Measurement of CF_2Cl_2 at Memanbetsu over the Period between October 1980 and March 1983

Michio Hirota and Hisafumi Muramatsu

Meteorological Research Institute, Tsukuba, Japan

Fumio Fukui, Fujio Muromatsu, Masahiko Hashimoto,
Masayuki Kuwashima, and Toshiharu Koike

Memanbetsu Magnetic Observatory, Memanbetsu, Japan

(Received Feb. 2, 1984; Revised May 18, 1984)

Abstract

In order to obtain the atmospheric lifetime of CF_2Cl_2 (τ), the measurements of CF_2Cl_2 were performed from October 1980 to March 1983 at Memanbetsu, Hokkaido.

The trend of monthly mean volume mixing ratios of CF_2Cl_2 when the wind directions were between NW and N was considered to represent the trend of the background mixing ratios. In this case, the mean increase rate from October 1980 to March 1983 was 1_5 ppt/year ($\text{ppt}=10^{-12}$).

From the increase rate obtained in this study and the release rate reported by the Chemical Manufacturers Association (1983), τ was calculated to be 24 ($5\sim\infty$) years. Such a short lifetime seems to be due to the overestimation of the release rate in 1980 and 1981.

1. Introduction

Chlorofluorocarbons (CF_2Cl_2 and CFCl_3) are being accumulated in the atmosphere. The lifetimes of these compounds against the photodissociation in the stratosphere are considered about 110 years for CF_2Cl_2 and 70 years for CFCl_3 (NAS, 1979). The persistent effect on the stratospheric ozone is based on their long lifetimes in the atmosphere.

No important tropospheric sinks have been identified for CF_2Cl_2 and CFCl_3 , though 10~20 years lifetimes for them could not be ruled out from the early measurements (Sze and Wu, 1976). Ausloos et al. (1977) only suggested that the photodecomposition on silica surface would be a possible sink for CF_2Cl_2 and CFCl_3 .

If there are other significant sinks for

CF_2Cl_2 and CFCl_3 , the lifetimes of these compounds will become much shorter and the effect on the stratospheric ozone will be much diminished. In 1978, Cunnold et al. (1978) proposed that the existence of unknown sinks can be checked through the analysis of long-term trends of the atmospheric burdens of CF_2Cl_2 and CFCl_3 .

In order to obtain the lifetime of CF_2Cl_2 , the gas-chromatographic measurement of CF_2Cl_2 was started in October 1980 at Memanbetsu, Hokkaido.

2. Method

The rate of change of the atmospheric burden of CF_2Cl_2 in either hemisphere can be given by (1) and (2) by assuming a two-box model (Chang and Penner, 1978).

$$\frac{dC_N}{dt} = S_N - \frac{1}{\tau_N} C_N - \frac{1}{\tau_m} (C_N - C_S) \quad (1)$$

$$\frac{dC_s}{dt} = S_s - \frac{1}{\tau_s} C_s + \frac{1}{\tau_m} (C_N - C_s) \quad (2)$$

where:

C_N and C_s are the hemispheric burdens of CF_2Cl_2 at time t (N ; north, S ; south). S_N and S_s are the hemispheric release rates.

τ_N and τ_s are the hemispheric lifetimes.

τ_m is the interhemispheric mixing time (≈ 1 year).

Assuming $\tau_N = \tau_s = \tau$, and $\tau_m = 1$ year,

$$C_N + C_s = \int_0^t (S_N(t') + S_s(t')) e^{(t'-t)/\tau} dt' \quad (3)$$

$$C_N - C_s = \int_0^t (S_N(t') - S_s(t')) e^{(t'-t)(1/\tau + 2/\tau_m)} dt' \quad (4)$$

$C_N(C_s)$ can be calculated from the data of $S_N(S_s)$ since the 1930's and the τ . If actual $C_N(C_s)$ can be estimated from the observation, τ can be obtained from $C_N(C_s)$ and $S_N(S_s)$.

