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Carbon monoxide in the antarctic atmosphere: Observations of decreasing concentrations

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vortex in November by continued monitoring of N₂O and O₃.

Finally, we have made an unsuccessful search for hydrogen peroxide (H₂O₂), resulting at least in a useful upper limit being placed for the first time on how much may be present in the polar night stratosphere.

In summary, we have obtained a large volume of unique data on several species (O₃, N₂O, HNO₃, NO₂, ClO, and H₂O₂) and have made some unanticipated observations that should prove to be of considerable significance in characterizing dynamical and chemical effects occurring in the heart of the antarctic winter vortex.

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Carbon monoxide in the antarctic atmosphere: Observations of decreasing concentrations

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Hydroxyl radicals remove hundreds, perhaps thousands, of organic gases from the atmosphere and are often regarded as an index of the oxidizing capacity of the Earth's atmosphere (Thompson 1992). In recent years, there have been growing concerns that, over the past century and now, human activities may be depleting hydroxyl concentrations by adding huge amounts of carbon monoxide and methane to the atmosphere. Reduction in the hydroxyl concentrations can then indirectly lead to more global warming, stratospheric ozone depletion, and other disturbances in atmospheric chemistry.

Carbon monoxide (CO) is a key component in the determination of hydroxyl radical (OH) concentrations: increases of CO would lead to a decline of OH. Global increases of CO had been observed in the 1980s (Khalil and Rasmussen 1985, 1988, 1990), but now it appears that the atmospheric concentrations of CO are falling. Here we will report data from Antarctica that suggest recent decreases in the concentration of CO.

Antarctic data are available between 1980 and 1992 from three experiments. Two experiments are part of our flask sampling program at the South Pole (90°S; 1983 to the present) and more recently at Palmer Station (64.46°S 64.05°W; 1988 to the present). The third experiment was conducted at Mawson Station (67.36°S 62.53°E; 1980–1984; Fraser et al. 1986). These experiments consist of taking (usually triplicate) flask samples, in specially prepared stainless steel containers, once a week. The samples are sent back to the laboratory to determine the concentrations of CO and other gases. For various reasons, samples are not available continuously or throughout the year from any of these sites; in fact, there are substantial gaps in the individual data sets. To determine trends and other features of trace gases in Antarctica, we first calculate monthly average concentrations. Concentrations of CO in Antarctica are reported in the table as a composite of the three experiments discussed above.

The salient features of these data are the seasonal cycles and trends as described below (from the table).

Carbon monoxide concentrations over Antarctica (in parts per billion by volume). (Dashes indicate data not available.)

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1980	—	—	32	35	—	44	—	43	52	—	44	—
1981	—	—	—	—	37	—	41	48	48	51	49	41
1982	30	27	—	—	—	—	—	—	—	—	—	—
1983	34	51	40	40	43	57	63	59	59	66	56	47
1984	40	34	31	39	—	44	54	56	50	51	46	42
1985	35	48	88	75	94	75	79	66	71	73	51	42
1986	38	49	62	41	62	46	62	70	62	65	53	39
1987	36	32	48	55	51	—	—	—	—	—	—	—
1988	—	62	60	61	51	60	63	58	64	64	66	44
1989	38	33	36	41	45	53	43	44	42	35	36	32
1990	33	34	30	34	32	33	36	39	44	44	41	38
1991	29	28	24	19	30	23	28	31	40	44	43	38
1992	28	24	26	26	30	34	38	39	38	41	—	—

