Chlorofluorocarbons in the atmosphere: trends and vertical profiles

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Abstract – Chlorofluorocarbons with extremely long atmospheric
lifetimes are responsible for both stratospheric ozone
depletion and global warming as they accumulate in the
atmosphere. Their average atmospheric concentrations in the
northern/southern hemisphere have been monitored since 1979 in
order to study their behaviors and the future trends of their
concentrations in the atmosphere:
1. An extremely clean analytical system has been developed for
accurate analysis of atmospheric chlorofluorocarbons, carbon
tetrachloride, methyl chloroform and other halocarbons.
Atmospheric samples were collected at the surface level by
grab-sampling and analyzed by ECD gas chromatography.
2. The background atmospheric concentrations of CCl_3F (CFC-11)
and CCl_2F_2 (CFC-12) in the mid-latitude northern hemisphere
have been increasing by 4% a year over the past decade. The
concentrations of CFC-11 and CFC-12 observed in Antarctica
have been 8-10% lower than those observed in the northern
hemisphere in accordance with the predominant emission of
chlorofluorocarbons in the northern hemisphere and the delay
(~2 years) in their diffusion into the southern hemisphere
across the Intertropical Convergence Zone. The CCl_2FCClF_2
(CFC-113) concentration in the atmosphere tends to increase
much faster than those of CFC-11 and CFC-12.
3. The vertical profiles of chlorofluorocarbons in the
stratosphere have also been measured by means of balloon grab-
sampling and cryogenic sampling. They reflect how efficiently
these compounds undergo UV-photolysis to release chlorine
atoms and end up with depletion of the ozone layer in the
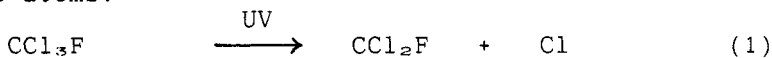stratosphere.

INTRODUCTION

Great concern has been felt about destruction of the stratospheric
ozone layer by very stable anthropogenic halocarbons (e.g.
chlorofluorocarbons) since the possible depletion of stratospheric
ozone by chlorofluoromethanes was first pointed out by Rowland and
Molina in 1974 (ref. 1). Extensive work has been done in the meantime
to confirm the possibility of ozone depletion by chlorofluorocarbons
and to assess the future environmental impact of the process. In fact,
such ozone loss has been observed recently in global trends of total
ozone (reported by the Ozone Trends Panel) as well as dramatic
depletion of the stratospheric ozone over Antarctica known as 'ozone
hole' (ref. 2). A very recent survey in the Arctic suggests that a
similar process may take place there, causing appreciable ozone loss.

Since chlorofluorocarbons cause stratospheric ozone depletion and
enhance the global warming, trends of their atmospheric concentrations
provide an important basis for assessing future global 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 (refs. 3-11). We have also been measuring vertical profiles of chlorofluorocarbons, which may reflect their photolytic behaviors in the stratosphere (refs. 11,12).

STRATOSPHERIC OZONE DEPLETION BY CHLOROFLUOROCARBONS

There is no removal process (sink) for chlorofluorocarbons (CCl_3F, CCl_2F_2, etc.) in the troposphere, and they accumulate in the atmosphere. After slow transport into the stratosphere, these molecules are decomposed by intense solar UV radiation to release chlorine atoms:

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

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

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

The released chlorine atom then decomposes ozone catalytically via chain reaction, leading to the depletion of the ozone layer:

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (4)$$

$$ClO + O \longrightarrow Cl + O_2 \qquad (5)$$
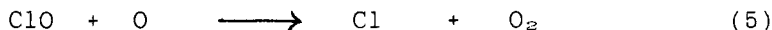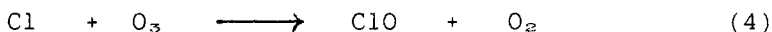
The essential part of reactions that take place in the stratosphere, involving chlorine, ozone and some other trace chemical species, is demonstrated schematically in Fig. 1.

