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STRATOSPHERIC OZONE DEPLETION: ITS IMPACT ON TROPOSPHERIC CHEMISTRY AND ON CLIMATE

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ABSTRACT

Observations have shown that there has been a long term decrease in stratospheric ozone on a global scale during the last two decades. Over the southern polar region the reductions are large and clearly connected to man made emissions of CFCs. There are mounting evidences that Northern Hemispheric ozone reductions observed since 1980 are connected to man made emissions of CFCs. Satellite observations give global average reductions of total ozone of the order 4% over the last 10 to 15 years. The reductions have been particularly large at mid and high northern latitudes after 1991. Furthermore, observations by ozone sondes have shown that the reductions occur in the lower stratosphere, during winter and spring months. For instance during the 1992/1993 winter ozone reductions up to 25 to 30%, compared to the long term mean, were observed. Measurements from the last winter (1994/1995) performed by the European SESAME campaign show similar decreases in the lower stratosphere. Model studies give strong indications that a substantial fraction of the reduction is due to enhanced chemical loss through chemical reactions involving chlorine compounds (ClO and Cl). The enhanced ozone loss which has occurred since 1991 coincides with enhanced particle formation in the stratosphere from the Mt. Pinatubo volcanic eruption in 1991, and enhanced formation of Polar Stratospheric Clouds (PSC) due to extremely low stratospheric temperatures, which were particularly pronounced in the winters of 1992/1993 and 1994/1995. Observations have also shown that the 11 year solar cycle variation affects stratospheric ozone on a short time scale (a few years) and has to be taken into account when observations are analysed.

Ozone has increased during the last two decades in the northern free troposphere, although there seem to have been a levelling off in the ozone increase since the mid 80s. Enhanced emissions of ozone precursors (NOx, CO and hydrocarbons) are the main cause for the ozone growth. Tropospheric ozone is also affected by the enhanced UV-B fluxes caused by reduced ozone column densities during the last five years. Model calculations give reduced ozone and methane levels in most of the free troposphere due to increased UV-B fluxes. Since both ozone and methane are greenhouse gases, reductions in stratospheric ozone are likely to have an impact on climate, not only due to stratospheric ozone changes, but also due to chemical changes in the troposphere.
INTRODUCTION

There are growing evidences that chemical processes induced by man made emission of chlorine and bromine compounds are effecting ozone distributions, not only in the southern polar region, where large ozone depletion in the spring months is a result of enhanced chlorine and bromine levels from man's activity, but also at mid- and high-northern latitudes where significant ozone reductions have been observed during the last decade. There are now significant long term reductions in the global average ozone values of the order of 3 % during the last decade (WMO, 1995).

In the Northern Hemisphere the largest reductions are found at mid- and high- latitudes. Particular large reductions have been observed during the last five years at northern latitudes during winter and spring months. This has drawn the attention to stratospheric particles and the role they play in the ozone destruction process in the lower stratosphere. This is where a significant part of the loss occurs via catalytic chlorine and bromine reaction (WMO, 1990; WMO,1992; WMO, 1995). Ozone sonde-, Umkehr- and satellite (SAGE)- observations all point to the lower stratosphere as the key region for the reduction in ozone column densities.

A major understanding of the ozone loss processes in the lower stratosphere has come as a result of the effort directed to understand polar ozone loss. It is, for instance, known that the enhanced ozone loss occurring each spring over Antarctica is in large part caused by catalytic chlorine and bromine reactions in connection with enhanced chemical activity due to the presence of Polar Stratospheric Clouds (PSC) in the lower stratosphere (WMO, 1990; WMO, 1992; WMO, 1995). The main loss prosesses which have been identified are those originally proposed by Solomon et al. (1986), McElroy et al./(1986), Toon et al. (1986). Significant chemical distortions, most likely due to similar catalytic loss reactions with enhancements of ozone loss, have been observed at mid - and high - northern latitudes (Weaver et al.,1993, Waters et al., 1993).

The last years decline in ozone column densities coincide with the large enhancement in sulfur particles that has been observed in the stratosphere after the Mt. Pinatubo eruption on the Phillipines in June 1991. The large enhancement in stratospheric sulfate loading is believed to significantly perturb the composition of the lower stratosphere significantly, and lead to enhanced ozone destruction (Granier and Brasseur, 1992).

