Stratospheric Ozone Depletion and Halocarbons

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ABSTRACT - Chlorofluorocarbons with extremely long atmospheric lifetimes cause depletion of the ozone layer in the stratosphere. We have been monitoring their average atmospheric concentrations in the northern/southern hemisphere since 1979: the background atmospheric concentrations of CCl_3F (CFC-11) and CCl_2F_2 (CFC-12) in the mid-latitude northern hemisphere had been increasing by 4% a year over a decade until 1989 but have started leveling off recently. The CCl_2FCClF_2 (CFC-113) concentration in the atmosphere increased much faster than those of CFC-11 and CFC-12 but its growth has also slowed down in the northern hemisphere. Vertical profiles of chlorofluorocarbons in the stratosphere have been measured by means of balloon grab-sampling and cryogenic sampling. The stratospheric ozone depletion causes increased UV-B exposure on the earth's surface, leading to deleterious biological impacts.

INTRODUCTION

Great concern has been felt about depletion of the stratospheric ozone layer by very stable man-made halocarbons (e.g. chlorofluorocarbons) since the possibility of the stratospheric ozone depletion by chlorofluoromethanes was first announced by Rowland and Molina in 1974 (Ref. 1). Numerous scientific evidences (laboratory experiments and field observations) have been accumulated in the meantime to confirm the possible ozone depletion by chlorofluorocarbons and to make assessment of the future environmental impact of such process. The ozone loss has been observed already in global trends of total ozone as well as dramatic depletion of the stratospheric ozone over Antarctica known as 'ozone hole' (Ref. 2). Recent survey in the Arctic suggests that a similar process may also take place there, causing substantial ozone loss. As the result of the stratospheric ozone depletion more UV-B penetrates onto the earth's surface, causing deleterious effects such as possible increases in human skin cancer and cataract and immune suppression as well as damaging effects on ecosystems.

Since chlorofluorocarbons cause stratospheric ozone depletion, trends of their atmosphericconcentrationsprovide a very important basis for assessing future environmental impact. We initiated very accurate measurements of trace halocarbons in the atmosphere as early as 1978–1979 in order to clarify their distribution and patterns (Ref. 3~12,16). We have also been measuring vertical profiles of chlorofluorocarbons, which may reflect their photolytic behaviors in the stratosphere (Ref. 11~13).

ULTRA-TRACE ANALYSES OF CHLOROFLUOROCARBONS AND HALOCARBONS IN THE ATMOSPHERE

We have developed an extremely clean, all-metal analytical system for accurate measurements of atmospheric concentrations of chlorofluorocarbons (CFC-11, CFC-12, CFC-113, etc.), carbon tetrachloride, methyl chloroform, and other halocarbons at 10~500 pptv level with 0.5% precision. We collected atmospheric samples at the surface level by grab-sampling in completely evacuated, extremely clean, all stainless steel canisters (of two-liter volume and equipped with a stainless steel bellows valve), and analyzed a portion of the sample by ECD gas chromatography in the laboratory. ˍFigure 1 demonstrates a typical gas chromatogram of a clean atmospheric air sample collected in Hokkaido.

Trends of Average Concentrations of Chlorofluorocarbons and Halocarbons in the Troposphere

At remote locations in Hokkaido, we have collected clean, well-mixed air samples free of local pollution every summer and winter since 1979 so as to monitor average (i.e. background) atmospheric concentrations of chlorofluorocarbons and halocarbons in the mid-lattitude northern hemisphere. Figure 2 shows the trends of background concentrations of chlorofluorocarbons and halocarbons in the atmosphere over Hokkaido since 1979. The concentrations of CCl_3F (CFC-11) and CCl_2F_2 (CFC-12) were increasing almost linearly by 4% a year over a decade until 1989. However, their growth has obviously slowed down since 1990 and they started leveling off in the northern hemisphere; this certainly reflects substantial reduction in emissions of these compounds due to the international controls. The atmospheric concentration of CCl_2FCClF_2 (CFC-113) was increasing by 10-20 % a year in 1980s, but it has also stopped growing recently in the northern hemisphere. We were the first to report such slowing-down of the growth rates of major chlorofluorocarbons in the atmosphere.

