The stratospheric distributions of long-lived atmospheric halocarbons over Kiruna and Sanriku observed by balloon-borne cryogenic sampling and subsequent GC analyses

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Abstract : The mixing ratios of HCFCs (HCFC-22, HCFC-142b), CFCs (CFC-11, CFC-12, CFC-113, CFC-114) and Halon-1211 in the stratosphere (up to 34 km) were obtained by gas chromatography / mass spectrometry (GC/MS) analysis of air samples collected by means of balloon-borne liquid-helium cryogenic samplers over Kiruna, Sweden (68° N) on February 22 and March 18, 1997, and over Sanriku, Japan (39° N) on May 30, 1997. Obtained vertical profiles of halocarbons clearly showed the photodissociation with altitude depending on their UV absorption cross sections. The reversed structure was sometimes shown, indicating the laminated structure in the lower stratosphere in early summer over Sanriku. The observation made at Kiruna showed higher mixing ratios for some compounds in the edge of the polar vortex when compared to those inside the polar vortex, suggesting the mixing of air from lower latitude at the vortex edge. Comparison of the vertical profiles over Kiruna and Sanriku showed latitudinal/seasonal differences in connection with meridional circulation of the atmosphere.

Keyword : cryogenic sampling, halocarbons, vertical profiles

1. Introduction

Halogenated hydrocarbons (halocarbons) play an important role in the stratospheric chemistry, since they are the source of halogen radicals that catalytically destroy stratospheric ozone and are also efficient greenhouse gases as they absorb thermal radiation in the spectral region of the "atmospheric window" between 8 and 12μm. Among these halocarbons, major chlorofluorocarbons (CFCs) like CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2) still have the greatest potential for both the stratospheric ozone depletion and the global warming, though their production and consumption have been strictly restricted by the international protocol since 1989. Hydrochlorofluorocarbons (HCFCs) like HCFC-

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142b (CH_3CClF_2) have been used as alternatives and their sharply increasing trends of tropospheric concentrations were observed these years (Shirai and Makide, 1998).

The stratospheric distributions of trace gases are controlled by the balance between transport and photochemical losses. CFCs and HCFCs can be effective tracers of chemistry and dynamics in the stratosphere as their sources and decomposition processes are relatively well understood. To observe their stratospheric distribution, the balloon-borne cryogenic sampling technique was developed and has been one of the most effective approach that has a great advantages in low detection limit, high precision and high accuracy compared to remote sensing techniques.

2. Experimental

Balloon experiments were successfully carried out over Kiruna, Sweden (68° N) on February 22 and March 18, 1997 (Photograph 1) and over Sanriku, Japan (39° N) on May 30, 1997 (Photograph 2). The air samples were collected by the balloon-borne cryogenic sampling system developed by the Institute of Space and Astronautical Science (ISAS), which consists of 12 evacuated stainless steel tubes submerged in liquid helium (Honda, et al., 1987 and 1996). The valves are remotely activated for sampling of air at 11 assigned altitudes. Sample collection was made during both ascending and descending of the balloons in order to shorten the flight time and avoid the contamination from the balloon during ascending at the higher altitude. The flight patterns and sampling altitudes are shown in Figures 1 and 2.

