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Atmospheric Concentrations of Halocarbons in Japan in 1979—1986

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The average atmospheric concentrations of halocarbons in the mid-latitude Northern Hemisphere have been measured accurately for 7 years from 1979 to 1986. Atmospheric samples were collected in summer and winter in Hokkaido (40—45°N), and the halocarbons at 10—400 pptv (pptv=10^{-12} v/v) concentrations were determined with 0.5% precision. The concentrations of halocarbons with long lifetimes have been increasing steadily (CCl_2F_2: 18 pptv/year, CCl_3F: 8—9 pptv/year, CH_3CCl_3: 4 pptv/year, CCl_4: 2 pptv/year); those of short-lived halocarbons ($CHCl{=}CCl_2$ and $CCl_2{=}CCl_2$) are low (<25 pptv) and show only seasonal variations.

A great concern has been shown for the change in the Earth's environment caused by increasing atmospheric concentrations of trace gases released by human activities. Among them, two groups of compounds should be watched most carefully: CO_2 which causes "greenhouse effect" as released in huge amounts,[1] and halocarbons (halogenated hydrocarbons) with extremely long atmospheric lifetimes, which cause depletion of the stratospheric ozone.[2]

Since the possibility of stratospheric ozone depletion by chlorofluoromethanes (CCl_2F_2 and CCl_3F) was pointed out in 1974,[3] extensive efforts have been made to assess the effect in the future.[2,4] The depletion of ozone in the middle and upper stratosphere has been detected recently.[4]

Halocarbon concentrations in the atmosphere were measured since 1978 at ALE (Atmospheric Lifetime Experiment) stations in Ireland (52°N, 10°W); Oregon, USA (1980—, 45°N, 124°W); the Barbados (13°N, 59° W); American Samoa (14°S, 171°W); and Tasmania (41° S, 145°E), and the data observed up to 1981 have been published.[5] However, such measurements had calibration problems,[6] and no systematic measurement of the atmospheric concentrations has been attempted in Asia. Furthermore, reliable statistics of the world production and emission of halocarbons is hardly available.[7] Since the comparison of models and measurements has shown some disagreements,[4] accurate monitoring of the atmospheric halocarbon concentrations has become more and more important.

In view of such a situation, we started measuring the average atmospheric concentrations of halocarbons in 1979 by analyzing atmospheric samples collected in Hokkaido in summer and winter. The preparation of primary standards was improved, and calibration was repeated carefully. In this paper we wish to report definite atmospheric halocarbon concentrations based on carefully established calibration standards and the trends in their concentrations over the 7 years from 1979 to 1986.

Experimental

Analytical System and Calibration. We have developed an extremely clean, all-metal analytical system for accurate measurement of ultratrace amounts of CCl_2F_2, CCl_3F, CH_3CCl_3, CCl_4, $CHCl{=}CCl_2$, and $CCl_2{=}CCl_2$ at 10—400 pptv (pptv: parts per trillion by volume, 10^{-12} v/v) concentration level in the atmosphere.[8,9] A new technique of preparing primary calibration standards was developed for relatively unstable compounds, such as CH_3CCl_3 and CCl_4.[10]

A portion of the atmospheric sample or the standard sample was introduced into an evacuated sample loop (50 ml) up to a pressure of about 1/3 atm and then transferred into a gas chromatograph. A Silicone OV-101 column was used as the preconcentration/separation column with the temperature programmed from −40 to 70 °C. Each halocarbon thus separated was determined by means of an electron capture detector. Methane was mixed into the extremely pure nitrogen carrier gas flow as a make-up gas just before the detector in order to improve the S/N ratio.

The primary calibration standard for each compound was carefully prepared by three-step static dilution with highly purified zero air to a concentration close to the atmospheric concentration. Zero air saturated with water vapor at room temperature was introduced into the flask before the final dilution step so that the water-vapor pressure in the primary standards eventually became about 1 kPa. Several ambient air samples stored in large sample containers were calibrated for all components against each primary standard; they were then used as the secondary standards in routine analysis.

Atmospheric Sampling. All samples were collected by grab-sampling in highly evacuated, extremely clean, all-stainless steel canisters (of two-liter volume and equipped with a stainless-steel bellows valve). In the field, sample air was introduced into the canister up to the ambient pressure by simply opening the valve; no pump or compressor, which would inevitably cause contamination, was employed.

Sampling locations in Japan were extensively surveyed in 1979: in the main and southern parts of Japan, it was found difficult to avoid the influence of regionally polluted air from Japan or Korea.[8] Thus we have collected well-mixed air free from local pollution (called averaged-concentration air, or background air) on a remote coast or point of land mainly in Hokkaido (but occasionally on the west coast of the Tohoku area) every summer (late July to early August) and winter (late January to early February) since 1979. Typical sampling locations are Wakkasakanai in Moor Sarobetsugenya (45°N, 142°E), Nosappu-misaki Point (43°N, 146°E), Setana in Oshima Peninsula (42°N, 140°E), and Nyudozaki Point (40°N, 140°E). Samples were collected against the wind blowing from the ocean.

