

GAS-CHROMATOGRAPHIC MEASUREMENTS OF ATMOSPHERIC
CF₂Cl₂, CFCl₃ AND N₂O FROM TOKYO TO SYOWA STATION LATE
IN 1983, AND AT SYOWA STATION BETWEEN FEBRUARY
1982 AND JANUARY 1984

Michio HIROTA, Yukio MAKINO, Masataka SHIOBARA,
Shigeru CHUBACHI and Hisafumi MURAMATSU

Meteorological Research Institute, 1-1, Nagamine, Yatabe-machi, Tsukuba-gun, Ibaraki 305

Abstract: Atmospheric CF₂Cl₂, CFCl₃ and N₂O were measured by a gas-chromatographic method in order to assess the influence of these gases on the stratospheric ozone. Air samples were successively obtained by the 24th and 25th Japanese Antarctic Research Expeditions.

From Tokyo to Syowa Station, volume mixing ratios of CF₂Cl₂ and CFCl₃ decreased toward the equator and were almost constant in the southern hemisphere. This is because most of CF₂Cl₂ and CFCl₃ have been released in the northern hemisphere. Volume mixing ratios of CF₂Cl₂ and CFCl₃ at Syowa Station as of January 1983 were lower by 6% than mean volume mixing ratios of them over Japan from October 1982 to February 1983. As for N₂O, no gradient in mixing ratio from Tokyo to Syowa Station was found. The mean value of total 19 samples was 302 ppb (=10⁻⁹ v/v).

Over the period between February 1982 to January 1984, CF₂Cl₂ and CFCl₃ showed a steady increase at Syowa Station, and their annual increases were 19.2 ppt (=10⁻¹² v/v)/year for CF₂Cl₂ and 10.2 ppt/year for CFCl₃. In the same period, N₂O was almost constant.

1. Introduction

Atmospheric chlorofluoromethanes (CF₂Cl₂ and CFCl₃) and dinitrogen oxide (N₂O) are major sources of the stratospheric ClO_x and NO_x. CF₂Cl₂ and CFCl₃ are released only by human activities, and they are being accumulated in the atmosphere. These gases (CF₂Cl₂, CFCl₃ and N₂O) are very stable in the troposphere. But in the stratosphere, they are decomposed by solar ultraviolet radiation and excited oxygen atom (O(¹D)), and then ClO_x and NO_x are produced (NATIONAL RESEARCH COUNCIL, 1982; WMO, 1981).

In order to assess the influence of these gases on the stratospheric ozone, we have measured these gases over Japan since 1978 (HIROTA *et al.*, 1984a). Measurements of the antarctic air samples or the southern hemispheric air samples are also indispensable to understanding the global distributions of these gases, because most of CF₂Cl₂ and CFCl₃ have been released in the northern hemisphere.

Antarctic air samples were obtained by the 23rd, 24th and 25th Japanese Antarctic Research Expeditions (JARE-23, -24 and -25), and analyzed by a gas-chromatographic method using an electron capture detector. Preliminary results were already

reported in the previous paper (HIROTA *et al.*, 1984b), and subsequent results will be reported here.

2. Experimental

Details of our air sampling and gas-chromatographic measurement are described in the previous paper. Only some changes will be given here.

In JARE-25, air samples from Tokyo to Syowa Station were collected on the bridge of an icebreaker SHIRASE. From February 1983 to January 1984 (JARE-24), air samples at Syowa Station were collected at 4 m above the ground surface on the northeast side of a hut of the Upper Atmosphere Physics Laboratory, when the wind directions were between NNE and E. One sample on April 11, 1983 was collected at Tottuki Point, and two samples on October 2, 1983 were collected at Lake Nurume in Langhovde. The locations are 15 km northeast and 25 km south from Syowa Station, respectively.

In the gas-chromatographic analysis, peak areas were used to calculate volume mixing ratios.

A primary reference gas for CF_2Cl_2 and CFCl_3 was changed to a new one (Seitetsu Kagaku). The accuracy of this gas was less than $\pm 5\%$. The preparation method of a reference gas for N_2O was changed. A mixed gas of 970 ppm ($=10^{-6}$ v/v) N_2O in air (Takachiho) was used as a primary reference gas for N_2O . In order to make a reference gas for practical use, this gas was diluted to 0.3 ppm with nitrogen gas (99.9995%) using a Standard Gas Generator SGGU-72AC3 (Standard Technology). Uncertainties in the measurements are summarized in Table 1. Precisions of measurements of these gases were all about 4~5% (=sum of the values in the last two lines in Table 1). Concentrations are all shown by volume mixing ratios where ppb= 10^{-9} and ppt= 10^{-12} .

