The Vertical Distributions of Atmospheric CF_2Cl_2 , CFCl_3 and N_2O over Japan

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Abstract

Tropospheric and stratospheric air samples were collected over Japan since 1978, and analyzed for CF_2Cl_2 , CFCl_3 and N_2O by a GC-ECD method.

Mean volume mixing ratios in the troposphere were 28₂ ppt for CF_2Cl_2 , 16₂ ppt for CFCl_3 , and 31₀ ppb for N_2O during October 1978 to March 1979. It was also found that the mean mixing ratios of CF_2Cl_2 and CFCl_3 increased by about 20% from 1979 to 1983.

The volume mixing ratios of CF_2Cl_2 , CFCl_3 and N_2O in the lower stratosphere decreased with increasing altitude in accordance with the vertical profiles calculated from a photochemical theory.

1. Introduction

The stratospheric ozone is produced by the photochemical reactions and destroyed by reactions with such minor constituents as O, NO, NO₂, OH, HO₂, Cl and ClO. If such species are released in large quantities by man's activities, natural balance of the ozone will be damaged (Johnston, 1971; Crutzen, 1970, 1971). The depletion of the stratospheric ozone will increase the biologically harmful UV radiation on the earth's surface, and will probably lead to the climate change (NAS, 1979a, b).

Halogenated hydrocarbons (CF_2Cl_2 , CFCl_3 , CH_3CCl_3 , CH_3Cl , etc.) and N_2O are considered as the major sources of the stratospheric ClO_x and NO_x respectively (Crutzen, 1970, 1971; Molina and Rowland, 1974). It is known that CF_2Cl_2 and CFCl_3 released by human activities are being accumulated in the troposphere (Love-lock, 1971; Su and Goldberg, 1973; Molina and Rowland, 1974). In order to assess the influence of these compounds on the natural ozone balance, concentrations and distributions of these compounds must be monitored.

In this paper, vertical distributions of CF_2Cl_2 , CFCl_3 and N_2O from 1978 to 1983 over Japan will be reported. Measurements of these compounds were performed using gas-chromato-

graphic methods.

2. Experimental

Details of our air sampling and gas-chromatographic measurement are described elsewhere (Muramatsu *et al.*, 1982a; Hirota *et al.*, 1982). Only a brief description will be presented here.

2.1 Sampling of air

Tropospheric air samples were collected on an aircraft by means of air-pumps into stainless steel cylinders (0.3, 0.5 and 1.0 l, Whitey) up to the pressure of 3.5~4.0 kg cm⁻². Flights were performed two times in Feb. and Mar. 1978, eight times between Oct. 1978 and Mar. 1979, ten times between Oct. 1979 and Feb. 1980, twelve times between Dec. 1980 and Mar. 1981, four times in Feb. 1982, and eight times between Oct. 1982 and Feb. 1983 from Chofu, Sendai, Haneda, and Yao Airports. In many cases, air was sampled far away from urban areas and at every kilometer of altitude.

Stratospheric air samples were obtained using balloon-borne stainless steel spheres (5 l). The valve (SS-4BKT, Nupro) of an evacuated sphere was operated using a baroswitch and two cutting heaters. Launching of the sampling system was made from the Aerological Observatory, and only in summer season in order to return the sampling sphere on land.

Table 1 Gas-chromatographic conditions.

Species	CF ₂ Cl ₂	N ₂ O	CFCl ₃
Column	glass column 3m x 3mm i.d.		
packing	molecular sieve 5A(30–60 mesh)		20% silicon oil DC-200 chromosorb WAW(60–80 mesh)
temp.	90°C	245°C	60°C
Carrier gas	ultra pure N ₂ (99.9995%) passed through a drier tube filled with molecular sieve 5A(1/16" pellets)		
flow rate	40 ml/min		
Detector	ECD ⁶³ Ni 10 mci		
pulse	width; 8 μ s, height: 40 V, freq.; 2.5 kHz		
temp.	320°C		
Sample size	2 ml		1 ml

Table 2 Errors in the gas-chromatographic analysis for the tropo-spheric air samples.