While the weather conditions are relatively stable in winter (i.e., a high atmospheric pressure overlying Siberia and a low atmospheric pressure overlying the North-west Pacific

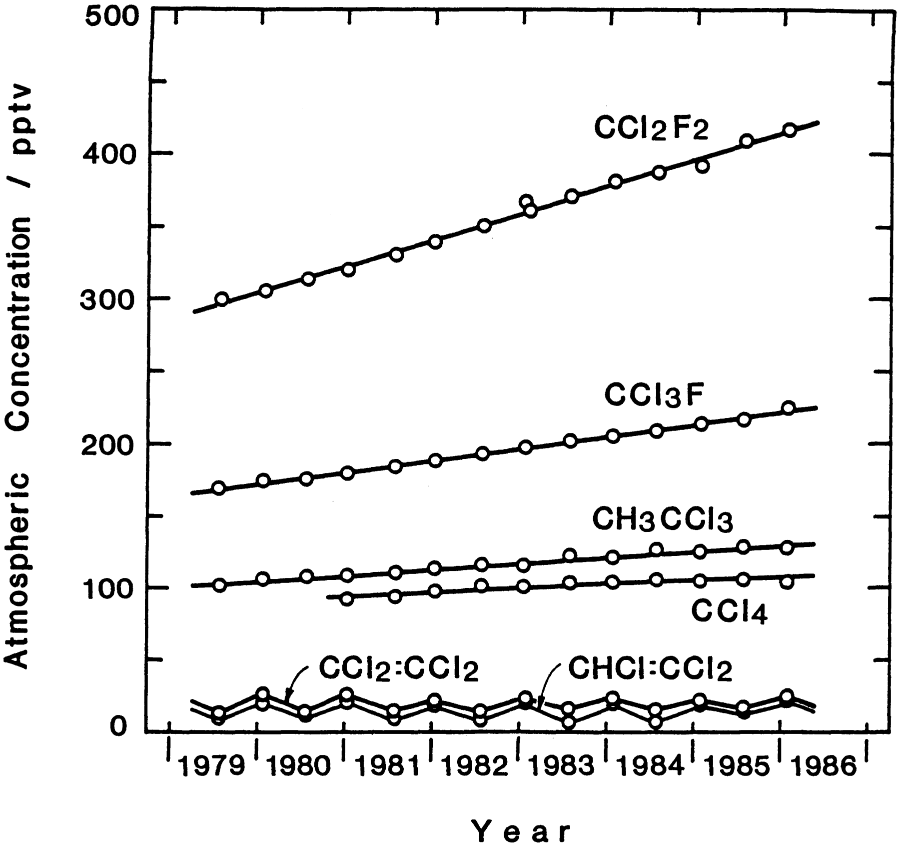

Fig. 1. Atmospheric concentrations of halocarbons in the mid-latitude Northern Hemisphere observed in Hokkaido (40—45°N) in 1979—1986. (pptv=10^{-12} v/v in dry air).

Ocean, causing strong west wind), they are changeable in summer according to the strength of the high atmospheric pressure over the Pacific Ocean. Thus, higher- or lower-latitude air was sometimes collected depending on the distribution of atmospheric pressure. All the collected samples were analyzed in our laboratory at the University of Tokyo within a few weeks of sampling.

Results and Discussion

Analysis. The primary standards for CCl_2F_2, CCl_3F, CH_3CCl_3, and CCl_4 were carefully prepared in different ways and repeatedly, and the concentration of each compound in a secondary standard was determined one by one. The calibration values for these compounds were determined definitely.

The precision of the measurement was within 0.5% at 100 pptv concentration level. The constancy of the calibration was often checked by using the same vacuum-line system and by analyzing several stored ambient air samples which contained enough water vapor to keep most components unchanged.

Trend of Halocarbon Concentrations Observed in Hokkaido. The atmospheric concentrations of CCl_2F_2, CCl_3F, CH_3CCl_3, CCl_4, $CHCl{=}CCl_2$, and $CCl_2{=}CCl_2$ observed in Hokkaido since 1979 are shown in Fig. 1.

The concentrations of CCl_2F_2, CCl_3F, and CH_3CCl_3 have been increasing almost linearly during the present period except for small fluctuations depending on the year, possibly due to the meteorological conditions and the limited number of samples. It is not clear whether or not such 2—3-year trends really reflect the variation in emission in the corresponding period.

The observed concentrations of CCl_2F_2 and CCl_3F at the end of January, 1986, were 417 and 225 pptv respectively. Our data of CCl_2F_2 and CCl_3F concentrations in 1980 agree reasonably well (within a possible range of accuracy: 4—5%) with those of the ALE measurements.[5] The increments of the CCl_2F_2 and CCl_3F concentrations we observed in the 6.5-year period were about 117 pptv (i.e., 18 pptv/year) and 56 pptv (i.e., 8.6 pptv/year) respectively; these values correspond to annual increase rates of 6.0 and 5.1% of the 1979 concentrations, or to those of 4.4 and 3.8% of the 1986 concentrations.