The air samples were analyzed in the laboratory at the University of Tokyo. An aliquot of the atmospheric sample was cryogenically preconcentrated and introduced into the gas chromatograph without contamination by using an extremely clean all stainless steel system. A 400-1000 ml of the sample air was introduced and preconcentrated by using a vacuum line passing through a cold trap at the liquid nitrogen temperature. The trapped constituents were desorbed from the first trap by warming and cryofocussed with a small-volume secondary trap at the liquid nitrogen temperature, and then desorbed rapidly by heating. GC separation was carried out using a PoraPLOT Q capillary column with purified helium carrier gas and the following temperature programming: isothermal at 40℃ for 4 min, then 5℃/min to 180℃. Each halocarbon thus separated was detected by a mass spectrometer. The concentrations
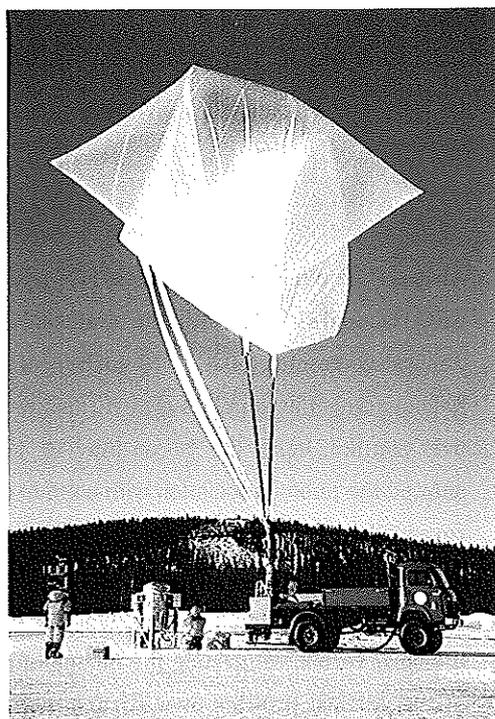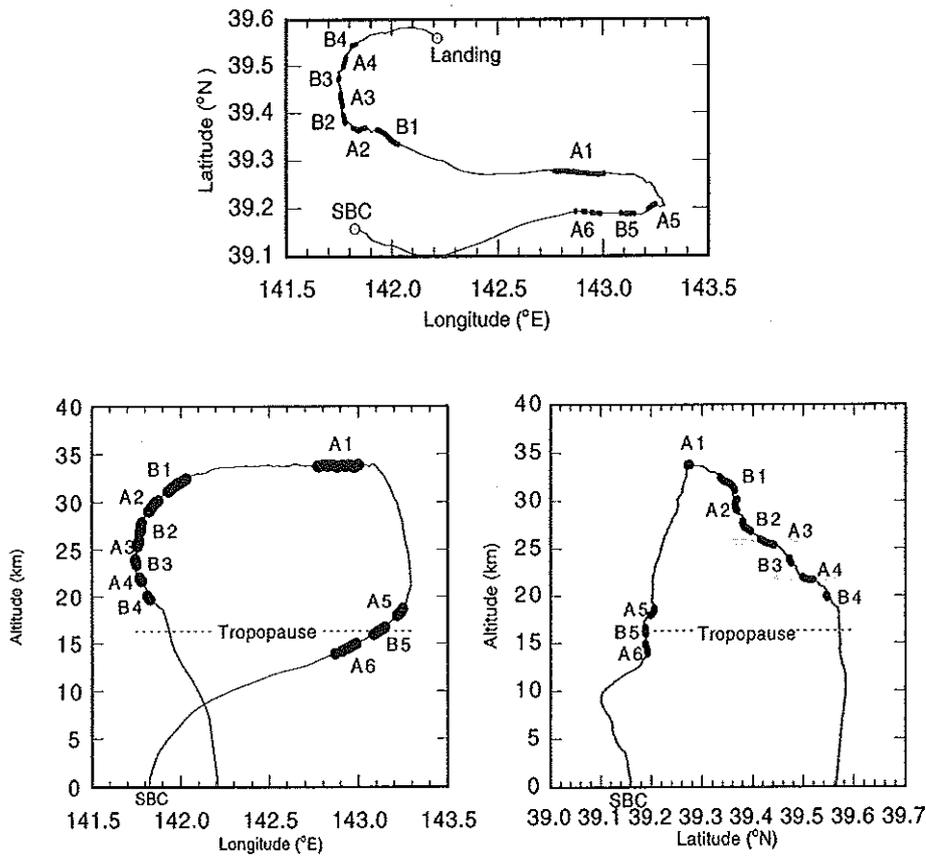

