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N91-27639

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PROPOSED REFERENCE MODELS FOR CO_2 AND HALOGENATED HYDROCARBONS

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ABSTRACT

The vertical distribution of carbon dioxide, halocarbons and their sink products, HCl and HF, have become available, mainly by means of balloon measurements. Most measurements were made at northern mid-latitudes, but some constituents were measured at tropical latitudes and in the southern hemisphere as well. This report attempts to combine the available data for presentation of reference models for CO_2, CCl_4, CCl_3F, CCl_2F_2, $CClF_3$, CF_4, $CCl_2F-CClF_2$, $CClF_2-CClF_2$, $CClF_2-CF_3$, CF_3-CF_3, CH_3Cl, $CHClF_2$, CH_3-CCl_3, $CBrClF_2$, $CBrF_3$, HCl and HF.

INTRODUCTION

CO_2 is a natural constituent of the atmosphere thought to be well mixed up to the turbopause. Due to the burning of fossil fuel, however, CO_2 abundances increase steadily at ground level resulting in CO_2 profiles which fall off with altitude in the stratosphere.

Halogenated hydrocarbons (halocarbons) are source gases for ClO_x, FO_x- and BrO_x-radicals in the stratosphere. Besides methyl chloride (CH_3Cl), the halocarbons discussed here originate almost entirely from anthropogenic sources: While CFC-10 (CCl_4), CFC-113 ($CCl_2F-CClF_2$), and CFC-140 (CH_3-CCl_3) are mainly used as solvents, CFC-22 ($CHClF_2$) and CFC-13 ($CClF_3$) are chiefly applied as refrigerants. CFC-114 ($CClF_2-CClF_2$), CFC-115 ($CClF_2-CF_3$), CFC-11 (CCl_3F), and CFC-12 (CCl_2F_2) are used as propellants and refrigerants, the two latter ones for foam blowing as well. CFC-14 (CF_4) and CFC-116 (CF_3-CF_3) are released from aluminium plants, but CF_4 is likely to have natural sources as well. The bromine containing species CFC-12BI ($CBrClF_2$) and CFC-13BI ($CBrF_3$) are released from fire extinguishers. Most halocarbons have long overall atmospheric life times. Thus the abundances of those emitted from anthropogenic sources are growing with time (see table 1). The same holds for the sink products HCl and HF.

EXPERIMENTAL

Stratospheric CO_2 and halocarbon data presented here were obtained by analyses of cryogenically collected air samples. CO_2 was analysed by infrared absorption /1/, while halocarbon analyses were made by gas chromatography (GC) employing electron capture detectors (ECD) as well as mass spectrometers (MS) for detection (e.g. /2-6/). The balloon-borne cryogenic whole-air samplers flown by the Max-Planck-Institut für Aeronomie (MPAE) and the Kernforschungsanlage Jülich (KFA) are described in /7/ and /8/, respectively. The stratospheric data are limited to balloon altitudes, i.e. up to about 35 km. Tropospheric data available from analyses of air samples collected aboard aircraft are also presented.

Vertical profiles of HCl and HF were obtained by various IR spectroscopic techniques, mainly through the efforts of the international Balloon Intercomparison Campaigns (BIC) conducted during 1982 and 1983. Since these are discussed in detail in the NASA Stratospheric Ozone Assessment Report 1985 /9/, they are not presented here.

RESULTS

CO_2

Cryogenically collected air samples from 3 balloon flights carried out at 44°N during November 1979, September 1982 and September 1984 were analysed for CO_2 using IR absorption. Employing this techniques, flask samples can be analysed with a total error of ±0.2 ppmV corresponding to ±0.06%. The results are plotted in fig.1 supplemented by aircraft data obtained close to the balloon site during the same time periods /10/. A striking feature of the CO_2 profiles is the overall similarity of the stratospheric portions above 20 km. Obviously, the general increase of the tropospheric abundance of CO_2, resulting from the burning of fossil fuel, is reflected by a stratospheric increase at a corresponding rate. Mid-stratospheric mixing ratios, as averaged over the height range above 22 km, are 325.4±0.5, 329.6±0.2, and 331.6±0.3 ppmV for 1979, 1982, and 1984, respectively. Average annual increase rates thus amount to 1.2 ppmV/y between 1979 and 1984

