

Simulation of the Influence of Ion-Produced NO_x and HO_x Radicals on the Antarctic Ozone Depletion with a One-Dimensional Model

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ABSTRACT

A one-dimensional time-dependent photochemical model is used to simulate the influence of ion-produced NO_x and HO_x radicals on the Antarctic ozone depletion in polar night and polar spring at a latitude of 73 degrees south.

Vertical transport and nitrogen-oxygen (NO_x), hydrogen-oxygen (HO_x) production by ionic reactions have been introduced into the model.

NO_x and HO_x produced by precipitating ions are transported into the lower stratosphere by vertical motion and have some effects in the development of the Antarctic ozone depletion.

From winter through spring the calculated ozone column decreases to 269.4 DU. However, this value is significantly higher than the total ozone observed at several Antarctic ozone stations.

1. INTRODUCTION

Ozone absorbs almost all solar ultraviolet radiation below 290 nm thus prevents that radiation from arriving at the Earth's surface. Penetration of solar ultraviolet radiation through the lower atmosphere depends upon the amount of stratospheric ozone as well as its absorption cross-section. A change in this ultraviolet absorption in the stratosphere would affect the modes of life and relations to their environments at the Earth's surface. It is certainly beyond the scope of this study to discuss the biological impact of changes in stratospheric ozone, which may be expected to occur as a result of various human activities.

Observations by Farman et al. (1985) reveal a remarkable depletion in total ozone over Antarctica, which has developed from 1975 to the present during the spring season. Analysis of satellite data shows that the phenomenon affects much of the cold cyclonic vortex found there, and that column abundances are among the lower recorded anywhere on the globe.

The dramatic springtime minimum in Antarctic ozone has challenged scientists to look for possible mechanisms which may have caused this Antarctic ozone depletion. Both heterogeneous chemical reactions, e.g. chlorine catalytic chemistry as well as nitrogen catalytic chemistry were suggested. Solomon et al. (1986) have calculated reductions of the total ozone through the heterogeneous reactions:

$\text{HCl} + \text{ClONO}_2 \rightarrow \text{HNO}_3 + \text{Cl}_2$ and $\text{H}_2\text{O} + \text{ClONO}_2 \rightarrow \text{HNO}_3 + \text{Cl}$ that can enhance the number densities of the radical species Cl and ClO in the stratosphere. Kruger et al. (1987) have calculated Antarctic ozone depletion based on accelerated photolysis of halogenated hydrocarbons during polar spring.

In this study we have investigated the role of nitrogen-oxygen and hydrogen-oxygen radicals in decreasing Antarctic ozone. The main sources of stratospheric NO_x and HO_x are neutral molecular reactions, for instance, for NO the main source is reaction $\text{N}_2\text{O} + \text{O}(^1\text{D}) \rightarrow$

2NO . Some NO_x and HO_x are formed directly through the interactions of ionizing particles with atmospheric nitrogen and hydrogen and by lightning. The major sources producing ionization in the middle atmosphere are solar electromagnetic radiation including extreme ultraviolet, X-ray and Lyman-Alpha above 60 km and charged particle components of the galactic cosmic rays below that height.

During solar proton events and auroral activities, solar flares eject high energy protons that can dominate the ionization levels of polar regions over the entire range of the middle atmosphere. These enhanced ionizations produce a large amount of NO in the middle atmosphere by ion chemistry. During solar proton events ionization rate is greatly enhanced.

Simulation of the ozone depletion requires accurate numerical chemical interaction of the trace elements and transport of trace species. In many such tracer-transport problems it is assumed that the global velocity field is given and that the tracer is transported passively along with the mean flow. Furthermore, the abundances of these tracers are regarded to be sufficiently small so that physical and chemical transformations which produce or destroy tracers do not change the general mass field. This paper presents a numerical simulation of the Antarctic ozone depletion using a 1-D time-dependent photochemical model.

II. MODEL

The 1-D photochemical model used for this study contains 113 reactions including 28 photochemical processes. For calculation of photolysis rates currently recommended solar flux data and absorption cross-sections are used. The temperature profiles used in these calculations are the August zonal averages for 80 degrees south given by Barnett and Corney. As initial concentrations of the constituents we used midlatitude profiles calculated for equinox by a time-dependent 1-D model for a steady state under 1985 conditions.

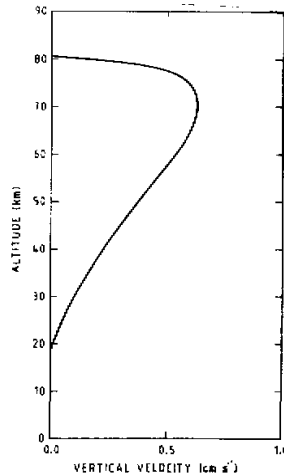


Fig. 1. The distribution of computed mean vertical velocity for the 73 degrees south water solstice.