It seems likely that stratospheric particles, particularly during periods following major volcanic eruptions, will affect stratospheric ozone densities at current chlorine and bromine levels at mid- and high- northern latitudes. The same is also the case when PSC formation in the polar region occurs over extended periods during winter and spring months as has been observed often during the last decade. Although the enhanced loss is triggered off by the presence of sulfate particles and PSCs, the direct cause for enhanced ozone loss is the presence of active chlorine and bromine compounds.

A key question is to understand the causes of recent years decreases in the ozone column
densities in the Northern Hemisphere. How can we separate natural changes like the 11 year solar cycle variations and other short term variations from the induced loss by increasing chlorine and bromine levels in the stratosphere?

An interesting consequence of reduced ozone in the stratosphere is that it lead to enhanced UV-B radiation that penetrates to the troposphere and causes significant changes in the oxidation process and in chemically and climatically important gases like O₃ and CH₄ (Fuglestvedt et al., 1994). This links stratospheric ozone depletion to tropospheric chemistry and climate processes.

CHEMICAL LOSS OF OZONE IN THE LOWER STRATOSPHERE

Ozone loss by catalytic chlorine and bromine reactions

A brief summary of the catalytics ozone destructing cycles involving chlorine and bromine compounds which are given below.

In the high latitude, lower stratosphere, the main ozone loss is given by the chlorine destructing cycle (Molina and Molina, 1987):

\[
\begin{align*}
\text{ClO} + \text{ClO} + \text{M} &\rightarrow \text{Cl}_2\text{O}_2 + \text{M} \\
\text{Cl}_2\text{O}_2 + \text{h} \nu &\rightarrow \text{Cl} + \text{ClO}_2 \\
\text{ClO}_2 &\rightarrow \text{Cl} + \text{O}_2 \\
2(\text{Cl} + \text{O}_3) &\rightarrow 2(\text{ClO} + \text{O}_2)
\end{align*}
\]

\[
\text{Net} \quad \text{O}_3 + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 + \text{O}_2
\]

Since the loss through ClO + ClO reaction is proportional to the square of the ClO concentration, the reaction becomes efficient in areas where the concentrations of ClO are significantly enhanced by heterogeneous reactions (e.g. in regions where the chemistry is strongly affected by the occurrence of PSCs) (Isaksen and Stordal, 1986).

Several chemical cycles involving bromine compounds have also been identified as ozone destructing mechanisms in the stratosphere (WMO, 1992; WMO, 1995). The main catalytics bromine cycles responsible for the ozone destruction in the lower stratosphere are (McElroy et al., 1986):

\[
\begin{align*}
\text{BrO} + \text{ClO} &\rightarrow \text{Br} + \text{Cl} + \text{O}_2 \\
\text{Cl} + \text{O}_3 &\rightarrow \text{ClO} + \text{O}_2 \\
\text{Br} + \text{O}_3 &\rightarrow \text{BrO} + \text{O}_2
\end{align*}
\]

\[
\text{Net} \quad \text{O}_3 + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 + \text{O}_2
\]
and (Solomon et al., 1986):

\[
\begin{align*}
BrO + HO_2 & \rightarrow HOBr + O_2 \\
HOBr + h\nu & \rightarrow Br + OH \\
Br + O_3 & \rightarrow BrO + O_2 \\
OH + O_3 & \rightarrow HO_2 + O_2
\end{align*}
\]

Net \quad O_3 + O_3 \rightarrow O_2 + O_2 + O_2

The first of these two cycles also involve ClO, thereby linking the stratospheric chlorine and bromine ozone destructing chemistry together. In this way future ozone loss by the bromine will depend on the development of chlorine. The two cycles involving bromine compounds is of importance outside the polar vortex where chemistry is moderately perturbed by heterogenous processes. Observations has shown that BrO is only moderately enhanced by PSCs in the vortex (Toohey et al., 1990).

**Heterogeneous reactions**

Heterogeneous reactions occuring on PSCs and sulfate aerosol particles which involve HCl, ClONO\textsubscript{2}, HOCl, N\textsubscript{2}O\textsubscript{5} and H\textsubscript{2}O, are believed to be the main reactions involved in converting reservoir compounds to active chlorine compounds (ClO). The following heterogeneous reactions which are believed to be the main reactions are included in the calculations:

\[
\begin{align*}
\text{ClONO}_2 + \text{HCl} & \rightarrow \text{Cl}_2 + \text{HNO}_3 \\
\text{ClONO}_2 + \text{H}_2\text{O} & \rightarrow \text{HOCl} + \text{HNO}_3 \\
\text{N}_2\text{O}_5 + \text{HCl} & \rightarrow \text{ClNO}_2 + \text{HNO}_3 \\
\text{N}_2\text{O}_5 + \text{H}_2\text{O} & \rightarrow \text{HNO}_3 + \text{HNO}_3 \\
\text{OHCl} + \text{HCl} & \rightarrow \text{Cl}_2 + \text{H}_2\text{O}
\end{align*}
\]

The reactions are found to significantly enhance the concentrations of ClO, and partly also BrO in the high latitude lower stratosphere, thereby enhancing the role of chlorine and bromine compounds as ozone depleting substances.