Table 1. Uncertainties in the gas-chromatographic measurement.

Species	CF_2Cl_2	CFCl_3	N_2O
Detection limit	15 ppt	4 ppt	10 ppb
Mixing ratio in reference gas	434 ppt	414 ppt	303 ppb
Error in repeated measurements of a reference gas	1.9%	0.6%	2.1%
Error in measurements of several reference gases	2.3%	3.2%	2.9%
Error in repeated measurements for samples	$\pm 1.0\%$	$\pm 0.9\%$	$\pm 2.0\%$

3. Results and Discussion

3.1. Latitudinal variation

Samples were collected late in 1983 from Tokyo to Syowa Station (69.0°S, 39.6°E) at intervals of about 5°. Latitudinal variation of CF_2Cl_2 is shown in Fig. 1, and those of CFCl_3 and N_2O are shown in Fig. 2. Vertical bars in Figs. 1 and 2 indicate the standard deviations for measurements of each reference gas.

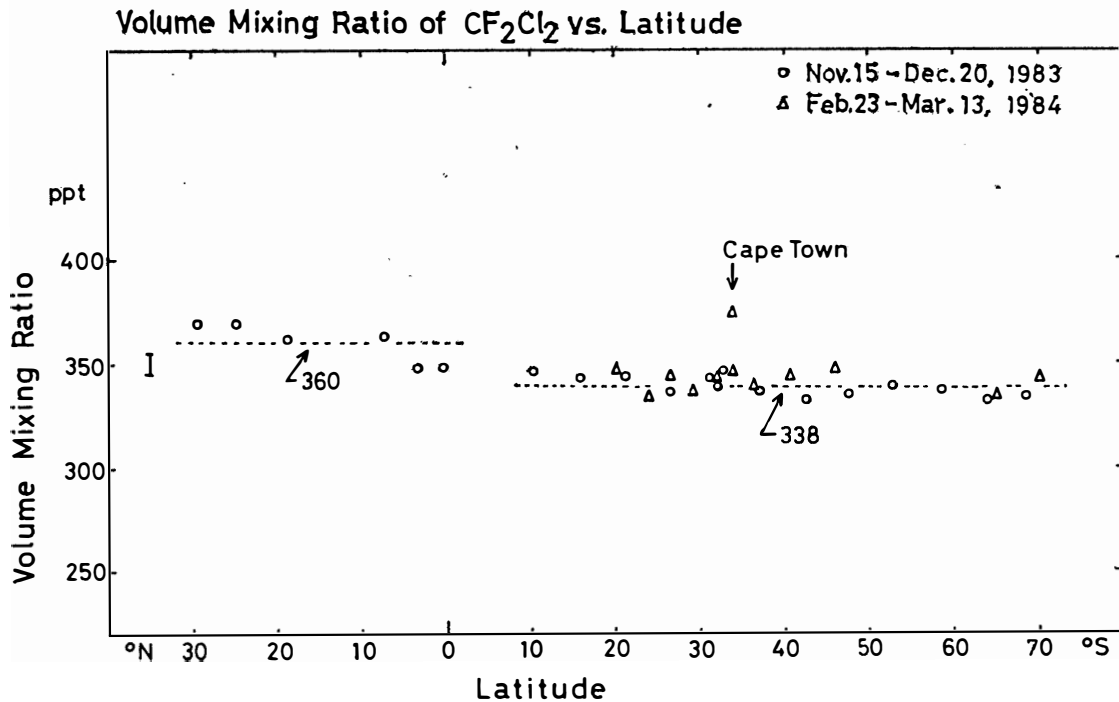


Fig. 1. Latitudinal variation of CF_2Cl_2 . ---; Mean volume mixing ratio in either hemisphere, I; precision of the measurements of a reference gas.