Photograph 1
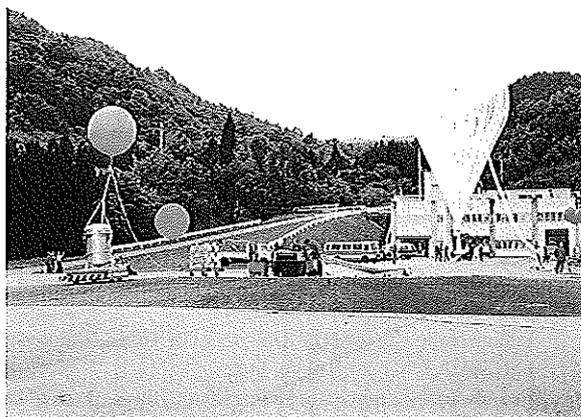
Photograph 2

Fig. 1   Trajectory of the balloon launched from SBC (Sanriku Balloon Center) on May 30, 1997. Samples are named A1, B1, ... for identification.
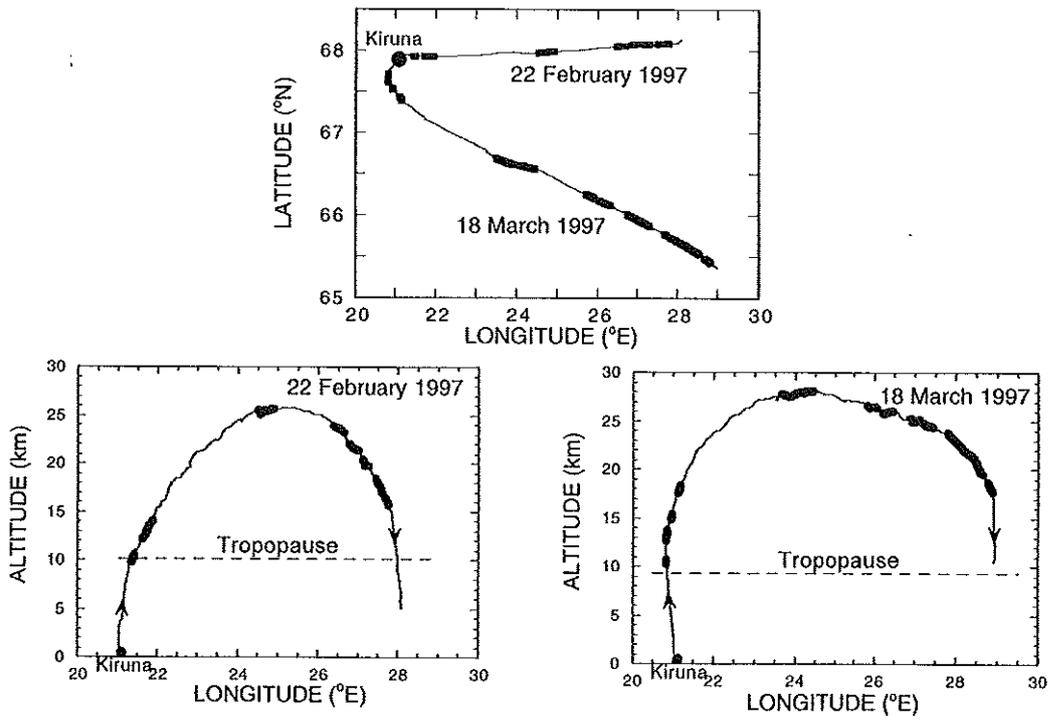

Fig. 2   Trajectory of the balloon launched from Kiruna (Esrange) on February 22 and March 18, 1997.

were determined by using calibrated secondary standards. Major halocarbons including CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), CFC-113 (CCl_2FCClF_2), 1.1.1-trichloroethane (CH_3CCl_3) and carbon tetrachloride (CCl_4) were also measured by GC/ECD (Electron Capture Detector) which has specific sensitivity to those compounds with high electron affinity. The compounds with less ECD sensitivity such as CFC-114 ($CClF_2CClF_2$), HCFC-22 ($CHClF_2$) and HCFC-142b (CH_3CClF_2), and some compounds of which the atmospheric concentrations are too low to be detected without preconcentration such as Halon-1211 ($CBrClF_2$) were measured only by GC/MS. The analytical results agreed very well with ECD and MS when measured, which indicates the reliability of the analytical procedures.

