

5. Nitrous Oxide and Halocarbons Division

S.A. MONTZKA (EDITOR), J.W. ELKINS, J.H. BUTLER, T.M. THOMPSON, W.T. STURGES, T.H. SWANSON, R.C. MYERS, T.M. GILPIN, T.J. BARING, S.O. CUMMINGS, G.A. HOLCOMB, J.M. LOBERT, AND B.D. HALL

5.1. CONTINUING PROGRAMS

5.1.1. FLASK SAMPLES

During 1991 air sample pairs continued to be collected and analyzed for CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), and nitrous oxide (N_2O). The collection sites were BRW, NWR, MLO, SMO, SPO, and ALT; their locations are shown in Figure 5.1. In May 1991, Cape Grim (CGO) Baseline Air Pollution Station, Tasmania (Latitude: 40.6822°S , Longitude: 144.6883°E) a part of CSIRO/DAR, was added to the NOAA flask sampling network making it the most southern, year round sampling site. ALT was upgraded to the higher pressure (3 atm) pump in May. All the sites are now equipped with this pump that provides sufficient pressure for the samples to be analyzed on four different instruments for numerous chemical constituents.

The automated flask analysis system has been routinely used throughout the year. This system greatly reduces the amount of operator time required for flask analyses. The old flask system requires manual sample injection and at most three pairs of flasks can be analyzed in an 8-hour day. The new system is capable of analyzing six pairs of flasks with only 1.5 hours of operator setup time. Once the setup is complete, the system automatically injects sample and

calibration gases, and records results. Data comparison between the old and new systems will continue into 1992 when the old system will be phased out.

Final NOAA scale mixing ratios for CFC-11, CFC-12, and N_2O have been assigned to the three calibration tanks used since 1977. The historic intercomparisons have been carefully checked and small drift corrections applied on the data from 1977 to 1985 as discussed in the standards section. The monthly mean mixing ratios calculated for the sample sites are presented in Tables 5.1-5.3. These values supersede all previous preliminary data.

The station time series have been combined into monthly global means and are graphed in Figure 5.2. The same GC was used throughout the entire sampling period, the only major modifications were automating the EC-GC, adding a pre-column, and replacing a gas sampling valve to permit backflushing and more rapid sampling in 1987. The gap in the CFC-12 record during 1984-1985 was due to a GC problem that only affected that compound.

Both CFCs, particularly CFC-11, showed a decrease in growth rate during the past few years that is apparent at all flask-sampling locations as a consequence of reduced production and release (Figure 5.3). Previous reports [Rasmussen and Khalil, 1986; Cunnold *et al.*, 1986; Elkins *et al.*, 1988] showed that the mean global growth rates between 1977 and 1984 were increasing linearly, and our results give rates of 9 ± 1 ppt yr^{-1} (one standard deviation; by mole fraction) for CFC-11 and 17 ± 3 ppt yr^{-1} for CFC-12. After a period of peak growth rates of 11 ± 1 ppt yr^{-1} for CFC-11 and 19.5 ± 2 ppt yr^{-1} for CFC-12 from 1985 to 1988, the growth rates have been decreasing rapidly, reaching levels in late 1991 of 4 ± 1 ppt yr^{-1} for CFC-11 and 14 ± 2 ppt yr^{-1} for CFC-12. The global slowdown of the growth rates observed after 1989 are also supported by estimates of reduced emissions [AFEAS, 1991; McFarland and Kaye, 1992] made by the CFC producers and are directly attributed to the international efforts of the Montreal Protocol [UNEP, 1987] and voluntary reductions from producers and users to reduce stratospheric ozone depletion. If the observed slowdown in growth rates continues at 1990-1991 levels, global atmospheric CFC-11 and -12 mixing ratios will reach a maximum well before the turn of the century, and thereafter begin to decline [Elkins *et al.*, 1992].

In contrast to the CFCs, the mean growth rate of N_2O has almost doubled from ~ 0.6 ppb yr^{-1} from the 1977-1985

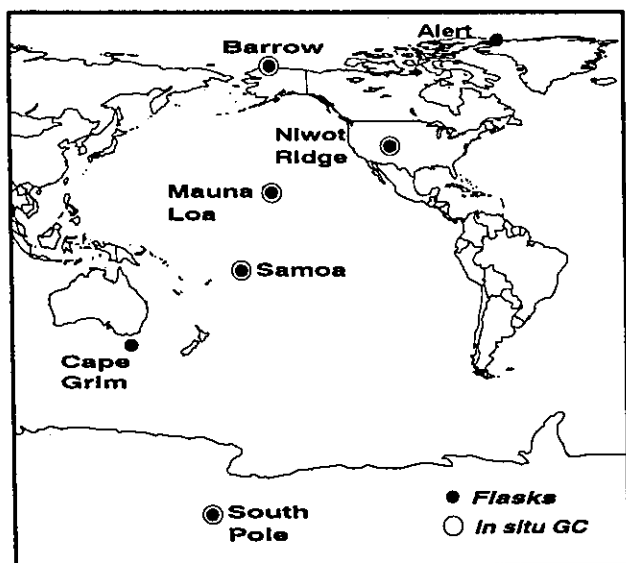


Fig. 5.1. Location of flask (solid circles) and in situ (open circles) sampling locations for nitrous oxide and selected halocarbons.

Table 5.1. Monthly Means of the Mixing Ratios of N₂O in ppb from the Flask Program

Year	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
<i>ALT N₂O</i>												
1988	—	307.7	307.9	308.2	308.8	308.3	308.2	308.1	308.7	309.5	308.7	309.5
1989	—	308.0	312.3	309.0	309.2	309.0	308.2	309.0	308.8	308.0	308.0	308.9
1990	309.2	309.3	310.4	310.3	312.1	311.1	311.6	310.4	309.7	309.7	310.7	309.9
1991	310.2	310.6	311.8	310.4	312.7	311.9	311.7	311.5	311.4	310.6	311.2	315.1
<i>BRW N₂O</i>												
1977	—	—	—	—	—	—	—	—	298.5	304.6	300.6	304.7
1978	303.9	302.8	301.7	301.9	302.2	302.2	302.4	301.8	303.3	302.1	301.7	301.5
1979	301.1	301.5	302.1	302.2	303.1	302.9	304.0	303.7	304.0	302.6	301.6	302.9
1980	302.6	303.1	302.0	301.8	303.1	302.7	302.4	304.9	302.9	300.9	301.5	302.9
1981	302.9	302.4	303.1	304.0	303.7	304.0	303.8	306.1	303.1	302.8	302.5	303.3
1982	301.8	304.2	303.9	304.7	304.8	304.2	305.2	305.3	304.7	303.7	304.1	304.3
1983	304.2	305.0	304.3	303.9	304.8	304.1	306.5	305.0	302.7	304.6	303.7	304.0
1984	304.5	304.0	303.7	304.5	305.2	305.5	305.1	306.5	305.2	305.4	305.8	306.1
1985	307.9	306.4	305.1	304.9	306.3	305.8	303.8	304.4	305.6	305.8	305.5	305.1
1986	305.2	305.3	305.2	306.2	306.6	307.7	309.0	308.8	307.1	306.4	306.5	305.7
1987	306.9	307.0	307.2	306.6	308.9	308.0	308.2	308.0	308.5	308.2	307.0	308.2
1988	307.5	307.0	308.6	307.5	307.3	307.0	307.3	306.2	308.4	307.5	307.7	308.2
1989	308.5	309.7	307.8	309.2	309.4	308.8	310.9	309.0	309.0	308.2	309.6	309.4
1990	308.7	309.2	309.3	310.1	309.9	309.7	308.8	310.5	312.2	310.5	309.4	309.8
1991	310.2	310.5	311.7	311.4	311.1	311.9	311.4	310.6	311.2	311.2	310.5	311.2
<i>NWR N₂O</i>												
1977	—	—	—	—	—	—	—	303.5	300.3	299.7	301.7	—
1978	—	302.3	302.1	302.8	303.3	301.9	301.7	301.9	302.9	302.5	302.9	303.6
1979	303.4	301.4	303.3	302.2	302.7	303.3	303.8	303.9	301.6	302.6	305.0	304.1
1980	306.7	304.3	303.2	303.8	304.0	305.3	302.8	306.2	304.2	303.3	304.1	303.0
1981	304.1	303.2	304.4	305.0	303.8	304.5	303.5	305.2	303.6	303.7	303.5	303.5
1982	304.8	303.4	304.2	306.1	305.6	305.4	306.2	307.5	305.6	304.9	306.3	305.9
1983	305.9	306.8	306.0	305.6	306.7	305.8	308.1	308.2	305.5	305.0	304.8	306.1
1984	305.2	305.0	304.4	305.2	306.0	307.7	308.1	309.1	307.1	306.9	307.3	308.1
1985	307.8	308.6	304.9	305.8	306.8	306.2	306.7	306.2	306.6	306.3	306.7	305.9
1986	306.0	306.0	306.0	306.1	306.4	306.3	307.8	306.8	306.9	307.4	306.5	306.8
1987	307.5	306.5	307.9	307.2	307.7	308.2	306.4	307.4	305.6	307.9	309.2	310.0
1988	309.6	308.0	309.7	306.7	307.5	307.0	309.8	309.7	307.6	308.7	309.4	309.6
1989	308.7	312.2	308.4	309.3	310.7	310.4	310.1	310.9	310.1	310.5	309.6	309.4
1990	311.3	310.4	310.0	309.5	310.1	310.4	309.5	312.9	313.0	311.7	311.4	311.1
1991	310.3	311.1	310.9	311.3	308.4	312.0	313.1	312.7	312.8	312.1	310.8	310.9
<i>MLO N₂O</i>												
1977	—	—	—	—	—	—	—	—	301.1	302.5	300.1	303.1
1978	302.4	301.5	303.1	300.5	299.5	301.1	300.1	300.8	301.5	300.9	301.2	300.8
1979	301.3	302.4	302.1	302.6	302.3	301.6	302.4	302.0	302.2	304.4	302.6	303.5
1980	303.4	302.3	304.3	301.8	303.2	303.3	301.9	301.0	302.7	304.0	301.8	302.6
1981	302.0	303.0	303.9	304.8	303.4	304.8	303.6	303.1	303.8	304.0	303.8	303.0
1982	304.3	303.9	304.4	305.2	304.7	304.7	304.7	307.0	304.7	306.0	305.0	304.3

Table 5.1. Monthly Means of the Mixing Ratios of N₂O in ppb from the Flask Program—Continued

Year	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
<i>MLO N₂O</i>												
1983	304.3	305.0	305.1	304.8	305.2	304.1	304.4	304.7	305.4	304.6	304.2	304.9
1984	305.2	304.5	304.3	306.4	305.6	304.9	307.8	306.4	305.6	306.7	307.3	306.3
1985	307.4	307.4	306.6	305.6	305.1	306.8	305.1	305.0	307.1	307.6	307.7	307.6
1986	306.7	306.3	308.2	306.9	307.5	307.0	308.9	308.5	308.8	308.9	308.0	307.6
1987	307.1	307.5	308.2	305.7	308.2	307.1	306.7	307.7	306.5	307.9	307.2	307.7
1988	306.8	307.8	306.4	307.9	307.3	307.3	308.2	307.1	306.9	308.0	309.8	307.2
1989	308.1	309.0	308.6	309.7	308.9	309.5	308.4	309.3	309.8	309.6	308.7	309.6
1990	310.8	310.0	311.2	309.4	308.5	308.3	309.1	312.2	311.0	311.03	311.4	311.4
1991	312.5	310.2	311.0	311.1	310.1	311.0	310.6	311.0	311.1	312.0	311.6	311.8
<i>SMO N₂O</i>												
1977	—	—	—	—	—	—	297.6	—	—	298.0	297.4	—
1978	297.2	298.9	299.1	299.8	300.7	300.1	299.6	298.8	299.1	298.9	300.1	299.5
1979	300.7	299.7	298.6	299.0	300.0	299.5	299.8	300.7	300.8	302.3	299.7	301.4
1980	301.5	302.0	300.5	299.4	299.5	300.4	299.0	299.5	300.3	300.1	298.2	299.2
1981	301.4	300.4	300.7	298.4	301.2	300.8	301.7	300.4	301.7	301.3	302.3	301.4
1982	299.4	299.8	300.6	302.5	302.7	303.0	301.8	302.2	303.3	302.6	302.6	302.3
1983	303.7	302.9	302.7	303.0	302.1	302.7	304.0	304.4	302.3	304.0	302.8	303.6
1984	304.2	304.0	303.9	303.7	303.1	303.7	303.7	304.0	304.0	303.7	303.2	304.8
1985	304.5	305.8	303.6	304.6	303.7	304.3	303.9	304.4	303.4	304.8	304.4	304.8
1986	303.9	305.0	304.5	305.0	303.9	305.5	305.0	305.4	305.4	304.5	305.9	305.1
1987	304.2	303.0	303.9	307.4	305.3	302.5	304.6	302.3	305.6	305.8	306.1	306.3
1988	306.9	306.4	305.3	304.5	305.4	305.1	305.4	305.6	305.7	305.2	306.4	308.1
1989	305.8	308.5	307.8	306.6	306.4	307.7	306.0	309.2	308.1	306.8	307.5	307.4
1990	—	309.5	308.5	307.6	307.0	307.2	307.4	308.1	310.9	309.0	307.1	309.6
1991	309.8	—	309.9	310.4	311.5	309.6	309.9	310.2	309.9	307.8	310.5	308.5
<i>CGO N₂O</i>												
1991	—	—	—	—	309.4	310.0	309.3	310.1	310.8	309.5	311.0	—
<i>SPO N₂O</i>												
1977	—	—	—	—	301.3	—	—	—	301.5	—	—	300.5
1978	300.5	302.3	—	302.4	298.5	301.4	301.8	301.7	299.5	—	300.5	300.9
1979	300.8	299.8	—	—	—	—	—	—	—	301.2	301.6	301.8
1980	301.6	—	301.8	301.3	303.5	300.0	300.0	302.7	—	300.5	300.8	300.1
1981	300.9	301.4	302.2	304.6	302.7	304.4	302.5	303.0	303.6	305.3	303.2	302.7
1982	304.1	—	—	—	—	—	—	—	—	—	302.8	303.5
1983	303.3	—	—	—	—	303.6	—	—	302.7	—	—	303.4
1984	303.5	303.8	—	—	—	—	—	—	—	—	304.7	305.7
1985	307.7	—	—	—	—	—	—	—	—	—	304.4	305.3
1986	306.6	—	—	—	—	—	—	—	—	—	305.4	305.1
1987	307.2	—	—	—	—	—	—	—	—	—	305.6	305.8
1988	307.0	306.8	—	—	—	—	—	—	—	—	—	306.1
1989	306.3	—	—	—	—	—	—	—	—	—	—	308.5
1990	309.9	—	—	—	—	—	—	—	—	—	—	309.3
1991	309.1	307.9	—	—	—	—	—	—	—	—	—	310.0