species	CF ₂ Cl ₂	CFCl ₃	N ₂ O
detection limit	15 ppt	4 ppt	10 ppb
mixing ratio in ref. gas	434 ppt	414 ppt	1000 ppb
error in repeated measure- ments of a ref. gas	1.9 %	0.6 %	0.9 %
error in measurements of several ref. gases	2.3 %	3.2 %	1.8 %
error in repeated measure- ments for samples	± 1.0 %	± 0.9 %	± 2.0 %

2.2 Gas-chromatographic analysis

CF₂Cl₂, CFCl₃ and N₂O in the sample air were analyzed using a Shimadzu Gas Chromatograph GC-6AM equipped with an electron capture detector (ECD). The sample air in the cylinder was transferred to a gas sampler (MGS-4, Shimadzu) and then to the gas chromatograph. Gas-chromatographic conditions are summarized in Table 1. The sample air in the 5 l sphere was concentrated in the gas sampler with a liquid nitrogen bath, and then warmed to the room temperature and transferred to the gas chromatograph.

2.3 Reference gas

The mixed gas of 20 ppm (in volume) CF₂Cl₂ and 20 ppm CFCl₃ in nitrogen gas (Nihon Sanso) was used as a primary reference gas. In order

to make a reference gas for practical use, 200 μ l of this gas was diluted with 10 l ultra pure nitrogen gas, which was passed through a U-shaped glass tube filled with active carbon (0°C), into a tedlar bag just before the analysis. The reference gas of 1.0 ppm N₂O was made by diluting 15 μ l of pure N₂O (>98%, Showa Denko) with 15 l of the air, which was passed through four U-shaped glass tubes filled with silica gel, drierite, ascarite and molecular sieve 5A (1/16" pellets, 0°C). Errors in the measurements of the tropospheric air are summarized in Table 2. Errors in the measurements of the stratospheric air was estimated to be about $\pm 15\%$. In 1982, the purity of N₂O was checked by a "standard gas" (99.5%, Gasukuro Kogyo), and those values previously reported were corrected (Tables 4 and 5).

3. Results and discussion

3.1 Distributions in the troposphere

Typical vertical distributions of CF_2Cl_2 and CFCl_3 are shown in Fig. 1. The higher mixing ratios by arrows were observed over the urban area up to the altitude of 2 km. Excluding these values, CF_2Cl_2 and CFCl_3 were well mixed in the troposphere as reported by Cronn *et al.* (1977), Sandalls and Hatton (1977), Seiler *et al.* (1978), and Fabian *et al.* (1979, 1981). The mean tropospheric mixing ratios of CF_2Cl_2 and CFCl_3 for

each observation period were calculated excluding those values up to the altitude of 2 km, and summarized in Table 3. The mean mixing ratios given in Table 3 are considered as the mean tropospheric mixing ratios over Japan. As for CF_2Cl_2 between Dec. 1980 and Mar. 1981, many samples were collected in Mar. 1981, and contained the air which had just come down from the stratosphere to the troposphere. Therefore, the value between Dec. 1980 and Mar. 1981 in Table 3 will be rather low for a typical mean tropospheric mixing ratio. CFCl_3 was not ana-

Fig. 1 Typical vertical distributions of CF_2Cl_2 , CFCl_3 and N_2O in the troposphere. Air samples were collected on Aerocommander 685.
 Δ ; CFCl_3 (ppt), $\circ$; CF_2Cl_2 (ppt), $\times$; N_2O (ppb).

Table 3 Mean tropospheric mixing ratios of CF_2Cl_2 and CFCl_3 .

sampling period	max. altitude (km)	number of samples		mean volume mixing ratio (ppt) ²⁾		standard deviation (ppt)	
		CF_2Cl_2	CFCl_3	CF_2Cl_2	CFCl_3	CF_2Cl_2	CFCl_3
Oct. 1978–Mar. 1979	7.4	51 ¹⁾	53 ¹⁾	28 ₂	16 ₂	2 ₁	1 ₉
Dec. 1979–Feb. 1980	7.6	13	11	29 ₉	17 ₉	2 ₆	7
Dec. 1980–Mar. 1981	9.3	62	12	(29 ₄)	18 ₄	1 ₀	1 ₃
Feb. 1982	8.1	17	21	(30 ₆)	18 ₈	5	5
Oct. 1982–Feb. 1983	8.2	19	16	33 ₅	19 ₄	7	7