It is difficult to obtain the absolute value of $C_N(C_s)$ from observations of the CF_2Cl_2 mixing ratio, X , because the accuracy of $C_N(C_s)$ is strongly dependent on systematic errors in the measurement, and also because background mixing ratios are not necessarily uniform in the atmosphere, i.e., the mean tropospheric mixing ratio, for example, is a little lower than that of the surface air (Rasmussen and Khalil, 1981).

The second method uses the time trend. The relative change of mixing ratios, $1/X \cdot dX/dt$, observed at a single station is compared with that of $C_N(C_s)$, i.e., $1/C_N \cdot \frac{dC_N}{dt}$, calculated from (3) and (4). In this case, accuracy of measurement is relatively unimportant. The trend in $1/X \cdot dX/dt$ at a single station will not be much different from the trend of the hemispheric burden, $C_N(C_s)$, if the station is far away from the sources of the atmospheric CF_2Cl_2 .

Gas-chromatographic measurement of CF_2Cl_2 was started in October 1980 at Memanbetsu, which is located on the coast of Lake Abashiri close to the Sea of Okhotsk in northeastern Hokkaido. The location of Memanbetsu is shown in Fig. 1. In Hokkaido, background mixing ratios had been frequently observed by Makide et al. (1981).

Fig. 1 Location of Memanbetsu

↑ : Memanbetsu. 1: Abashiri. 2: Kitami.

3. Experimental

An air sampler (Tokyo Electron) and a Perkin-Elmer Gas Chromatograph Sigma 1-Sigma 10 system were set up at the Memanbetsu Magnetic Observatory, which is situated in the eastern suburbs of Memanbetsu.

Air 2.5 m above the ground surface was sampled through a copper tube (1/8" o.d.) by means of an air pump into a 2ml gas sampling tube, and was then transferred into a stainless steel column (6ft x 1/8" o.d.) filled with Porasil B (80~100 mesh). An electron capture detector (ECD, ^{63}Ni 15 mCi) was used at 300°C. A 95% Ar-5% CH_4 mixture was used as the carrier gas at a flow rate of 25 ml/min. The reference air, which was filled into a 50-l stainless steel container up to the pressure of 7 kg/cm² by an oil-free compressor and which could be used for 40~50 days, was first analyzed. Then, after an hour, the outdoor air was sampled and analyzed. This pair of measurements was repeated every 6hrs. The mixing ratio of CF_2Cl_2 in the reference air was determined at the Meteorological Research Institute by a previously reported method (Hirota et al.,

Fig. 2 Wind roses at Memanbetsu in 1981

(A): Jan.-Mar. (B): Apr.-Jun.

(C): Jul.-Sep. (D): Oct.-Dec.

1982).

The variation coefficient in the repeated measurements of the reference air was about 4%, and the detection limit was about 2₅ ppt ($=10^{-12}$). The total precision in the measurements was estimated to be about $\pm 7\%$.

The measurements were often interrupted by troubles in the controlling system. From May to September 1982, measurements were stopped owing to trouble in the timer which controlled the gas sampler.

When the outdoor air was sampled, wind direction and wind velocity were also mea-

sured.

4. Results and Discussion

Wind roses for every three months of 1981 are shown in Fig. 2. Through the year, winds from SSE and S were predominant, and winds between NW and N were also predominant from January to March. Nearly the same trends were observed in other years. Therefore, the effect of polluted air from Abashiri City or Kitami City was considered to be small (see Fig. 1). Frequency histograms for volume mixing ratios for every three

Fig. 3 Frequency histograms for volume mixing ratios of CF_2Cl_2 at Memanbetsu between Oct. 1980 and Mar. 1983.

Fig. 4 Monthly mean volume mixing ratios of CF_2Cl_2 at Memanbetsu. $\pm$: mean and SD. $\bullet$: mean when the wind directions were SSE and S. $\circ$ and ---: mean when the wind directions were between NW and N, and their linear trend calculated by the method of least squares.