Table 1
Average vertical distribution of halocarbons at northern midlatitudes, units: pptV (10^{-12} by volume). These profiles correspond to the times given at the bottom of each column. Overall atmospheric lifetimes, N/S ratios and trends are also given. Trend values marked by an asterisk were derived from time-dependent model computations, they are as yet not confirmed by measurements.

layer	CCl_4 (CFC-10)		CCl_3F (CFC-11)		CCl_2F_2 (CFC-12)		$CClF_3$ (CFC-13)		CF_4 (CFC-14)		$CClF-CClF_2$ (CFC-113)		$CClF_2-CClF_2$ (CFC-114)	
surface & lower troposphere	130		190		350		4		70		23		11	
10-11 km	96.5		177.7		329.3						21.93		10.36	
11-12 km	86.5		171.7		321.8						20.71		10.02	
12-13 km	80.1	±10%	171.3		314.7						20.68		9.89	
13-14 km	73.2		167.2		310.7	±5%					21.68	±20%	9.57	
14-15 km	69.3		163.7		307.4		3.9		65.2		21.95		9.31	
15-16 km	66.0		156.9	±6%	298.5						22.83		9.03	±8%
16-17 km	60.8	±17%	147.2		284.4						22.32		8.59	
17-18 km	52.4	±21%	133.5		267.4						20.99		8.17	
18-19 km	44.2	±28%	118.3		246.9		3.5		66.6		17.81		7.62	
19-20 km	34.1	±36%	98.0		218.2	±7%					15.51		6.91	
20-21 km	22.5	±46%	76.0		189.7						12.25		6.13	
21-22 km	13.6	±59%	53.9	±36%	160.3						10.01		5.53	
22-23 km	8.9	±73%	35.7	±40%	137.4	±12%	3.0	±10%	66.5		8.43	±32%	5.17	
23-24 km	4.9	±90%	20.3	±47%	113.3	±22%				±10%	7.40		4.79	
24-25 km	2.3		11.1	±50%	93.6	±25%					6.54		4.28	
25-26 km	1.2	±100%	5.8	±64%	81.5	±28%					5.49		4.39	
26-27 km	0.3		3.5	±79%	69.2		2.7		58.0		4.79		4.16	
27-28 km	0.1		1.4	±90%	55.9	±18%					3.94		3.79	
28-29 km			0.6		46.1	±50%	2.5				3.15		3.65	±18%
29-30 km			0.5	±100%	40.5						2.46		3.72	
30-31 km			0.3		29.9						1.90		3.33	
31-32 km			0.2	±50%	24.3	±30%	2.3		61.8		1.39	±65%	3.16	
32-33 km			0.2		16.9						1.03		3.04	
33-34 km					15.6						0.54		2.85	
34-35 km														
Corresponding to time	Sept/Oct. 1982-83		Sept./Oct. 1980-83		Sept./Oct. 1980-83		Sept. 1980		Sept. 1980		Sept./Oct. 1982-84		Sept./Oct. 1982-84	
overall life time	60-100y		55-93 y		105-169y		180-450y		10000y		63-122y		126-310y	
N/S ratio	1.07		1.12		1.07		~1		~1		1.12		1.05	
trend	2%/y		6%/y		5%/y		5%/y*		2%/y*		10%/y*		6%/y	

which is quite comparable with those observed at tropospheric levels. Annual means of tropospheric CO_2, for the years discussed here, were found to be in excess of 6.8±0.9 ppmV over the stratospheric mixing ratios corresponding to a time lag of 5.2±0.8 years. The transition occurs between 10 and 22 km altitude, while there is almost no height dependence of the CO_2 VMR above that height.

The tropospheric CO_2 profiles shown in fig. 1 are representative of late summer/fall conditions, when the cumulative uptake of CO_2 by plants reaches its maximum. Thus at ground level, an annual minimum is obtained in August/September. In late winter/spring, when CO_2 is returned to the atmosphere, a maximum occurs in April/May. This seasonal variation, having a total amplitude of about 7 ppmV in the northern troposphere, is almost undetectable within the lower stratosphere.

