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THE VERTICAL DISTRIBUTIONS OF ATMOSPHERIC CF_2Cl_2, $CFCl_3$ AND N_2O OVER SYOWA STATION IN 1983

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Abstract: Air samples were collected on an aircraft over Syowa Station up to an altitude of 7.3 km on January 24, April 5, October 18 and December 12, 1983. Trace gases (CF_2Cl_2, $CFCl_3$ and N_2O) were measured by a GC-ECD method. These gases were vertically mixed well. Seasonal variation of vertical profiles could not be detected.

1. Introduction

There are only a few observations of vertical distributions of trace gases in Antarctica (GOLDAN *et al.*, 1980; ROBINSON *et al.*, 1982, 1983). GOLDAN *et al.* (1980) reported the vertical distributions of CF_2Cl_2, $CFCl_3$ and N_2O in the stratosphere, which were obtained by balloon-borne air samplings, and there was only one tropospheric air sample in each flight. Using an aircraft (C-130) and a helicopter, ROBINSON *et al.* (1982, 1983) observed higher mixing ratios of trace gases (CF_2Cl_2, $CFCl_3$, N_2O, CCl_4 and CH_3CCl_3) in the upper troposphere than at the surface during the austral spring season. They suggested that these phenomena were brought about by the mid-latitude air mass advection over Antarctica through the upper troposphere.

In 1983, four flights were performed over Syowa Station, and air samples up to an altitude of 7.3 km were collected on "Pilatus PC-6" by the 24th Japanese Antarctic Research Expedition (JARE-24). In this paper, vertical distributions of tropospheric CF_2Cl_2, $CFCl_3$ and N_2O over Syowa Station will be reported.

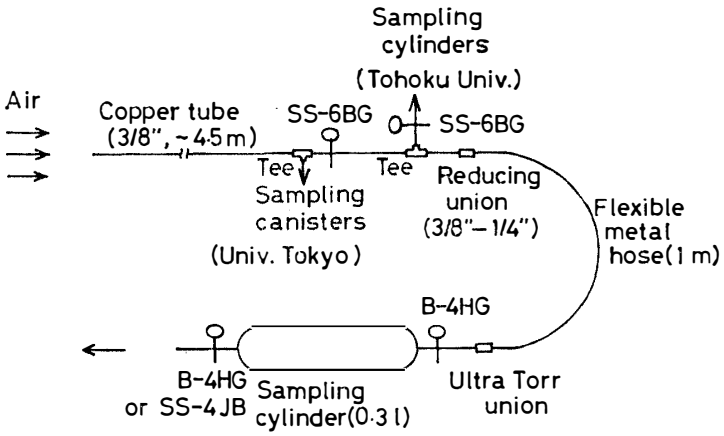

Fig. 1. Air sampling apparatus on the aircraft "Pilatus PC-6". After the first flight, sampling canisters (University of Tokyo) and SS-6BG valve between two Tees were removed.

2. Experimental

Air sampling method and gas-chromatographic measurement are described elsewhere (HIROTA *et al.*, 1984, 1985). On the aircraft, a copper tube (3/8″) was installed in the stay of the wing in order to avoid the exhaust gas from the engine, and air was taken utilizing dynamic pressure as shown in Fig. 1 (HIROTA *et al.*, 1984).

After the first flight, sampling canisters (University of Tokyo) and SS-6BG valve between two Tees were removed.

As air samples were collected at atmospheric pressure, peak areas of gas chromatograms were corrected by the pressure of sample air.