1) 4 samples which were collected on Mar. 1978 were included.
2) Samples which were collected up to the altitude of 2 km were excluded.

lyzed for samples collected in Mar. 1981. The mean mixing ratio of CF_2Cl_2 obtained in Feb. 1982 was also rather low. The reason is not clear. It may be noted that a column of the gas chromatograph was replaced with new one before analysis.

During 4 years, the tropospheric CF_2Cl_2 increased about 5₃ ppt (19%), and CFCl_3 about 3₂ ppt (20%). In Japan, Tazawa *et al.* (1967) reported that the background mixing ratio of CF_2Cl_2 in Nagoya was about 0.15 ppb in 1967. However, this value is too high. Judging from the values in 1973 and 1974 reported by Lovelock (1974) and Heidt *et al.* (1975), the mean tropospheric mixing ratio of CF_2Cl_2 would be less than 100 ppt in 1967. The tropospheric

CF_2Cl_2 , therefore, was considered to increase about triply in the 15 years. In comparison with the data of Rasmussen *et al.* (1981), the increasing rates of CF_2Cl_2 and CFCl_3 from 1979 to 1983 was lower than those from 1976 to 1980. This will be due to the pause of the increasing CF_2Cl_2 and CFCl_3 releases to the atmosphere since about 1975.

Typical vertical distribution of N_2O is also shown in Fig. 1. No vertical gradient of the mixing ratio at lower altitudes was observed for N_2O as reported by Pierotti and Rasmussen (1977), Goldan *et al.* (1978), Seiler *et al.* (1978), Roy (1979), and Fabian *et al.* (1979, 1981). This would be due to the more uniform distribution and weaker strength of the sources of N_2O than

Table 4 Mean tropospheric mixing ratios of N_2O .

sampling period	max. altitude (km)	number of samples	mean volume mixing ratio (ppb)	standard deviation (ppb)
Fed. Mar. and Oct. 1978	7.0	8	31 ₈ ¹⁾	1 ₉
Oct. 1978–Mar. 1979	7.4	90	31 ₀	1 ₄
Oct. 1979–Feb. 1980	13.6	88	32 ₅ ²⁾	1 ₃
Dec. 1980–Mar. 1981	9.3	45	32 ₁ ²⁾	1 ₂
Feb. 1982	7.2	35	32 ₅	9
Dec. 1982–Feb. 1983	8.2	30	31 ₈	7

1) measured by a concentration method.

2) corrected value (see text).

Table 5 Mixing ratios of N_2O in surface air.

sampling period	sampling point	number of samples	mean volume mixing ratio (ppb)	standard deviation (ppb)
Mar.–Jun. 1979	Koenji(Tokyo) ¹⁾	16	32 ₇	9
Jul.–Sep. 1980	Yatabe ²⁾	60	31 ₉ ^{3,4)}	8
Jan. 1981 (6 days)	Hachijojima	6	31 ₉	4
Jan. 1981 (7 days)	Chichijima	7	31 ₄	5
Dec. 1981 (7 days)	Hachijojima	7	31 ₅	6
Dec. 1981 (7 days)	Chichijima	7	31 ₈	5
Dec. 1982 (3 days)	Kawasaki–Miyazaki ⁵⁾	6	31 ₃	6

1) MRI before removal.

2) MRI

3) Porapak Q and QS were used as column packing.

4) corrected value (see text).

5) Air was sampled on the upper deck of Mimitsu-maru, Nippon Car Ferry.

those of CF_2Cl_2 and CFCl_3 . Mean mixing ratios of N_2O for each observation period are summarized in Table 4. In addition to these results, atmospheric N_2O was also measured on the ground (Table 5). All these results showed that the tropospheric N_2O was almost constant from 1979 to 1983 over Japan in the range of the experimental uncertainties. Small increasing rates less than 2 ppb/year, however, were reported by Goldan *et al.* (1980), Weiss (1981), and Khalil and Rasmussen (1983) around the same period.