Table 5.2. Monthly Mixing Ratios of CFC-12 in ppt From the Flask Program

Year	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
<i>ALT CFC-12</i>												
1988	—	458.6	453.4	464.0	466.7	461.0	—	465.2	468.5	—	473.1	477.8
1989	—	472.9	—	477.2	488.8	—	475.8	483.4	484.9	489.4	488.3	494.4
1990	490.8	492.2	493.1	498.2	495.6	—	493.2	492.0	487.8	495.7	497.4	497.3
1991	501.6	501.2	504.5	507.0	502.0	497.1	506.4	509.3	508.4	508.4	510.2	526.5
<i>BRW CFC-12</i>												
1977	—	—	—	—	—	—	—	—	—	—	—	—
1978	—	—	—	290.7	—	—	287.8	—	292.7	296.4	299.7	296.8
1979	298.0	296.1	299.9	295.8	295.2	299.4	300.9	299.8	307.7	303.8	309.1	311.2
1980	312.8	308.2	310.7	316.5	316.3	314.3	310.7	314.7	320.0	318.8	327.6	335.9
1981	323.1	323.5	327.2	330.8	333.3	328.9	335.7	345.6	336.1	339.9	341.7	344.5
1982	344.7	345.6	347.1	349.4	350.4	345.6	350.1	351.4	353.1	358.2	361.5	361.2
1983	363.9	364.4	363.4	363.9	366.1	363.2	364.0	366.5	374.6	378.8	375.9	375.2
1984	381.3	385.3	375.5	—	—	—	—	—	—	—	—	—
1985	—	405.1	390.5	392.8	397.7	405.5	391.2	394.1	406.8	414.6	417.9	419.9
1986	419.1	421.1	422.6	424.0	421.1	423.7	422.0	419.7	421.8	430.3	433.3	437.3
1987	435.5	436.3	444.1	442.5	441.4	439.1	447.4	443.1	452.9	456.2	458.3	458.9
1988	457.8	459.1	461.5	461.8	458.6	460.8	461.1	462.9	468.9	470.8	482.7	476.5
1989	479.0	473.7	475.3	476.4	477.7	474.5	482.9	478.8	482.1	485.5	492.2	493.2
1990	495.3	503.1	491.1	490.4	490.4	493.4	486.7	490.7	490.9	496.4	497.4	497.8
1991	501.2	501.9	505.1	501.5	496.2	502.2	501.0	502.7	507.5	510.9	512.0	519.0
<i>NWR CFC-12</i>												
1977	—	—	—	—	260.5	268.1	255.8	263.6	287.0	288.7	281.6	279.3
1978	285.0	269.6	275.4	—	—	292.5	298.2	301.4	—	286.7	294.1	290.3
1979	285.0	287.2	296.6	304.9	292.3	294.2	294.5	296.4	310.9	294.4	300.0	304.3
1980	309.9	312.5	316.2	311.1	315.2	308.9	308.7	309.7	313.0	312.3	312.8	317.3
1981	317.5	315.3	323.7	324.8	326.8	328.4	331.9	333.5	334.3	339.5	331.0	334.2
1982	338.2	335.6	339.9	349.4	342.4	346.8	353.3	349.6	349.6	353.0	353.6	352.9
1983	354.3	357.5	359.5	360.1	362.2	363.5	377.0	364.4	372.1	373.2	373.8	377.1
1984	374.7	371.1	368.9	—	—	—	—	—	—	—	—	—
1985	—	—	383.8	383.3	390.6	391.2	388.2	395.9	405.3	405.8	414.8	408.6
1986	408.8	408.7	411.9	410.4	418.2	418.6	416.4	421.3	415.7	422.8	422.2	424.6
1987	427.2	425.4	438.2	435.5	—	443.2	441.9	441.6	450.7	453.6	452.7	452.7
1988	454.7	450.8	450.8	459.0	459.8	456.4	468.6	469.8	465.0	462.5	474.2	466.6
1989	465.7	473.9	461.1	469.8	473.7	476.8	480.6	483.0	482.5	478.8	485.9	482.8
1990	482.5	491.3	485.7	483.0	489.4	494.1	491.0	490.8	502.4	494.0	497.0	497.0
1991	495.3	493.4	492.1	500.8	492.3	501.0	504.4	504.6	509.5	511.1	503.4	505.7
<i>MLO CFC-12</i>												
1977	—	—	—	—	272.4	—	261.8	—	260.6	267.1	267.9	277.6
1978	277.7	272.8	276.7	284.4	—	287.8	282.8	284.9	282.6	282.7	287.2	293.6
1979	295.9	288.9	291.3	289.4	295.6	296.3	299.8	—	304.7	—	304.8	306.3
1980	311.8	321.1	305.9	311.4	300.0	307.9	309.0	309.9	308.7	318.6	317.1	314.1
1981	311.7	318.5	318.4	329.1	332.8	330.8	335.9	334.6	339.2	338.2	337.2	348.6
1982	341.7	342.4	338.6	339.9	340.8	341.7	339.8	343.8	347.8	349.3	349.7	352.9
1983	347.1	354.3	353.5	354.1	353.9	356.3	363.9	358.2	367.6	367.5	372.6	370.5
1984	368.4	376.3	363.9	—	—	—	—	—	—	—	—	—

Table 5.2. Monthly Mixing Ratios of CFC-12 in ppt From the Flask Program—Continued

Year	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
<i>MLO CFC-12</i>												
1985	—	381.3	383.3	378.7	387.9	398.6	385.5	387.0	403.0	409.2	403.6	409.8
1986	407.2	404.2	411.4	413.8	413.5	415.1	412.2	417.7	419.6	428.9	426.9	427.5
1987	428.7	420.2	441.0	431.6	—	432.9	432.6	437.5	447.7	448.2	448.9	442.3
1988	441.7	446.7	444.4	452.7	452.0	452.9	456.0	456.3	459.7	460.7	—	468.0
1989	467.9	461.2	465.0	468.8	468.0	468.5	468.3	472.8	475.6	478.9	477.6	474.2
1990	482.9	480.1	482.2	487.5	484.1	483.8	482.7	486.1	489.9	488.7	489.4	491.4
1991	492.4	485.5	491.9	496.6	495.0	498.4	497.3	498.9	498.7	503.3	505.5	504.0
<i>SMO CFC-12</i>												
1977	—	—	—	—	234.8	232.3	237.4	242.7	241.4	243.9	244.2	250.9
1978	251.1	255.9	249.3	—	259.3	259.4	257.2	258.6	262.0	262.9	266.9	266.8
1979	273.7	273.2	272.8	273.8	271.8	272.4	275.2	276.7	280.1	280.1	283.5	280.6
1980	284.9	284.6	284.6	287.9	286.0	288.6	288.8	288.2	292.2	293.5	293.0	296.9
1981	299.2	302.7	303.5	306.1	306.8	305.7	312.1	313.1	311.7	315.3	317.7	318.5
1982	322.7	326.0	323.7	326.1	322.9	324.9	328.1	329.8	330.0	333.4	332.6	333.0
1983	338.1	339.2	342.8	342.1	341.5	341.8	342.0	348.1	351.7	354.6	356.1	357.4
1984	356.9	362.8	358.6	—	—	—	—	—	—	—	—	—
1985	—	373.1	369.8	371.0	379.2	379.1	375.1	373.8	387.6	389.5	389.6	392.8
1986	395.1	399.2	397.3	397.8	398.2	403.0	401.6	403.4	405.3	405.2	405.3	409.1
1987	411.6	414.2	420.9	414.3	418.4	409.8	418.2	—	—	421.7	425.6	426.3
1988	428.7	432.3	429.1	437.5	434.6	432.9	440.7	441.1	440.7	445.2	449.4	447.8
1989	450.5	454.1	448.2	451.4	453.8	445.4	457.5	457.3	459.7	461.8	460.6	465.2
1990	474.4	463.8	469.9	468.4	467.6	471.5	469.2	471.4	473.8	475.7	478.6	481.9
1991	486.7	—	486.7	487.9	491.8	485.8	488.3	490.4	493.1	493.5	494.6	492.8
<i>CGO CFC-12</i>												
1991	—	—	—	—	480.3	481.4	485.2	486.7	490.1	492.0	488.8	—
<i>SPO CFC-12</i>												
1977	—	234.6	—	—	—	232.4	—	—	—	—	—	253.1
1978	—	—	—	—	—	—	—	—	—	255.3	257.1	263.3
1979	263.7	259.3	—	—	—	—	—	—	—	—	290.8	280.9
1980	280.8	—	—	283.6	284.4	289.0	287.0	—	304.3	295.2	291.8	294.2
1981	294.0	299.7	—	—	302.9	—	—	—	—	—	—	320.0
1982	317.3	—	—	—	—	—	—	—	—	—	344.5	—
1983	343.7	—	—	—	—	—	—	—	—	—	—	343.8
1984	—	357.1	—	—	—	—	—	—	—	—	—	—
1985	—	—	—	—	—	—	—	—	—	—	386.1	389.0
1986	392.9	—	—	—	—	—	—	—	—	—	401.9	404.8
1987	408.1	—	—	—	—	—	—	—	—	—	420.4	419.9
1988	417.6	—	—	—	—	—	—	—	—	—	436.6	435.6
1989	439.6	—	—	—	—	—	—	—	—	—	—	459.6
1990	464.7	—	—	—	—	—	—	—	—	—	—	472.6
1991	474.8	472.1	—	—	—	—	—	—	—	—	486.7	488.5

Table 5.3. Monthly Mean Mixing Ratios of CFC-11 in ppt from the Flask Program

Year	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
<i>ALT CFC-11</i>												
1988	—	256.3	—	258.1	—	255.8	—	—	—	—	264.6	263.0
1989	—	—	—	—	267.8	268.7	—	267.2	—	272.5	270.7	276.1
1990	273.9	277.2	276.8	275.5	—	274.6	272.1	275.9	273.6	276.6	274.9	277.4
1991	279.2	277.4	275.1	279.0	282.9	278.9	278.0	275.2	275.5	276.0	281.0	282.6
<i>BRW CFC-11</i>												
1977	145.5	148.1	144.1	145.5	150.8	143.6	—	147.3	148.2	154.9	155.0	157.9
1978	156.5	155.6	156.7	159.0	156.9	157.3	158.3	159.0	163.7	163.3	167.9	165.9
1979	164.8	165.3	167.9	167.4	166.4	166.1	166.9	166.4	168.9	172.4	173.3	175.0
1980	175.8	174.6	176.6	175.2	174.8	176.2	175.7	176.7	177.5	178.5	176.4	181.3
1981	181.1	185.1	182.5	183.6	182.8	184.2	184.2	184.9	183.7	188.0	190.1	192.3
1982	190.6	193.2	193.7	192.3	190.5	190.2	191.7	192.5	194.2	195.4	197.0	198.0
1983	199.6	199.0	199.1	200.8	—	201.8	202.6	200.5	204.2	204.5	207.6	205.8
1984	209.2	209.7	208.8	206.9	208.9	208.2	209.7	209.7	211.5	214.1	215.6	218.5
1985	219.2	224.9	220.6	223.1	221.1	218.4	219.4	222.8	223.2	227.9	229.9	230.2
1986	230.9	230.6	231.7	237.8	232.3	232.3	232.0	234.6	232.9	239.0	239.3	243.0
1987	242.2	242.3	243.7	245.3	245.9	245.2	247.8	247.3	249.0	253.1	255.4	256.3
1988	254.3	256.4	256.6	258.6	256.1	256.5	256.4	257.6	258.8	261.5	266.4	265.4
1989	263.9	265.6	266.4	267.0	265.7	264.7	265.3	264.1	266.9	272.0	276.9	275.6
1990	275.7	277.4	274.1	272.6	271.0	272.6	269.5	271.7	271.1	272.6	273.8	276.1
1991	277.3	277.8	278.6	275.2	274.6	274.6	273.7	274.8	274.7	277.0	277.0	279.8
<i>NWR CFC-11</i>												
1977	151.6	149.4	143.7	146.6	148.1	140.4	144.2	146.6	145.2	151.6	148.8	155.6
1978	150.1	154.2	152.0	—	159.0	152.9	157.4	160.0	164.9	160.6	162.0	159.5
1979	159.3	157.6	163.1	161.3	160.8	163.4	163.4	165.3	163.0	168.6	169.9	168.6
1980	169.0	168.8	177.6	172.3	176.3	173.2	175.1	—	173.3	175.3	177.7	174.5
1981	177.3	177.1	179.3	176.8	180.9	181.1	180.7	182.2	183.4	185.2	182.9	183.8
1982	184.9	183.7	187.2	189.1	188.5	188.8	191.9	189.3	190.9	190.6	194.8	195.0
1983	193.0	195.9	196.2	199.5	199.0	198.4	199.2	199.3	201.3	202.8	201.9	205.0
1984	203.5	201.5	206.7	204.8	206.3	206.6	206.5	206.0	208.8	212.7	210.6	214.2
1985	213.8	212.2	215.9	216.3	218.2	215.9	215.6	218.9	223.6	224.5	225.1	223.9
1986	223.3	227.5	225.9	226.5	228.2	230.0	226.9	231.2	228.9	233.7	237.0	233.5
1987	234.0	236.4	237.1	238.0	240.7	242.2	240.8	243.7	246.1	251.3	249.6	251.3
1988	251.5	250.7	252.2	253.1	258.2	254.5	257.3	258.7	255.1	254.5	262.5	258.9
1989	258.2	262.6	257.9	260.7	260.8	262.0	268.6	266.1	267.3	264.8	269.3	265.7
1990	267.1	268.8	270.6	267.0	267.6	268.8	267.7	269.0	269.1	270.2	272.0	270.6
1991	269.2	273.0	269.2	273.8	270.1	273.2	274.5	273.0	274.6	273.4	273.9	275.4
<i>MLO CFC-11</i>												
1977	140.0	139.3	140.3	135.8	135.6	142.1	140.0	143.3	145.7	144.7	145.3	147.0
1978	149.0	148.7	148.7	149.4	150.1	150.3	151.4	152.1	155.4	153.4	155.1	154.9
1979	157.1	158.9	159.1	158.6	157.6	157.9	160.3	—	164.0	168.2	166.9	165.4
1980	167.5	167.1	168.8	170.2	166.4	170.5	171.9	171.5	170.6	173.6	174.6	173.3
1981	172.4	175.6	176.6	177.6	177.1	178.2	180.6	179.8	180.6	182.6	182.1	184.0
1982	182.3	182.1	183.6	184.0	185.6	185.4	184.7	187.2	188.7	189.6	189.6	188.5
1983	190.0	191.3	193.0	193.2	194.7	196.9	198.0	197.9	198.4	199.0	198.8	201.5
1984	200.9	202.0	200.9	202.5	202.2	202.8	204.1	204.9	206.6	208.9	213.2	210.9