Atmospheric samples have also been collected at nearby Syowa Station in Antarctica so as to clarify the behaviors and lifetimes of these compounds and
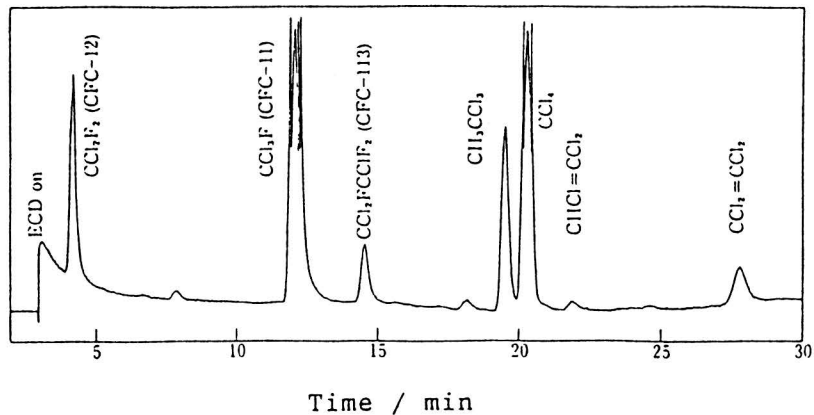
Fig. 1 Typical ECD chromatogram of a clean atmospheric air sample collected in Hokkaido, Japan (January, 1988).
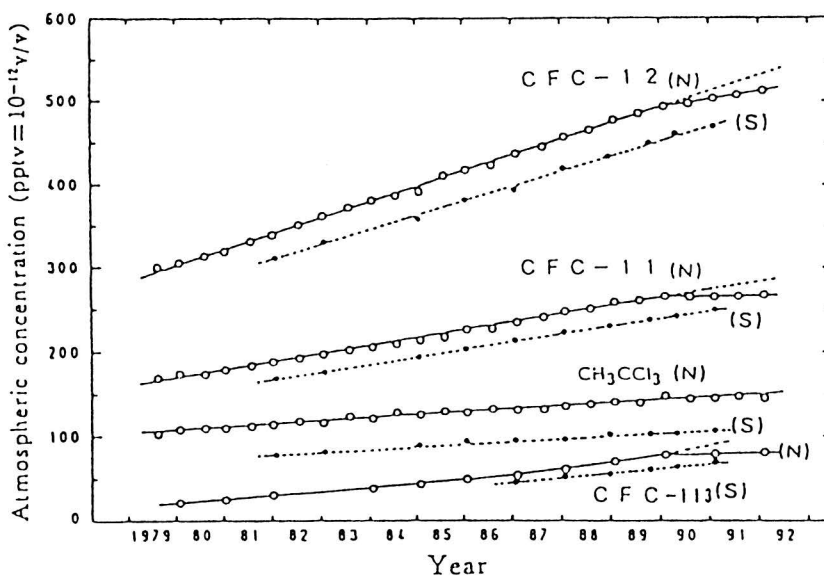

Fig. 2 Observed atmospehric concentrations of major halocarbons in the mid-latitude Northern Hemisphere (N: Hokkaido) and Southern Hemisphere (S: Antarctica) (Ref. 9~12,15).

to estimate their global concentrations. In Fig. 2 are represented the atmospheric concentrations of major chloro-fluorocarbons both in the northern hemisphere (Hokkaido) and in the southern hemisphere (Syowa Station in Antarctica). The chlorofluorocarbon concentrations observed in Antarctica have been 8~10 % lower than those in Hokkaido in accordance with the predominant emission of chlorofluorocarbons in the northern hemisphere and the delay time (1~2 years) for their diffusion into the southern hemisphere across the Intertropical Convergence Zone. For CFC-113, which was growing much faster than CFC-11 and CFC-12, the difference between concentrations in the northern and the southern hemisphere was larger (~20 %) than those for CFC-11 and CFC-12, reflecting a very rapid increase in its production/ emmission during 1980's.

The global tropospheric concentrations of CFC-11, CFC-12 and CFC-113 can be obtained as the average of their concentrations in either hemisphere, respectively. While the chlorofluorocarbons' concentrations in the northern hemisphere now start leveling off, thier concentrations in the southern hemisphere still keep growing constantly. Accordingly, their global tropospheric concentrations are increasing by 1~2 % a year and then are expected to reach the maximum, or level off, within a few years. Their stratospheric concentrations will reach the maximum several years later, or nearly in the year 2000.

