Chlorine-Containing Gases in Antarctica

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Chlorine-containing gases in Antarctica

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In recent years, there has been considerable interest in chlorine-containing trace gases in the atmosphere, particularly in Antarctica because of the relationship between chlorofluorocarbons and the antarctic ozone hole. All chlorine-containing trace gases, whether produced by human activities or by natural processes, have a potential for destroying ozone in the stratosphere. This is a complex environmental problem, but it is clear that manmade chlorine-containing gases are the driving force behind the antarctic ozone hole and, by extension, reductions of stratospheric ozone over other parts of the world [World Meteorological Organization (WMO) 1989, 1991, 1995].

We have taken measurements of the major chlorine-containing gases in Antarctica for more than 20 years, first at Amundsen–Scott South Pole Station and more recently at Palmer Station (64.46°S 64.04°W). Here we report the results of this work. During recent years, major changes in the concentration of ozone-depleting compounds have taken place in Antarctica because of the Montreal Protocol, which is designed to phase out the production of chlorofluorocarbons and related compounds, to prevent the destruction of the ozone layer (WMO 1995).

The production and emissions of chlorofluorocarbons have been declining in recent years [Alternative Fluorocarbon Environmental Acceptability Study (AFEAS) 1997]. These changes are quite dramatic, and in the last year or so, the production of the major chlorofluorocarbons has fallen to between 10–20 percent of the peak values in the 1980s; emissions have fallen accordingly. These changes in industrial emissions are clearly observable in the antarctic atmosphere. The concentrations of many chlorine-containing compounds are either increasing very slowly compared to previous years or are decreasing. Consequently, for the first time in the 20 years of observations, the total chlorine concentrations in Antarctica have declined from one year to the next during the last 2 years. The trends we discuss for Antarctica are also representative of the global changes, although the magnitudes may be different at other latitudes.

Trends of chlorinated compounds in Antarctica

Chlorinated compounds can be classified as "reactive" or "unreactive." Reactive gases are taken to be those that are removed in the troposphere (approximately surface to 12 kilometers). Gases that are not removed in the troposphere have the greatest potential for destroying the ozone layer. Such gases are classified as unreactive.

"Reactive chlorine" gases are the following: methylchloroform (CH_3CCl_3) and chlorodifluoromethane ($CHClF_2$, F-22), which are entirely manmade, and methylcloride (CH_3Cl), which is thought to be mostly natural, but substantial amounts are known to be emitted from biomass burning. Small amounts of "other chlorine-containing gases" are also expected to exist in the antarctic atmosphere, namely trichloroethylene (C_2HCl_3), tetrachloroethylene (C_2Cl_4), chloroform ($CHCl_3$), dichloroethane ($C_2H_4Cl_2$), dichloromethane (CH_2Cl_2), and bromochloromethane (CH_2BrCl), because these have been measured at latitudes down to about 45°S. Many of these gases have some natural emissions, mostly from the oceans. All known natural emissions of chlorine-containing gases are from this group (Khalil in press).

"Unreactive" gases in the troposphere are dichlorofluoromethane (CCl_2F_2, F-12), trichlorofluoromethane (CCl_3F, F-11), carbon tetrachloride (CCl_4), and the fully halogenated ethanes ($C_2Cl_3F_3$, F-113; $C_2Cl_2F_4$, F-114; C_2ClF_5, F-115).

Figure 1*A* shows the chlorine composition for the antarctic atmosphere. It is determined as the concentration times