3. Results and Discussion

Air samples were collected over Syowa Station (68.7–69.4°S, 39.4–40.2°E) up to the

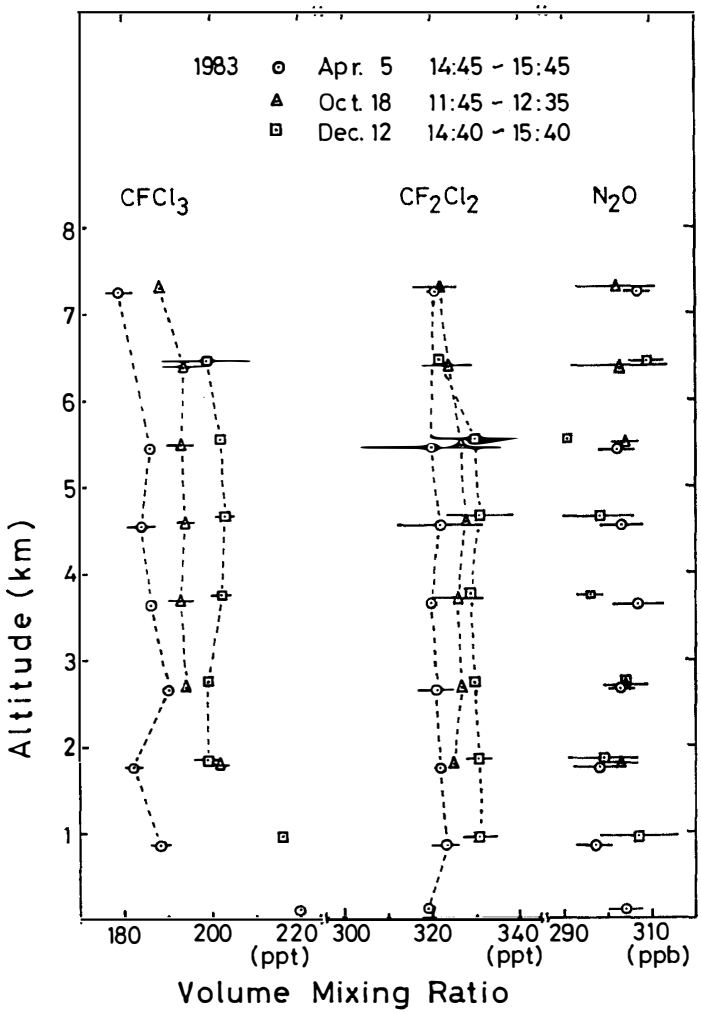

Fig. 2. Vertical distributions of CF_2Cl_2, $CFCl_3$ and N_2O over Syowa Station. Differences of two measurements (>3 ppt for CF_2Cl_2 and $CFCl_3$, and >3 ppb for N_2O) for each sample are shown by error bars.

Table 1. Mean volume mixing ratios of CF_2Cl_2, $CFCl_3$ and N_2O over Syowa Station and their standard deviations.*

Date	CF_2Cl_2(ppt)	$CFCl_3$(ppt)	N_2O(ppb)	Tropopause height** (km)
1983				
January 24	321(3)	180(3)[a)]	298(2)	8.6
April 5	321(1)	185(4)[a)]	303(4)	8.9
October 18	326(2)	193(2)[b)]	303(1)	12.2
December 12	329(3)	201(2)[c)]	301(6)	8.2

* Values in parentheses. ** Sonde data at 1500 LT.
a) The value at 0.1 km was excluded.
b) The value at 1.8 km was excluded.
c) The value at 0.9 km was excluded.

altitude of 7.3 km on January 24, April 5, October 18 and December 12, 1983. Air samples of the first flight were carried back by JARE-23 prior to those of the later flights. The results of the first flight were reported in the previous paper (HIROTA *et al.*, 1984). Those of the second, third and fourth flights are shown in Fig. 2. Air sampling altitudes overlapped each other in all flights, data points are slightly shifting in Fig. 2. Differences of two measurements (>3 ppt for CF_2Cl_2 and $CFCl_3$, and >3 ppb for N_2O) for each sample are indicated by error bars. Large error bars are generally seen in samples of higher altitudes. This would be due to smaller amounts of higher altitude samples according to lower atmospheric pressure. Mean values and standard deviations in each flight are shown in Table 1 together with the tropopause heights at 1500 LT.