3. Results and Discussion

The vertical profiles of the trace gases obtained by the flight from Sanriku on May 30, 1997 are shown in Figure 3a. All the CFCs, HCFCs and halons originate entirely from anthropogenic activity on the surface. As shown in Figure 3, the observed mixing ratios of fully halogenated hydrocarbons like CFCs and halon were almost uniform below the tropopause because they are inert to the hydroxy radicals and not removed in the troposphere. They are transported into the stratosphere, dissociated by photochemical processes, and release free chlorine/bromine atoms, which them catalytically destroy stratospheric ozone. Since they are decomposed by the photolysis, their mixing ratios clearly showed decreases with altitude corresponding to their UV cross sections (Figure 4). The similar decreasing gradients of CFC-12 and CFC-113 can be explained by their close UV absorption cross sections. Halon-1211 and CFC-11 are rapidly decomposed by relatively long wavelengh light, while CFC-114 showed much smaller gradient, reflecting its smaller UV cross section.

HCFCs, which contain hydrogen atoms, are decomposed with hydroxyl radicals in the troposphere and partly removed before reaching the stratosphere. They showed rapid decrease in the upper troposphere and the lower stratosphere, while in the midstratosphere they decreased only slightly reflecting their smaller UV cross sections than those of CFCs. They showed even reversed structure affected by dynamics as shown in Figure 1. The considerably lower mixing ratios for those compounds at heights of 25 km and 22 km suggest the intrusion of laminated air masses with different histories in the corresponding altitude. These anomalies were also found in the previous observations and lower concentrations of other trace gases such as CO_2, CH_4, and N_2O in the same samples analyzed by different methods (Aoki et al., 1998), which eliminates the possibility of measurement errors. These laminated structures
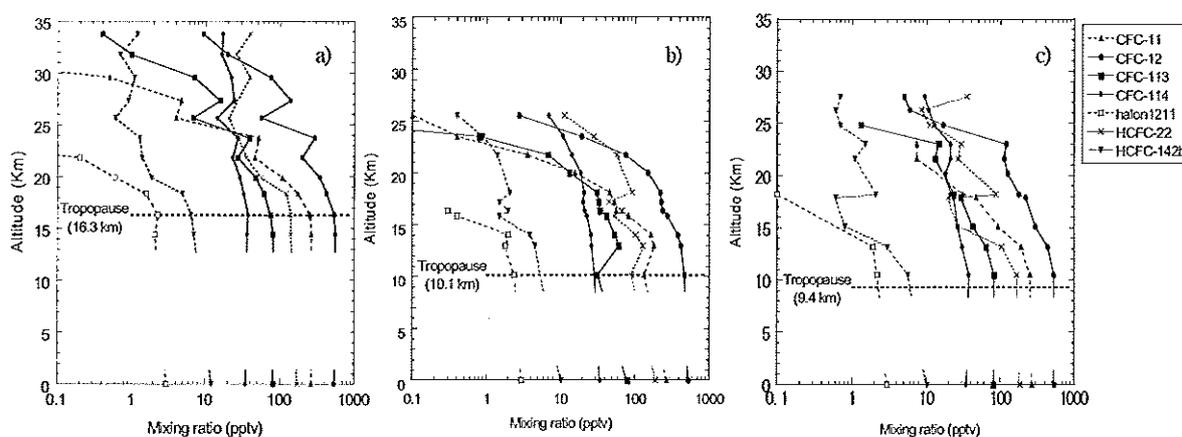

Fig. 3   Observed vertical profiles of halocarbons over a) Sanriku (Japan, 39° N) on May 30, 1997, b) Kiruna (Sweden, 68° N) on February 22, 1997, and c) Kiruna (Sweden, 68° N) on March 18, 1997. The surface concentrations are average concentrations obtained by samples collected in Hokkaido (42-45° N)

observed over Sanriku showed the inactivity of vertical mixing in the lower stratosphere in the early summer.

