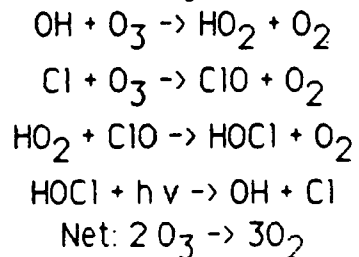# On the depletion of Antarctic ozone

Susan Solomon, NOAA Aeronomy Laboratory, Boulder, CO
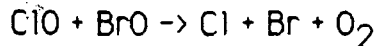NASA trends workshop, Boulder, CO, March 5-7, 1986

Farman et al. (1985) have shown that total ozone abundances in Antarctica have decreased substantially (about 30-50%) in the spring in recent years. Satellite observations (Krueger and Stolarski, 1985) have revealed similar depletions over a very extended region in general agreement with Farman et al.'s ground based data. These large depletions seem to be confined to high latitudes during Antarctic spring; no such dramatic depletions are observed in Antarctica during other seasons, nor in the Northern hemisphere.

Further information regarding the vertical profile of the ozone perturbation is essential to an understanding of the origin of the observed total column changes. Antarctic balloonsonde data are available from the Syowa (69S, 39E) ozonesonde station for several years in the late 1960's and early 1970's, and for 1982. These data show that the ozone perturbation occurs during August and September, (but not during the polar night period) and that the largest changes in the vertical profile occur near 15-20 km, where the observed percentage changes are about 30-50%. At these low altitudes, the ozone photochemical time scale is of the order of several years using presently accepted homogeneous photochemistry. If the observed depletions are the result of a chemical process, then the said process must obey the following constraints: 1) it must be essentially confined to the southern hemisphere, 2) it must be a fairly strong function of latitude, 3) it must produce an acceleration of the ozone chemical loss rate from a time scale of years to a few months near 15-20 km, and 4) it must increase with time over the past twenty years or so. Constraint 4) clearly suggests that we examine the chemistry of atmospheric chlorine.

At the low altitudes where the ozone perturbation is observed, chlorine can (in principle) destroy ozone through the process
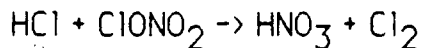
$$OH + O_3 \rightarrow HO_2 + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$HO_2 + ClO \rightarrow HOCl + O_2$$
$$HOCl + h\nu \rightarrow OH + Cl$$
$$\text{Net: } 2\,O_3 \rightarrow 3\,O_2$$

and by (McElroy et al., 1986):

$$ClO + BrO \rightarrow Cl + Br + O_2$$

In practice, however, these processes are not very effective near 20 km for presently accepted photochemistry since very little of the available chlorine is expected to be present in the form of ClO at these altitudes. Rather, the bulk of the available chlorine resides in the form of the reservoirs, HCl and $ClONO_2$ for presently accepted chemistry. Indeed, each of these reservoirs is predicted to be present in about 100 times greater abundance than ClO near 20 km. To appreciably enhance the density of ClO, the equilibrium between ClO and its reservoirs must be dramatically disturbed. If chlorine chemistry is the cause of the Antarctic ozone phenomenon, then the crux of the problem is the identification and validation of a process that can perturb these equilibria sufficiently to allow ClO to become the major chlorine species at 20 km. Under these circumstances (ie., ClO abundances of the order of ppbv; HCl and $ClONO_2$ greatly reduced from typical levels), the calculated ozone changes would be comparable to those observed.

It is likely that the reaction between HCl and $ClONO_2$ takes place rapidly on surfaces (Rowland, 1984):

$$HCl + ClONO_2 \rightarrow HNO_3 + Cl_2$$

If this reaction is heterogeneous, it presumably takes place in the stratosphere only in the presence of stratospheric aerosol, and indeed, it is well known that the stratospheric aerosol surface area increases substantially in the vicinity of polar stratospheric clouds. Furthermore, these clouds are very common in the cold environment of Antarctic winter and early spring near 10-20 km, where their occurence frequency is far greater than in the warmer Northern hemisphere (McCormick, 1983), suggesting that this process should be enhanced specifically in Antarctic spring. It will be shown that this reaction can lead to ozone depletions that are similar to those observed insofar as their vertical, latitudinal, and temporal characteristics are concerned. Furthermore, the implications of this process for the behavior of NO_2 and HNO_3 are consistent with observations by McKenzie and Johnston (1984) and Williams et al. (1982), providing an independent check on inferences drawn from ozone observations. This and other mechanisms capable of producing the observed changes in ozone will be discussed and contrasted. Implications for other species in Antarctic spring will be described.

References

Farman, J. C., Gardiner, B. G., and J. D. Shanklin, Nature, 315, 207-210, 1985.

Krueger, A. J., and R. S. Stolarski, Trans. AGU, 66, 838, 1985.

McCormick, M. P., Adv. Space Res., 2, 73-86, 1983.

McElroy, M. B., Salawitch, R. J., Wofsy, S. C., and J. A. Logan, submitted to Nature, 1986.

McKenzie, R. L., and P. V. Johnston, Geophys. Res. Lett., 11, 73-75, 1984.

Rowland, F.S., paper presented at NASA meeting on the stratosphere, Feldafing, 1984.

Williams, W. J., Kosters, J. J., and D. G. Murcray, J. Geophys. Res., 87, 8976-8980, 1982.