High values of $CFCl_3$ in lower altitudes were excluded in the calculation of mean values (see footnotes of Table 1). These high values could not be expected from the contamination from Syowa Station, because high values were observed up to the altitude of 2 km and because high values of CF_2Cl_2 were not observed from the same sample. As air samples were collected in the descent flight, it was impossible to take the contaminated air in the sampling tube into the sampling cylinder at lower altitude. These high values of $CFCl_3$ would be due to the adsorption of $CFCl_3$ on metal surface of the sampling tube, which was cooled below $-35°C$ at about 6–7 km. With increasing temperature in the descent flight, $CFCl_3$ on metal surface would be desorbed and be taken into the sampling cylinder. In accordance with this speculation, these high values were observed only when the outer temperature was higher than $-10°C$. The lack of similar phenomena for CF_2Cl_2 would be due to its lower boiling temperature than $CFCl_3$ by 54°C.

Mean values of CF_2Cl_2 and $CFCl_3$ in Table 1 show that these gases were increasing during 1983 as was shown at the surface at Syowa Station (HIROTA *et al.*, 1985). That of N_2O was almost constant within the range of experimental uncertainty.

Figure 2 shows that these gases were vertically well mixed up to the altitude of 6 km in spring, summer and autumn including the results on January 24. Above this level, CF_2Cl_2 and $CFCl_3$ seemed to decrease slightly. This would be due to the lower tropopause heights on April 5 and December 12. On October 18, the tropopause height was 12.2 km. Its variation, however, was rather large and the mean value for

five days before and after the day was 10.5 km. Then a sudden increase of total ozone in this year was first observed on October 25 (ATMOSPHERIC ENVIRONMENT SERVICE OF CANADA, 1984). Generally the Antarctic tropopause is indistinct and frequently dissipates in winter and spring. Therefore, the tropospheric/stratospheric mixing might have been rather active around the middle of October 1983 before the sudden increase of total ozone.

ROBINSON *et al.* (1983) reported that higher mixing ratios of trace gases (CF_2Cl_2, $CFCl_3$, N_2O, CCl_4 and CH_3CCl_3) in the upper troposphere and rather low values at the surface were observed during spring. They suggested that these phenomena were brought about by the mid-latitude air mass advection over Antarctica through the upper troposphere. Similar result was observed only for $CFCl_3$ on December 12 over Syowa Station. This result, however, could not be significant considering the experimental uncertainty. In the observations of ROBINSON *et al.* (1983), statistically significant results were obtained only for CF_2Cl_2 (Fig. 2 in ROBINSON *et al.*, 1983). In order to ascertain the long-range transports of trace gases over Antarctica, more precise measurement is needed.

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References

ATMOSPHERIC ENVIRONMENT SERVICE OF CANADA (1984): Ozone Data for the World, **25**, 373–499.

GOLDAN, P. D., KUSTER, W. C., ALBRITTON, D. L. and SCHMELTEKOPF, A. L. (1980): Stratospheric $CFCl_3$, CF_2Cl_2, and N_2O height profile measurements at several latitudes. J. Geophys. Res., **85**, 413–423.

HIROTA, M., CHUBACHI, S., MAKINO, Y. and MURAMATSU, H. (1984): Gas-chromatographic measurements of atmospheric CF_2Cl_2, $CFCl_3$ and N_2O in Antarctica. Mem. Natl Inst. Polar Res., Spec. Issue, **34**, 20–27.

HIROTA, M., MAKINO, Y., SHIOBARA, M., CHUBACHI, S. and MURAMATSU, H. (1985): Gas-chromatographic measurements of atmospheric CF_2Cl_2, $CFCl_3$ and N_2O from Tokyo to Syowa Station late in 1983, and at Syowa Station between February 1982 and January 1984. Mem. Natl Inst. Polar Res., Spec. Issue, **39**, 57–62.

ROBINSON, E., CRONN, D. R., CLARK, D. and MENZIA, F. (1982): Gaseous trace compounds in the Antarctic atmosphere. Antarctica: Weather and Climate, comp. by N. W. YOUNG. Parkville, Univ. Melbourne, 149–156.

ROBINSON, E., CRONN, D. R., MENZIA, F., CLARK, D., LEGG, R. and WATKINS, R. (1983): Trace gas profiles to 3000 m over Antarctica. Atmos. Environ., **17**, 973–981.

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