The existence of a shaped CO_2 profile as shown in fig. 1 may be relevant for satellite sounders that use the assumption of well-mixed CO_2 in the stratosphere to retrieve temperatures from infrared spectral features.

Halogenated hydrocarbons (halocarbons)

Vertical profiles of halocarbons are plotted in figures 2-12. Every data point corresponds to an air sample with sampling altitude ranges typically varying between 1-2 km at 35 km and about 0.2-0.4 km at 10 km. The plotted altitudes correspond to the centers of the sampling ranges. A careful error analysis has to take into account the following

Table 1 contd.

layer	$CClF_2$-CF_3 (CFC-115)	CF_3-CF_3 (CFC-116)	CH_3Cl (CFC-40)	$CHClF_2$ (CFC-22)	CH_3-CCl_3 (CFC-140)	$CBrClF_2$ (CFC-12B1)	$CBrF_3$ (CFC-13B1)
surface & lower troposphere	4.1	4	617	73	175	1.3	1.0
10-11 km				60.8	101.4	1.32	0.9
11-12 km				55.9	80.6	1.23	
12-13 km				56.2	76.0 ±10%	1.26	
13-14 km				53.8	69.1	1.15 ±20%	
14-15 km	3.1		424	53.0	67.1	1.08	0.68
15-16 km			372.4	52.0	69.7	0.99	
16-17 km			348.1	50.6	66.7 ±20%	0.84	±10%
17-18 km			306.3 ±20%	48.1	61.0	0.68	
18-19 km	2.3	3.7	262.6	45.8	56.5	0.56	
19-20 km	±10%		214.9	42.6 ±11%	49.8	0.40 ±26%	
20-21 km			161.5	38.6	29.7 ±30%	0.28	0.44
21-22 km			125.4 ±35%	34.9	19.5	0.15 ±50%	
22-23 km	1.7	3.47	110.4	32.0	11.4	0.06	0.17
23-24 km			100.9	29.8	6.32 ±50%	0.07	
24-25 km			83.3 ±50%	27.6	3.96		
25-26 km		±10%	75.8	27.0	2.16		
26-27 km	1.36	3.12	65.1	26.1	1.24		0.06
27-28 km			42.1	25.3	0.1 ±100%		
28-29 km	1.26	2.92	30.5	24.0			
29-30 km			29.6	24.6			
30-31 km			22.9 ±30%	23.5			
31-32 km			20.9	21.7			
32-33 km	1.0	2.53	19.8	19.7			
33-34 km							
34-35 km							
Corresponding to time	Sept. 1980	Sept. 1980	Sept./Oct. 1980-83	Sept. 1982/83	Sept./Oct. 1982/83	Sept./Oct. 1982-84	Sept. 1980
overall life time	230-550y	10 000 y	2-3 y	12-20y	5.7-10y	29-42y	62-117y
N/S ratio	≈1	≈1	1	1.18	1.36	1.43	?
trend	9%/y*	6%/y*	-	12%/y	8%/y	20%/y	5%/y*

contributions: The sampling altitude range and its errors due to the fact that measured pressures were converted into altitudes using the temperature distribution of a standard atmosphere, the statistical errors related to sampling, possible contamination and analysis leading to an overall precision of ± (5-10)%, and the errors of the absolute calibration which are ±10% or less. The lowest detection limits are about 0.02 pptV for CFC-12B1, 0.1 pptV for CFC-10, CFC-11, CFC-113, CFC-140, and CFC-13B1, and 1 pptV for CFC-12, CFC-13, CFC-14, CFC-114, CFC-115, CFC-116, CFC-40, and CFC-22.

The data points of the figures show a scatter, however, which is often considerably larger than the quoted precision of 5-10%. This certainly reflects some natural variability, but no seasonal effects as all data represent September/October conditions. The scatter is particularly large in those portions of the profiles which show a large vertical gradient of the mixing ratio suggesting that sampling height errors may be involved. CH_3Cl (fig. 9) is exceptional in revealing extremely large scatter between 20 and 30 km altitude. It is not clear whether real natural variability or sample contamination may account for this effect.