Table 5.3 Monthly Mean Mixing Ratios of CFC-11 in ppt from the Flask Program—Continued

Year	Jan.	Feb.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
<i>ALT CFC-11</i>												
1985	212.6	212.6	217.4	214.8	215.7	216.3	215.5	217.9	218.4	222.1	220.2	224.7
1986	219.6	222.3	225.2	228.4	227.1	226.2	228.5	227.6	233.2	234.0	232.2	233.5
1987	233.2	—	236.3	238.1	—	236.8	238.5	239.1	242.3	245.0	244.9	242.4
1988	241.5	246.4	242.7	247.9	248.5	249.6	249.3	250.5	252.8	253.3	257.9	—
1989	257.7	255.0	256.5	259.6	259.0	260.4	258.9	261.4	263.4	262.7	262.2	264.0
1990	265.0	263.5	264.9	263.4	263.8	267.5	265.5	265.4	264.9	267.8	267.3	270.5
1991	270.4	265.8	269.1	271.2	271.4	268.6	270.3	270.5	269.6	269.7	271.8	274.4
<i>SMO CFC-11</i>												
1977	130.6	130.2	125.0	130.0	129.6	130.2	131.8	133.7	134.5	135.2	134.5	133.5
1978	138.3	137.7	139.2	141.1	141.3	141.1	141.1	143.3	143.2	144.9	147.7	146.6
1979	149.3	152.0	149.9	151.2	149.9	149.6	151.6	152.2	152.0	156.2	155.3	155.4
1980	157.9	158.7	158.8	158.7	159.2	160.8	159.5	159.8	163.2	162.0	161.6	163.1
1981	165.2	166.4	165.4	167.5	167.4	167.8	168.5	170.4	171.5	171.9	174.1	173.7
1982	175.4	175.1	175.7	177.3	177.1	176.1	178.5	180.2	179.8	181.2	181.2	180.8
1983	185.3	182.7	186.5	186.0	185.6	187.2	187.3	186.2	187.8	190.6	189.0	193.4
1984	194.7	196.5	193.2	196.1	195.3	193.6	194.5	195.2	199.3	199.1	197.6	203.9
1985	204.4	206.9	206.8	207.7	206.8	205.3	207.0	208.0	209.7	210.2	209.5	212.9
1986	216.5	210.5	213.9	216.9	219.2	219.5	219.1	220.7	221.0	220.9	221.1	223.5
1987	223.2	229.0	226.6	225.6	230.1	226.6	227.5	—	233.0	231.0	233.8	234.7
1988	236.1	237.3	235.0	239.6	237.4	239.1	239.4	242.1	239.1	242.4	244.2	248.6
1989	248.9	248.7	247.4	249.6	249.7	249.4	250.0	252.3	253.8	253.6	253.5	255.1
1990	258.0	254.2	258.0	257.0	255.5	258.0	258.6	260.7	260.5	258.8	261.3	265.3
1991	263.8	—	264.9	264.9	265.4	264.3	265.8	267.2	267.9	267.7	267.8	266.8
<i>CGO CFC-11</i>												
1991	—	—	—	—	—	269.9	264.4	—	265.8	267.5	—	—
<i>SPO CFC-11</i>												
1977	134.3	125.9	—	—	—	—	—	—	—	—	—	—
1978	143.2	—	—	—	—	—	—	151.9	—	—	158.3	150.3
1979	147.6	149.5	—	—	—	—	—	—	—	—	155.1	164.0
1980	156.7	—	—	157.2	169.7	158.1	—	—	—	170.5	160.1	164.9
1981	164.2	164.8	—	—	178.1	—	—	—	—	186.5	167.6	178.4
1982	181.5	—	—	—	—	—	—	—	—	—	192.9	193.7
1983	192.9	—	—	—	—	—	—	—	—	—	—	187.5
1984	—	190.5	—	—	—	—	—	—	—	—	198.5	205.1
1985	206.5	—	—	—	—	—	—	—	—	—	211.0	216.1
1986	—	—	—	—	—	—	—	—	—	—	222.3	—
1987	222.8	—	—	—	—	—	—	—	—	—	232.4	231.0
1988	—	—	—	—	—	—	—	—	—	—	239.8	237.0
1989	—	—	—	—	—	—	—	—	—	—	—	251.1
1990	253.4	—	—	—	—	—	—	—	—	—	—	260.6
1991	261.4	258.3	—	—	—	—	—	—	—	—	—	264.6

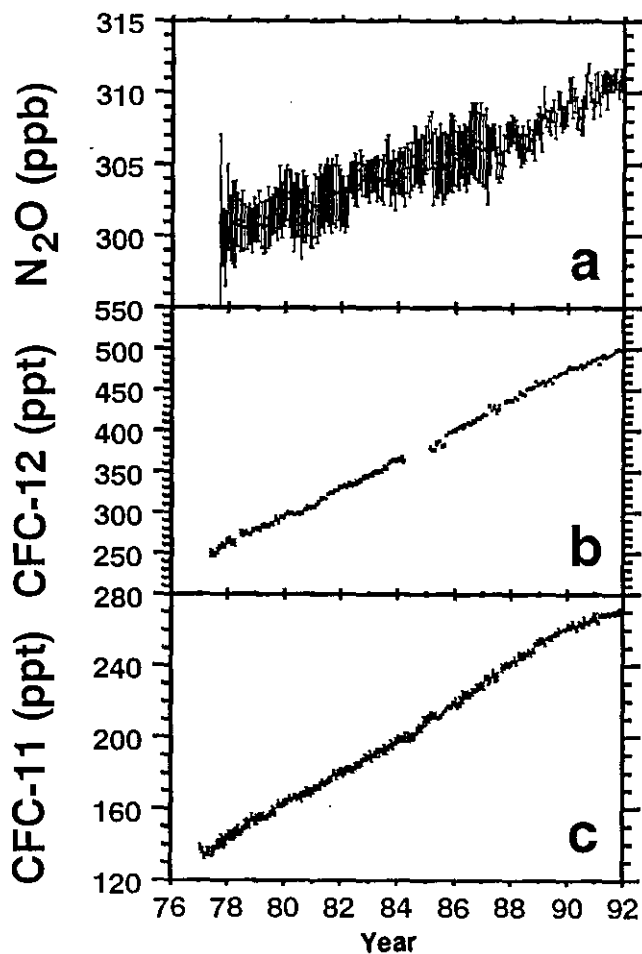


Fig. 5.2. Global monthly mean mixing ratios of (a) N_2O in ppb, (b) CFC-12 in ppt, and (c) CFC-11 in ppt. The standard deviation for each monthly mean is also shown. The global mean is determined from the monthly data at ALT, BRW, NWR, MLO, SMO, CGO, and SPO when available. Tic marks on the abscissa are the beginning of the year, January 1.

time period to ~ 1.1 ppb yr^{-1} in recent years (1988-1992). The reason for this apparent rise in growth rate is unknown since the magnitudes of sources from human activities and oceans are uncertain.

5.1.2. RITS CONTINUOUS GAS CHROMATOGRAPH SYSTEMS AT CMDL STATIONS AND NIWOT RIDGE

In situ analysis of air continued at BRW, MLO, NWR, SMO, and SPO using EC-GC. The schematic of the in situ GC system is shown in Figure 5.4. There are three separate channels on each system: (1) N_2O , (2) CFC-12, and (3) CFC-11, CFC-113 ($CCl_2F-CClF_2$), methyl chloroform (CH_3CCl_3), and carbon tetrachloride (CCl_4). Each channel has a 10-port gas sampling valve that is configured for backflushing the analytical column after the peaks of

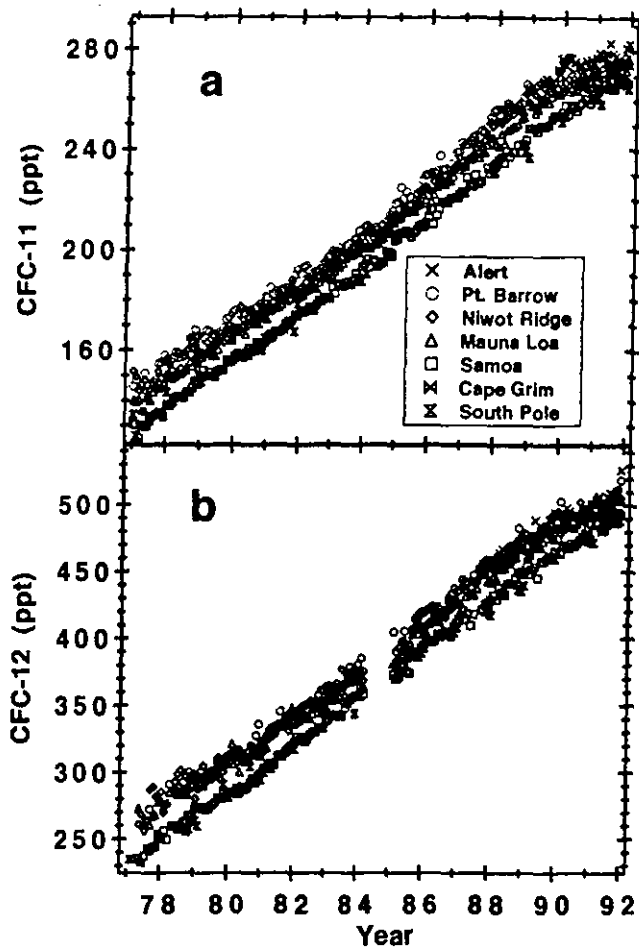


Fig. 5.3. Monthly means of the observed mixing ratio (ppt) measured in flask pairs from CMDL and cooperative stations for (a) CFC-11 and (b) CFC-12. Upon request, a color version of this figure is available from the NOAA Division.

interest are detected by the ECD. These automated systems analyze one sample of air every hour, 24 times each day.

During scheduled maintenance trips in May and June, a new air sampling inlet system was installed at BRW, MLO, and SMO. Figure 5.5 is a diagram of this system. It consists of 0.93 cm outside diameter, Dekabond tubing running from the top of the meteorological tower to a continuously operating pump mounted near the gas chromatographs. A stream select valve allows air to be sampled either from this line or from the normal gas sampling stack and calibration gas cylinders. A comparison of the two air streams is underway in an effort to understand sources of contamination and boundary layer gradients.

Analysis of N_2O measurements at SMO in 1990 and early 1991 indicated chromatographic problems associated with

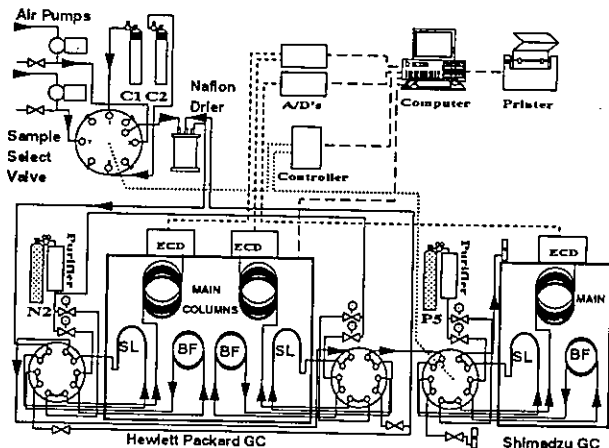


Fig. 5.4. Schematic layout of the RITS GC system. A/Ds are analog to digital converters (PE-Nelson), BF is a backflush column, C1 and C2 are calibration tanks, N2 is nitrogen carrier gas, P5 is 95% argon-5% methane carrier gas, and SL is a sample loop (~2.5 mL).

electric power fluctuations. Although the station power is augmented by a backup generator, adequate station power continued to be a problem. The generator would turn on during blackouts but not during brownout situations. In May 1991, a 4.1 kVA UPS was installed at SMO. This unit has enough capacity to maintain power for the entire chromatographic system during power disruption before the generator turns on and also conditions both voltage and frequency during brownout conditions. Figure 5.6 shows the residual N_2O mixing ratios averaged for the hours of

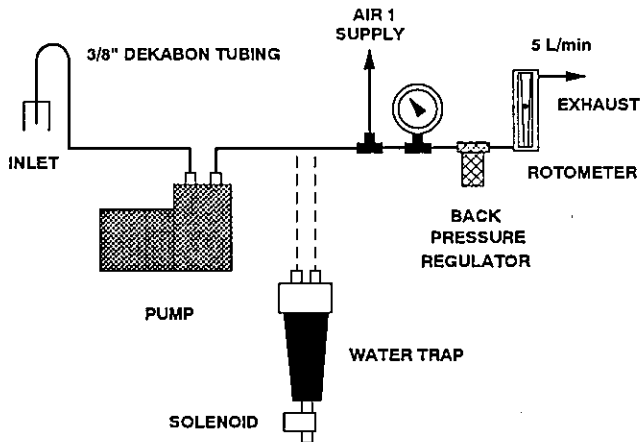


Fig. 5.5. New inlet system installed at BRW, MLO, and SMO. The water trap is installed only at SMO and MLO. At the end of the trap is a solenoid valve that periodically releases water that has accumulated in the trap.