In the stratosphere over Antarctica in winter, water vapor freezes to form fine ice particles (polar stratospheric cloud, or PSC) in the very low temperatures. On the surface of the PSC, inactive chlorine species (e.g. $ClONO_2$, or HCl) can be effectively converted to active chlorine species (e.g. Cl_2, or HOCl), which then quickly decompose ozone in the presence of solar radiation. Such ice-enhanced processes may have played an important role in the rapid and extensive destruction of the ozone layer over Antarctica (ref. 13).
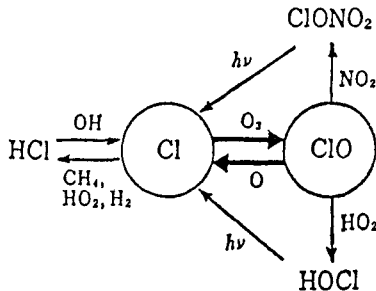

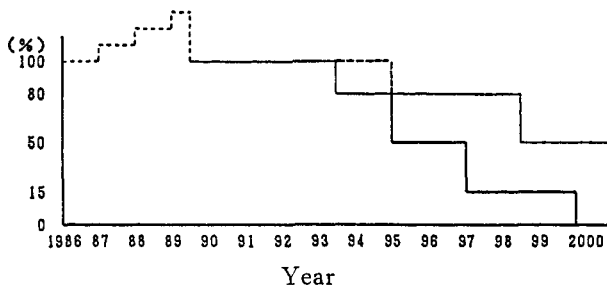Fig.1. Stratospheric ozone depletion by Cl-ClO chain reactions

Fig.2. Worldwide control of production/ consumption of chlorofluorocarbons based on the Montreal Protocol

—— : Current control schedule
——— : Newly adopted adjustments to the schedule

As a consequence of ozone depletion, more UV-B radiation penetrates through the ozone layer and reaches the surface of the earth. Increased UV-B levels on the earth will affect biological species: a typical example is the increase in incidence of skin cancer (ref. 14). The increase in chlorofluorocarbons in the atmosphere will have another global impact known as the greenhouse effect: together with other trace gases such as carbon dioxide and methane, chlorofluorocarbons also trap some of the infrared radiation escaping from the earth and thus contribute partially to the global warming.

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 international agreement, the worldwide control of chlorofluorocarbon production and consumption entered into force in 1989: reductions in stages of chlorofluorocarbon production/consumption, to 50% of 1986 rates by 1998 (Fig. 2).

However, even larger cuts in emissions of chlorofluorocarbons and other long-lived halocarbons have been suggested to be necessary as the result of 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, suggesting that chlorofluorocarbons are suspected as its major cause (ref. 2). Over Antarctica, an 'ozone hole' has been developing in the 1980s, 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 loss, a complete phase-out of chlorofluorocarbons 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).

Accurate monitoring of trace gases such as chlorofluorocarbons and halocarbons in the atmosphere has now become even more important as the emission of chlorofluorocarbons is being controlled and alternatives are being introduced.
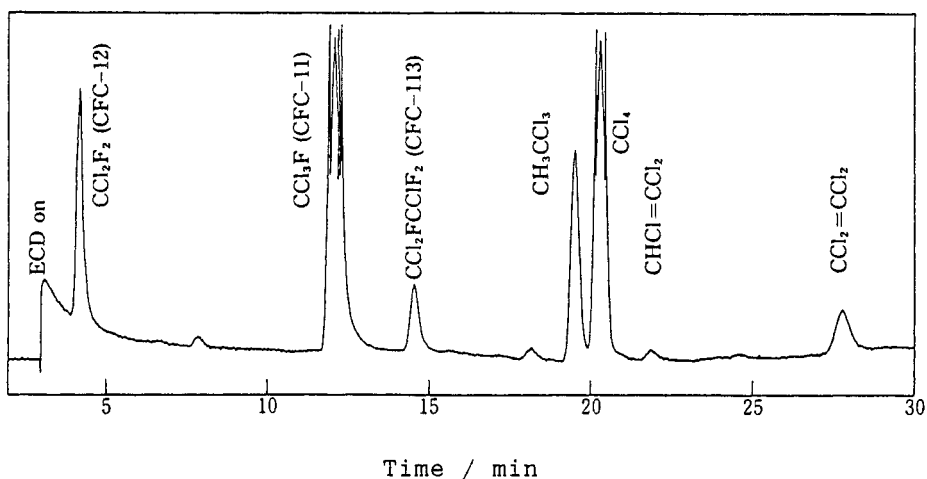

Time / min

Fig.3. Typical ECD chromatogram of a background atmospheric air sample collected at Nosappu-misaki in Hokkaido (January, 1988)

ULTRA-TRACE ANALYSES OF CHLOROFLUOROCARBONS AND HALOCARBONS IN THE ATMOSPHERE

An extremely clean, all-metal analytical system has been used for accurate measurements of atmospheric concentration of chloro-fluorocarbons (CFC-11, CFC-12, CFC-113, etc.), carbon tetrachloride, methyl chloroform and other halocarbons at the 10-400 pptv level with 0.5% precision. Atmospheric samples at the surface level were collected 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 a portion of the samples was analyzed by ECD gas chromatography in the laboratory. A typical gas chromatogram of a clean atmospheric air sample collected in Hokkaido is shown in Fig. 3.