To consider the seasonal and latitudinal differences, the vertical profiles observed over Kiruna on February 22 and March 18, 1997 are shown in Figures 3b and 3c, respectively. Compared to the flight over Sanriku, the profiles observed over Kiruna showed substantially larger vertical gradients: the falloff occurs at lower altitudes. To remove the effect of the latitudinal difference of tropopause height and air density, and to consider the isentropic transport of the air masses in the stratosphere, we compared those profiles by plotting with a potential temperature as a vertical
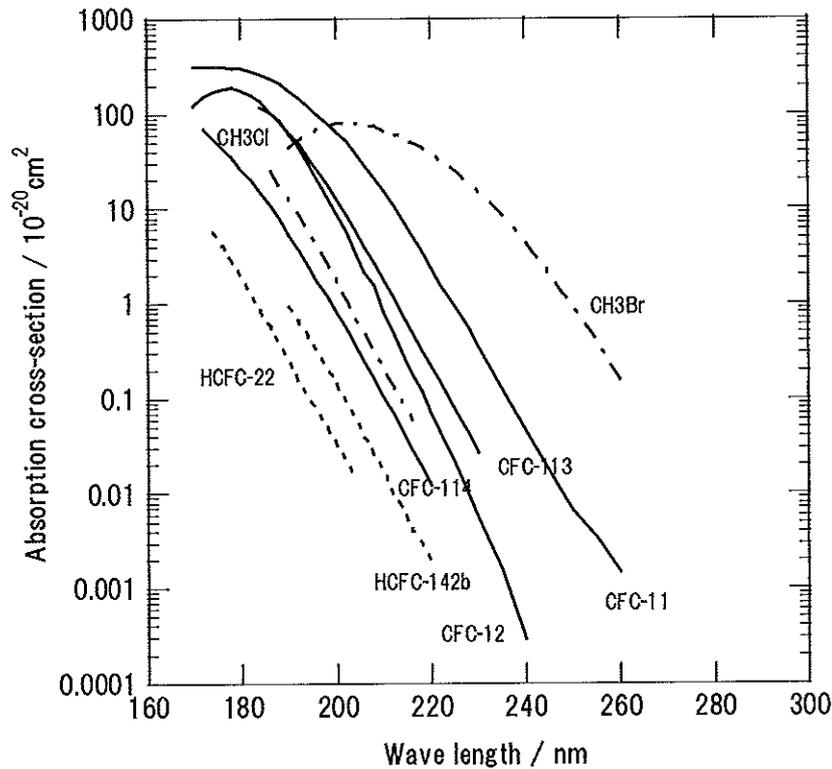