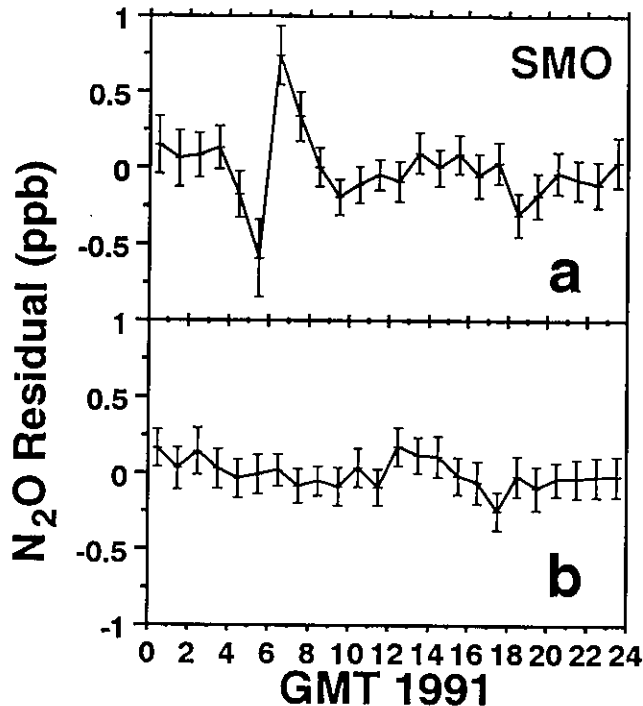


Fig. 5.6. Residual N_2O mixing ratios in ppb at SMO during 1991 before the UPS was installed (a) and after (b). The residuals were averaged for each hour of the day and the bars represent the 95% confidence interval of the mean.

day before and after the UPS was installed. It appears that the voltage fluctuations in the island power did affect a few of the N_2O measurements, and, with the addition of the UPS, the problem has been resolved.

Late in 1991, a new data collection system was purchased for SPO to be installed in January 1992. This system consists of a 386 IBM PC with IEEE-488 card, PE-Nelson interface box, and printer. The computer runs the same controlling software as the other sites and allows the storing of raw chromatograms, not just reported results. This allows for data reprocessing in Boulder, should the need arise.

The daily means for N_2O , CFC-12, CFC-11, and CCl_4 from the in situ systems are shown in Figures 5.7-5.10, respectively. Additional support for the deceleration of atmospheric growth rates of CFC-11 and CFC-12 is confirmed from in situ EC-GC measurements [Swanson *et al.*, 1992].

5.1.3. LOW ELECTRON ATTACHMENT POTENTIAL SPECIES (LEAPS)

One objective of the LEAPS program has been to estimate recent trends in the growth of H-1211 and H-1301

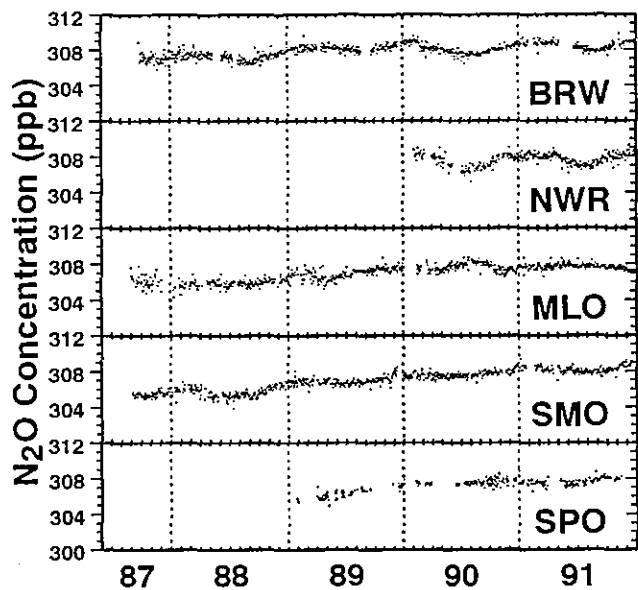


Fig. 5.7. Daily average N_2O mixing ratios in ppb from the in situ GCs.

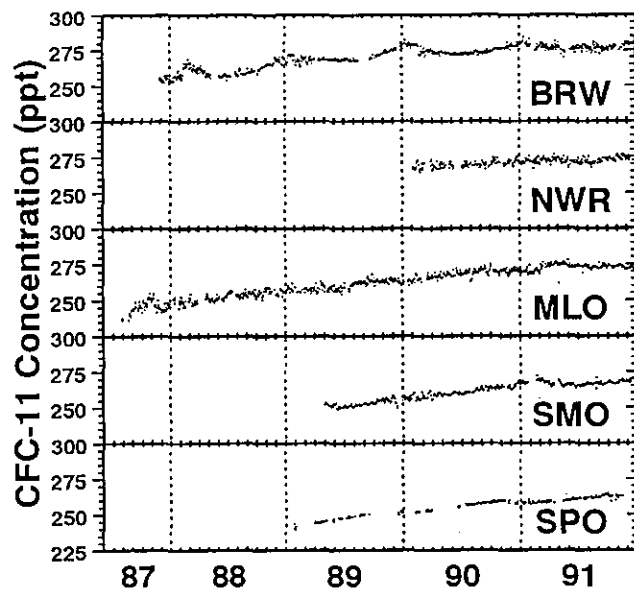


Fig. 5.9. Daily average CFC-11 mixing ratios in ppt from the in situ GCs.

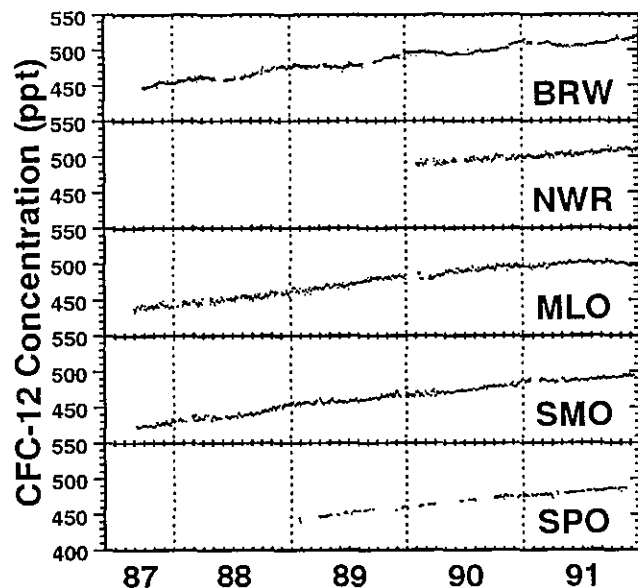


Fig. 5.8. Daily average CFC-12 mixing ratios in ppt from the in situ GCs.

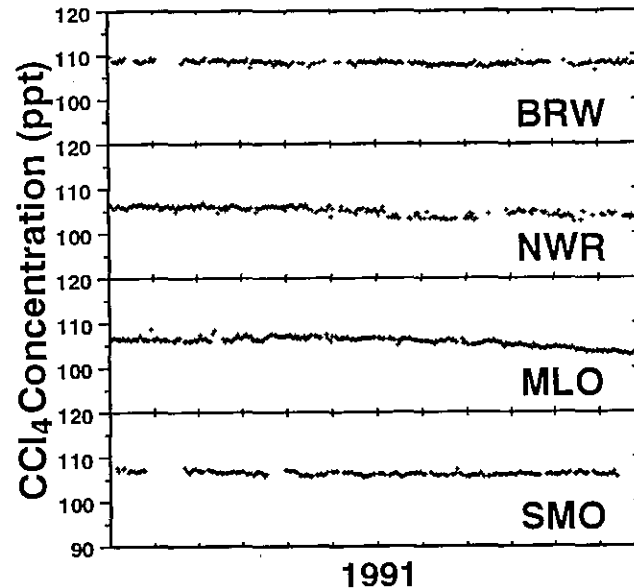


Fig. 5.10. Daily average CCl_4 mixing ratios in ppt from the in situ GCs.

from flask samples collected at NOAA's climate monitoring stations and cooperative flask sampling sites (Table 5.4), and on research cruises in the Pacific Ocean (Table 5.5).

Halons H-1211 ($CBrClF_2$) and H-1301 ($CBrF_3$) are introduced into the atmosphere almost solely as fire extinguishants; other uses, such as etching with H-1301 and

dispersing from towers as atmospheric tracers, are currently minimal. These trace gases are of interest because they have very high ozone depletion potentials [Solomon *et al.*, 1992]. Although each of the halons is present at only 1-2 ppt, both are persistent in the troposphere with estimated mean lifetimes of about 65

Table 5.4. Atmospheric Measurements of Halon-1301 and Halon-1211 [Butler et al., 1992]

Station	Year	H-1301	SE-1301*	H-1211	SE-1211*	Station	Year	H-1301	SE-1301*	H-1211	SE-1211*
ALT	91.359	2.23	0.15	2.44	0.08	MLO	90.200	1.70	0.07	2.53	0.19
ALT	91.529	1.77	0.09	1.91	0.16	MLO	90.444	1.78	0.06	1.67	0.03
ALT	91.759	1.89	0.07	2.27	0.04	MLO	90.523	1.48	0.03	—	0.01
ALT	91.874	1.92	0.04	—	—	MLO	90.679	1.80	0.07	1.94	0.11
BRW	89.589	1.62	0.32	—	—	MLO	90.830	1.88	0.12	2.07	0.07
BRW	89.668	1.64	0.09	2.56	0.19	MLO	90.942	2.03	0.02	2.52	0.15
BRW	89.767	1.82	0.10	1.86	0.09	MLO	91.227	1.59	—	2.15	—
BRW	90.304	1.86	0.02	2.12	0.16	MLO	91.038	1.60	0.09	2.14	0.05
BRW	90.455	1.77	0.04	2.14	0.05	MLO	91.184	1.67	0.08	2.26	0.20
BRW	90.455	1.90	0.03	2.12	0.09	MLO	91.230	1.58	0.22	2.03	0.09
BRW	90.589	1.85	0.01	2.11	0.05	MLO	91.518	1.55	0.11	2.28	0.17
BRW	90.704	1.99	0.03	2.28	0.01	MLO	91.690	1.82	0.04	2.00	—
BRW	90.858	2.01	0.02	2.55	0.05	MLO	91.781	1.86	0.03	—	—
BRW	91.126	2.08	0.02	—	—	MLO	91.866	1.82	0.03	2.26	0.05
BRW	91.173	1.79	0.00	2.30	—	MLO	91.921	1.89	0.02	2.32	0.07
BRW	91.225	2.22	0.02	—	—	SMO	89.515	1.51	0.03	2.26	0.36
BRW	91.225	2.01	0.02	2.32	0.16	SMO	89.515	1.27	0.03	—	—
BRW	91.449	1.96	0.05	2.64	0.12	SMO	89.767	1.45	0.03	2.00	0.07
BRW	91.625	1.79	0.05	2.00	0.08	SMO	89.693	1.38	0.04	1.87	0.04
BRW	91.770	2.02	0.07	1.95	0.31	SMO	90.282	1.83	0.03	1.74	0.03
BRW	91.855	1.83	0.05	—	—	SMO	90.112	1.92	0.11	2.53	0.21
BRW	91.953	2.08	0.04	2.57	0.19	SMO	90.512	1.58	0.01	2.02	0.03
NWR	89.641	1.56	0.07	1.96	0.07	SMO	90.438	1.63	0.04	2.11	0.08
NWR	89.756	1.54	0.03	1.88	0.01	SMO	90.690	1.55	0.02	1.94	0.05
NWR	89.852	1.60	0.01	1.99	0.03	SMO	90.833	1.72	0.03	2.51	0.03
NWR	90.101	1.50	0.02	1.96	0.21	SMO	90.956	1.84	0.08	2.64	0.16
NWR	90.178	1.77	0.07	2.03	0.04	SMO	91.112	1.55	0.04	1.90	0.08
NWR	90.449	1.65	0.03	1.92	0.09	SMO	91.233	1.84	—	2.18	—
NWR	90.523	1.85	0.17	2.03	0.28	SMO	91.447	1.77	0.07	2.35	0.11
NWR	90.526	1.71	0.10	1.92	0.08	SMO	91.405	1.72	0.02	—	—
NWR	90.871	2.07	0.03	1.95	0.01	SMO	91.619	1.43	0.03	1.99	0.11
NWR	90.945	1.75	0.04	2.32	0.05	SMO	91.699	1.66	0.14	1.87	—
NWR	91.022	1.59	0.07	2.03	0.12	SMO	91.866	1.69	0.06	2.16	0.08
NWR	91.148	1.79	0.00	2.45	0.32	CGO	91.359	1.65	0.03	2.10	0.15
NWR	91.214	1.73	0.03	2.06	0.04	CGO	91.452	1.68	0.05	—	—
NWR	91.521	1.74	0.07	2.26	0.05	CGO	91.537	1.59	0.10	1.86	0.03
NWR	91.616	1.85	0.02	1.96	0.07	CGO	91.696	1.67	0.04	—	—
NWR	91.712	2.28	0.09	2.28	0.05	CGO	91.825	1.73	0.03	—	—
NWR	91.901	1.96	0.02	2.53	0.04	SPO	90.068	1.56	0.04	1.80	0.03
MLO	89.504	1.14	0.11	—	—	SPO	90.008	1.50	0.03	2.04	0.09
MLO	89.600	1.28	0.02	—	—	SPO	90.213	1.38	0.02	2.10	0.08
MLO	89.677	1.60	0.02	1.92	0.03						

*The error in the measurement is reported as the standard error, SE-1301 and SE1211.

years for H-1301 and 16 years for H-1211 [Burkholder et al., 1991]. Because of the long atmospheric lifetimes, these gases carry a significant amount of bromine up to the

stratosphere where it can destroy O₃ catalytically. Recent reports indicate that reactions involving BrO and ClO may be responsible for 20-25% of the springtime depletion of

Table 5.5. Mean Atmospheric Measurements of Halon-1301(H-1301) and Halon-1211(H-1211) From Research Expeditions in the Pacific Ocean [Butler et al., 1992]

Expedition	Year	H-1301	H-1211
SAGA-2	87.5	0.96	1.91
RITS 89	89.2	1.45	2.01
SAGA-3	90.3	—	1.89

stratospheric O₃ over the Antarctic [Anderson et al., 1989]. The manufacture of both gases is to be discontinued globally by the end of the year 2000 according to the Montreal Protocol on Substances that Deplete the Ozone Layer [UNEP, 1987], and perhaps sooner, owing to unilateral action by users, manufacturers, and producing countries.