Table 1. Monthly mean volume mixing ratios of atmospheric CF_2Cl_2 at Memanbetsu (ppt)

month	Case 1 ¹⁾			Case 2 ²⁾		Case 3 ³⁾	
	n	m	SD	n	m	n	m
Oct.+Nov. 1980	84	31 ₈	1 ₉	23	32 ₃	10	31 ₀
Dec. 1980	165	32 ₇	3 ₄	33	32 ₇	39	31 ₄
Jan. 1981	150	32 ₂	1 ₆	40	32 ₃	39	31 ₅
Feb. "	132	32 ₁	1 ₈	25	32 ₅	24	31 ₄
Mar. "	170	32 ₆	1 ₉	34	32 ₆	55	32 ₅
Apr. "	172	33 ₈	1 ₈	45	33 ₉	40	33 ₀
May. "	92	33 ₂	1 ₉	44	33 ₂	18	33 ₄
Jun. "	42	33 ₃	1 ₄	26	33 ₄	4	33 ₇
Jul. "	79	32 ₈	1 ₇	36	33 ₁	10	31 ₇
Aug. "	40	31 ₅	1 ₈	9	32 ₆	10	30 ₈
Sep. "	118	31 ₉	1 ₇	49	32 ₃	10	31 ₂
Oct. "	104	32 ₄	1 ₉	40	33 ₀	19	31 ₄
Nov. "	66	32 ₉	1 ₇	21	33 ₅	17	32 ₄
Dec. "	112	34 ₁	2 ₀	41	34 ₁	18	33 ₇
Jan. 1982	122	33 ₅	1 ₈	32	33 ₂	23	32 ₈
Feb. "	109	33 ₄	1 ₆	18	33 ₉	12	33 ₃
Mar. "	47	33 ₆	1 ₅	8	34 ₄	11	32 ₆
Apr. "	34	32 ₉	1 ₅	12	32 ₁	9	33 ₂
Oct. 1982	33	34 ₆	2 ₁	7	34 ₅	5	34 ₈
Nov. "	67	32 ₇	2 ₂	16	32 ₉	21	32 ₅
Dec. "	71	34 ₅	2 ₆	25	34 ₂	8	34 ₆
Jan. 1983	113	35 ₃	1 ₆	32	35 ₁	14	34 ₇
Feb. "	29	35 ₅	2 ₁	4	35 ₆	5	35 ₆
Mar. "	4	35 ₈	1 ₈	1	36 ₃	3	35 ₆

1) all samples

2) samples when the wind direction was SSE or S

3) samples when the wind direction was NW, NNW or N

n: number of samples. m: mean.

SD: standard deviation

months are shown in Fig. 3. The patterns of these histograms are roughly symmetrical, and this also indicates that the effect of local air pollution is small. If the effect of local air pollution is rather large, the envelope is very extended toward the side of higher mixing ratios (Penkett et al., 1979). When high mixing ratios of CF_2Cl_2 were observed, those of other halocarbons were mostly high. The measurement results of other halocarbons will be given elsewhere.

The lowest mixing ratios were often

Table 2. Calculated annual increase rates of the northern hemispheric CF_2Cl_2

	Case 1	Case 2	Case 3
Wind direction	all	SSE, S	NW, NNW, N
Annual increase rate (ppt/year)	9.8	8.8	14.7
Mean mixing ratio on Jan. 1981 (ppt)	325.1	326.6	317.7

observed when the wind directions were between NW and N, especially when the winds from the Sea of Okhotsk were lasting, i.e., the winter monsoon was prevailing. Therefore, we considered that the trend of monthly mean mixing ratios when the wind directions were between NW and N represented the trend of background mixing ratios.

Monthly mean mixing ratios and their standard deviations (SD) are shown in Table 1 (Case 1) and Fig. 4. Mean values range from 31₅ ppt to 35₅ ppt, and the SDs are about 2₀ ppt, which is roughly equal to the precision of the measurement. Monthly mean mixing ratios when the wind directions were SSE and S (Case 2) and between NW and N (Case 3) are also shown in Table 1 and Fig. 4. From monthly mean mixing ratios, increase rates for three cases were calculated by the method of least squares. In these calculations, $n/\Sigma n$ were used as weighting factors. The results are shown in Table 2. The increase rate in Case 3 was 4.6 %/year in January 1981. The variance of the residuals of the monthly mean values to the linear trend was 9 ppt in Case 3. Including this value, the increase rate in Case 3 ranged from 2.2 %/year to 7.1 %/year in January 1981.

