	212.0	--
Jan	191.4	183.3	181.7	172.6	169.5	Jul	229.1	223.3	222.2	213.8	--
Feb	190.1	183.3	181.3	173.0	168.8	Aug	225.0	223.5	221.4	211.7	--
Mar	192.5	--	184.3	174.8	--	Sep	226.6	224.6	219.7	213.6	--
Apr	190.9	187.6	183.9	174.3	--	Oct	230.1	226.3	223.4	217.4	--
May	191.0	--	181.3	177.4	187.1	Nov	233.9	227.6	223.3	215.8	--
Jun	192.2	--	185.6	178.5	--	Dec	231.9	231.0	217.8	221.2	209.8