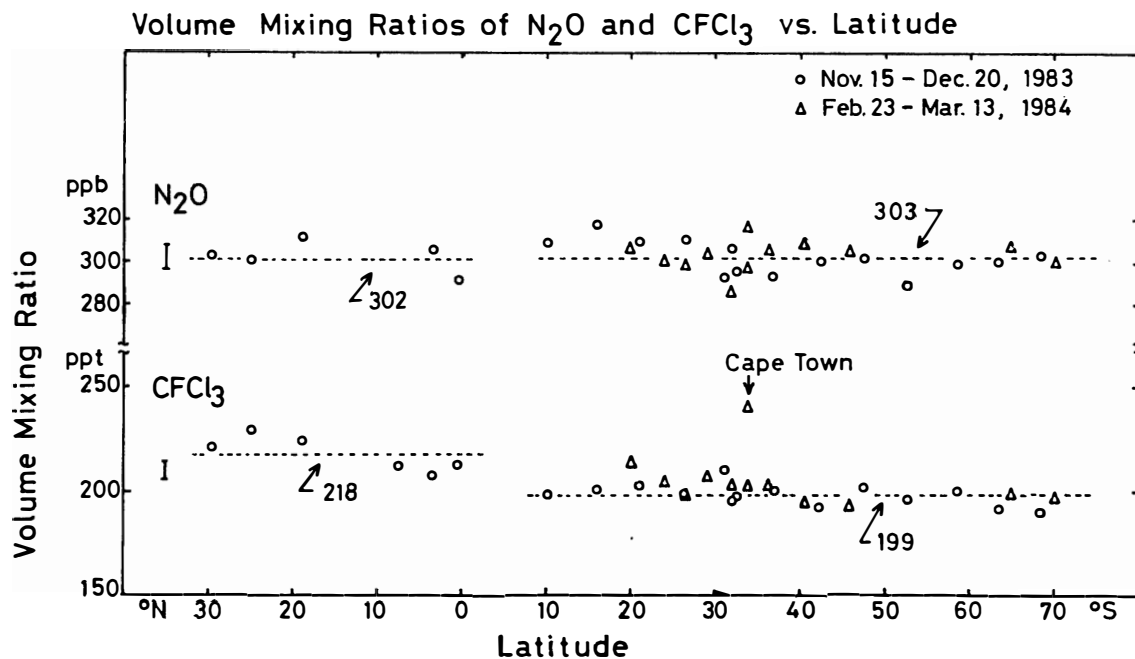


Fig. 2. Latitudinal variations of CFCl_3 and N_2O . --- and I; Same as Fig. 1.

Mixing ratios of CF_2Cl_2 decreased from 30°N to the equator, and were almost constant in the southern hemisphere. From cloud images of the GMS, ITCZ was recognized between the equator and 10°S late in November 1983. Although there was no samples between the equator and 10°S , the change in volume mixing ratio across

the ITCZ seemed to be smooth and not so steep as was observed in December 1982 (Fig. 1 in HIROTA *et al.*, 1984b). The change across the ITCZ would be different year by year.

The mean volume mixing ratio of CF_2Cl_2 was 360 ppt in the northern hemisphere and 338 ppt in the southern hemisphere, which was 6% lower than that in the northern hemisphere. In the return voyage, air samples were also collected from Syowa Station to the Mauritius Island (20.2°S , 57.5°E). Results are shown by open triangles. The mean was 341 ppt, except the value at Cape Town (33.9°S), where a polluted air from urban area might be sampled. The average increase of 3 ppt within three months is consistent with the increasing trend of CF_2Cl_2 at Syowa Station within the experimental uncertainties (see Section 3.2).

Like CF_2Cl_2 , volume mixing ratios of CFCl_3 also decreased from 30°N to the equator, and were almost constant in the southern hemisphere. The mean value was 218 ppt in the northern hemisphere and 199 ppt in the southern hemisphere, which was 9% lower than that in the northern hemisphere. Correlation coefficient between CF_2Cl_2 and CFCl_3 was 0.90. In the return voyage, the mean was 201 ppt. The average increase of 2 ppt within three months in the southern hemisphere is also consistent with the increasing trend of CFCl_3 at Syowa Station within the experimental uncertainties.

As for N_2O , no gradient in mixing ratio was found. The mean value of total 19 samples was 302 ppb. In the return voyage, the mean was 303 ppb.

3.2. Time variation

Time trends of CF_2Cl_2 , CFCl_3 and N_2O at Syowa Station are shown in Fig. 3. Air samples were collected more frequently in the latter half of 1983. The value of CF_2Cl_2 in August 1982 was too high. Except this, CF_2Cl_2 and CFCl_3 showed a steady increase, and a change in the air sampling method in February 1983 (HIROTA *et al.*, 1984b) would have no effect on the results.