Thus, for calculating reference models for the different species, the individual errors were not analysed for every data point. Instead, the points were averaged within 1-km layers, and the standard deviations from the respective mean values were calculated. It appears that this mean standard deviation is a reasonable estimate of all statistical errors within each layer. The average profiles thus obtained and the standard deviations are plotted in the figures. They are also compiled in table 1.

For CFC-13, CFC-14, CFC-115, CFC-116, and CFC-13B1, only one measured profile was available at all (see fig. 5, 6, 12, data points compiled in table 1). Thus no averaging was possible. More data points will become available soon. At MPAE, air samples collected during balloon flights made 1983, 1984 and 1985 have already been analysed for those constituents. The absolute calibration, however, has not been finished yet. It can be concluded, however, that these new data confirm the vertical slopes of the species, shown

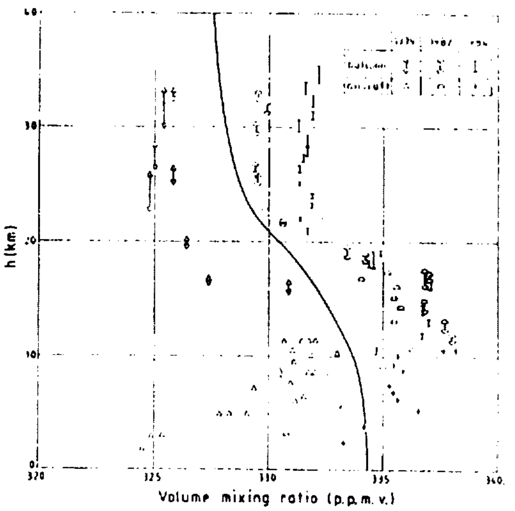

Figure 1. Vertical distribution of CO_2 between the ground and 35-km altitude as analysed by infrared absorption of whole air samples collected aboard balloon and aircraft platforms, for 1979, 1982, and 1984. The height range of the balloon samples is shown by the symbols. The modelled profile (solid line) computed by means of a one-dimensional time-dependent model corresponds to 1980 conditions /10/.

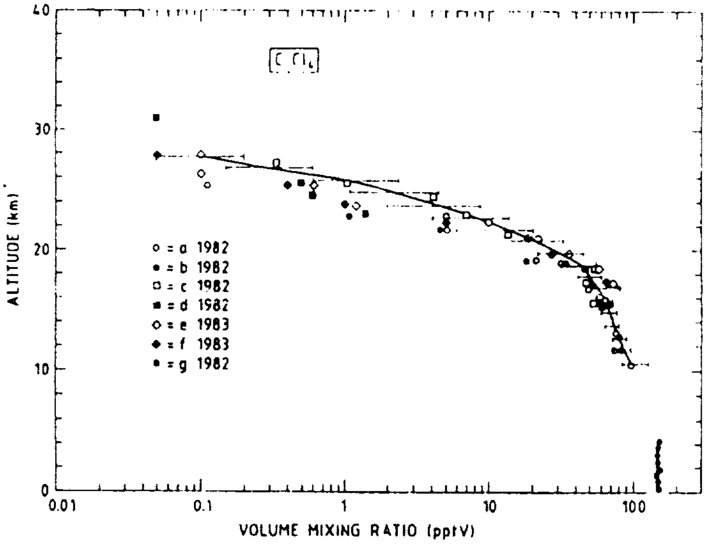

Figure 2. Vertical distribution of CCl_4 (CFC-10) at northern midlatitudes. Every data point represents one whole-air sample collected during the year listed in the figure. Each symbol represents data from a different flight or group of investigators, respectively. The average profile and its error bars were obtained by averaging all data points within 1 km layers. The points of this profile are compiled in Table 1. Sources: a,b /4/; c-f /6/; g /11/.