Paired samples have been collected every 1-2 months in electropolished, stainless-steel flasks since mid-1989 at four of the five CMDL flask network sites: BRW, NWR, MLO, and SMO. The fifth station, SPO, was sampled only during the summers of 2 years; hence the record from that station is not continuous. In 1991 sample collection for halons was begun at ALT and CGO. Flasks were also filled on research cruises from SAGA-2 in 1987 (45°N to 30°S), RITS-89 in 1989 (50°N to 60°S), and SAGA-3 in 1990 (20°N to 15°S) in the remote Pacific Ocean.

The mean difference in H-1301 mixing ratio between samples collected within the same latitudinal bands on the first two cruises suggests a growth rate of 0.29 ± 0.04 ppt yr⁻¹ for 1987-1989 (Figure 5.11a). This high growth rate is also supported by the mean interhemispheric difference of 0.28 ppt in the cruise samples. Because the atmospheric lifetime of 65 years for H-1301 is long compared to the interhemispheric exchange time of about 1 year and because it is highly likely that most of the H-1301 is emitted in the northern hemisphere, the mean latitudinally weighted, interhemispheric difference should approximate the annual growth rate (Table 5.6). Strictly calculated, this would represent a growth rate of about 0.25 ppt yr⁻¹ during this interval.

Data from the CMDL flask network show a significantly lower rate of growth for H-1301 from 1989 through 1991 (Figure 5.11a, Table 5.6). The rate of increase varied among individual stations from 0.11 to 0.19 ppt yr⁻¹, with a mean of 0.17 ± 0.06 ppt yr⁻¹. The mean interhemispheric difference during this time was 0.18 ppt, which represents an atmospheric growth rate of 0.15 ppt yr⁻¹, consistent with the observed trends.

The growth rate of atmospheric H-1211 was relatively constant at 0.08 ± 0.02 ppt yr⁻¹ for 1987-1991 (Figure 5.11b). Although the mean interhemispheric difference for H-1211 of 0.11 ppt supports an atmospheric growth rate

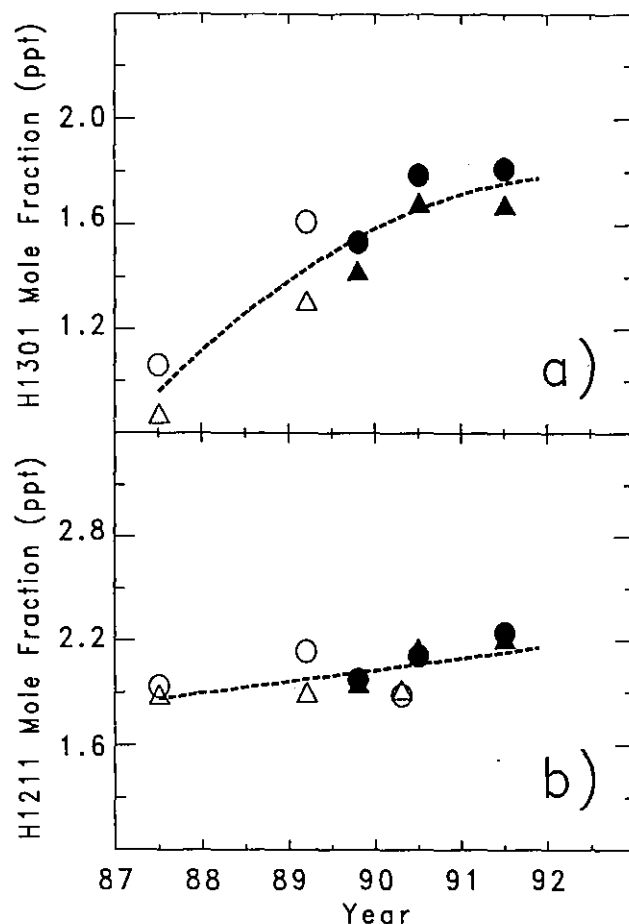


Fig. 5.11. Dry atmospheric mixing ratios of (a) H-1301 and (b) H-1211 from 1987 to 1992 [Butler et al., 1992]. Circles denote the northern hemisphere and triangles represent the southern hemisphere. Open symbols are latitudinally weighted means of data from cruises in the remote Pacific Ocean; and filled symbols are latitudinally weighted, calendar-year averages of monthly measurements from fixed sites. (Measurements of H-1301 were not obtained for the 1990 cruise.)

much closer to zero, H-1211 is not as well-suited to this calculation as is H-1301; the lifetime of H-1211 is much shorter and its emission pattern may be more variable. The mean growth rate of 0.08 ppt yr⁻¹, however, is much less than those reported by other investigators for earlier periods (Table 5.6). It is clear from these data that the atmospheric growth rates of both halons have decreased dramatically in recent years, both in absolute and relative terms.

Production of both halons began declining after 1988; however, it is more uncertain exactly when, and to what extent, releases started dropping off. Annual growth rates for 1960-1990 were calculated from emission data in McCulloch [1992] with a simple, one-box, finite-increment model:

Table 5.6. Atmospheric Growth Rates of H-1301 and H1211 (ppt yr⁻¹) 1978-1992

Year	Location	H-1301		H-1211	
		(ppt yr ⁻¹)	(% yr ⁻¹)	(ppt yr ⁻¹)	(% yr ⁻¹)
1981	Pacific Ocean* [Singh et al., 1983]	0.1	13%	—	—
1982-1984	Upper troposphere [Lal et al., 1985]	—	—	0.12	20%
1979-1985	South Pole† [Khalil and Rasmussen, 1985]	—	—	0.16	21%
1979-19987	Upper troposphere‡ [Singh et al., 1988]	0.05	4.5%	0.16	12%
1978-1987	Oregon coast [WMO, 1988]	0.05 - 0.21	18%	0.16 ± 0.01	7-15%
1987-1989	Pacific Ocean	0.29 ± 0.04	16%	0.08 ± 0.02	3%
1989-1991	CMDL observatories	0.17 ± 0.06	10%	0.08 ± 0.02	3%

*Growth rate estimated from interhemispheric difference:

$$\frac{dX}{dt} = \frac{\Delta X}{\tau_e} - \frac{X}{\tau}$$

where X is the halon mixing ratio in the southern hemisphere (ppt), ΔX is the latitudinally weighted interhemispheric difference in mixing ratio (ppt), τ_e is the interhemispheric exchange time, and τ is the atmospheric lifetime of the halon. This equation requires that emissions in the southern hemisphere are insignificant.

†Because data from the various studies were not standardized by intercalibration, the absolute growth rates have been adjusted to match the NOAA scale, where possible. Relative growth rates (% yr⁻¹), however, are not affected by differences in calibration scales.

‡Based upon only three data points; large relative uncertainty in mixing ratios.

$$\Delta X(t+1) = \frac{\Delta t}{\tau} \left[(t-0.5) \frac{fE(t+1)}{M_a} \right] - X(t)$$

where $\Delta X(t+1)$ is the mean change in tropospheric mixing ratio for time increment $t+1$, Δt is 1 year, τ is the mean lifetime in the atmosphere, f is the fraction of total atmospheric halon in the troposphere divided by the fraction of total atmospheric mass in the troposphere, $E(t+1)$ is the total annual emission, M_a is the mass of the atmosphere, and $X(t)$ is the average tropospheric mixing ratio in a given year. The fraction, f , was calculated as 1.13 for H-1301 and 1.17 for H-1211 from data given in Lal et al. [1985] and Singh et al. [1988]. The emission scenarios predict 1990 mixing ratios to within 6% of the measured values, indicating excellent agreement between NOAA measurements, emission rates from McCulloch [1992], and lifetimes from Burkholder et al. [1991]. The recent downward trends in the growth rates of both halons are also supported by emission data, although there is some disagreement in the absolute rates (Figure 5.12, Table 5.6). Growth rates calculated from atmospheric data are associated with some error, but the uncertainties in estimating annual emissions are much greater. This is particularly true for the late 1980s and early 1990s, when mandatory and voluntary reductions in use of the halons have dramatically reduced their release to the atmosphere. McCulloch [1992] simply estimated emissions as fractions

of production over three intervals from 1960 through 1990. Today, considerable effort is being made to limit releases, and much of the halon already produced remains in extinguishers or has been stockpiled. Hence, recent growth rates calculated from measurements of atmospheric mixing ratios are probably more reliable than estimates from release scenarios.

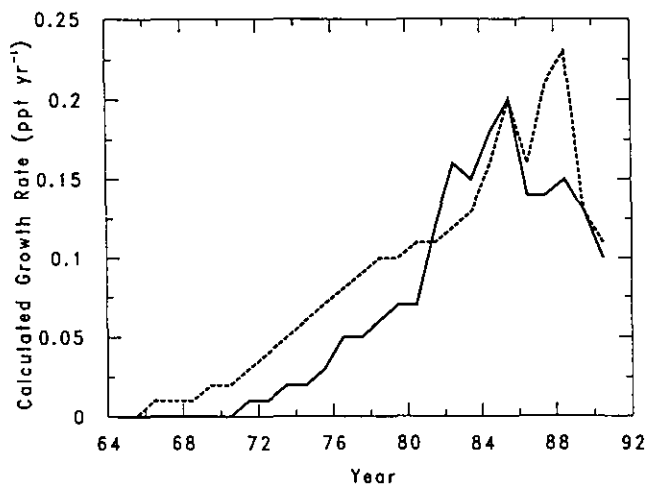


Fig. 5.12. Tropospheric growth rates for H-1301 (solid line) and H-1211 (dashed line), calculated from emission data given in McCulloch [1992].

5.1.4. ALTERNATIVE HALOCARBON MEASUREMENTS

Chlorine-mediated ozone destruction in the stratosphere has provided the impetus for eliminating the use of CFCs within the next decade. The Montreal Protocol for Substances that Destroy Ozone [UNEP, 1987] was the first treaty in which target dates were set for reduction and gradual elimination of different CFCs such as CFC-12, CFC-11, CFC-113, CFC-114 (CClF₂-CClF₂), CFC-115 (CClF₂-CF₃), methyl chloroform, carbon tetrachloride, and the halons. Additional agreements and individual nations have pushed these target dates even earlier.

A combination of different compounds are expected to replace the CFCs, including hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). HCFCs contain chlorine, but less of this chlorine will be released in the stratosphere than that released by CFCs. One HCFC, HCFC-22 (CHClF₂), is readily available as it has been used extensively in refrigeration and air conditioning applications since the 1970s. The ozone depletion potential (ODP) of HCFC-22 is much less than the CFCs that it replaces, however, models suggest that its impact on stratospheric ozone could be significant if its use is allowed to continue unabated [Solomon *et al.*, 1992]. As a result, the HCFCs are viewed as temporary replacements for CFCs until better alternatives are developed, such as the HFCs. HFCs contain no chlorine and are expected to have ODPs of zero. Until recently, however, these compounds were not readily available and the hazards associated with their use were unknown. Within the last year, one of these compounds, HFC-134a, has been introduced in automobile air conditioners.

Global measurements of HCFC-22, other HCFCs, and HFCs allow for monitoring the buildup of these compounds in the atmosphere. Such measurement programs help validate models used to understand chemical and dynamic processing within the atmosphere on a global scale.

The alternative halocarbon measurement program at CMDL is based on two different approaches (1) flask sampling of air from around the globe, and (2) the use of absorbent tubes to collect large volumes of air at remote sites. Both of these approaches require that samples be analyzed in Boulder. In 1991 techniques were developed using gas chromatography with mass spectrometric detection (GC-MS) to measure HCFC-22 and other compounds in flasks. Further developmental work was undertaken to optimize the collection of large amounts of ambient air on various absorbent materials and to screen different alternative halocarbons for their response by ECD and oxygen-doped ECD.

GC-MS Measurements of Hydrohalocarbons

Techniques were developed in 1991 for the analysis of ambient air by GC-MS. One to two hundred cm³ of dry air

are cryogenically collected onto an uncoated length of fused silica tubing at reduced pressure and directly injected onto a capillary chromatography column. This method affords good precision (relative standard deviation of ~1%) for measurements of compounds present at sub-ppb levels in background tropospheric air. For compounds present at levels as low as 1-10 ppt, collection of larger volumes of air is often necessary and will be accomplished with larger flasks and/or the use of absorbents.

Routine analysis of air from the CMDL stations, NWR, CGO, and ALT, using the GC-MS instrument, was begun in November 1991 by sampling air from flasks that are currently collected and analyzed by our LEAPS program (Table 5.7). Measurements of nine compounds were performed on each flask sample including HCFC-22. Tests conducted in this laboratory indicate that the integrity of HCFC-22 is maintained in these flasks for periods of at least 2 months.

Preliminary results indicate that the global average mixing ratio of HCFC-22 at the end of 1991 was approximately 100 ppt. The northern hemisphere contained 10-15 ppt more HCFC-22 than the southern hemisphere (after latitude weighting). These results are fairly consistent with calculations that use emission and lifetime estimates to generate global mixing ratios [Midgley and Fisher, 1992]. However, these results are substantially lower than have been reported previously for ground-based chromatographic measurements [WMO, 1988]. It is likely that this difference is due to a discrepancy in calibration scales. We believe that our current scale is accurate to within 5%, and further work in 1992 will help define these uncertainties further.

In an attempt to describe the growth of HCFC-22 in the past, archived air collected from SAGA-2 (Table 5.8) and NWR (Table 5.9) and stored at CMDL has been analyzed by GC-MS. Although rigorous testing of the stability of compounds such as HCFC-22 in different containers has not yet been completed, results of these analyses are reported in

Table 5.7. Atmospheric Measurements of HCFC-22 Reported as Dry Mixing Ratios in ppt (by Mole Fraction)

Station	Collection Date	No. of Flasks	HCFC-22 (ppt)
ALT	1991.87397	2	110.2
BRW	1991.95342	1	109.2
NWR	1991.98082	2	103.3
MLO	1991.99726	2	102.9
SMO	1991.90411	2	96.2
SMO	1991.99726	2	94.2
CGO	1991.88767	2	93.0
CGO	1991.91233	2	91.9
SPO	1991.95068	1	92.0

Table 5.8. Atmospheric Levels of HCFC-22 Measured in Flasks Collected During SAGA-2

Date	Latitude	Longitude	HCFC-22 (ppt)
1987.3836	36.8	-160.0	79.0
1987.3918	23.3	-160.0	75.5
1987.4027	1.7	-160.0	71.5
1987.4247	-22.2	-160.0	67.9
1987.4301	-29.4	-170.0	67.2

Figure 5.13 for air collected at NWR after mid-1988 in a number of different types of containers, with and without drying agents in line. For unknown reasons, contamination of these samples is a problem for air collected prior to mid-1988. However, for samples collected after this time, a growth rate of 6.4 ppt yr^{-1} (or $7.0\% \text{ yr}^{-1}$) can be estimated from these data. This is very similar to growth rates that have been reported in the literature for HCFC-22 for the years 1985-1990 [WMO, 1988, Rinsland *et al.*, 1990] and calculated from emission estimates [Midgley and Fisher, 1992]. This is an indication that the growth of HCFC-22 has been fairly constant over the past 2 years despite the drastic reduction in use and emission of CFC-11 and CFC-12 during this time [Elkins *et al.*, 1992].