Mean mixing ratios of N_2O in Table 4 are higher than those reported by Weiss (1981), Goldan *et al.* (1981), and Khalil and Rasmussen (1983), *i.e.*, about 300 ppb and lower than those reported by Roy (1979) and Fabian *et al.* (1979, 1981), *i.e.*, about 330~340 ppb. In order to obtain more reliable data, some improvements in the calibration process of the reference gas are now in progress.

3.2 Distributions in the stratosphere

Vertical distributions of CF_2Cl_2 , CFCl_3 and N_2O in the stratosphere are shown in Figs. 2~4. Though from 4 to 9 samples were collected in every year since 1978, several high values, which were probably due to the contamination in the

GC measurements, were excluded. In 1978, air samples were collected in plastic bags of 250 l, and N_2O was measured by a concentration

Fig. 3 Vertical distribution of CFCl_3 in the stratosphere. Legends are the same as in Fig. 2.

Fig. 2 Vertical distribution of CF_2Cl_2 in the stratosphere. In 1978, air samples were collected in plastic bags of 250 l. —; vertical profile calculated from a 1-D model (36°N , summer solstice), ; range of the tropospheric mixing ratios.

Fig. 4 Vertical distribution of N_2O in the stratosphere. Legends are the same as in Fig. 2. ; Ram air was sampled on DC-9, TDA over Osaka on Jan. 8, 1979.

Fig. 5 Relation between volume mixing ratios of O₃ and CF₂Cl₂. O₃ was measured by Dasibi Model 1008 PC ozone meter. O₃ rich and CF₂Cl₂ poor air (right hand side) was observed around the altitudes of 6~8 km.

method (Hirota, 1978). In 1981, samples at altitudes of 18 km and 15 km were recovered after a half year and one year from launching respectively.

As expected from the photochemical decomposition by the solar UV radiation, mixing ratios of these compounds decreased with increasing altitude. This is illustrated in Figs. 2~4 by solid lines, which were calculated from a one-dimensional photochemical diffusive model in summer condition (Muramatsu *et al.*, 1982b). The measured values are consistent with the model calculation, though the measurements are sparse and data points are rather scattered. At least, our values were within the range of many values measured over mid-latitude of the northern hemisphere (Pierotti and Rasmussen, 1977; Ehhalt, 1978; Fabian *et al.*, 1979, 1981; Goldan *et al.*, 1980; Vedder *et al.*, 1981; Gallagher *et al.*, 1983). Annual increases in the stratospheric mixing ratios of these compounds could not be observed due to the experimental uncertainties.

Since mixing ratios of these compounds in the stratosphere is lower than in the troposphere, these can be used as tracers for the mass transfer process between the stratosphere and troposphere. Measurement results of O₃ and CF₂Cl₂ on Mar. 10, 1981 are shown in Fig. 5. O₃ rich and CF₂Cl₂ poor air (right hand side in Fig. 5) was observed around the altitude of 6~8 km. This indicates that the intrusion of the stratospheric air into the troposphere occurred. Detailed analysis for the intrusion process will be given elsewhere (Muramatsu *et al.*, 1983).

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日本上空における CF_2Cl_2 , CFCl_3 および N_2O の鉛直分布

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日本上空における対流圏および成層圏空気試料の採集を1978年から開始し、 CF_2Cl_2 , CFCl_3 および N_2O の分析を GC-ECD 法によって行った。

1978年10月から翌年3月にかけて、対流圏の平均体積混合比は CF_2Cl_2 が 28₂ ppt, CFCl_3 が 16₂ ppt, N_2O が 31₀ ppb であった。また CF_2Cl_2 と CFCl_3 の1979年から1983年までの増加率は共に約20%であった。

下部成層圏における CF_2Cl_2 , CFCl_3 および N_2O の体積混合比は高度が増すとともに減少しており、その傾向は光化学理論から計算された高度分布にほぼ一致した。