Rapidly Increasing Concentrations of CFC Alternatives (HFC-134a, HCFC-141b, and HCFC-142b) in the Atmosphere as Observed in Hokkaido and Antarctica

Tomoko Shirai and Yoshihiro Makide
Radioisotope Center, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113-0032

(Received January 19, 1998; CL-980042)

Sharply increasing trends were observed for recent atmospheric concentrations of CFC alternatives by GC/MS analysis of samples collected in Hokkaido, Japan and Syowa Station, Antarctica. These trends were consistent with those calculated based on the world production/release statistics for HFC-134a and HCFC-141b, but inconsistent for HCFC-142b, suggestive of some inaccurate release estimations.

Hydrochlorofluorocarbons (HCFCs) containing carbon-hydrogen bonds are subject to OH radical attack in the troposphere resulting in shorter atmospheric lifetimes and a fairly reduced potential for stratospheric ozone depletion compared to ozone-depleting chlorofluorocarbons (CFCs). Hydrofluorocarbons (HFCs) with no chlorine atoms are not involved in the ozone depletion.

HFC-134a (CH_2FCF_3) and HCFC-142b (CH_3CClF_2) have been used as alternatives to CFC-12 (CCl_2F_2). HCFC-141b (CH_3CCl_2F) is primarily an alternative to CFC-11 (CCl_3F) and partly an alternative to CFC-113 (CCl_2FCClF_2). The use of these compounds was relatively newly developed and their productions are sharply increasing among the CFC substitutes.[1]

However, the production of HCFCs has been capped since 1996 and is scheduled to be phased out by 2020 in developed countries by the revised Montreal Protocol on Substances That Deplete the Ozone Layer due to their small but relatively high short-term ODPs.[2] On the other hand, the production and release of non ozone-depleting HFCs will be controlled by international regulation for the prevention of global warming[3] in the coming years due to their relatively high potential for global warming. While it is important to assess their affects on the global environment, only a few measurements[4-9] have been reported.

We developed an analytical system for the accurate determination of trace amounts of these HCFCs and HFCs in the atmosphere at the pptv level (pptv = 10^{-12} v/v). By analyzing the stored atmospheric samples collected in Hokkaido and Antarctica, a time series of the tropospheric concentrations of HFC-134a, HCFC-141b and HCFC-142b in the mid/high-latitude Northern Hemisphere (NH) and the high-latitude Southern Hemisphere (SH) were obtained. The observed results were compared with the anticipated tropospheric concentrations which we calculated by a two-box model based on the atmospheric release estimations reported by AFEAS.[1]

The analytical system consists of a stainless steel vacuum line for sample introduction and a capillary gas chromatograph-mass spectrometer (GC/MS) for the separation and determination of HCFCs and HFCs. A 100 - 400 ml air sample was cryogenically preconcentrated prior to GC separation. A detailed procedure is published elsewhere. Atmospheric samples were collected by grab-sampling in 2 or 12 L stainless-steel canisters on a remote coast or points in Hokkaido, Japan (42-45°N, 140-146°E) and at Syowa Station, Antarctica (69°S, 40°E).

The calibration standards were prepared from 1 ppmv standard gases by a two-step static dilution using different vacuum lines according to the concentration levels. The final concentrations of the standard gases were around 10 pptv. Several ambient air samples in large canisters were calibrated and used as secondary standards in the measurements.

Figure 1 shows the observed HFC-134a tropospheric concentration since 1994. HFC-134a, which is exempt from the Montreal Protocol, is mainly used as a CFC-12 substitute refrigerant in the air conditioning of automobiles and in refrigerators. The rapid shift from CFC-12 to HFC-134a has taken place since 1990 and the production of HFC-134a has continued to grow rapidly. The atmospheric concentration of HFC-134a showed the most rapid growth among the major CFC substitutes: a global mean growth rate at 83 ± 6% yr^{-1} for the period from July 1994 to January 1997 by an exponential fitting of the data. The global mean atmospheric concentration in January 1997 was 5.9 ± 1.2 pptv.

