Vertical Profiles of CCl_3F, CCl_2F_2, and CH_4 in the Stratosphere and Troposphere over Japan as Observed by Balloon Grab-Sampling and by Gas-Chromatographic Analysis

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Synopsis. Stratospheric and tropospheric air samples were collected by means of a balloon-borne grab-sampler launched from Sanriku (39°N, 142°E) in the late summers of 1981, 1983, and 1984. The mixing ratios of CCl_3F and CCl_2F_2 were determined precisely by using gas chromatography with ECD, and that of CH_4, by gas chromatography with FID. The vertical profiles of these compounds are presented and compared with the model calculations.

Large amounts of chemical species have been released into the atmosphere from human activities; their atmospheric concentrations increase depending on the released amounts and tropospheric lifetimes. Among them, entirely man-made chlorofluoromethanes, CCl_3F and CCl_2F_2, both with extremely long lifetimes, are believed to have a severe impact on the Earth's environment; the stratospheric ozone is depleted by chlorine atoms released from these compounds in the stratosphere.[1–3] In this connection, we have been measuring the background concentrations of several halocarbons in the atmosphere in Hokkaido since 1979 and have observed that the CCl_3F and CCl_2F_2 concentrations increase by 4—6% a year.[4]

We have also observed that the atmospheric concentration of methane increases gradually as well (about 1% a year); in the troposphere, it will cause an elevation of the surface temperature (i.e., a "greenhouse effect"),[5] and a depletion of the tropospheric OH radical concentration leading to prolonged lifetimes of many air pollutants susceptible to OH attack.[6]

In this paper we report the vertical profiles of CCl_3F, CCl_2F_2, and CH_4 over Japan obtained by the analysis of air samples collected by means of a balloon-borne large-volume grab-sampler. While the vertical distributions of these compounds have often been observed in the USA[7,8] and southern France,[9] no systematic measurements have been attempted to date in Asia.

Experimental

Stratospheric Air Sampling. A balloon-borne grab-sampling system for collecting stratospheric whole air samples was developed; the details have been described elsewhere.[10]

Six 30-l sample cylinders were installed in a sealed large aluminum container called a "scientific gondola" (0.9 m in diameter, 1.3 m in height, and weighing 150 kg), together with a sampling manifold, a monitor circuit, and a valve-controller. A motor-driven stainless-steel bellows valve was installed between each sample cylinder and the sampling manifold; it was operated at the desired altitude by command signal from the ground station. The sampling manifold was connected to an outside air-intake tube (4-m-long flexible tubing equipped with a glass-sealed end for ensuring a high vacuum and extremely clean conditions).

In order to avoid contamination by halocarbons from the components (cylinder, valve, manifold, etc.), all parts were cleaned thoroughly before they were assembled. The inside of the electropolished sample-cylinder was further passivated by silanization with hexamethyldisilazane, and then evacuated for several hours at 150 °C.

After launching, the scientific gondola was reeled down to 100 m below the control gondola/15000 m^3 balloon in order to avoid contamination from these systems and from the helium gas to be released from the balloon. Then, the end glass-seal was cut off and the 4-m intake tubing was extended downward. Sampling was performed when the balloon system was descending, and the inlet port was continuously flushed with ambient air. The sampling system was launched in the early morning on September 2nd, 1981, on August 28th, 1983, and on September 7th, 1984, from the Sanriku Balloon Center on the Pacific coast (39.16°N, 141.83°E). In the beginning, it flew east over the Pacific Ocean while ascending (at 300 m min^{-1}) on the west wind in the troposphere; it then returned to the west at an altitude of about 28 km on the weak east wind in the stratosphere. After 2—4 h flight for degassing and returning to over Sanriku, it was made to descend at 50—100 m min^{-1}; five stratospheric samples were collected in the meantime. Then the balloon was cut off, and one tropospheric sample was collected during descent by parachute. The scientific gondola alighted on the sea near Sanriku and was recovered within an hour.

Analysis. The sample cylinders were returned to the laboratory, and an aliquot of the atmospheric sample was introduced into an extremely clean, evacuated sample loop for precise and accurate analysis with the gas chromatographic system we had developed.[11,12] The halocarbons were determined with an ECD (electron capture detector), while methane was determined with an FID (flame ionization detector).

Results and Discussion

Since the atmospheric pressure decreases with the altitude, the concentration is expressed in terms of the volume mixing ratio (molar ratio of each component to dry air, in units of pptv=10^{-12} v/v or ppmv=10^{-6} v/v).