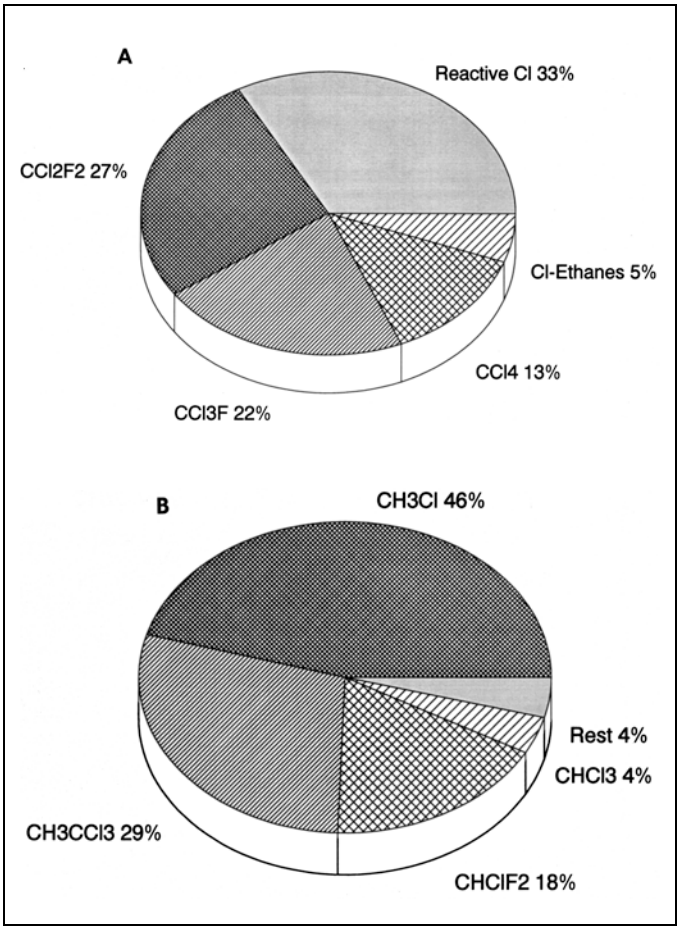

Figure 1. *A*. The distribution of chlorine in the gas phase in Antarctica. About two-thirds is from the manmade chlorofluorocarbons and at least half of the "reactive chlorine" group are also from human activities. The graph shows the concentration as the percent of chlorine contributed by each gas to the total chlorine composition of the antarctic atmosphere (see text). *B*. The reactive chlorine gases in the antarctic atmosphere. All known natural emissions of chlorine-containing gases are from this group.