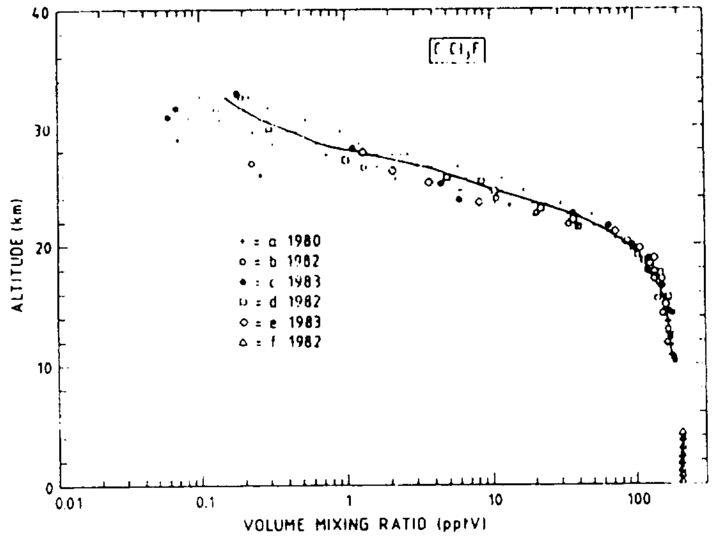

Figure 3. Same as Figure 2 but for CCl_3F (CFC-11). Sources: a /3/; b /12/; c,e /13/; d /6,8/; f /11/.

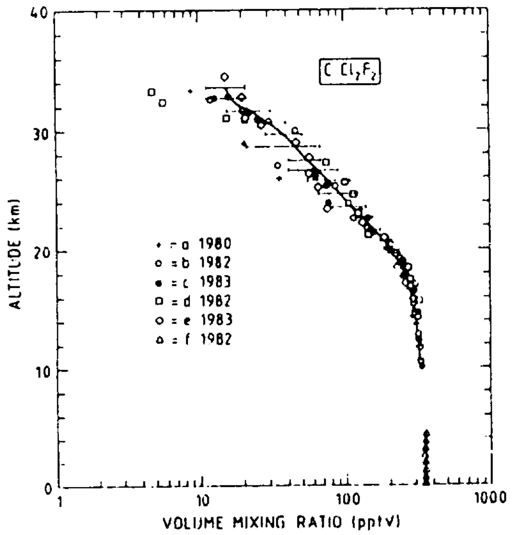

Figure 4. Same as Figure 2 but for CCl_2F_2 (CFC-12). Sources: a /3/; b /12/; c,e /13/; d /6,8/; f /11/.

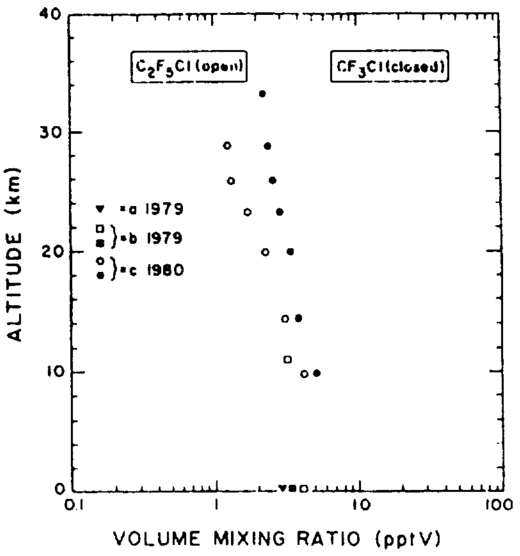

Figure 5. Vertical distribution of $CClF_3$ (CFC-13) and $CClF_2$-CF_3) (CFC-115) at northern midlatitudes. Sources: a /14/; b /15/; c /3/.