The observed mixing ratios of CCl_3F and CCl_2F_2 (1981, 1983, and 1984), and CH_4 (1983 and 1984) are shown in Fig. 1, together with the observed concentrations on the surface (background concentrations observed in Hokkaido in August).[4]

While these compounds were distributed uniformly in the troposphere, the mixing ratios of halocarbons decreased rapidly in the stratosphere because of the slow transport into the stratosphere and the photodissociation by intense solar radiation with short wave-

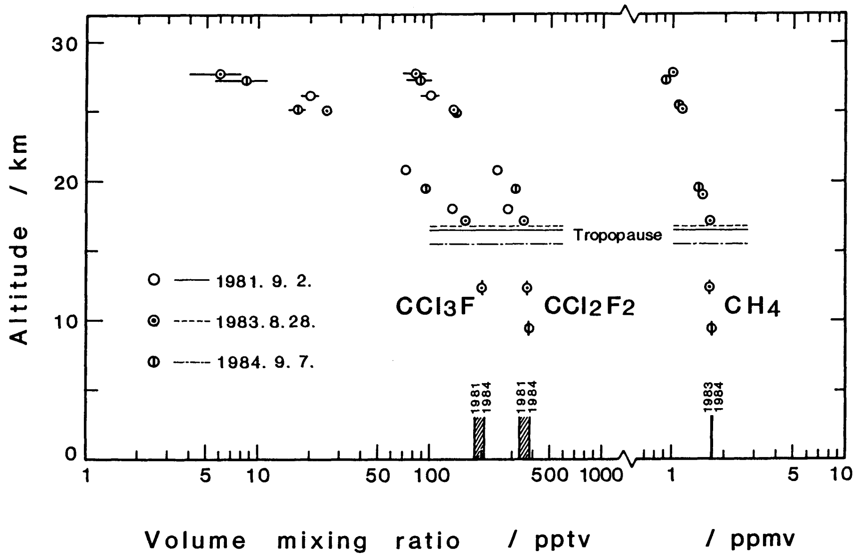

Fig. 1. Observed vertical distribution of halocarbons and methane in the stratosphere and troposphere over Sanriku (39°N, 142°E) in summers of 1981, 1983, and 1984.

lengths (190—220 nm). As compared with CCl_2F_2, CCl_3F, with a larger photodissociation cross-section, indicated a quicker decrease in the mixing ratio.

Since no removal process (sink) for CCl_3F and CCl_2F_2 has been found in the troposphere (i.e., no photodissociation with sunlight (>280 nm), no reaction with OH, no dissolution into rain or sea water, etc.), their tropospheric lifetimes have been confirmed to be extremely long, more than several hundred years.[13)] In the stratosphere, however, ultraviolet solar radiation not absorbed by stratospheric ozone can decompose CCl_3F (at about <230 nm) and CCl_2F_2 (at about <220 nm) effectively, with maximum dissociation at altitudes of about 25 and 30 km respectively. The photodissociation of CCl_3F and CCl_2F_2 ($CCl_3F+h\nu \rightarrow Cl+CCl_2F$, and $CCl_2F_2+h\nu \rightarrow Cl+CClF_2$) is followed by the release of all the Cl atoms in the molecule, and the released Cl joins the ClO_x-catalyzed decomposition of ozone ($Cl+O_3 \rightarrow ClO+O_2$, and $ClO+O \rightarrow Cl+O_2$), leading to the depletion of the stratospheric ozone.[1—3)]

By contrast, methane is decomposed mainly in the troposphere by the reaction with the OH radical ($CH_4+OH \rightarrow H_2O+CH_3$), with a tropospheric lifetime of about 10 years.[6)] In the lower stratosphere, the observed mixing ratio of CH_4 decreases only slowly due to the low OH and $O(^1D)$ concentrations, the small photodissociation cross-section with UV, and the upward diffusion to the upper stratosphere. As compared with the CH_4 profile, it is obvious that CCl_3F and CCl_2F_2 are decomposed effectively in the lower and mid stratospheres.

The vertical profiles of the stratospheric mixing ratios observed in this work (Fig. 1) agree reasonably well with those calculated on the basis of recent atmospheric models.[14—17)] A two-dimensional (2-D) atmospheric model calculation[14)] suggests, for summer at latitude 38°N, that the CCl_3F mixing ratio will drop to 1/10 and 1/100 (of the tropospheric value) at altitudes of about 25 and 28 km respectively, while the CCl_2F_2 mixing ratio will fall to 1/10 at about 31 km. Our measurements at 39°N in summer indicate that the CCl_3F mixing ratio fell to 1/10 and 1/100 at altitudes of 25—26 km and 28—29 km, while that of CCl_2F_2 fell to 1/10 at 30—31 km. The 2-D model calculation[14)] similarly suggests that the CH_4 mixing ratio decreases to 1/2 (of the tropospheric value) at about 30 km; this is also in agreement with the value of 29—30 km in the observed profile (Fig. 1).