Table 5.9. Atmospheric Levels of HCFC-22 Measured in Archived Gas Cylinders*

Collection Date	HCFC-22 (ppt)	Type of Container and Method	Moisture
1988.8932	85.0	0	0
1988.8932	84.5	0	0
1989.2986	86.2	1	0
1990.3863	95.7	2	0
1990.9123	98.3	3	0
1991.1616	99.7	2	0
1991.7781	109.5	3	1
1991.942	107.9	2	2

*All cylinders were pumped at NWR. The types of sample containers are described by the following types: 0 = electropolished, stainless steel, 33-L container initially filled to 300 psig with ambient air; 1 = Aculife treated (Scott Specialty Gases, Plumsteadville, Pennsylvania), 49.9-L steel gas cylinder filled to 2000 psi with ambient air; 2 = Aculife treated, 29.5-L aluminum gas cylinder filled to 2000 psi with ambient air; and 3 = Aculife treated, 5.9-L aluminum gas cylinder filled to 2000 psi with ambient air. The moisture was removed with either Aquasorb (moisture = 0, support coated P_2O_5 , Mallinckrodt, Paris, Kentucky) or Sicapent (moisture = 1, support coated P_2O_5 , EM Science, Gibbstown, New Jersey) to dewpoints below -80°C . One cylinder was filled without a dryer (moisture = 2).

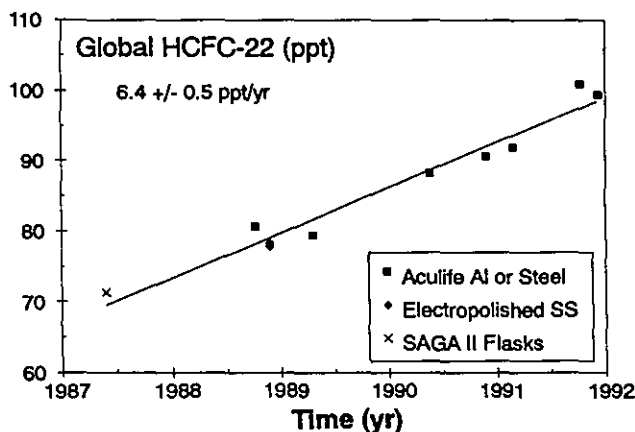


Fig. 5.13. Global estimates of HCFC-22 (by GC-MS) in archived air samples collected at NWR and during the SAGA-2 cruise. For the NWR samples, mixing ratios were divided by 1.086 to approximate the global average of HCFC-22 at that time. Five samples taken during the SAGA-2 cruise between 30°S and 37°N and between 160°E and 170°E were latitudinally weighted to determine a global mean (Table 5.8).

Absorbent Tube and O_2 -Doped ECD Measurement of Hydrohalocarbons

Further screening of potential absorbent materials for concentrating halocarbons and hydrohalocarbons from large air samples was continued in 1991. The present design for an absorbent trap consists of a 35 cm long, 0.63 cm outside diameter steel tube packed with a 9 cm length of Carbosieve S-II (Supelco), 5 cm of Carboxen 1000 (Supelco), and 16 cm of HayeSep D_B (Hayes Separations). Samples were collected on the tube at ambient temperature ($25\text{-}30^\circ\text{C}$), and desorbed at 200°C . The desorbed compounds were cryogenically refocused and analyzed with the LEAPS GC. The LEAPS GC has two ECDs in series; the second detector is doped with oxygen-in-nitrogen to $0.2\% \text{ O}_2$.

Analytical precision for some halocarbons and HCFC-22 are shown in Table 5.10. Peak areas showed standard errors (1σ , $n = 3$) of about 2-4%. Normalizing to CFC-12 improved precision to $\sim 1\%$ or less.

Figure 5.14 shows a calibration curve for CFC-12 collected on the trap from a range of NOAA gas standards. Two measurements of CFC-12 in a cylinder filled at NWR are also shown in this figure. Using the standard curve shown gave a CFC-12 mixing ratio of 479 ± 6 ppt. An earlier analysis using our flask GC system gave a CFC-12 mixing ratio of 461 ± 3 ppt for this cylinder.

The ECD responds only weakly to HFCs and some HCFCs. We have determined, however, that a number of HCFCs and HFCs can be detected using O_2 -doping of an ECD. When used in conjunction with absorbent tubes,

TABLE 5.10. Analytical Precision for Some Halocarbons and HCFC-22 in NOAA-191 (1-16 ppb Mixture in Air)*

Compound	Precision (Sample Standard Error, n = 3), %	
	Peak Area	Ratio to CFC-12
CFC-12	2.8	—
CFC-11	3.3	0.47
CFC-113	3.7	1.26
CH ₃ CCl ₃	2.2	0.57
CCl ₄	2.5	0.28
HCFC-22 (O ₂ -doped ECD)	4.3	0.86

*Loops were swept onto an absorbent trap (Carbosieve S-II, Carboxen 1000, HayeSep D_B) with 400 mL of N₂ at 30°C, and then desorbed with backflush at 200°C.

detection of these compounds using an O₂-doped ECD should be possible at the ppt level. Figure 5.15 illustrates the measurement of the only HFC currently used by industry: HFC-134a (CH₂FCF₃). While HFC-134a is not detected in the undoped ECD, oxygen doping enhances the response of this compound dramatically. Measurement of lower level standards suggests that a detection limit (three times the RMS noise) of around 3 ppt is possible in a 10-L air sample.

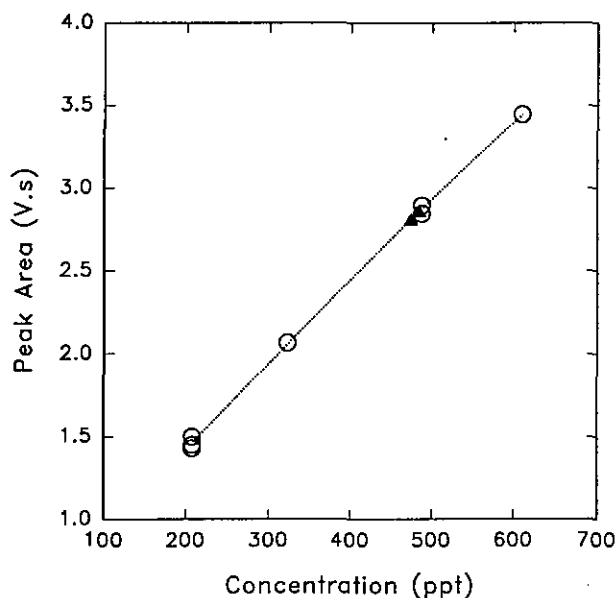


Fig. 5.14. CFC-12 gas standards (open circles) of varying concentrations trapped on an absorbent tube (10 mL of standard and 550 ml of N₂) and then desorbed at 200 °C into the LEAPS GC. Also shown (solid triangles) are two similar analyses of air from a cylinder filled at NWR.

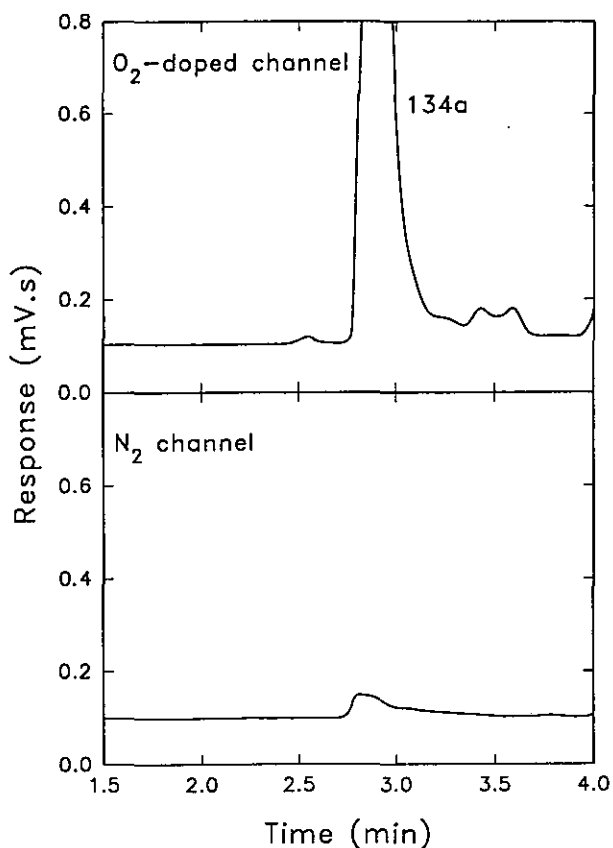


Fig. 5.15. Chromatograms from non-doped and O₂-doped ECDs in series from the same injection of 10 mL of a 156 ppm HFC-134a standard (balance air).

Figure 5.16 shows the chromatograms obtained from a 1 µL injection of "pure" HCFC-142b (CClF₂CH₃). This compound has already been detected in the atmosphere at the ppt level. As is the case with HFC-134a, a high degree of signal enhancement is possible with O₂-doping. The bulk sample contains CFC-11 and HCFC-141b (CCl₂FCH₂) as impurities. The HCFC-141b is also clearly visible in the O₂-doped ECD response. We do not as yet have standards for this compound to determine detection limits, but from the response observed in Figure 5.16 for high concentrations, we expect to be able to detect ppt levels with sample enrichment using absorbent tubes.

HCFC-123 (CF₃CHCl₂) has a similar response on both the doped and non-doped detector. The inherently lower noise of the non-doped channel makes this the choice for lowest detection limit. The detection limit was estimated to be 0.06 ppt in a 10-L air sample.

The LEAPS GC program has already established that O₂-doping enhances the response of HCFC-22 in an ECD. Therefore, it will be possible to measure HCFC-22, HCFC-123, HCFC-142b, HCFC-141b, and HFC-134a using O₂-

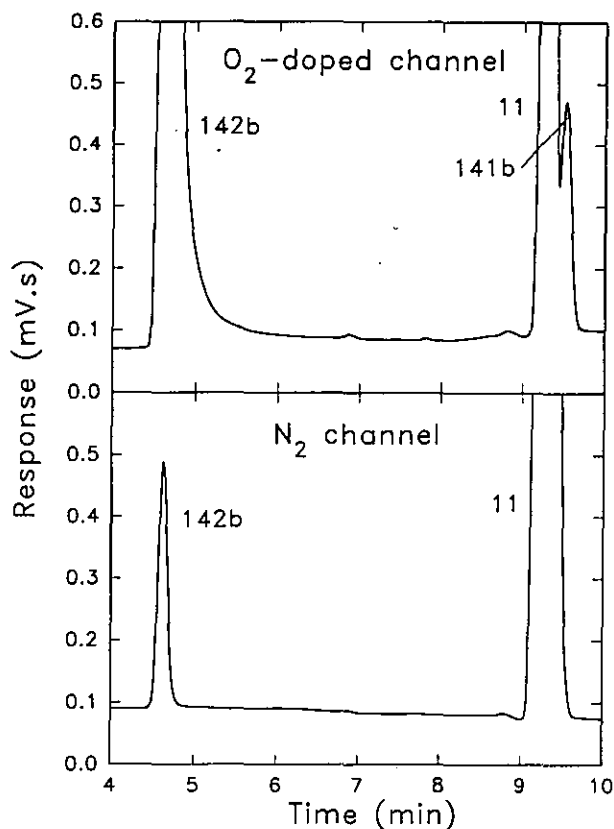


Fig. 5.16. Chromatograms from non-doped and O_2 -doped ECDs in series from the same injection of $1 \mu L$ of "pure" HCFC-142b. CFC-11 and HCFC-141b are present as impurities.

doped ECD and absorbent tube sample concentration. This gives us another viable technique, along with mass selective detection, for monitoring hydrohalocarbons. In addition, absorbent tube technology can enhance sampling flexibility of other detection methods, including mass selective.