TRENDS OF AVERAGE CONCENTRATIONS OF CHLOROFLUOROCARBONS IN THE TROPOSPHERE

In an extensive survey of sampling locations in 1979, it was difficult to avoid the influence of locally polluted air in the main and southern parts of Japan. For example, weekly measurements for 2 years in the Noto Peninsula indicate that chlorofluorocarbons and longer-lived halocarbons remain stably at low concentrations in winter, with its strong northwest winds from Siberia, while in summer their concentrations are often affected by local pollution (Fig. 4).

Thus we have collected clean, well-mixed air samples free of local pollution at remote locations in Hokkaido (Fig. 5) every summer and winter since 1979 so as to monitor average (or background) atmospheric concentrations of chlorofluorocarbons and halocarbons in the mid-lattitude northern hemisphere.

Figure 6 shows the background concentrations of chlorofluorocarbons and halocarbons in the atmospheric samples collected in Hokkaido since 1979. The concentrations of CCl_3F (CFC-11) and CCl_2F_2 (CFC-12) have been increasing almost linearly by 4% a year over a decade. However,
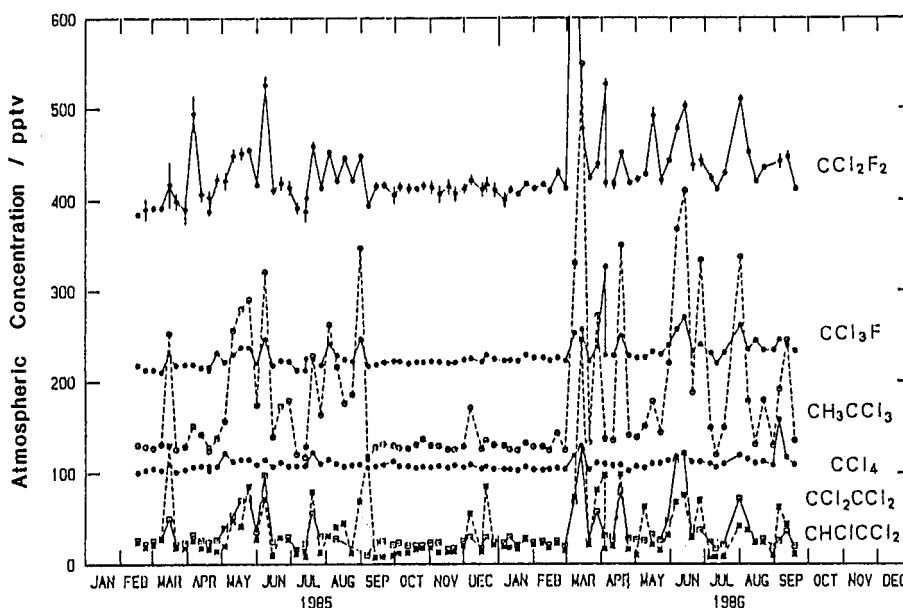

Fig.4. Weekly change of halocarbon concentrations observed in northwestern Noto Peninsula (January 1985 - December 1986)

it appears in Fig. 6 that the increasing rate has slowed somewhat very recently; whether this reflects reduced emission of these compounds due to the international controls (Fig. 2) is still uncertain.