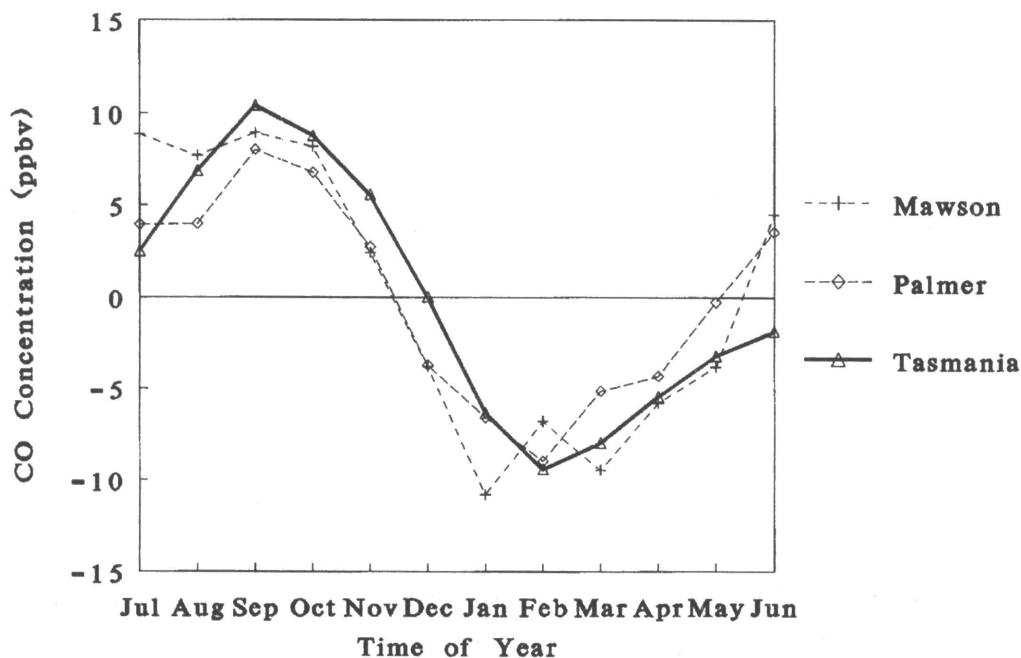


Figure 1. The seasonal variations of carbon monoxide at sites in Antarctica. The cycle at Cape Grim, Tasmania, is shown for comparison. The results are deviations from the average concentrations, which amount to about 8 ppbv above average during October and 9 ppbv below average during January.

There are prominent seasonal cycles in the concentrations, as shown in figure 1. In Antarctica, these cycles are driven mostly by seasonal variations of OH with additional contributions from seasonality of emissions and atmospheric formation of CO. The antarctic data are sparse, but the cycle is very similar to seasonal variations observed over many years at Cape Grim, Tasmania (42°S). The average concentration of CO at the antarctic sites during the course of these experiments was about 44 parts per billion by volume (ppbv) with seasonal variations of 8 ppbv higher than average in October and 9 ppbv lower than average in January.

Concentrations increase during the first half of the data (1980–1986) and decrease in the second half (1986–1992). We use the monthly average data (table) and subtract the seasonal cycles (as in figure 1), then calculate the linear trends during these two periods. The result is that between 1980 and 1986, concentrations increased an average of 3.4 ± 1.4 ppbv per year, and between 1986 and 1992 concentrations decreased at -5 ± 1 ppbv per year (the \pm values are 90 percent confidence limits of the trends).

Overall, the decrease in recent years has more than compensated for the increases in earlier years so that CO concentrations now (1991–1992) are lower by about 10 ± 3 ppbv, compared with concentrations a decade ago (1980–1981). The annual average concentrations are shown in figure 2, reflecting the decline of concentrations.

Although it seems that the data make a strong case for recent decreases of CO concentrations, there are reasons for caution. There are several factors that can affect the conclusions. The first is the stability of calibration standards: these have been checked and corrections have been made to the data. The second is the stability of CO in flasks over the long

periods of time required for the antarctic experiments. The antarctic data were checked against measurements at Cape Grim, and no anomalies were found. Finally, the data are still quite sparse and variable, creating a possibility of artifacts in trends over the relatively short duration of this experiment.

Although the trends are shown here only for Antarctica, similar trends exist in the other long-term data from our flask sampling network, which spans tropical, middle, and polar latitudes of both hemispheres.

Carbon monoxide can decrease if emissions from anthropogenic activities decrease or if OH is increasing (also due to human activities). The decrease of CO may be occurring

from the combined effect of both these processes, although we believe that the decrease of sources is probably the larger contribution or perhaps even the full explanation.