A profile of vertical velocity (Fig. 1) calculated by three-dimensional model was used. The runs were performed as a simulation of the polar night for 90 days, in 5-day steps, and for simulation of the polar spring in 1-hour steps, at a latitude of 73 degrees south. The profiles of temperature, NO_x , HO_x production rates and vertical velocity were held constant for the whole calculations.

III. RESULTS AND DISCUSSION

Using the one-dimensional time-dependent photochemical model we made two sets of calculations: one run without NO_x and HO_x production by ionic reactions, the other run with NO_x and HO_x production by ionic reactions effective in the upper stratosphere. We assumed production rates of 50 molecules $\text{cm}^{-3}\text{s}^{-1}$ for 50 to 80 km altitude. For this height range, Sheldon et al. (1985) found ion production rates as high as 10 ion pairs $\text{cm}^{-3}\text{s}^{-1}$ and more, at high southern latitudes. Although the number of NO_x and HO_x produced by every single ion pair is not known exactly, the production rate assumed for our study appears to lie within the right order of magnitude.

Results of these calculations are illustrated in Figures 2 through 6. The variation of the total column amount of ozone in springtime at 73 degrees south is shown in Fig. 2. The solid line indicates the variation of total ozone calculated without NO_x and HO_x production by precipitating ions. It shows a decrease in the ozone column which reaches a minimum of 270.1 DU on September 15. After this time an increase of total ozone is observed. The dashed line indicates the variation of total ozone which was calculated with introducing NO_x and HO_x production by ionic reactions. It shows that the decrease of the ozone column is slightly deeper than that calculated without NO_x and HO_x production by ionic reactions. A minimum of 269.4 DU is observed on September 19 with subsequent increase thereafter. Fig. 2 demonstrates that the slight decrease in total ozone is essentially monotonic both with and without NO_x , HO_x production by ionic reactions. In addition, it appears that the effect of NO_x , HO_x production by ionic reactions has almost no effect on the Antarctic ozone depletion in comparison with other sources of catalytic compounds, as well as active chlorine radicals, reactive halogenated hydrocarbons in the stratospheric Antarctic chemistry.

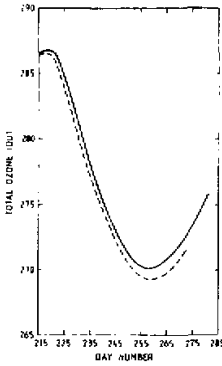


Fig. 2. Ozone columns in the Antarctic spring at 73°S for calculations; with and without NO_x , HO_x production by ionic reactions.

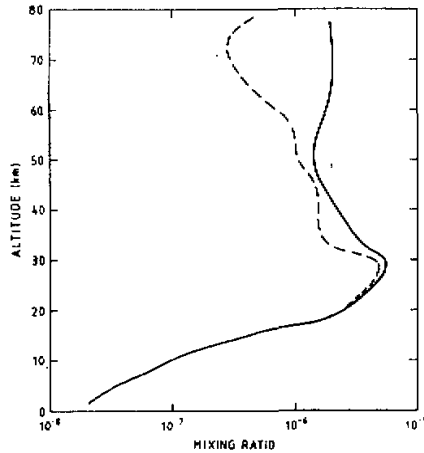


Fig. 3. Vertical distribution of the ozone mixing ratio for two calculations; with and without NO_x , HO_x production by ionic reactions in polar spring on August 20.

Farman et al. (1985) have reported a rapid decrease of the total column amount of ozone over Halley Bay (76°S). The decrease was most pronounced in October. For this month the mean ozone columns observed over Halley Bay were 221 DU (1982), 199 DU (1983), and 190

DU (1984). Stolarski et al. (1986) reported measurements from SBUV and TOMS aboard the Nimbus 7 satellite, which show that the decrease occurs during September reaching a minimum in mid-October.

The ozone depletion calculated in this study is smaller than the variations of total ozone observed at Halley Bay for October of 1982–1984. Furthermore, the minimum appears earlier than suggested by the observations.

Fig. 3 indicates the vertical distributions of ozone computed for polar spring (on August 20). The solid portion shows the ozone distribution calculated without production of NO_x and HO_x by ionic reactions, the dashed lines shows the vertical ozone distribution calculated including ionic reactions. The influence of NO_x and HO_x production by ionic reactions is largest above 50 km, where ionic reactions are assumed to be effective. Some NO_x and HO_x are transported to lower levels by vertical motion reaching 20 km (below 20 km the vertical velocity is put zero). So at levels below 50 km we can see a slight effect of NO_x , HO_x produced by ionic reactions, too.

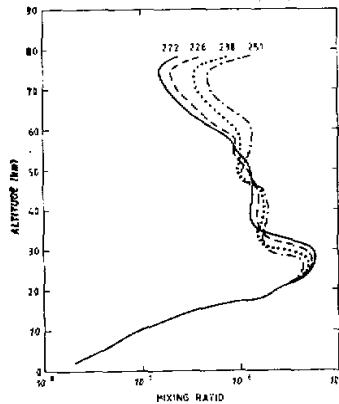


Fig. 4. Vertical distributions of the ozone mixing ratio for calculations: with NO_x , HO_x productions of ionic reactions in polar spring on August 12, 16, 28 and September 10.