Atmospheric samples have also been collected at nearby Syowa Station in Antarctica so as to clarify the behaviors and lifetimes of these compounds and to estimate their global concentrations. In Fig. 7 the concentrations of major chlorofluorocarbons in the northern hemisphere (Hokkaido) are compared with those in the southern hemisphere (Syowa Station in Antarctica). The chlorofluorocarbon concentrations observed in Antarctica have been 8-10% lower than those observed in Hokkaido in accordance with the predominant emission of chlorofluorocarbons in the northern hemisphere and the delay (1-2 years) in their diffusion into the southern hemisphere across the Intertropical Convergence Zone. It is also evident in Fig. 7 that the CCl_2FCClF_2(CFC-113) concentration tends to increase much faster (10-20% a year) than CFC-11 and CFC-12. The difference between
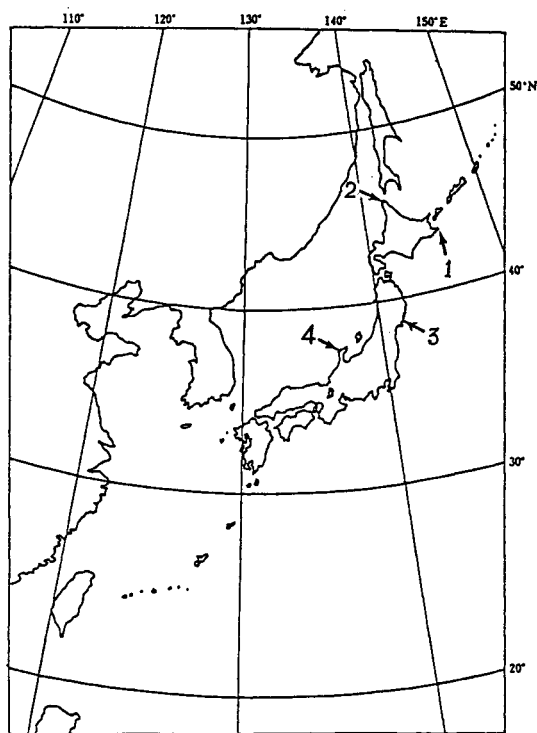

Fig.5. Sampling locations in Japan
1. Nosappu-misaki (Hokkaido)
2. Wakkasakanai (Hokkaido)
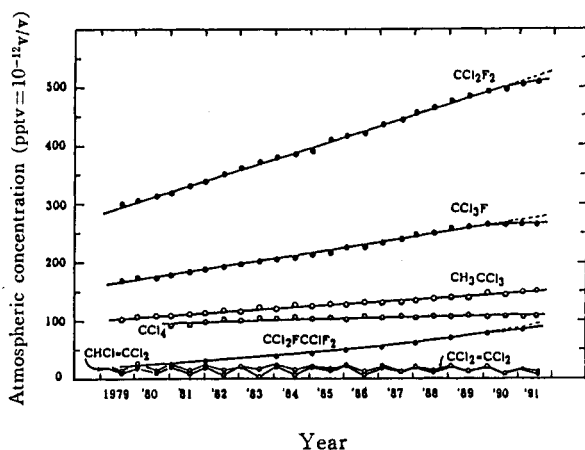3. Sanriku Balloon Center
4. Noto Peninsula

Fig.6. Surface level atmospheric concentrations of halocarbons in the mid-lattitude northern hemisphere (Hokkaido, Japan) for the period 1979-1991
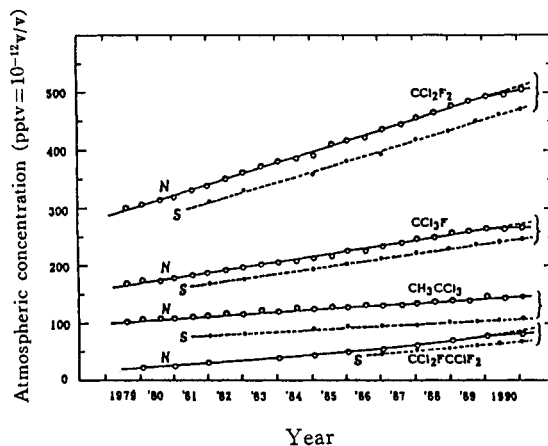

Fig.7. Surface level atmospheric concentrations of major chlorofluorocarbons in the northern hemisphere (Hokkaido, Japan) and the southern hemisphere (Antarctica)

N: Northern hemisphere
S: Southern hemisphere

concentrations observed in the northern and the southern hemisphere is also larger (-20%) for CFC-113, reflecting a very rapid increase in its production/emmission during the last several years. Thus the average (global) tropospheric concentrations of CFC-11, CFC-12 and CFC-113 were estimated to be 260, 480 and 70 pptv, respectively, in 1990.