The atmospheric concentration of methyl chloroform (CH_3CCl_3) has been increasing by about 3% a year; its concentration has been nearly 30% lower in Antarctica than in Hokkaido in accordance with its relatively short atmospheric lifetime (6~7 years) due to the reaction with tropospheric OH radicals. The atmospheric concentration of carbon tetrachloride increases rather slowly (by 1% a year, or less).

Effect of Montreal Protocol and Future Prospects of Chlorofluorocarbons' Concentrations

An international approach to protection of the stratospheric ozone layer was initiated by UNEP as early as in 1980, and resulted in adoption of the 'Vienna Convention for the Protection of the Ozone Layer' (1985) and the 'Montreal Protocol on Substances that Deplete the Ozone Layer' (1987). Based on the international agreement, the worldwide control of chlorofluorocarbon production/ consumption started in 1989: reductions in stages of chlorofluorocarbon production/consumption, to 50% of 1986 rates by 1998 (Fig. 3).

However, larger cuts in emissions of chlorofluorocarbons and other long-lived halocarbons were suggested as necessary owing to the remarkable progress in ozone science in the post-Protocol years. The Ozone Trends Panel (1987 ~1988) reanalyzed global ozone data and reported a downward trend in total

ozone in the northern hemisphere over the last two decades, suspecting the chlorofluorocarbons as its major cause. Over Antarctica, the 'ozone hole' has been steadily developing and ice-enhanced chemical reactions involving man-made chlorine have proved to be responsible for the ozone loss. In view of such observations of ozone depletion, a complete phase-out of chlorofluoro-carbons by the end of this century was proposed in 1989, and the following adjustments and amendment to the Montreal Protocol were adopted in 1990: reductions in stages ending with complete phase-out of chlorofluorocarbons, halons, and carbon tetrachloride by 2000 (and methyl chloroform by 2005). Moreover, it has been further agreed in November 1992 that the time limit for the phase-out should be moved up to 1996 in order to stop the ozone depletion as soon as possible (Fig. 3).

In evaluating the effects of such international regulations in the future, the atmospheric risk for ozone depletion was expressed in terms of the total chlorine (and bromine) concentration in the atmosphere as its surrogate (Fig. 4). After the complete phase-out of chlorofluorocarbons, the total chlorine concentration will reach its maximum and then start decreasing; the atmospheric risk (or ozone depletion) will be stalilized and then start decreasing very slowly down to the level where the ozone hole first appeared (2 ppbv). However, it will take several decades before the atmosphere (or ozone layer) eventually recovers that state.

Accurate monitoring of chlorofluorocarbons and other ozone-depleting substances becomes more and more important at this moment when we are approaching such a turning point. In the first place, it is useful for confirming whether we understand correctly their atmospheric lifetimes and behaviors on which the model calculations are based. Secondly, we can monitor and check if the worldwide control due to the Montreal Protocol works effectively, since annual emissions of chlorofluorocarbons may be estimated from the trends of their global concentrations. In fact, CFC-11 and CFC-12 emissions were estimated as being reduced by nearly 40% from 320,000 and 480,000 tons a year before 1989 to 190,000 and 310,000 tons a year after 1990 respectively; such an estimate is well compatible with reported reduction (about 40%) in world production in the meantime (1986 to 1990).