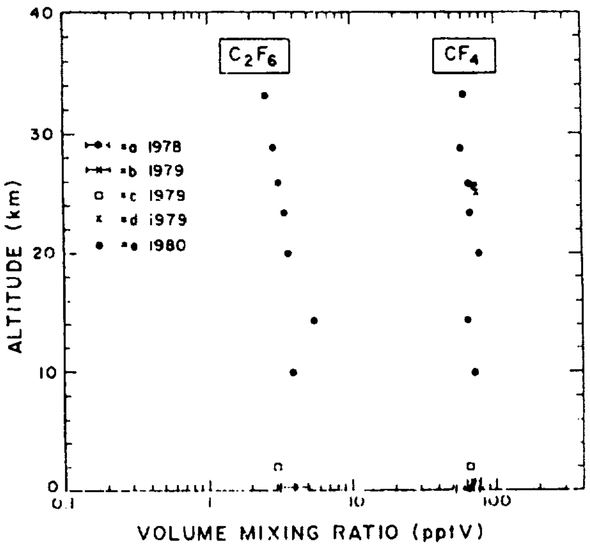

Figure 6. Vertical distribution of CF_4 (CFC-14) and CF_3-CF_3 (CFC-116) at northern midlatitudes. Sources: a/16/; b /15/; c /14/; d /17/; e /3/.

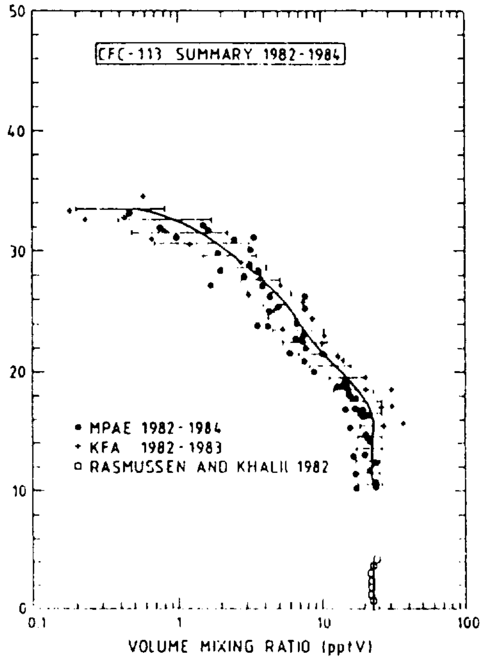

Figure 7. Same as Figure 2 but for $CCl_2F\text{-}CClF_2$ (CFC-113). Source: /18/.

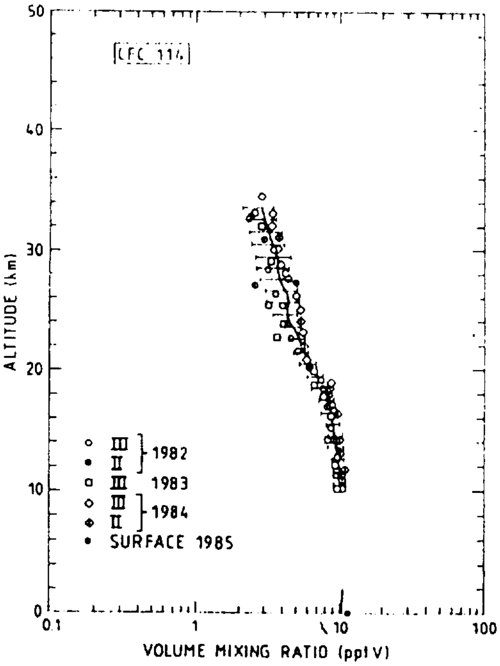

Figure 8. Same as Figure 2 but for $CClF_2\text{-}CClF_2$ (CFC-114). Source: /19/.

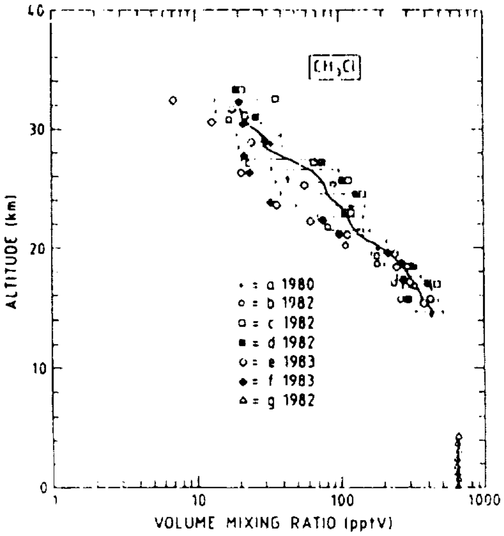

Figure 9. Same as Figure 2 but for CH_3Cl (CFC-40). Sources: a /3/; b /12/; c-f /6/; g /11/.