Based on the release estimation data in the AFEAS report[1] and its atmospheric lifetime,[2] the anticipated concentrations of HFC-134a (dashed lines in Figure 1) were calculated for mid/high latitudes in the both hemispheres by the 2-box model adopting longer interhemispheric exchange time. The atmospheric concentrations were observed about half a year ahead of the statistical estimations, possibly suggesting its shorter term release. Since HFC-134a is mainly used as CFC-12 substitute in automobile air conditioning and its release into the atmosphere will supposedly occur in about a decade, the currently observed

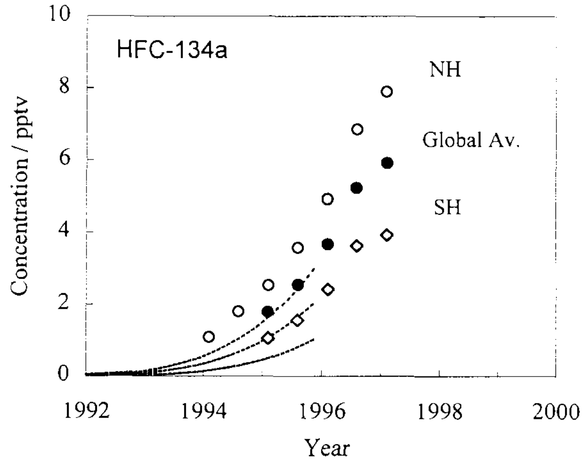

Figure 1. Observed atmospheric concentrations of HFC-134a in the Northern Hemisphere (○: Hokkaido) and the Southern Hemisphere (◇: Syowa Station), and their global average (●). Dashed lines represent corresponding concentrations anticipated by a 2-box model calculation based on the statistics of world production and release estimation data.[1]

growth of the atmospheric concentration will thus continue for at least a few decades until a new compound/technique or complete recovery system is established. Long term monitoring hereafter will be important to estimate the change of atmospheric HFC-134a in the future and make adequate policies about its regulation.

Figure 2 shows the observed tropospheric concentrations of HCFC-141b since 1994 with estimates from the AFEAS release data.[1] The atmospheric concentration of HCFC-141b has shown a non-linear growth: a global mean growth rate at 63 ± 9% yr^{-1} for the period from July 1995 to January 1997 by an exponential fitting of the data. Its global mean atmospheric concentration in January 1997 was 5.7 ± 0.6 pptv.

The concentrations calculated agreed with those observed within the analytical error, which means that the AFEAS estimation[1] is reasonable up to a point in the case of HCFC-141b. Production of HCFC-141b has shown a sharp increase since the early 1990's. Since HCFC-141b contained in a closed-cell foam as a substitute of CFC-11 is released to the atmosphere very slowly, the recently seen rapid increasing trend can be accounted for by HCFC-141b replacing the CFC-113 in solvent use which is released to the atmosphere in much shorter period.

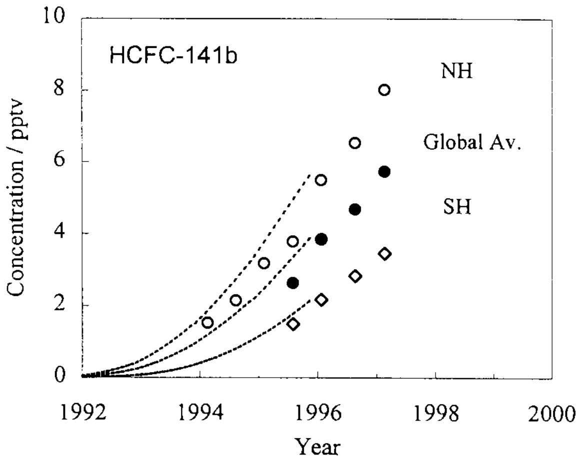

Figure 2. Observed atmospheric concentrations of HCFC-141b. Symbols and lines are as described in Figure 1.

Figure 3 shows the observed tropospheric concentrations of HCFC-142b since 1993. The global mean atmospheric concentration of HCFC-142b in January 1997 was 10.4 ± 1.1 pptv. The globally averaged growth rate for the period 1995-1997 was 1.6 ± 0.1 pptv yr^{-1} by a linear fitting or 20 ± 0.4% yr^{-1} by an exponential fitting of the data. The higher atmospheric concentrations and smaller growth rate of HCFC-142b compared with HFC-134a and HCFC-141b are corresponding to its use, which began about 10 years ahead of the other two and has not grown as remarkably as those compounds that have appeared recently.

