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The Chemistry of Antarctic Ozone 1960 – 1987

by

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The ozone abundance over Antarctica has declined rapidly during spring in recent years (Farman et al., 1985), with nearly complete removal between about 11 and 20 km by early October in 1986 and 1987 (Hofmann et al., 1987; Farman et al., in press 1988). Marked declines in ozone were first observed during the 1970's, and rates of depletion appear to have accelerated after 1980 (Farman et al., 1985; Krueger et al., 1987). The present paper examines the factors that influence Antarctic ozone with a view to understanding the observed historical trend. We show that reduced ambient temperatures can dramatically enhance the efficiency of chemical removal processes. Attention is focused on positive feedback between levels of ozone, temperature, and rates for heterogeneous chemical reactions.

Chemical models using recent kinetic data predict rapid loss of Antarctic ozone after sunrise (McElroy et al., 1988, Salawitch et al., 1988, Wofsy et al., 1988), consistent with observations from 1986 and 1987. Key chemical steps require very low temperatures, needed to condense ice containing HCl and HNO_3 to form the polar stratospheric clouds (PSCs). Heterogeneous reactions on PSC particles convert inorganic chlorine to reactive forms in the gas phase, mainly ClO and $(ClO)_2$ and odd nitrogen species are efficiently scavenged from the gas phase (Molina et al., 1987; Tolbert et al., 1987, 1988; Leu, 1988). Trace gas concentrations predicted by these models are consistent with the observations of Farmer et al. (1987) and Solomon et al. (1987), from the 1986 NOZE campaign, and the models yield concentrations of ClO consistent with the ER-2 data of Anderson, Brune and coworkers. About 75% of the computed O_3 removal is associated with reactions of ClO and its dimer (Molina and Molina, 1987), and about 25% with reactions of ClO and BrO (McElroy et al., 1986b).

Model results exploring effects of nighttime heterogeneous chemistry are shown in Figure 1. Conditions at the beginning of polar night were estimated on the basis of detailed photochemical simulations of stratospheric chemistry at various latitudes in fall (June), scaling to Antarctic latitudes along preferred mixing surfaces (McElroy et al., 1986b). Condensation was assumed to begin on July 1, corresponding to the first appearance of PSCs (McCormick and Trepte, 1986). The composition of the ice was fixed at 2 mole % HCl (Wofsy et al., 1988) during the early stages of condensation and HNO_3 was assumed to be completely scavenged from the gas phase (Toon et al., 1986; Crutzen and Arnold, 1986; McElroy et al., 1986a).

Four key heterogeneous reactions were assumed to operate at rates given by Leu (1988) (reactions 1 and 2) and by Tolbert et al. (1988) (reactions 3 and 4):

$$ClNO_3 + HCl(s) \rightarrow HNO_3(s) + Cl_2 \qquad (1)$$

$$ClNO_3 + H_2O(s) \rightarrow HNO_3(s) + HOCl \qquad (2)$$

$$N_2O_5 + HCl(s) \rightarrow ClNO_2 + HNO_3(s) \qquad (3)$$

$$N_2O_5 + H_2O(s) \rightarrow 2HNO_3(s), \qquad (4)$$

where (s) denotes solid phase species. Production of nitryl chloride is seen to represent an important component of the net loss of HCl, while odd nitrogen is converted mainly to solid-phase HNO_3. At stratospheric sunrise chlorine species are rapidly converted to

ClO and its dimer, and high levels of these gases are maintained until the clouds evaporate, on 15 September for the simulation shown here.

Concentrations of chlorine radicals decline after the clouds dissipate. The model assumed that 50% of the $HNO_3(s)$ returned to the gas phase when the clouds evaporated, while 50% was removed by precipitation, consistent with the observations of Farmer et al. (1987) in 1986 (McElroy et al., 1988). Photolytic destruction of HNO_3 yields NO_2, which binds chlorine as relatively unreactive $ClNO_3$. Significant conversion of radicals to HCl also occurred, by reaction of Cl with CH_4.

Analysis of these results shows that ozone losses are sensitive to several of our assumptions, most of which relate to the formation and persistence of the PSCs:

(1) If the clouds last longer into the spring, high concentrations of radicals will persist and ozone losses will continue longer, producing larger reductions of ozone by mid-October.

(2) If less nitric acid is returned to the gas phase, formation of $ClNO_3$ would be retarded, high concentrations of ClO would persist, and loses of ozone would be larger.

(3) If the rate of reaction of Cl with CH_4 were slowed, formation of HCl would be retarded. A slower rate could reflect an abundance of CH_4 less than assumed here, or a lower temperature resulting in a slower rate for reaction of Cl and CH_4.

(4) If the height range of the region influenced by clouds were extended, losses of column ozone would be correspondingly increased.

The persistence of the polar vortex itself may give rise to an observational bias, particularly in comparison of model results with monthly averaged data for ozone column in October as reported, for example, by Farman et al. (1985). If the breakdown of the vortex is delayed the October mean concentration of O_3 will be more strongly influenced by the springtime depletion.

The factors cited above all respond in the same way to reductions in stratospheric temperatures. Colder temperatures would extend the time duration and the height range for PSCs. Colder temperatures also would provide efficient precipitation of solid-phase HNO_3. There are intriguing hints that temperatures might indeed have declined in the Antarctic stratosphere, reflecting perhaps reduced solar heating associated with ozone reductions. Persistence of the vortex and downwelling in the vortex (which would bring in air depleted in CH_4) might also be strengthened by diminished heating at low O_3.