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 relative 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).
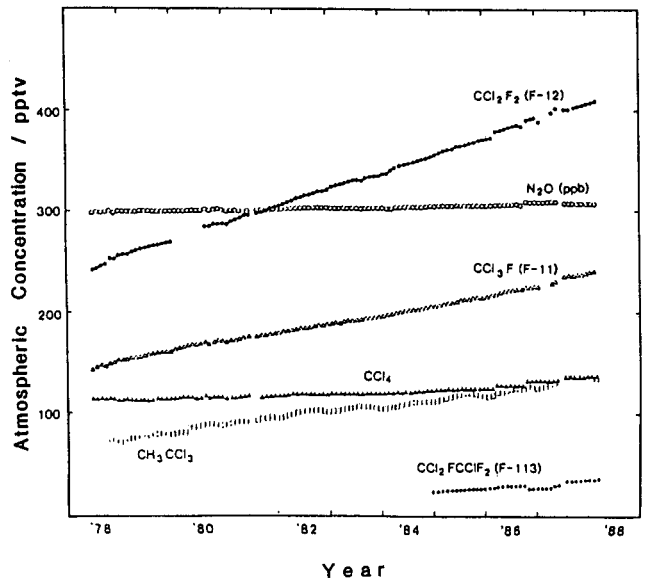

Fig.3. Concentrations of trace gases monitored at Cape Grim, Tasmania(ref.14)

Atmospheric concentrations of trace gases were also measured at ALE/GAGE stations. For instance, Fig. 8 demonstrates trace gas concentrations monitored by one of such stations at Cape Grim, Tasmania (ref. 14). While ALE/GAGE values for CFC-11 and CFC-12 concentrations are generally in agreement with our data, their values for CFC-113 concentration are nearly 30% lower than ours, possibly due to calibration problems in their measurements. Their values for carbon tetrachloride and methyl chloroform are overestimated possibly because of calibration difficulties: we have solved the problem by adding water vapor in the preparation of calibration standards (ref. 7).

VERTICAL PROFILES OF CHLOROFLUOROCARBONS IN THE STRATOSPHERE

In order to obtain vertical profiles of chlorofluorocarbons, stratospheric (and tropospheric) air samples were collected with a balloon-borne grab-sampler launched from the Sanriku Balloon Center in collaboration with the Institiue of Space and Astronautical Science. The mixing ratios of CFC-11 and CFC-12 were also determined by ECD gas chromatography (Fig. 9). 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.
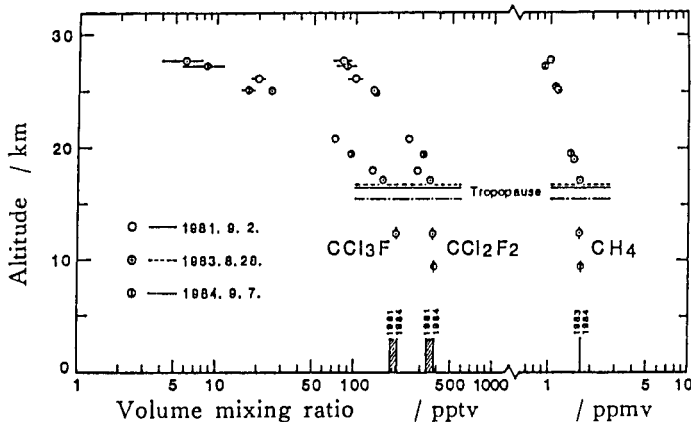

Fig.9. Vertical profiles of chlorofluorocarbons and methane in the stratosphere and troposphere over Sanriku in summers 1981-1984 (by grab-sampling)
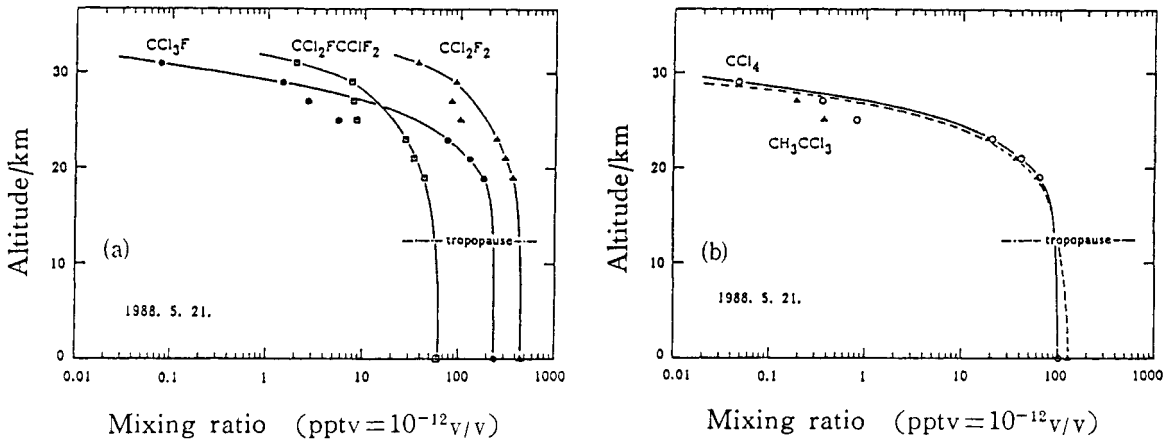
Fig.10. Vertical profiles of (a) chlorofluorocarbons and (b) carbon tetrachloride and methyl chloroform in the stratosphere over Sanriku in 1988 (by cryogenic sampling)