5.1.5. GRAVIMETRIC STANDARDS

A major effort was placed on refining our calibration of CFC-11 and CFC-12 over the past year because of the observed slowdown in their growth rates. Primary calibration of flask measurements involved only three gas standards throughout the entire period. These standards, filled with air from the NWR region, were recalibrated recently on a NOAA scale based on gravimetric standards prepared in our laboratory since 1986. All gravimetric standards agreed to better than 1%. The analysis of long-term drift of the three working standards revealed that only one standard (cylinder no. 3072), which was used from 1977 to 1985, had a statistically significant drift rate for both CFC-11 and CFC-12 (Figure 5.17). On the basis of

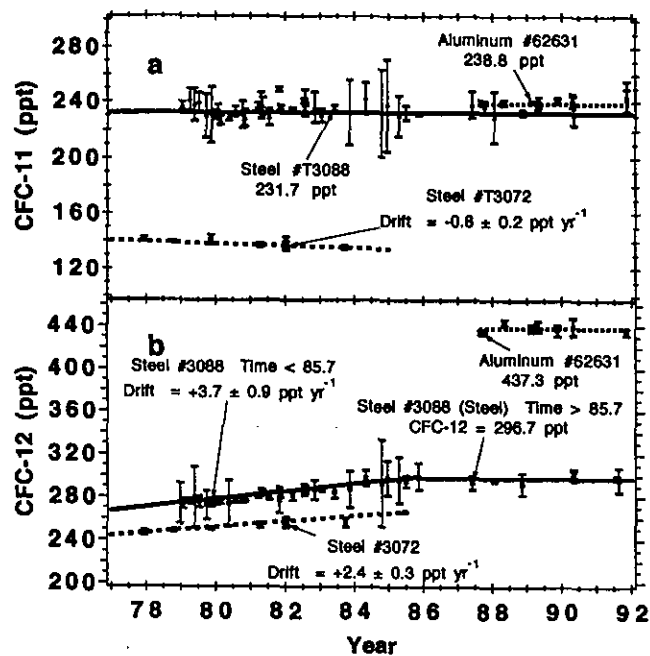


Fig. 5.17. History of NOAA calibration scale for (a) CFC-11 and (b) CFC-12. Steel cylinder no. 3072 was the only cylinder used for calibration from 1977 to 1985 and it drifted in mixing ratio starting in 1977 to 1985 for both CFC-11 and -12. However, cylinder no. 3088 has not drifted significantly since 1985 for CFC-12. Cylinder no. 3072 was emptied accidentally in 1985; therefore, only cylinder no. 3088 and no. 62631 have been used to calibrate the flask measurements. Error bars are 95% C.I.

comparisons with primary standards maintained by OGIST [Rasmussen and Khalil, 1986], we have estimated that the mixing ratio of CFC-12 was increasing at 2.4 ± 0.3 (one standard deviation) ppt yr^{-1} and CFC-11 was decreasing at $0.8 \pm 0.2 \text{ ppt yr}^{-1}$ in that first standard. In last year's report [Ferguson and Rosson, 1991], the three working standards were put on the NOAA scale, and the drift was incorrectly assumed to be insignificant for all cylinders at all times. Although we recently have corrected our data, the effect of drift in standards during 1977-1985 does not affect the more recent slowdowns of CFC growth rates that are reported here. Our absolute values for CFC-12 are about $3.4 \pm 1.5\%$ higher, and for CFC-11 about $3.2 \pm 1.3\%$ lower than those measured by the ALE/GAGE [Cunnold et al., 1986] based on a comparison of data from a jointly occupied station at SMO. Results from a recent laboratory intercomparison of two cylinders showed that our scale for CFC-12 is 1.3% higher and for CFC-11 is 0.1% higher than the SIO scale [Bullister and Weiss, 1988].

Twenty-seven primary calibration standards were prepared during 1991 in the standards laboratory (see Table 5.11). Sixteen of the standards were prepared as multi-

Table 5.11. Summary of Gravimetric Standards Prepared in 1991

Compounds	Qty	Concentration Range	Prepared For
CFC-11, CFC-113, CFC-12, CH ₂ Cl ₂ , CCl ₄ , HCFC-22, N ₂ O	16	ppm, ppt	ACATS and NOAH
HCFC-22	2	ppm, ppb	NOAH
HCFC-123	3	ppm, ppb	NOAH
HFC-134a	1	ppb	NOAH
CH ₄	3	percent, ppm	CC
CH ₄ , N ₂ O	2	ppm, ppb	JPL

component mixtures specifically for the ACATS project, but were also used in other NOAH projects. Six standards were prepared for use in the Alternative Halocarbon Measurements' project. Three methane standards were prepared for the Carbon Cycle Division including two at the percent-level and one at ambient levels. The percent-level standards will be used to generate a suite of primary standards above and below atmospheric mixing ratios for future use as a primary calibration scale. Two standards, one containing N₂O and the other CH₄, were prepared for JPL. Four NWR air secondary standards were prepared and analyzed for the RITS project. Two were used to replace GC calibration standards at SMO, and two were used to replace the GC calibration standards at NWR.

A nickel oxide catalyst was installed on the Shimadzu FID-GC model GC-8 for the measurement of CO and CO₂. The addition of the GC-MS to the NOAH group has greatly enhanced the standards laboratory capabilities to evaluate impurities of reagents used in preparing standards and also in detecting contamination problems in cylinders and in the blending manifold. A new manifold heated to 300°C has been built for transferring pure gases. After each use, it is purged with high-purity N₂ while placed inside an oven. An additional manifold currently being built, has been designed for preparing ppt level standards.

During 1991, we continued to develop a primary calibration scale for HCFC-22. Earlier measurements by chromatographic techniques (WMO, 1988) have suggested substantially higher mixing ratios than observed here at CMDL or by long-path infrared (Rinsland *et al.*, 1990), or expected from estimates of emissions (Midgley and Fisher, 1992). The GC-MS has been used to verify linearity of the standards from ppt to ppb levels. Further work is planned to expand this result to the high ppm level in 1992.

Accurate standard preparation also hinges on knowing the purity of reagent materials. Analysis of pure HCFC-22 from two different manufacturers was performed by GC-

MS and FT-IR. Small amounts (1-2 µL) of pure material were injected directly onto a capillary column and analyzed. The chromatograms are presented in Figure 5.18 and indicate, when combined with the results of FT-IR analysis (performed by the AL), that the purity of both of these reagents is better than 99.9%.

One of the special projects that required the preparation of numerous standards was the ACATS project where trace gases (CFC-11 and CFC-113) were measured real-time via a gas chromatograph installed on one of NASA's ER-2 aircraft. In-flight calibrations were performed with a gravimetrically prepared calibration gas mixture. Two standards were initially prepared using pure aliquots of CFC-11, CFC-12, CFC-113, methyl chloroform, carbon tetrachloride, and HCFC-22. The resulting mixing ratios of the gases ranged from high parts per billion to low parts per million levels. Eight standards were then prepared from these two standards to provide a suite of calibration standards that contained mixing ratios above and below the atmospheric levels of these gases. Four additional standards were prepared as bulk mixtures contained in 46.4-L cylinders. The mixing ratios of components in these standards were targeted to approximate the range of levels expected from the lower troposphere to the upper stratosphere. A listing of the standards and their gravimetrically assigned mixing ratios are shown in Table 5.12. The suite of eight calibration standards and one of the bulk standards were intercompared using the ACATS GC. Figures 5.19 and 5.20 show a plot of response versus gravimetric mixing ratio of CFC-11 and CFC-113 respectively.

5.2. SPECIAL PROJECTS: AIRBORNE CHROMATOGRAPH FOR ATMOSPHERIC TRACE SPECIES (ACATS)

Measurement of vertical profiles of trace gases, in particular CFCs, has gained more importance in the research activities of CMDL. Expanding our program to

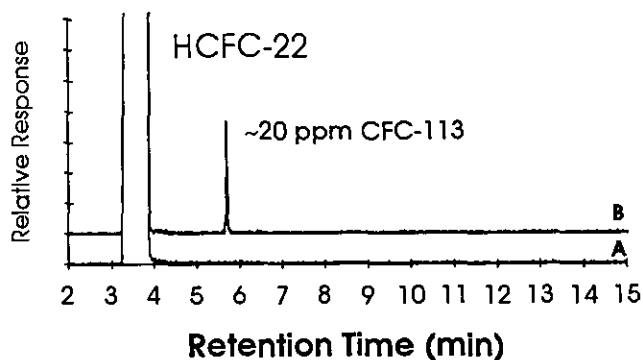


Fig. 5.18. GC-MS chromatograms of "pure" HCFC-22 from two different manufacturers, (a) Scott Specialty Gas and (b) PCR Inc.

Table 5.12. Gravimetrically Prepared Standards Used for ACATS Project

Standard Number	CFC-11	CFC-113	CFC-12	CH ₃ CCl ₃	CCl ₄	HCFC-22	N ₂ O
NOAA-192	478 ppb	132 ppb	1.58 ppm	761 ppb	754 ppb		
NOAA-190	282 ppb	119 ppb	1.46 ppm	599 ppb	954 ppb	469 ppb	
NOAA-191	3.02 ppb	1.28 ppb	15.7 ppb	6.42 ppb	10.2 ppb	5.03 ppb	
NOAA-215	4.33 ppb	1.83 ppb	22.5 ppb	9.21 ppb	14.7 ppb	7.23 ppb	4.83 ppm
NOAA-204	303 ppt	128 ppt	1.57 ppb	644 ppt	1.03 ppb	505 ppt	
NOAA-203	235 ppt	99.3 ppt	1.22 ppb	499 ppt	795 ppt	391 ppt	
NOAA-202	118 ppt	50.1 ppt	615 ppt	252 ppt	401 ppt	197 ppt	
NOAA-196	136 ppt	37.5 ppt	451 ppt	217 ppt	215 ppt		
NOAA-193	55.6 ppt	23.5 ppt	289 ppt	118 ppt	188 ppt	92.9 ppt	
NOAA-194	69.2 ppt	19.1 ppt	229 ppt	110 ppt	109 ppt		
NOAA-195	49.5 ppt	13.6 ppt	164 ppt	78.7 ppt	78.0 ppt		
NOAA-197	23.5 ppt	6.48 ppt	77.8 ppt	37.5 ppt	37.1 ppt		
BULK-1	33.5 ppt	14.2 ppt	173.8 ppt	71.2 ppt	113 ppt	55.7 ppt	
BULK-2	131 ppt	55.6 ppt	682 ppt	279 ppt	445 ppt	219 ppt	
BULK-3	77.2 ppt	32.6 ppt	400 ppt	164 ppt	261 ppt	129 ppt	
BULK-4	102 ppt	43.0 ppt	528 ppt	216 ppt	344 ppt	169 ppt	113 ppb

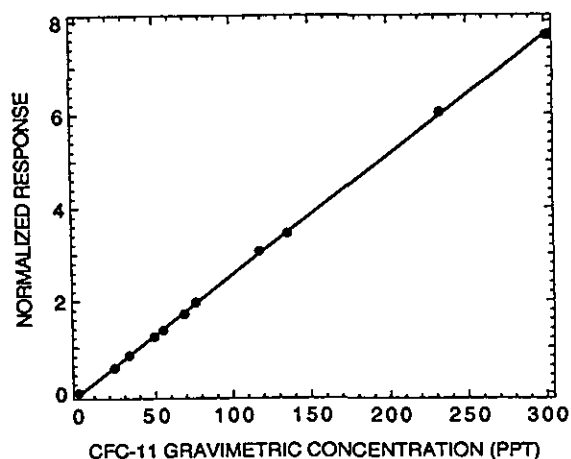


Fig. 5.19 CFC-11 gravimetric mixing ratios versus normalized instrument response of the ACATS GC using during AASE-II. Note the near-zero intercept and linear calibration of the GC over the range of the measurements.

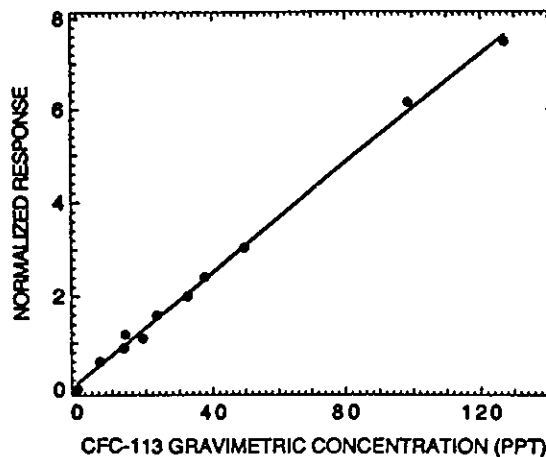


Fig. 5.20. CFC-113 gravimetric mixing ratios versus normalized instrument response of the ACATS GC using during AASE-II.

include measurements of CFC vertical profiles has become a major element of the RITS program at NOAA and a key responsibility of NOAA to the National Global Climate Change Program [GCRP, 1990]. Vertical profiles of CFCs are useful for comparing observed tropospheric mixing ratios to those calculated using industry estimates of emissions and simple box models. Specifically, knowledge of vertical profiles permits calculation of the fraction (f) of total CFC mass in the troposphere (see LEAPS section).

In 1991 our principal effort was the development of a new GC for measuring CFC-11 and CFC-113 every 2

minutes on the NASA ER-2 aircraft. This GC was built as a joint project between CMDL and AL. The schematic layout of the ACATS GC is shown in Fig. 5.21. Improvement in the sampling frequency over commercially available GCs was made possible by the addition of a two-position, 12-port gas sampling valve (GSV). The GSV injects a 5 cm³ sample onto two separation columns coupled in series (SP 2100, Supelco), a main column and a pre-column. The use of two columns prevents air from entering the ECD and allows for backflushing of the pre-column after CFCs of interest enter the main column. The

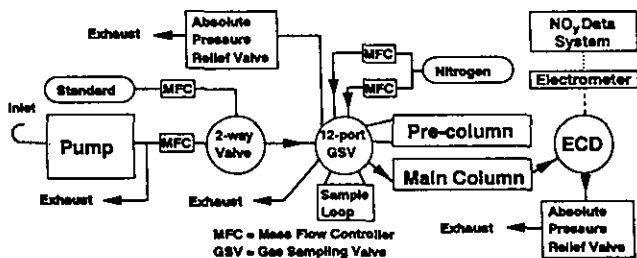


Fig. 5.21. Schematic layout of the ACATS GC.

net result is a chromatogram that contains two CFC peaks but no signal associated with air or other heavier halocarbons. The GC was mounted inside the NO_y instrument [Fahey et al., 1989] in the main aft instrument compartment of the plane behind the cockpit (Q-bay). Because of limited space and weight considerations, both instruments shared a number of key components, including the onboard IBM PC, pump motor, and power lines.

The technological requirements for the airborne GC were demanding. In less than 6 months, a two-channel GC was built to fit within a 50 L volume (note that the equivalent station GC takes up a standard 2 m lab bench and weighs over 150 kg). The airborne GC's electrical and mechanical systems were required to meet or exceed military specifications for safety, and its design included several automatic shutdown features rarely found on commercial GCs. Special engineering was required so that the instrument response was independent of the wide pressure (250-1000 mb) and temperature (3-33°C) variations experienced in the Q-bay during a single flight.

The first application of ACATS on the ER-2 aircraft was to measure CFC-11 and CFC-113 for the NASA Arctic Airborne Stratospheric Expedition-II (AASE-II) that ran from August 1991 through March 1992. The goal of AASE-II was to investigate the formation, maintenance, and breakup of the arctic vortex and to quantify the amount of ozone depletion in the northern hemisphere resulting from the presence of CFCs. The expedition began in August with a series of test flights at the NASA Ames Research Center, Moffett Field, California. The initial flights occurred in September. During both test flight periods, flights were made south and east to measure the stratospheric extent of the volcanic plume from the Mt. Pinatubo eruption that had occurred in June. In order to measure the background levels of tracers and other reservoir species in the stratosphere prior to the formation of the arctic vortex, a series of flights were based out of Fairbanks, Alaska, in October and out of Bangor, Maine, in November and December. The formation, maintenance, and breakup of the vortex were monitored between December 1991 and March 1992. Several flights were directed south (as far south as 23°N) to examine the extent

of ozone depletion and the influence of aerosols from Mt. Pinatubo into the mid-latitudes.