While the Chemical Manufacturers Association (CMA) gave estimates of world production and emission for CCl_2F_2 and CCl_3F up to 1982, it then discontinued the world estimates because of the alleged difficulty in estimating the production in the USSR and in Eastern European countries. The CMA data on CCl_2F_2 reported in 1981 were, however, revised upward in the following year,[7] corresponding to the comments that the observed atmospheric concentrations were much higher than those expected from the 1981 CMA emission values.[11] The CMA attributed the revised amount mainly to unknown USSR emission.

In the 1980's, the world production of CCl_2F_2 and CCl_3F appears to have been roughly constant, or to be gradually increasing.[12] Even if the current emission level is maintained constant in the future (a very conservative assumption), the atmospheric concentrations of CCl_2F_2 and CCl_3F will keep increasing up to above 3000 and 1000 pptv respectively. If the emission of these halocarbons increases, as has been reported recently, the concentrations will become extremely high in the future[13] and a catastrophic change in the ozone layer can be anticipated.[14] The greenhouse effect is also predicted as a result of the strong IR absorption of halocarbons not overlapping with CO_2 absorption bands.[15]

The atmospheric concentration of CH_3CCl_3 has been increasing by about 4 pptv/year, reaching about 130 pptv in 1986. While the production and atmospheric release of CH_3CCl_3 (about 500 kilotons/year) exceed those of CCl_2F_2 and CCl_3F, the increment in its atmospheric concentration is smaller because CH_3CCl_3 is decomposed, mainly by the reaction with OH in the troposphere, and so has only a 6—7 year lifetime.[16]

The atmospheric concentration of CCl_4 increases rather slowly (about 2 pptv/year) because of its large accumulation in the atmosphere as a result of prolonged use since the 1920's, a smaller amount of release (about 100 kilotons/year) in recent years, and its lifetime of about 30 years.[10]

While our data on CCl_2F_2 and CCl_3F concentrations for the 1979—1981 period are similar to the ALE data, the CH_3CCl_3 and CCl_4 values were both about 30% lower than the ALE's.[5] Such large discrepancies in the observed CH_3CCl_3 and CCl_4 concentrations may be attributed to the calibration difficulties in their data, as we have previously pointed out.[6,10] Our new calibration method has solved the problem by adding water vapor in the preparation of standards for CH_3CCl_3 and CCl_4: otherwise, these compounds are readily adsorbed on the vessel's inner wall in extremely pure, dry gases in primary standards, thus mistakenly leading to apparently low concentrations in the standards and, consequently, high atmospheric concentrations, as might be the case with the ALE measurements.

While the $CHCl{=}CCl_2$ and $CCl_2{=}CCl_2$ concentrations in Tokyo often exceed 1000 pptv, those observed in Hokkaido were below 25 pptv, according to their short lifetimes (of a few weeks to a few months) in the troposphere; also, they showed seasonal variation (i.e., they were high in winter and low in summer). This seasonal variation in concentrations may reflect the seasonal difference in the photochemical activity (i.e., the higher OH radical concentration and faster reaction rate in summer) or a difference in the longitudinal transport of air masses from Europe to Hokkaido in the mid-latitude Northern Hemisphere (i.e., faster in winter than in summer). Such an obvious seasonal variation in $CHCl{=}CCl_2$ and $CCl_2{=}CCl_2$ concentrations has not been reported before. By analyzing the seasonal variation coupled with meteorological data, useful information regarding the photochemical activity and/or the global circulation of air masses can be obtained.

In addition to the halocarbons mentioned above, we have also observed other halocarbons, such as $CClF_2CClF_2$, CCl_2FCClF_2, and $CHCl_3$, in the same analytical run,[8,9] although their concentrations have not been determined quantitatively (because of the low concentration, contamination, or instability). CCl_2FCClF_2 has recently been increasingly used for cleaning fine electronic parts, etc. The stainless steel bellows valves of our sample canisters (Nupro SS-4H) had also been washed with this solvent (a standard procedure for meeting NASA specifications). Since we noticed that the CCl_2FCClF_2 concentration increased gradually and slightly in stored samples, even in carefully prepared sample canisters, we discontinued the quantitative determination of the CCl_2FCClF_2 concentration. However, its concentration in freshly collected samples has also been increasing because of its long atmospheric lifetime exceeding several decades.

The contamination of underground water with $CHCl{=}CCl_2$ and $CCl_2{=}CCl_2$ released by the semiconductor industry or dry cleaning has recently been observed in the USA and Japan, and more stable chlorofluorocarbons (e.g., CCl_2FCClF_2) have been proposed as substitutes for such unstable chlorocarbons. Although CCl_2FCClF_2 might be less toxic for human bodies if uptaken, it will instead contribute to the depletion of stratospheric ozone, as does CCl_2F_2. Accordingly, the use of halocarbons with extremely long lifetimes should be strictly checked for the protection of the Earth's atmosphere.

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