Tominaga and Makide (1983) reported that the increase rate of the background mixing ratios of CF_2Cl_2 in Hokkaido was about 15 ppt/year for the last few years, which was in agreement with our value in Case 3. This also shows that the trend in Case 3 is considered to be the trend of the background mixing ratios.

The lifetime of CF_2Cl_2 was estimated using the increase rate for Case 3 and the atmospheric release rate of CF_2Cl_2 since

Fig. 5 Atmospheric release rate of CF_2Cl_2 (CMA, 1983). The annual release rate has a maximum in 1974. After July 1971, its fraction in the southern hemisphere was assumed to be 7% for the total release rate.

1931 (Fig. 5, Chemical Manufacturers Association (CMA), 1983, which is the same data as used by Cunnold et al., 1983). The northern hemispheric burdens of CF_2Cl_2 were calculated for various lifetime values. The increase rate of 4.6 (2.2~7.1) %/year for the northern hemispheric burden of CF_2Cl_2 in 1980 corresponded to the lifetime of 24 (5~ ∞) years. Considering the rather large experimental errors, this value was not necessarily unreasonable. However, this value (24 years) was too small to explain the high increase rate (> 6%) up to 1979 (Cunnold et al., 1983). Cunnold et al. (1983) reported a lifetime of 769 years (lower limit of 81 years) using the Atmospheric Lifetime Experiment (ALE) data from July 1978 to June 1981. However, a lifetime of 13 years could be calculated from the data of the third year (Table 6 in Cunnold et al., 1983). They concluded that the trend analysis of the ALE data gave results that were reasonably consistent with the release data of CMA (1983), and suggested that the release rates in 1980 and 1981 would be overestimated by CMA (1983). Thus, a short lifetime of 24 years obtained in this study would be due to the overestimated release rates after 1980 rather than the underestimated release rates before 1979. If the lifetime is 81 years, the increase rate of 4.6%/year in January 1981 corresponds to the 7~8% reduction of the release rate in 1981.

In the model calculation, the trend was not so sensitive to the interhemispheric mixing time (τ_m). When τ_m was changed from 1 year to 2 years with fixed lifetimes ($\tau=5, 24$ and 1000 years), the increase rates on 1980 was changed by only 0.1%, i.e., for example, 4.5 %/year instead of 4.6 %/year for the lifetime of 24 years. The ratio between two hemispheric burdens was sensitive to τ_m .

5. Conclusion

In order to obtain the atmospheric lifetime of CF_2Cl_2 (τ), trend analysis was applied to the gas-chromatographic measurements of CF_2Cl_2 , which were performed from October 1980 to March 1983 at Memanbetsu, Hokkaido.

The trend of monthly mean volume mixing ratios of CF_2Cl_2 , when the wind directions were between NW and N, was considered to represent the trend of the background mixing ratios. In this case, the mean increase rate from October 1980 to March 1983 was 1.5 ppt/year, which corresponded to the increase rate of 4.6 %/year in January 1981.

From the increase rate obtained in this study and the atmospheric release rate reported by CMA (1983), τ was calculated to be 24 (5~ ∞) years. Such a short lifetime seems to be due to the overestimation of the release rate in 1980 and 1981 in comparison with the ALE data (Cunnold et al., 1983).

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北海道・女満別における大気中 CF_2Cl_2 の測定

——1980年10月～1983年3月——

広田道夫・村松久史・福井史雄*

室松富二男*・橋本雅彦*・桑島正幸*・小池捷春*

CF_2Cl_2 の大気中での寿命を求めるために、 CF_2Cl_2 の測定を北海道・女満別において1980年10月から1983年3月まで行った。

風向がNWからNの場合の月平均体積混合比がバックグラウンドの変化傾向を表していると考えられたが、この場合の年平均増加率は 1.5 ppt/年 ($\text{ppt} = 10^{-12}$) であった。

ここで得られた年増加率と大気放出率のデータ (CMA, 1983) から大気中での寿命は24年 (5年 $\sim\infty$) と計算された。この値は従来推定されてきた値に比較して短かいが、これは1980年、1981年の放出量が多目に見積られているためであると考えられる。

*地磁気観測所女満別出張所