Fig. 4 indicates the vertical ozone distribution for days August 12, 16, 28, and September 10 calculated with productions of precipitating ions. It shows that at altitudes from 20 to 30 km the ozone concentration decreases rapidly during springtime.

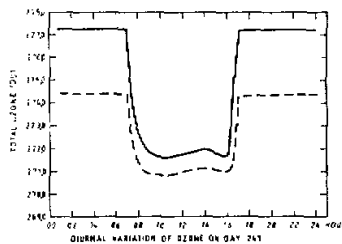


Fig. 5. Calculated diurnal variations of ozone on September 6 at 73°S latitude.

Above 50 km the ozone concentration increases with time. From the fact that decrease in ozone concentration mainly occurs at 20–30 km altitude. This lead us to conclude that the main role in decrease of the ozone column is the depletion of ozone concentration at 20–30

km altitude.

Fig. 5 shows the diurnal variation of the Antarctic ozone on September 6 (solid line and dashed line are calculated without and with NO_x , HO_x production by ionic reactions, respectively). Throughout 24 hour interval, the ozone column amount calculated without NO_x , HO_x production by ionic reactions is larger than the ozone column calculated with NO_x , HO_x production. During the night the difference is larger than during daytime.

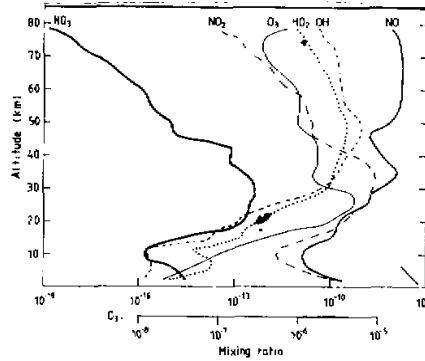


Fig. 6. The computed vertical distributions of NO , NO_2 , NO_3 , OH , HO_2 , O_3 in Antarctic atmosphere on day August 28 at 73 degrees south.

Fig. 6 shows the vertical distribution of O_3 , NO , NO_2 , NO_3 , OH and HO_2 in the atmosphere as computed for day August 28. Comparing the ozone distribution with NO_x and HO_x profiles it appears obviously that NO , OH and HO_2 are responsible for the reduction of ozone concentration in stratosphere. Whereas NO_2 and NO_3 have not clear influence on the change of ozone during daytime.

All these calculations demonstrate that NO_x and HO_x production by ionic reactions in the upper stratosphere contributes to the development of the ozone depletion. This effect is more pronounced in springtime above 50 km (Fig. 3). In the depletion of total ozone only a slight effect is observed.

The ionizations of NO and O_3 are responsible for maintaining the night time E region ionization at 80–100 km. Ions produced in the ionosphere are precipitated downward into the stratosphere of the winter hemisphere. Further transport to mid-stratospheric levels occurs principally in the Southern Hemisphere within the polar night vortex. During the continuing downward motion within the stratosphere ions of ionospheric origin can interact with the species of stratospheric origin. At high latitudes formation of NO_x and HO_x in the upper stratosphere by ion chemistry, due to increased amounts of protons during large solar proton events, could reduce stratospheric ozone. Nitrogen-oxygen and hydrogen-oxygen produced by ion chemistry are transported further downward to altitudes of about 20–30 km, a region which contributes significantly to the Antarctic ozone depletion.

Mcpeters et al. (1981) noted that a long term ozone depletion following the August 1972 Solar Proton Event was very clear and lasted at least a month in both northern and southern polar regions. Thomas et al. (1983) have detected a clear decrease of ozone density during the Solar Proton Event of July 13 1982; a maximum depletion of $\sim 70\%$ was observed in the northern high latitudes. Solomon and Crutzen (1981) examined the effects of the August 1972 Solar Proton Event on stratospheric ozone using model including the effect of temperature

feedback. The calculated ozone decreases are expected to produce temperature decreases, and consequently affect the reaction rate constants. A balloon-borne ion mass spectrometer provided ion composition data between 13 and 42 km (Max-Planck-Institut für Kernphysik, Heidelberg, FRG, A. Krieger, P. Arnold, 1987).

IV. CONCLUSION

1. NO_x and HO_x produced by ionic reactions give a little contribution to the decrease in total ozone by weighting average at ozone maximum levels.

2. The influence of ion-produced NO_x and HO_x on ozone concentration becomes more effective above 50 km.

3. Destruction of ozone molecule by NO_x and HO_x radicals is much more at night time due to NO_2 , NO_3 catalytic chemistry.

4. NO , OH and HO_2 productions are responsible for reduction of ozone concentration in the stratosphere during daytime.

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