The sources of CO that may be slowing down are direct emissions from automobiles, biomass burning and other combustion processes, and indirect sources such as the atmospheric oxidation of methane and other hydrocarbons. In the United States and many European countries, urban emissions of CO (mostly from automobiles) have declined

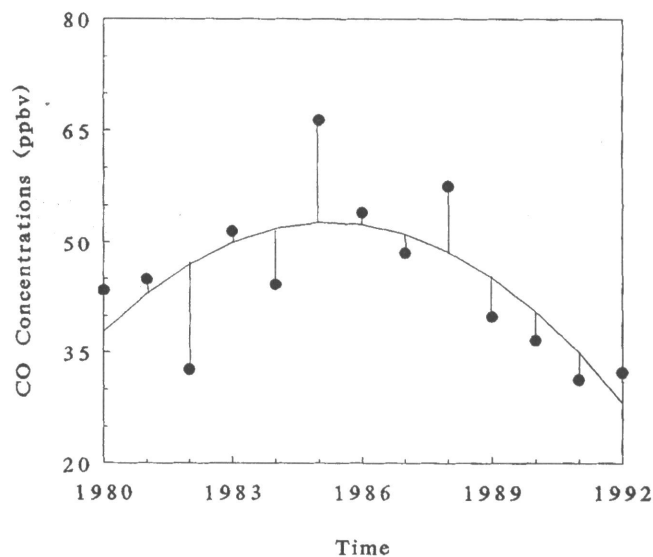


Figure 2. Annual average concentrations of CO in Antarctica. These data show that concentrations increased during the first half of the experiment and are decreasing now. The line is C (ppbv) = $37.8 + 5.68t - 0.54t^2$, where t is in years and is 0 in 1980.

dramatically during recent years because of legislative controls, enacted because CO is regarded as a highly undesirable pollutant that leads to adverse health effects and urban pollution (EPA 1990; Khalil and Rasmussen 1990). Reactive hydrocarbons that can lead to the atmospheric formation of CO are also controlled. The other process, increase of OH, which causes a greater removal of CO thus leading to declining concentrations, can occur because of possible reduction of stratospheric ozone that allows more ultraviolet radiation to reach the troposphere where it stimulates the production of OH (Madronich and Granier 1992). The possibility that OH is increasing in recent years is a reversal of earlier concerns that it may be depleted by human activities. At present, there is no direct or indirect experimental evidence for changes in OH.

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Atmospheric measurements of HCFC-22 at the South Pole

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Concern for stratospheric ozone depletion in polar regions and around the globe has prompted many nations to agree to phase out production and use of fully halogenated chlorofluorocarbons (CFCs) over the next few years (UNEP 1987). Because of this action, the atmospheric growth rates of CFCs and bromine-containing halons have declined in recent years (Butler et al. 1992; Elkins et al. 1993). Partially hydrogenated chlorofluorocarbons, also known as hydrochlorofluorocarbons (HCFCs), are among the different classes of compounds used as replacements for CFCs. HCFCs are preferred to CFCs because model calculations predict that HCFCs will have shorter atmospheric lifetimes and release less reactive chlorine to the stratosphere. The HCFCs are viewed only as interim replacements for CFCs, however, because they still have some potential to destroy ozone. Ozone-depletion potentials of HCFCs are generally predicted to be less than 15 percent, by weight, of those for the CFCs that they will replace (Solomon et al. 1992).

The major HCFC in use today is HCFC-22 (CHClF₂). This compound is used primarily for refrigeration and air-conditioning applications and, to a lesser extent, as a blowing

agent for open- and closed-cell foams (Midgley and Fisher 1993).

We have measured HCFC-22 in air samples collected at seven remote stations around the globe since the end of 1991. In the Southern Hemisphere, samples are collected at three different remote locations: Amundsen-Scott South Pole Station, at the South Pole (90°S); Cape Grim Baseline Air Pollution Station, Australia (40.7°S 144.8°E); and Cape Matatula, American Samoa (14.3°S 170.6°W). Here, we report measurements made at the South Pole through the end of 1992 and discuss them in light of results obtained at the next nearest station, Cape Grim.

Paired samples of air were collected monthly in 0.85-liter (L) electropolished stainless-steel flasks. Flasks were filled to a maximum pressure [approximately 25 pounds per square inch, gauge (psig) for South Pole samples and approximately 40 psig for Cape Grim samples] without drying agents in line. Samples were analyzed by capillary gas chromatography with mass spectrometric detection. Detailed procedures for collection and analysis of air for HCFCs are described elsewhere (Montzka et al. 1992, 1993, in press). Data are not reported for