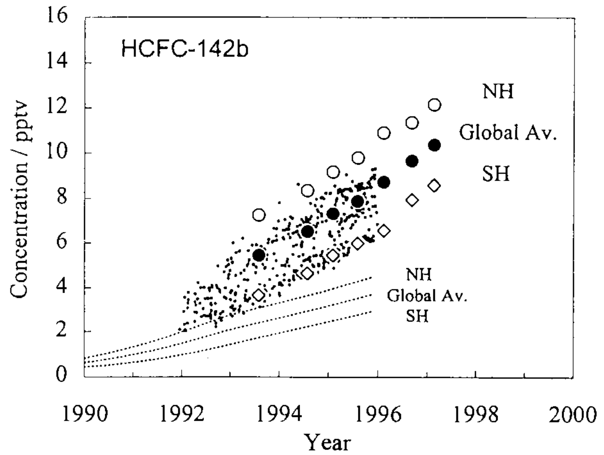

Figure 3. Observed atmospheric concentrations of HCFC-142b. Symbols and lines are as described in Figure 1. Observation made by NOAA group[10] at seven sampling sites is plotted with small dots.

In the case of HCFC-142b, our measurements gave values of more than 2 times higher than those calculated from data based on the release estimation by Midgley and Fisher in the AFEAS report.[1] The large differences between concentrations observed and those calculated cannot be explained by only unreported production and/or the time lag between production and release. Since the NOAA group has also shown similar concentrations (small dots in Figure 3), this discrepancy cannot be explained by calibration problems, either. Our result thus indicates that this compound is released to the atmosphere over a much shorter period than estimated by Midgley and Fisher.[1] The uncertainties are supposed to lie in the release estimation of long-term use, into which most of HCFC-142b is categorized as a blowing agent for closed-cell foams. There are possibilities of underestimation of the release at early stages in the process of foam manufacturing. A higher release rate is also possible for some kinds of foam uses.

In the case of HCFCs used for blowing closed-cell foams like HCFC-141b and HCFC-142b, the release from such long-term use will continue over the next few decades from previously manufactured products and determine their atmospheric concentrations in the future as the phasing out of HCFCs proceeds. As the use patterns are various and changing, we should check carefully the correlation between the change of production statistics and the trends of their atmospheric concentrations to make the release patterns clearer and allow for a more accurate prediction of atmospheric concentrations in the future.

References and Notes

1 AFEAS, " Production, Sales and Atmospheric Release of Fluorocarbons through 1995", (1997).
2 World Meteorological Organization, "Scientific Assessment of Ozone Depletion: 1994", Report No. 37 (1995).
3 Kyoto Protocol to the United Nations Framework Convention on Climate Change (December 1997).
4 S. A. Montzka, R. C. Myers, J. H. Butler, and J. W. Elkins, *Geophys. Res. Lett.*, **21**, 2483 (1994).
5 S. M. Schauffler, W. H. Pollock, E. L. Atlas, L. E. Heidt, and J. S. Daniel, *Geophys. Res. Lett.*, **22**, 819 (1995).
6 D. E. Oram, C. E. Reeves, S. A. Penkett, and P. J. Fraser, *Geophys. Res. Lett.*, **22**, 2741 (1995).
7 S. A. Montzka, R. C. Myers, J. H. Butler, J. W. Elkins, L. T. Lock, A. D. Clarke, and A. H. Goldstein, *Geophys. Res. Lett.*, **23**, 169 (1996).
8 D. E. Oram, C. E. Reeves, W. T. Strurges, S. A. Penkett, P. J. Fraser, and R. L. Langenfelds, *Geophys. Res. Lett.*, **22**, 1949 (1996).
9 S. A. Montzka, J. H. Butler, R. C. Myers, T. M. Thompson, T. H. Swanson, A. D. Clarke, L. T. Lock, and J. W. Elkins, *Science*, **272**, 1318 (1996).
10 ftp data archive of NOAA/CMDL (URL:ftp://ftp.cmdl.noaa.gov/noah/hcfcs/hcfc142b/142B_MS.DAT).