Meteorological conditions should be taken into consideration for a closer examination of the vertical distribution of these compounds in the stratosphere. The heights of the tropopause were about 16.5, 16.8, and 15.5 km respectively at the time of the flights in 1981, 1983, and 1984. The flights were made in more or less similar seasons and under similar weather conditions, because these factors were chosen to ensure the recovery of the sampler on the sea off Sanriku; the stable combination of a tropospheric west wind and a stratospheric east wind is possible only in early and late summer.

Since the tropopause moves upward or downward with the air, the observed mixing ratios were plotted against the height above the tropopause in Fig. 2; the tropopause height was normalized to 16.5 km. With such normalization, less scattered and more reasonable plots were obtained. The atmospheric pressure-temperature curves on the sampling day were very similar in 1981 and 1983, and a clear turning point corresponding to the tropopause was observed, whereas there was a gradual change in the temperature around the tropopause in 1984, indicating that the profile around the tropopause was affected by air mass motions. Our data are less scattered and indicate a slower fall-off in the lower stratosphere than those reported over the USA (41°N)[7)] or southern France (44°N).[9)] Such a discrepancy of vertical profiles may be attributed to the difference in the dynamic processes in this altitude region (lower stratosphere) depending on

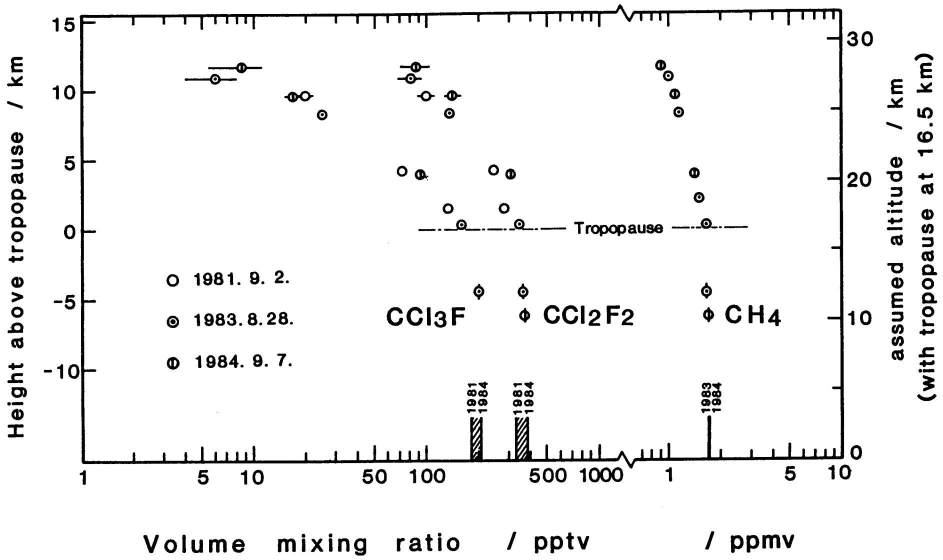

Fig. 2. Vertical distribution of halocarbons and methane vs. height above tropopause.

the latitude, season, and meteorological conditions.

The observed atmospheric concentrations of CCl_3F and CCl_2F_2 on the surface increased by about 12 and 15% respectively in these 3 years (1981—1984).[4] While the mixing ratios of these halocarbons in the stratosphere may also tend to increase slightly (Fig. 2), it is still difficult, in view of variable meteorological conditions, to indicate the trend in the stratosphere quantitatively on the basis of 3 years' data. A long-term monitoring is needed to determine unequivocally the trend of their stratospheric concentrations. Since stratospheric air samples from higher altitudes should be analyzed for a more detailed comparison with models, a balloon-borne liquid-helium-cooled cryogenic-sampler has been developed to collect sufficient amounts of samples at lower-pressure altitudes.[18]

Conclusion

The vertical profiles of CCl_3F, CCl_2F_2, and CH_4 were determined by the analysis of the air samples collected by means of a balloon-borne grab-sampler. The mixing ratios of halocarbons decreased sharply in the stratosphere, indicating the emission of large amounts of Cl atoms, which in turn cause the depletion of stratospheric ozone: this situation will persist for several tens to hundreds of years in view of the increasing tropospheric concentrations of halocarbons with extremely long lifetimes.

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