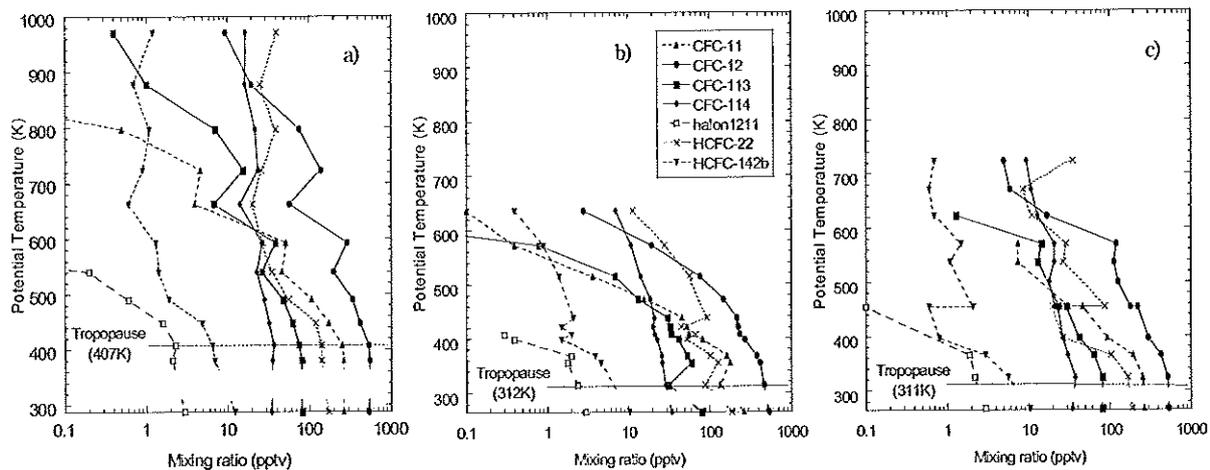Fig. 4   Absorption cross sections of halocarbons at 295-298K

Fig. 5   Observed vertical profiles of halocarbons plotted versus potential temperature over a) Sanriku (Japan, 39° N) on May 30, 1997, b) Kiruna (Sweden, 68° N) on February 22, 1997, and c) Kiruna (Sweden, 68° N) on March 18, 1997. The surface concentrations are average concentrations obtained by samples collected in Hokkaido (42-45° N)

coordinate instead of geopotential height (Figure 5). As the result, all the compounds observed over Kiruna still showed significantly lower mixing ratios than over Sanriku for the same potential temperature, suggesting longer transport time of the air masses at higher latitudes, as the tropospheric air enters the stratosphere predominantly through the tropical tropopause, and moves upward then poleward in the stratosphere.

The profiles obtained from two flights over Kiruna agreed fairly well with each other for the lower altitudes but higher mixing ratios are observed at the higher altitudes for the flight on March 18. As shown in Figure 2, the samples were collected during both ascending and descending, and the samples collected above 18km were taken in the latter part of the flight (after the level flight) when the balloon was flying further southeast from the first half of the flight. This local effect was clearly shown by the large gaps between the mixing ratios of HCFCs in the two samples collected at approximately 18km altitude. Assuming that those samples represent different air masses, the form of the polar vortex was inverstigated on each day of the flight. Figure 6 shows the Ertel's potential vorticity distribution (Nash, et al., 1996) of February 22 and March 18. Geographical distribution of the polar vortex was very different for those two days. The trajectories of the balloon flights indicate that the balloon flew entirely inside the polar vortex on February 22 while it flew in the vortex boundary region on March 18. The samples collected during descent at southeast from Kiruna showed higher concentrations, suggesting the mixing of the air from lower latitude outside the polar vortex.

Transport in the stratosphere has been viewed as the Eulerian zonal-mean circulation, which is upward in the tropics and downward at high latitudes. Various observations made using aircraft, balloons, and satellites have given estimated the descent rates of a few kilometers per month within in the polar votex in winter (Loewnstain, et al., 1990, Schmidt, et al., 1991, Bauer, et al., 1994). The effect of such diabatic subsidence of air in the polar vortex can be estimated by the temporal variation of the vertical profiles of the trace gases which means that the downward shift is expected to be found towards late winter. However, when comparing the two profiles observed over Kiruna in this study, those were nearly identical for the lower altitude and rather elevated concentrations were observed for the higher stratosphere. The higher mixing ratios in the higher altitude has been explained by the effect of the air advected from outside of the vortex. However, similar profiles seen in the lower altitudes can be explained by the