A balloon-borne cryogenic sampler (cooled by liquid helium) has been developed recently to collect sufficient amounts of stratospheric air samples at higher altitudes. The cryogenic sampling, together with other improvements in the analytical system, has enabled us to determine concentrations of CFC-113 and some other less abundant halocarbons in the stratosphere (Fig. 10).

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

FUTURE PROSPECT

Accurate monitoring of chlorofluorocarbons and other ozone-destroying compounds such as carbon tetrachloride and methyl chloroform has become more and more important since we are now approaching a turning point: the observed change in their increasing rates may reveal whether the atmospheric risk (in terms of organochlorine concentration as its surrogate) is being stabilized or reduced in accordance with the international controls (Fig. 11). Monitoring of alternatives (HCFCs, etc.) will also become important shortly since they may be partially responsible for the global warming or ozone depletion if they tend to accumulate in the atmosphere. Preliminary measurements of such compounds are also in progress in our laboratory.
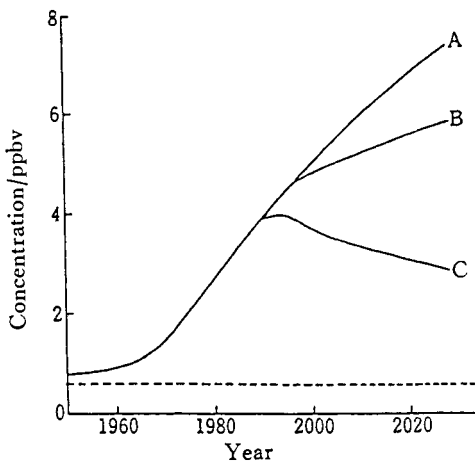

Fig.11. Calculated future organochlorine concentrations in the atmosphere according to the following chlorofluorocarbon (CFC) emission levels (by F. S. Rowland)

A: Constant CFC emissions at 1986 level

B: Stepwise reduction of CFCs down to 50% of 1986 level in 1998 (current Montreal Protocol)

C: Complete phase-out of CFCs, carbon tetrachloride and methyl chloroform by 2000 (revised Montreal Protocol)

REFERENCES

1. M.J. Molina and F.S. Rowland, Nature 249, 810-812 (1974).
2. Executive Summary of Ozone Trends Panel (1988).
3. Y. Makide, T. Tominaga and F.S. Rowland, Chem. Lett. 1979, 355-358.
4. Y. Makide, Y. Kanai and T. Tominaga, Bull. Chem. Soc. Jpn. 53, 2681-2682 (1980).
5. Y. Makide, Y. Kanai and T. Tominaga, Nippon Kagaku Kaishi 1981, 133-144.
6. Y. Makide, A. Yokohata and T. Tominaga, J. Trace Microprobe Tech. 1, 265-292 (1982/1983).
7. A. Yokohata, Y. Makide and T. Tominaga, Bull. Chem. Soc. Jpn. 58, 1308-1314 (1985).
8. Y. Makide, Y. Kubo, A. Yokohata and T. Tominaga, Mem. Natl. Inst. Polar Res., Spec. Issue No. 45, 94-95 (1986).
9. Y. Makide, A. Yokohata, Y. Kubo and T. Tominaga, Bull. Chem. Soc. Jpn. 60, 571-574 (1987).
10. Y. Makide, Y. Kubo and T. Tominaga, Proc. NIPR Symp. on Polar Meteorology and Glaciology No. 1, 146 (1987).
11. T. Tominaga and Y. Makide, Nippon Kagaku Kaishi 1991, 351-357.
12. Y. Makide, A. Yokohata, T. Tominaga, H. Honda, H. Kubo and T. Itoh, Bull. Chem. Soc. Jpn. 60, 1540-1542 (1987).
13. S. Solomon, Nature 347, 347-354 (1990).
14. UNEP: Scientific Assessment of Stratospheric Ozone 1989 (1990).