Solid lines in Fig. 3 show linear trends of these compounds calculated by the method of least squares. From February 1982 to January 1984, annual increases of 19.2 ppt/year for CF_2Cl_2 and 10.2 ppt/year for CFCl_3 (6.1 and 5.6%/year at January 1983, respectively) were obtained. Correlation coefficients were 0.87 for CF_2Cl_2 and 0.82 for CFCl_3 . Similar trends ($\sim 5\%$ /year) were also observed over Japan (HIROTA *et al.*, 1984a). Though correlation coefficient between CF_2Cl_2 and CFCl_3 was 0.83, clear seasonal variation of them were not observed.

Annual increase of N_2O was 2.2 ppb/year in the same period (0.7%/year at January 1983). In other words, N_2O was almost constant in this period within the range of experimental uncertainty.

In Fig. 3, solid circles indicate the results of MAKIDE *et al.* (1983) and YOKOHATA *et al.* (1984). Cross marks indicate those at Palmer Station (65.5°S , 64.1°W) (ROBINSON and BAMESBERGER, 1983) which are weekly average values. In the measurements of MAKIDE *et al.* (1983) and YOKOHATA *et al.* (1984), increases for CF_2Cl_2 and CFCl_3 from February 1982 to January 1983 were 19 and 7 ppt respectively, which were in good agreement with ours. Although observations at Palmer Station did not cover a whole year, annual increase for CFCl_3 (12.8 ppt/year) was also in agreement with ours.

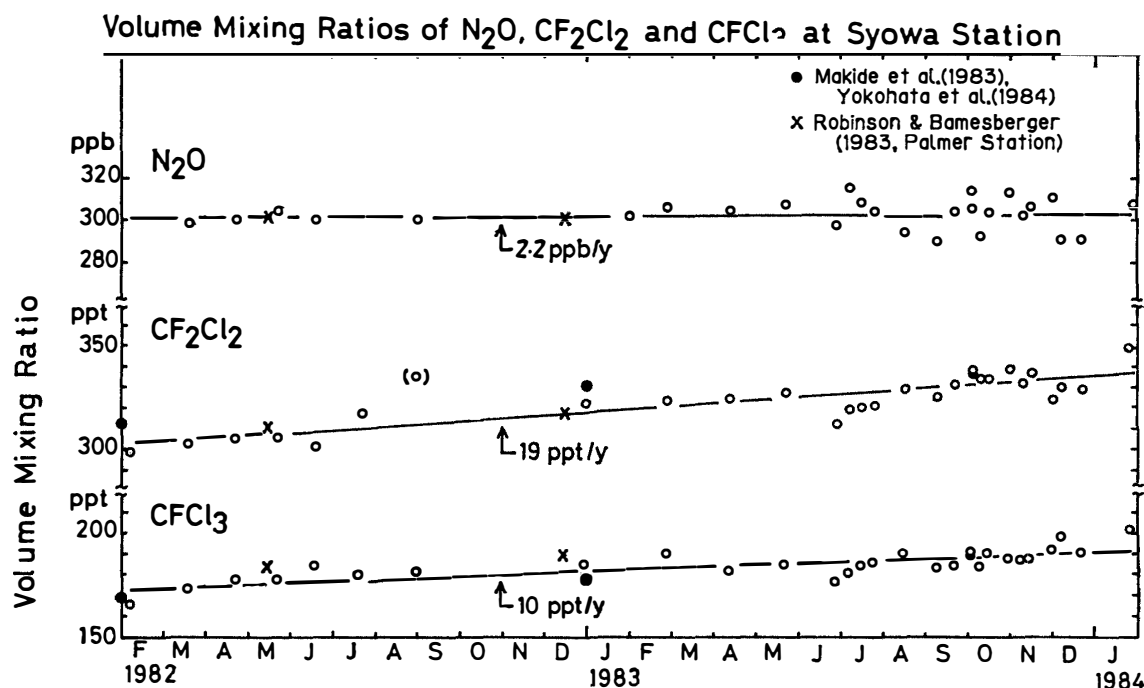


Fig. 3. Time variations of CF₂Cl₂, CFCl₃ and N₂O at Syowa Station. —; Linear trend calculated by the method of least squares.

That for CF₂Cl₂ (13.2 ppt/year), however, was a little lower than ours. Values of N₂O at Palmer Station were in good agreement with ours.