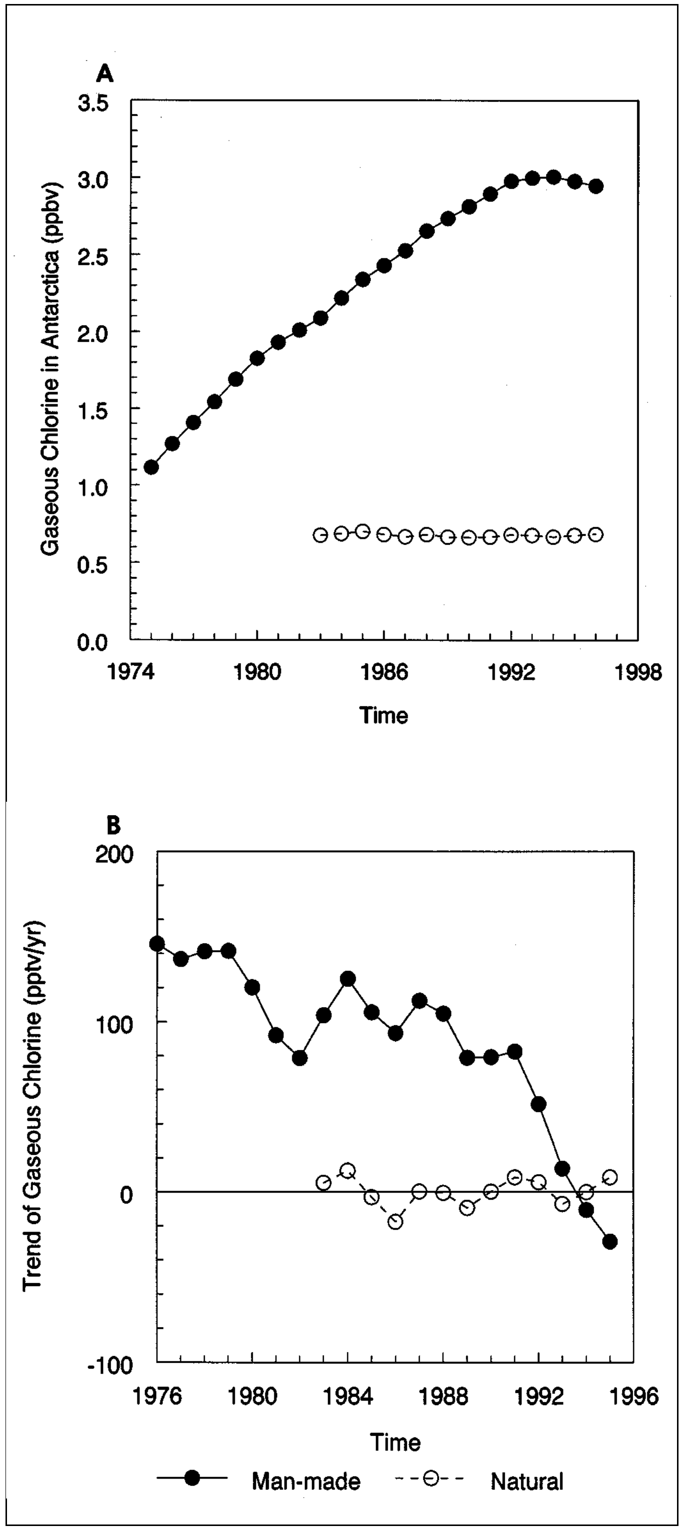

Figure 2. *A*. The 20-year record of total gaseous chlorine in Antarctica. Concentrations are in parts per billion (ppbv) chlorine. *B*. The rate of change (trend) of chlorine containing gases in parts per trillion per year (pptv/yr). During the last 2 years, the concentration of total chlorine has begun to drop in Antarctica.

the number of chlorine atoms in the molecule of the gas. The "reactive chlorine" component is further expanded in figure 1*B*. It is not clear as to how much gaseous chlorine comes from natural processes. There are, however, no documented natural sources of the unreactive compounds, and from the reactive chlorine group, there are no known natural sources of methylchloroform and chlorodifluoromethane, so at least 80–85 percent of the chlorine present in the antarctic atmosphere is of anthropogenic origins. The remainder is mostly methylchloride and chloroform, and there is about 50 parts per trillion by volume (pptv) of the "other chlorine-containing gases" mentioned above. We are designating these as "natural," although it is not proven to be so, and some may be manmade.The record of annually averaged concentrations of chlorine in the antarctic atmosphere is shown in figure 2*A* representing 20 years of observational data. It is determined as the sum of the concentrations of each gas times the number of chlorine atoms in each molecule of the gas and given in parts per billion. In figure 2*B*, we show the trends at year *t*, where trend $(t)=[C(t+1)+C(t-1)]/2$ in parts per trillion per year. Sources of data are Rasmussen and Khalil (1986), Khalil and Rasmussen (1992), and continuation of these experiments and Montzka et al. (1996) for $CHClF_2$. For F-113 and F-22, there are no measurements before 1986 and 1992, respectively. For the calculations here, concentrations were estimated by linear backward extrapolation based on the earliest 4 years of data. Concentrations of both these gases were small during the early periods and, thus, do not greatly affect the total chlorine shown here.

The results show a pattern that is being observed worldwide. Because most of the gases involved are produced in the middle northern latitudes, these changes are delayed at Antarctica by 1–2 years. Concentrations of methylchloroform (CH_3CCl_3), which has been used as a de-greasing solvent, are declining rapidly because it has a relatively short lifetime of about 6 years. Carbon tetrachloride, which was used for the production of fluorocarbons, is declining because these compounds are no longer being produced. The trend of F-11, one of the major chlorofluorocarbons implicated in the depletion of the ozone layer, is also beginning to decline. F-113 is no longer increasing in the atmosphere. Only chlorofluorocarbon-12 continues to increase, but the trend is much less than in previous years.

Conclusions

New chemicals are now being used instead of the chlorofluorocarbons we have discussed here. The main new compounds are HCFC-141b ($C_2H_3Cl_2F$), HCFC-142b ($C_2H_3ClF_2$), and HCFC 134a ($C_2H_2F_4$). These and $CHClF_2$ (F-22) are taking over the usages of chlorofluorocarbons in air conditioning, refrigeration, and blowing insulating foams and as solvents. These gases belong to the group of "reactive chlorine." Most of the emissions will be removed in the troposphere and will never reach the stratosphere where they may affect the ozone layer.

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