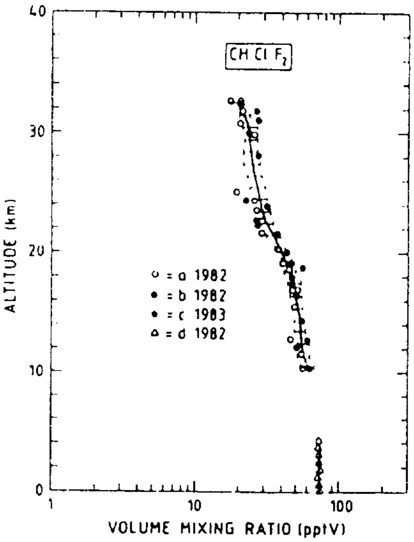

Figure 10. Same as Figure 2 but for $CHClF_2$ (CFC-22). Sources: a-c /20/; d /11/.

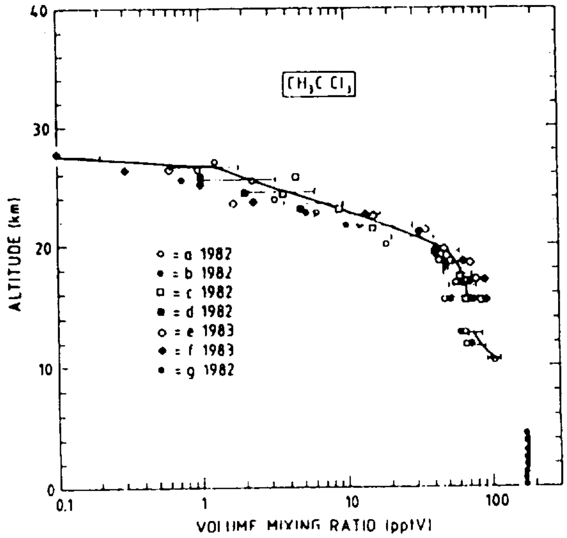

Figure 11. Same as Figure 2 but for CH_3-CCl_3 (CFC-140). Sources: a,b /4/; c-f /6/; g /11/.

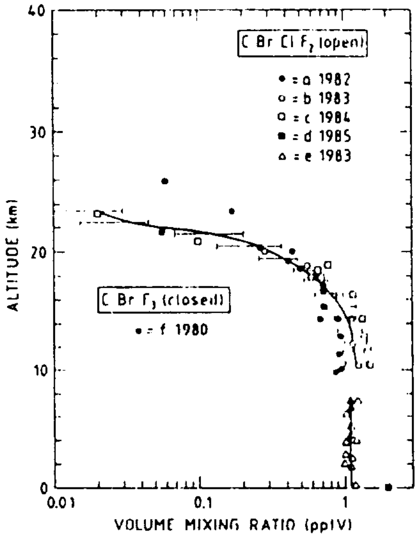

Figure 12. Same as Figure 2 but for $CBrClF_2$ (CFC-12BI). Vertical distribution of $CBrF_3$ (CFC-13BI) is also given. Sources: a-d /21/; e /11/; f /3/.

in figures 5,6, and 12.

The proposed reference models of halocarbons are compiled in table 1. Due to the errors related to the absolute calibration, every profile is accurate to within ±10% for the time period given at the bottom of the respective column. The same accuracy may be assumed for the surface and lower tropospheric mixing ratios shown in the first line of table 1. These were obtained by averaging all published field data.

Since all stratospheric measurements presented here were made during September/October, the tabulated values correspond to this time of year. On the basis of measurements made at KFA, Schmidt et al. /8/ have argued that seasonal variations do occur. These are small, however, and thus most likely included in the quoted standard deviations.