VERTICAL PROFILES OF CHLOROFLUOROCARBONS IN THE STRATOSPHERE

In order to obtain vertical profiles of chlorofluorocarbons, stratospheric/ tropospheric air samples were collected by means of balloon-borne grab-samplers launched from the Sanriku Balloon Center in collaboration with the Institiue of
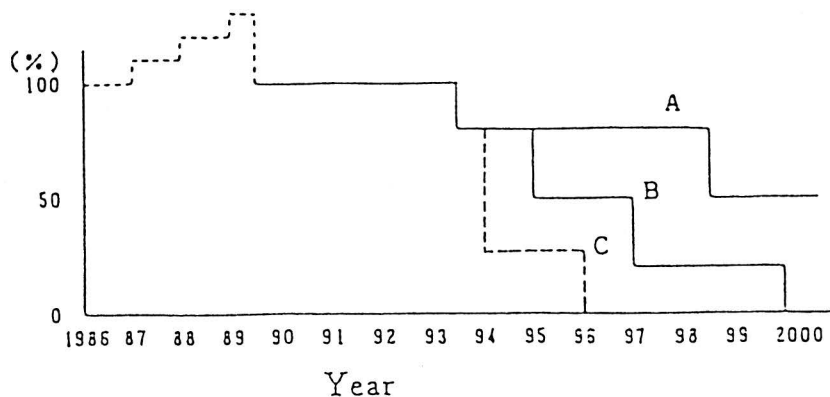
Fig. 3 Worldwide control of production/consumption of chlorofluorocarbons based on the original Montreal Protocol (**A**), its 1990 revisions (**B**), and 1992 revisions (**C**).
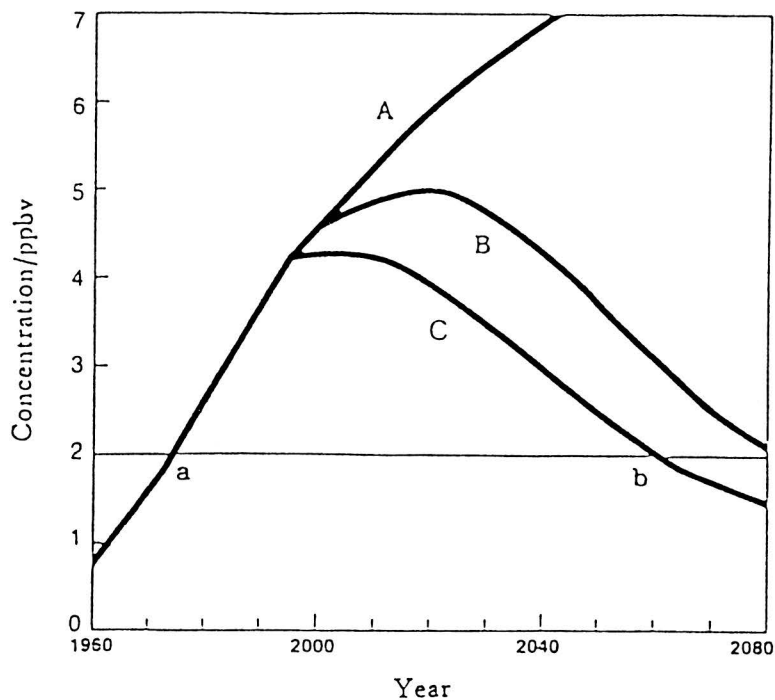

Fig. 4 Observed and projected chlorine abundances in the atmosphere based on the original Montrial Protocol (**A**), its 1990 revisions (**B**), and 1992 revisions (**C**). Antarctic ozone hole appeared at **a** and may disappear at around **b**. (Source: World Meteorological Organization)

Space and Astronautical Science. The mixing ratios of CFC-11 and CFC-12 were also determined by ECD gas chromatography (Fig. 5). While CFC-11 and CFC-12 were distributed uniformly in the troposphere, their mixing ratios decreased rapidly in the stratosphere because of the slow transport into the stratosphere and the photodissociation by solar UV radiation.

A balloon-borne cryogenic sampler (cooled by liquid helium) has been developed to collect sufficient amounts of stratospheric air samples at higher altitudes. The cryogenic sampling, together with other improvements in the analytical systems, has enabled us to determine concentrations of CFC-113 and other less abundant halocarbons in the stratosphere (Fig. 6).