In Table 2, the values estimated from the linear trend as of January 1983 at Syowa Station are compared with the mean values observed over Japan (38–34°N, altitude 2–9 km) from October 1982 to February 1983 (HIROTA *et al.*, 1984a). With an improvement in the calibration method, the mean value of N₂O was revised. The mean values of CF₂Cl₂ and CFCl₃ at Syowa Station were lower than those observed over Japan by 6%. This is because that most of CF₂Cl₂ and CFCl₃ have been released in the northern hemisphere. Rather large values (8–11%), however, were reported by MAKIDE *et al.* (1983) and YOKOHATA *et al.* (1984). This difference would be due to the difference in latitude where air samples were collected in Japan, because CF₂Cl₂ and CFCl₃ have been released mostly from advanced industrial nations in mid-latitudes of the northern hemisphere. Our samples were collected on aircraft between 34 and 38°N, while those of MAKIDE *et al.* (1983) and YOKOHATA *et al.* (1984) were collected on the ground surface in Hokkaido (42–45°N). Absolute values cannot be compared directly, because the difference includes the systematic error between them. Fortunately we were measuring CF₂Cl₂ continuously at Memanbetsu (43.9°N) in Hokkaido from October 1980 to March 1983 (HIROTA *et al.*, 1984c). Background concentration of

Table 2. Mean volume mixing ratios of CF₂Cl₂, CFCl₃ and N₂O.

Species	CF ₂ Cl ₂ (ppt)	CFCl ₃ (ppt)	N ₂ O(ppb)
Over Japan (October 1982–February 1983)	335(7)*	194(7)*	301(7)*
At Syowa Station (January 1, 1983)	316	182	302

* Standard deviations are shown in ().

CF₂Cl₂ at Memanbetsu as of January 1983 was 347 ppt. A value of CF₂Cl₂ as of January 1983 at Syowa Station was 9% lower than this value.

The difference of 6% between at Syowa Station and over Japan (Table 2) was smaller than those expected from the results mentioned in Section 3.1, where the *mean* values in the southern hemisphere were lower than those from 30°N to the equator by 6 or 9%. This would be probably due to the limited number of samples in the northern hemisphere or to the long-range transport of the polluted air from Japan and/or eastern Asia by the winter monsoon.

There was no difference in values of N₂O in Table 2. This would be due to the more uniform distribution of the sources of N₂O than those of CF₂Cl₂ and CFCl₃.

Acknowledgments

The authors wish to express their thanks to the members of JARE-23, -24 and -25 for their support to the air sampling operations. They also thank Prof. S. KAWAGUCHI and Dr. T. YAMANOUCHI of the National Institute of Polar Research for their kind advice in planning these observations.

References

- HIROTA, M., MURAMATSU, H., MAKINO, Y., SASAKI, T. and TOYAMA, Y. (1984a): The vertical distributions of atmospheric CF₂Cl₂, CFCl₃ and N₂O over Japan. *J. Meteorol. Soc. Jpn.*, **62**, 158–164.
- HIROTA, M., CHUBACHI, S., MAKINO, Y. and MURAMATSU, H. (1984b): Gas-chromatographic measurements of atmospheric CF₂Cl₂, CFCl₃ and N₂O in Antarctica. *Mem. Natl. Inst. Polar Res., Spec. Issue*, **34**, 20–27.
- HIROTA, M., MURAMATSU, H., FUKUI, F., MUROMATSU, F., HASHIMOTO, M., KUWASHIMA, M. and KOIKE, T. (1984c): Measurement of CF₂Cl₂ at Memanbetsu over the period between October 1980 and March 1983. *Pap. Meteorol. Geophys.*, **35**, 63–69.
- MAKIDE, Y., YOKOHATA, A. and TOMINAGA, T. (1983): Atmospheric concentrations of halocarbons in Antarctica (abstract). *Mem. Natl. Inst. Polar Res., Spec. Issue*, **29**, 225.
- NATIONAL RESEARCH COUNCIL (1982): Causes and Effects of Stratospheric Ozone Reduction; An Update. Washington, D. C., National Academy Press, 339p.
- ROBINSON, E. and BAMESBERGER, W. L. (1983): Air chemistry monitoring at Palmer Station. *Antarct. J. U. S.*, **18**, 253–254.
- WMO (1981): The Stratosphere 1981, Theory and Measurements. Geneva, WMO, 503p. (WMO Global Ozone Research and Monitoring Project Report, No. 11).
- YOKOHATA, A., MAKIDE, Y. and TOMINAGA, T. (1984): Atmospheric concentrations of halocarbons and methane in Antarctica (abstract). *Mem. Natl. Inst. Polar Res., Spec. Issue*, **34**, 231.

(Received April 1, 1985; Revised manuscript received August 3, 1985)