Figure 2 illustrates the influence of the above factors on column ozone, for levels of inorganic chlorine appropriate for the time period between 1960 to 1987. The upper curve shows the relatively modest declines in ozone preducted with the model in Figure 1. The lower curve shows the very low ozone columns if PSCs persist to the end of September, if CH_4 is 50% less than assumed in Figure 1, and if 90%, rather than 50%, of stratospheric HNO_3 is assumed to precipitate. The effects of particular changes in model parameters are also shown in Figure 2 (see caption).

The magnitude of the O_3 loss is shown to be sensitive to the efficiency with which HNO_3 is removed from the stratosphere by precipitation and to the persistence and altitude extent of PSCs. Loss of O_3 may be expected to diminish the role of solar heating in October, extending the lifetime of the polar vortex and promoting colder temperatures. These factors could account for the accelerated removal of O_3 observed over the past several years.

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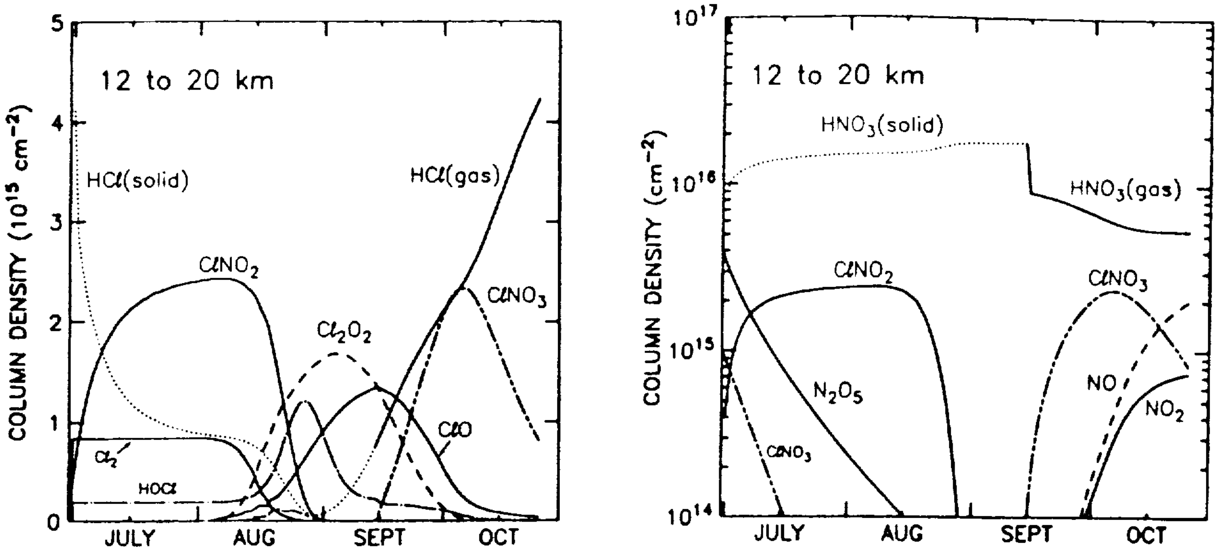

FIGURE 1 COLUMN DENSITY vs TIME

The evolution of the column density between 12 and 20 km for species of the chlorine family (left panel) and nitrogen family (right panel). The calculation used a latitude of 78°S and assumed 3.3 ppb of Cl_x at high altitude, appropriate for 1985. Results are shown for local noon. Polar stratospheric clouds were assumed to exist prior to September 15, with heterogeneous reactions (1) – (4) occurring and HCl and HNO_3 existing in the solid phase. Further details are provided in the text.

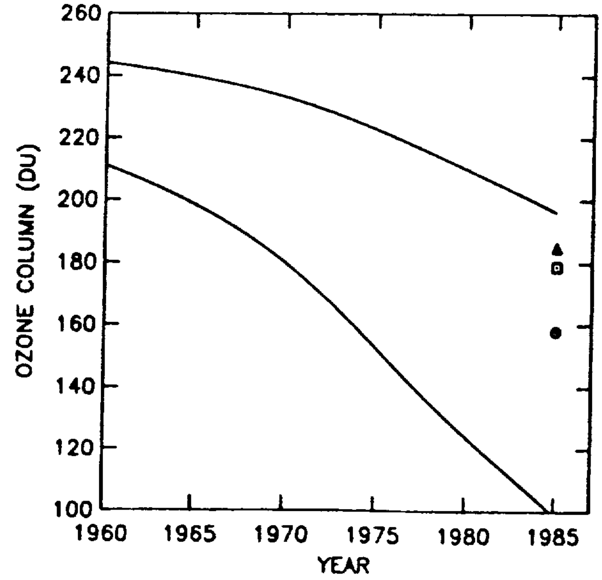

FIGURE 2 OZONE COLUMN vs YEAR, 1960–1987

The ozone column calculated for October 15 at 78°S, using levels of Cl_x appropriate for each year (1.0 ppb for 1960, 1.55 ppb for 1970, 2.4 ppb for 1978, and 3.3 ppb for 1985). The upper curve shows results using the same assumptions used for Figure 1. The points show the effects of changing various model assumptions: the triangle represents reducing the level of CH_4 in the model by 50%; the box represents extending the height range of the ozone loss to 11 to 25 km (vs. 12 to 20 km); the circle represents precipitation of 90% of $HNO_3(s)$ (vs. 50%). The lower curve combines all three of these changes. The effects are not additive due to the non-linearity of the ClO–ClO loss process.