The vertical profiles of chlorofluorocarbons demonstrate how effectively they undergo UV-photolysis to release chlorine atoms (equations (1) to (3)) and end up with depletion of the ozone layer in the stratosphere (equations (4) and (5)).

$$CCl_3F \quad \xrightarrow{UV} \quad CCl_2F + Cl \quad\quad (1)$$

$$CCl_2F_2 \quad \xrightarrow{UV} \quad CClF_2 + Cl \quad\quad (2)$$

$$CCl_2FCClF_2 \quad \xrightarrow{UV} \quad CClFCClF_2 + Cl \quad\quad (3)$$

The released chlorine atom in turn decomposes ozone catalytically via chain reaction, triggering the stratospheric ozone depletion:

$$Cl + O_3 \quad \rightarrow \quad ClO + O_2 \quad\quad (4)$$

$$ClO + O \quad \rightarrow \quad Cl + O_2 \quad\quad (5)$$

The above chain reaction is interrupted by the reactions of Cl and ClO with other chemical species such as CH_4, HO_2 and NO_2 to yield HCl, HOCl and $ClONO_2$ (i.e. chlorine reservoir compounds) which do not destroy ozone directly; thus stratospheric chlorine may generally spend most of its lifetime in the form of such reservoir compounds. In the stratosphere over Antarctica in winter, however, water vapor freezes and forms fine ice particles (polar stratospheric cloud, or PSC) at very low temperatures. On the surface of the PSC, inactive chlorine species (e.g. $ClONO_2$, or HCl) are converted effectively to active chlorine species (e.g. Cl_2, or HOCl), which then quickly decompose ozone on the return of the spring sun light. These ice-enhanced processes may have
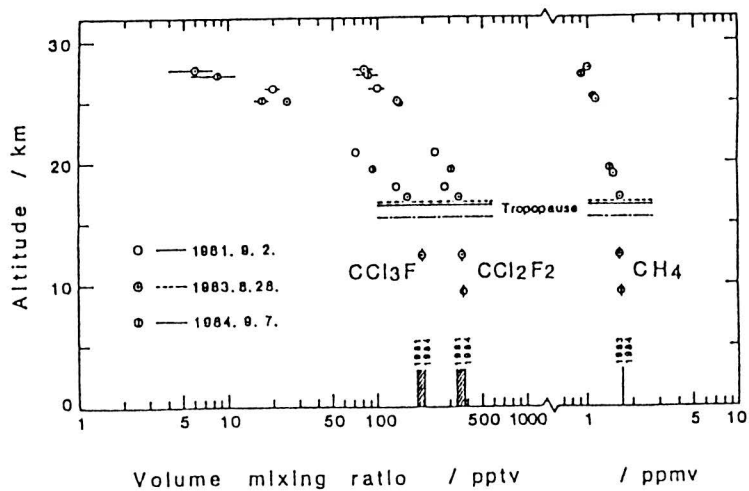
Fig. 5 Vertical profiles of CFC-11, CFC-12, and methane in the stratosphere and troposphere over Japan in summers 1981–1984 measured by grab-sampling (Ref. 11~13).
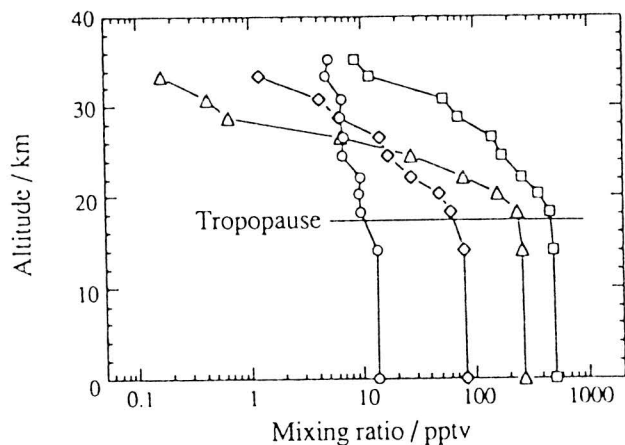

Fig. 6 Vertical profiles of chlorofluorocarbons in the stratosphere and troposphere over Japan (August 1991) measured by cryogenic sampling.

　　□ : CFC-12,　△ : CFC-11,　◇ : CFC-113,　○ : CFC-114.

played an important role in the rapid and extensive destruction of the ozone layer over Antarctica (Ref. 14).

Similar heterogeneous reactions are believed to take place on other types of aerosols such as nitric acid trihydrate and sulphate particles in the stratosphere, which may well account for substantial part of the stratospheric ozone loss over the Arctic and the temperate zone. Further studies of such heterogeneous reactions will be necessary for improvement of our understanding of global ozone depletion mechanisms.

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