The scientific motivations for measuring CFC-11 and CFC-113 on the AASE-II were: (1) to define the CFC tracer field during the mission from 23° to 90°N; (2) to estimate the chemical ozone loss within the arctic vortex; (3) to record the evolution of organic chlorine (CCl_y , e.g. CFCs) and to support calculation of inorganic chlorine (Cl_y , e.g. ClO , ClONO_2 , HCl) in the arctic vortex; and (4) to calculate local ODPs expected for HCFCs given the in situ measurements of CFCs by ACATS and CH_4 by ALIAS [Webster et al., 1990], and the chemical model of Solomon et al. [1992]. Typical vertical profiles of CFC-11 and CFC-113 as measured by ACATS are shown in Figure 5.22 from a flight between Fairbanks and Moffett Field on October 14. Approximately 90% of the total atmospheric CFC-11 and CFC-113 reside in the troposphere. While the mixing ratio of CFC-113 is linearly correlated with N_2O measured by ATLAS [Loewenstein et al., 1989], CFC-11 shows considerable curvature (Figure 5.23). The degree of curvature observed in these plots gives an indication of the local photochemical lifetime of the CFC relative to mixing times. A linear relationship indicates that local mixing times are shorter than the time for local photochemical loss. Non-linearity denotes more rapid local chemical loss of the tracer than can be resupplied by mixing. The relationship between N_2O , a long lived tracer with an atmospheric lifetime of ~130 years, and molecules with shorter lifetimes will be non-linear at low N_2O values, and this is consistent with the results shown in Figure 5.23 given that the accepted lifetime for CFC-11 is ~55 years and for CFC-113 is ~110 years.

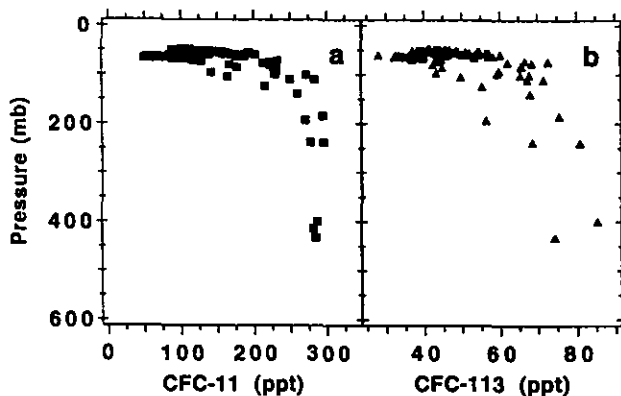


Fig. 5.22. Vertical profiles of (a) CFC-11 in squares and (b) CFC-113 in triangles measured using the ACATS GC on board the NASA ER-2 aircraft on October 14, 1991, during a ferry flight from Fairbanks, Alaska, to Moffett Field (NASA Ames Research Center), California. Note that the high values (>80 ppt) of CFC-113 were observed on the approach to Moffett Field over San Jose, California, an area where large amounts of CFC-113 are used by the electronics industry.

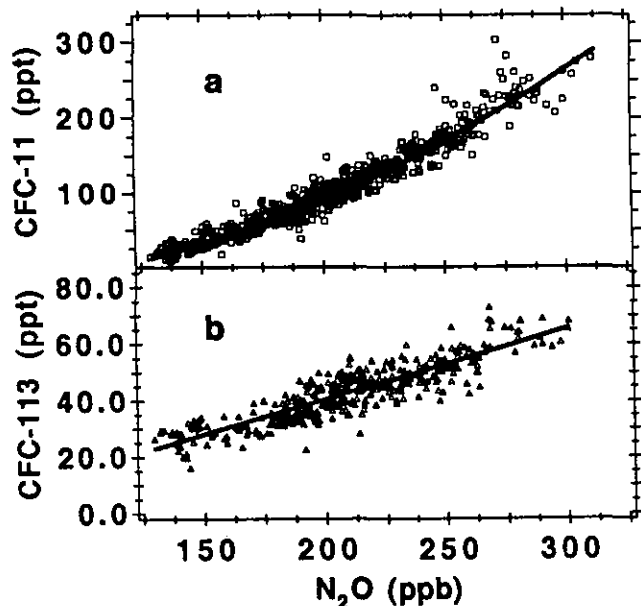


Fig. 5.23. Tracer plots from the AASE-II in 1991 for (a) CFC-11 versus N_2O and (b) CFC-113 versus N_2O . Both sets of data are preliminary. Data for N_2O were obtained from the ATLAS instrument (private communication, Max Loewenstein, NASA, Ames).

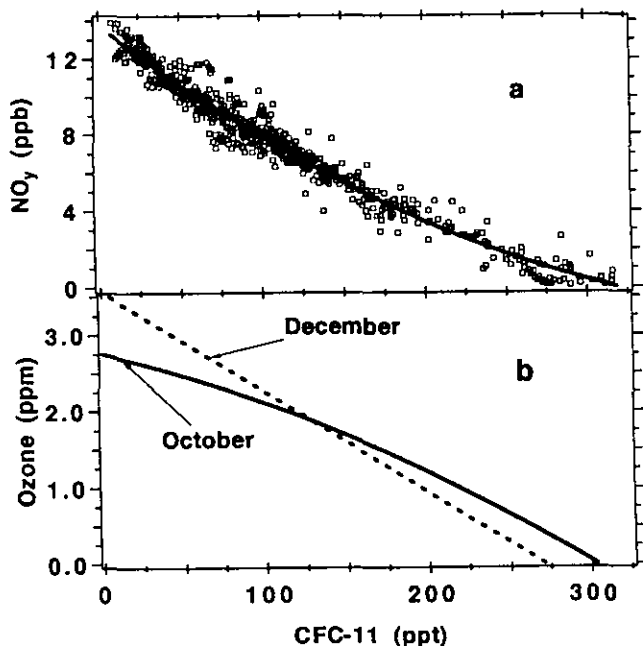


Fig. 5.24. Relationships of (a) reactive nitrogen (NO_y) versus CFC-11 and (b) ozone versus CFC-11 fitted curves for October and December. All sets of data are preliminary (NO_y [private communication David Fahey, NOAA/AL] and O_3 [private communication Michael Proffitt, CIRES].)

Mixing ratios of CFC-11 are inversely correlated with ozone [Proffitt *et al.*, 1992] and NO_y [Fahey *et al.*, 1989] (Figure 5.24). The low ozone (O_3) values observed in October when CFC-11 was also low are associated with summertime loss of O_3 in the higher latitude regions (Figure 5.24b.). Plots of O_3 versus tracers (for example, CFC-11 and N_2O) and their relationships establish a relative climatology for predicting O_3 mixing ratios, thereby permitting estimates of loss and production of this important trace gas over the period of the mission.

5.3. REFERENCES

- AFEAS (Alternative Fluorocarbons Environmental Acceptability Study), *Chlorofluorocarbons (CFC's) 11 and 12*, Report prepared for AFEAS by Grant Thornton, Washington, DC, 1991.
- Anderson, J.G., W. H. Brune, S. A. Lloyd, D. W. Toohey, and S. P. Sander, Kinetics of O_3 destruction by ClO and BrO within the antarctic vortex: An analysis based on in situ ER-2 data, *J. Geophys. Res.*, **94**, 11480-11520, 1989.
- Burkholder, J.B., R.R. Wilson, T. Gierczak, R. Talukdar, S.A. McKeen, J.J. Orlando, J.J., Vaghjani, G.L., and A.R. Ravishankara, Atmospheric fate of CF_3Br , CF_2Br_2 , CF_2ClBr , and CF_2BrCF_2Br , *J. Geophys. Res.*, **96**, 5025-5043, 1991.
- Bullister, J.L. and R.F. Weiss, Determination of CCl_3F and CCl_2F_2 in seawater and air, *Deep Sea Res.*, **35**(5), 839-853, 1988.
- Butler, J.H., J.W. Elkins, T.M. Thompson, B.D. Hall, and C.M. Brunson, N_2O and Halocarbons Group, in *Geophysical Monitoring for Climatic Change No. 17, Summary Report, 1988*, edited by J.W. Elkins, and R.M. Rosson, pp. 64-70, NOAA Environmental Research Laboratories, Boulder, CO, 1989.
- Butler, J., J.W. Elkins, B.D. Hall, S.O. Cummings, and S.A. Montzka, A decrease in the growth rates of atmospheric halon concentrations, *Nature*, **359**, 403-405, 1992.
- Cunnold, D.M., R.G. Prinn, R.A. Rasmussen, P.G. Simmonds, F.N. Alyea, C.A. Cardelino, A.J. Crawford, P.J. Fraser, and R.D. Rosen, Atmospheric lifetime and annual release estimates for $CFCl_3$ and CF_2Cl_2 from 5 years of ALE data, *J. Geophys. Res.*, **91**, 10,797-10,817, 1986.
- Elkins, J.W., T.M. Thompson, B.D. Hall, K.B. Egan and J.H. Butler, NOAA/GMCC halocarbons and nitrous oxide measurements at the South Pole, *Ant. J. U. S.*, **23**, 76-77, 1988.
- Elkins, J.W., T. M. Thompson, T. H. Swanson, J. H. Butler, S. O. Cummings, B. D. Hall, D. A. Fisher, and A.G. Raffo, Slowdown in the atmospheric growth rates of chlorofluorocarbon-11 and -12, submitted, *Nature*, 1992.
- Fahey, D.W., D.M. Murphy, K.K. Kelly, M.K. W. Ko, M.H. Proffitt, C.S. Eubank, G.V. Ferry, M. Loewenstein, and K. R. Chan, Measurements of nitric oxide and total reactive nitrogen in the antarctic stratosphere: Observations and chemical implications, *J. Geophys. Res.*, **94**, 16,655-16,681, 1989.
- Ferguson, E.E. and R.M. Rosson (Eds.), *Climate Monitoring for Climate Monitoring and Diagnostics Laboratory, No. 19: Summary Report 1990*, pp 19, NOAA Environmental Laboratories, Boulder, CO, 1991.
- GCRP (Global Change Research Program), *Our Changing Planet: The FY 1991 Research Plan, The U.S. Global Change Research Program*, Report by the Committee on Earth Sciences, 120 pp., U.S. Geological Survey, Reston, VA, 1990.
- Khalil, M.A.K., and R.A. Rasmussen, The trend of bromochlorodifluoromethane and the concentrations of other bromine-containing gases at the South Pole., *Ant. J. U. S.*, **20**, 206-207, 1985.

- Loewenstein, M., J.R. Podolske, K.R. Chan, and S.E. Strahan, Nitrous oxide as a dynamical tracer in the 1987 Airborne Antarctic Ozone Experiment, *J. Geophys. Res.*, *94*, 11,589-11,598, 1989.
- Lal, S., R. Borchers, P. Fabian, and B.C. Krüger, Increasing abundance of CBrClF₂ in the atmosphere, *Nature*, *316*, 135-136, 1985.
- McFarland, M., and J. Kaye, Annual reviews, Chlorofluorocarbons and ozone, *J. Photochem. Photobiol.*, *55*, 911-929, 1992.
- Midgley, P.M., and D.A. Fisher, The production and release to the atmosphere of chloro-difluoromethane (HCFC-22), submitted, *Atmos. Environ.*, 1992.
- McCulloch, A. Global production and emissions of bromochlorodifluoromethane and bromotrifluoromethane (Halons 1211 and 1301), *Atmos. Environ.*, *26A*, 1325-1329, 1992.
- Proffitt, M.H., S. Solomon, and M. Loewenstein, Comparison of 2-D model simulations of ozone and nitrous oxide at high latitudes with stratospheric measurements, *J. Geophys. Res.*, *97(D1)*, 939-944, 1992.
- Rasmussen, R.A. and M.A.K. Khalil, Trends and distributions over the last decade, *Science*, *232*, 1623-1624, 1986.
- Rinsland, C.P., A. Goldan, F.J. Murcray, R.D. Blatherwick, J.J. Kusters, D.G. Murcray, N.D. Sze, and S.T. Massie, Long-term trends in the concentrations of SF₆, CHClF₂, and COF₂ in the lower stratosphere from analysis of high-resolution infrared solar occultation spectra, *J. Geophys. Res.*, *95*, 16,477-16,490, 1990.
- Singh, O.N., R. Borchers, P. Fabian, S. Lal, and B. H. Subbaraya, Measurements of atmospheric BrO_x radicals in the tropical and mid-latitude atmosphere, *Nature*, *334*, 593-595, 1988.
- Singh, H.B., L.J. Salas, and R.E. Stiles, Selected man-made halogenated chemicals in the air and oceanic environment, *J. Geophys. Res.*, *88*, 3675-3683, 1983.
- Solomon, S., M. Mills, L.E. Heidt, W.H. Pollock, and A.F. Tuck, On the evaluation of ozone depletion potentials, *J. Geophys. Res.*, *97*, 825-842, 1992.
- Swanson, T.H., J.W. Elkins, T.M. Thompson, S.O. Cummings, J.H. Butler, and B.D. Hall, Decline in the accumulation rates of atmospheric chlorofluorocarbons 11 and 12 at the South Pole, submitted, *Ant. J. U. S.*, 1992.
- UNEP (United Nations Environmental Program), *Montreal Protocol to Reduce Substances that Deplete the Ozone Layer Report, Final Report*, New York, 1987.
- Webster, C.R., R.D. May, R. Toumi, and J.A. Pyle, Active nitrogen partitioning and the nighttime formation of N₂O₅ in the stratosphere: Simultaneous in situ measurements of NO, NO₂, HNO₃, O₃, and N₂O using the BLISS Diode Laser Spectrometer, *J. Geophys. Res.*, *95*, 13,851-13,866, 1990.
- WMO (World Meteorological Organization), *Report of the International Ozone Trends Panel, 1988*, Vol. 2, Global Ozone Research and Monitoring Project Report No. 18, Geneva, Chapter 8, 1988.