The given halocarbon profiles reflect northern midlatitude conditions. Corresponding southern midlatitude data may be obtained by applying the N/S ratios also given in table 1, which were derived from all available tropospheric halocarbons measurements. Tropical profiles of CFC-11 and CFC-12 are known to fall with height less rapidly than midlatitude profiles /22/ as upward motion partly counteracts decomposition in this region. A similar effect can be expected for other halocarbons, but except for a few first exploratory data /23/ no conclusive measurements are documented yet.

Due to continuing anthropogenic emission, atmospheric halocarbon abundances increase with time. Present annual increase rates were evaluated and also listed in table 1. These trend values base, wherever available on measured data. The trend values marked by an asterisk were derived from time-dependent model computations at MPAE based on available global emission scenarios.

ACKNOWLEDGEMENT

The source gas research program at the Max-Planck-Institut für Aeronomie has been sponsored by the Federal Ministry of Research and Technology through grants No.FKW-03 and KBF-MT-0450-0704563 2.

REFERENCES

/ 1/ Bischof, W., Tellus 29, 435 (1977)
/ 2/ Penkett, S.A., Toxicol.Environ.Chem. 3, 291 (1981)
/ 3/ Fabian, P., Borchers, R., Penkett, S.A., Prosser, N.J.D., Nature 294, 733 (1981)
/ 4/ Borchers, R., Fabian, P., Penkett, S.A., Naturwiss. 70, 514 (1983)
/ 5/ Fabian, P., Gömer, D., Fresenius Z. Anal.Chem. 319, 890 (1984)
/ 6/ Knapska, D., Schmidt, U., Jebsen, C., Kulessa, G., Rudolph, J., Penkett, S.A., Atmospheric Ozone (C.S. Zerefos, A. Ghazi, Eds.) 117, Reidel-Dordrecht (1985)
/ 7/ Fabian, P., Adv. Space Res. 1, 17 (1981)
/ 8/ Schmidt, U., Khedim, A., Knapska, D., Kulessa, G., Johnen, F.J., Adv. Space Res. 4, 131 (1984)
/ 9/ NASA, Stratospheric Ozone Assessment Report 1985, Washington, D.C. (1986)
/10/ Bischof, W., Borchers, R., Fabian, P., Krüger, B.C., Nature 316, 708 (1985)
/11/ Rasmussen, R.A., Khalil, M.A.K., Dept.of Env. Sci. Oregon Grad. Center, Beaverton, manuscript (1983)
/12/ Borchers, R., Fabian, P., unpublished data.
/13/ Schmidt, U., Kulessa, G., Klein, E., Röth, E.P., Fabian, P., Borchers, R., to appear in Plan. Space Sci. (accepted 1986)
/14/ Rasmussen, R.A., Khalil, M.A.K., in M. Nicolet, A.C. Aikin (eds.) NATO Adv. Study Inst. Atmosph. Ozone, Report FAA-EE-80-20, 209 (1984)
/15/ Penkett, S.A., Prosser, N.J.D., Rasmussen, R.A., Khalil, M.A.K., J. Geophys. Res. 86, 5172 (1981)
/16/ Rasmussen, R.A., Penkett, S.A., Prosser, N.J.D., Nature 277, 549 (1979)
/17/ Goldman, A., Murcray, D., Murcray, F., Cook, G., van Allen, J., Bonomo, F., Blatherwick R., Geophys. Res. Lett. 6, 609 (1979)
/18/ Borchers, R., Fabian, P., Krüger, B.C., Lal, S., Schmidt, U., Knapska, D., Penkett, S.A., to appear in Plan. Space Sci. (accepted 1986)
/19/ Fabian, P., Borchers, R., Krüger, B.C., Lal, S., J. Geophys. Res. 90, 13091 (1985)
/20/ Fabian, P., Borchers, R., Krüger, B.C., Lal, S., Penkett, S.A., Geophys. Res. Lett. 12, 1 (1985)
/21/ Lal, S., Borchers, R., Fabian, P., Krüger, B.C., Nature 316, 135 (1985)
/22/ Ehhalt, D.H., Proc. Ozone Symposium Boulder 1980 (J. London, Ed.) 728 (1981)
/23/ Borchers, R., Fabian, P., Lal, S., Subbaraya, B.H., Acharya, Y.B., Jayaraman, A., this issue