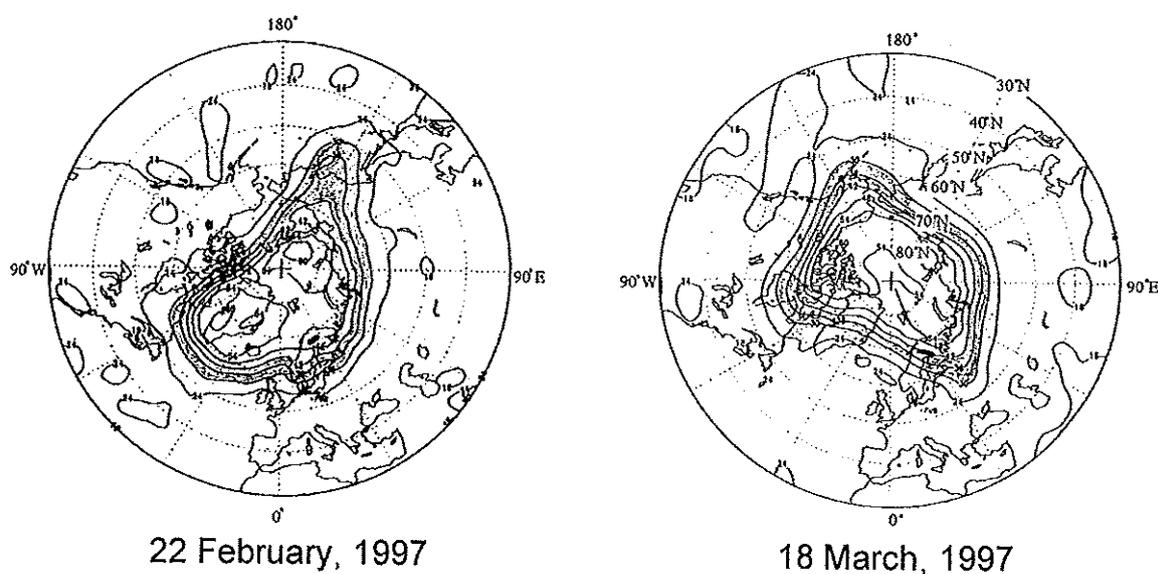22 February, 1997　　　　　　　　　　　　18 March, 1997

Fig. 6　The potential vorticity on the 475K isentropic level on February 22 and March 18, 1997.

following two reasons. Firstly, diabatic decent rate inside the polar vortex was very slow over the period (from mid-February to mid-March) consistent with previous studies (Knudsen, et al., 1998, Rex, et al., 1999). Secondly, there might have been some warming events to make midlatitude air intrudes inside the polar vortex period, which compensated the lowering of concentrations at certain altitude due to subsidence.

4. Conclusion

The vertical profiles of halocarbons in the stratosphere (up to 34km altitude) in mid-latitude early summer and polar winter in the Northern Hemisphere were obtained by balloon-borne cryogenic sampling and subsequent laboratory analysis using GC/MS. Observed latitudinal/seasonal difference among the profiles demonstrated both photochemistry and transport of those trace constituents in the troposphere and stratosphere. Vertical gradients of the mixing ratios of the compounds due to the decomposition with altitude were not necessary monotonic and rather showed step-wise pattern, indicating layer structure in lower stratosphere. The flight crossed the edge of the polar vortex showed a gap of the mixing ratios at the approximate altitude depending on the relative location of the vortex, indicating the gradient of trace gas mixing ratios at the vortex edge. Compared to the mid-latitude early summer, lower mixing ratios were observed in the polar winter even with the correction of the different air density. This can be explained by isolation and downward motion of air within the polar vortex as part of the meridional circulation in the stratosphere (upwelling in the tropics and subsidence in middle and high latitudes). No clear indication of downward motion inside the polar vortex was observed between the two vertical profiles over Kiruna with an interval of approximately one month, suggesting the low rate of subsidence in mid-February and mid-March and occasional intrusion of the air from outside of the vortex at the time of warming events.

5. Acknowledgments

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