**PSC and sulfate particles in the lower stratosphere**

Parameterization of PSC distribution and their interaction with the gaseous compounds in the lower polar stratosphere is done in the same way as in previous studies (Isaksen et al.,
1990), based on observations of PSC occurrences.

Sulfate aerosols which are present in the lower stratosphere have been measured routinely over northern hemispheric locations during the last two decades, and global measurements have been performed from satellites since 1978 (SAGE I, SAGE II). A long term basis for stratospheric aerosol loading has been established, which shows that there are significant variations over time associated with volcanic eruptions (WMO, 1992). Major volcanic eruptions (e.g. El Chicon in Mexico in 1982 and Mt. Pinatubo on the Phillipines in June 1991) have enhanced the aerosol surface areas in the lower stratosphere significantly. There seems to be only shorter time periods (1978-1979, 1989) which can be characterized as "quiescent" periods where the particle loading is not affected significantly by volcanic eruptions (Hofmann, 1990; WMO, 1992). Observations of PSCs in the polar regions, particularly in the Arctic has shown that, although PSCs occur almost every year, their frequency and duration of occurrence during the winter months vary strongly from year to year.

It is therefore clear that there are large variations in the impact of sulfate particles and PSCs on the ozone destructing process, which are reflected in the variation in ozone from year to year.

OBSERVED OZONE CHANGES DURING THE LAST DECADE

Reductions in ozone column densities

Satellite observations (WMO, 1995) have revealed that there has been a gradual decrease in global ozone column densities during the 1980s and more pronounced during the first years of the 90s (Figure 1).

![Graph showing percent deviation from monthly average ozone column densities from 1980 to 1994.]

Figure 1. Changes in ozone column densities (%) between 1979 and 1994 as observed from the SBUV-2 satellite for the latitude interval 60°S-60°N (Ref.: WMO, 1995).
Ozone column densities may show large year to year variations due to variations which is likely to be a result of year to year variations in the heterogenous process connected to PSC and sulfate aerosol formation as described above. Figure 2 shows observed variation in ozone column densities over the 3 year period 1992 through 1994 for latitude belts 30°N-50°N and 20°S to 20°N. The 1993 low ozone values at northern latitudes occurred at a time when sulfate aerosol loading after the Mt. Pinatubo volcanic eruption was high, along with extended PSC formation. This was in contrast to the higher ozone levels in 1994, when there were less sulfate aerosols and less PSC formation. As will be shown below, this agrees with model calculated ozone variations when observed levels of PSCs

Figure 2. Observed ozone column densities for the latitudinal belts 30°N to 50°N and 20°S to 20°N for the years 1992, 1993, 1994. The range for the period 1979 to 1990 is also given in the figure (Ref.: WMO, 1995).
and sulfate aerosols are taken into account in the calculations of heterogenous processes. At low latitudes ozone is little affected by year to year variations in the PSC formation in the Arctic winter.

Studies of the trend in the vertical distribution of ozone have clearly shown that the most significant reductions have occurred in the lower stratosphere. Satellite, Umkehr and sonde data indicate ozone reductions of the order of 5 % or more during the 1980s for heights below 25 km. in the stratosphere. Similar reductions (in %) is found in the upper stratosphere. However, ozone densities are low, the reduction contributes therefore less to total ozone column depletion than the lower stratospheric loss.

Ozone increases in the troposphere

In contrast to stratospheric ozone reductions, ozonesonde observations from northern latitudes show ozone increases at most heights in the troposphere over the two last decades. However, several of the observations show reduced increase in free tropospheric ozone during the last few years, indicating changes in the ozone production process. Southern hemispheric ozone has shown a clear downward trend in the troposphere during the last decade, which is particular large at high southern latitudes.

Figure 3 shows ozone changes at clean air stations at different latitudes for the 1970s and 1980s. At mid- and high- northern latitudes there is a positive trend in ozone, while mid- and high- southern latitudes show a negative ozone trend. The positive trend at northern latitudes are dominated by the increase during the 1970s.

![Figure 3. Trends in tropospheric ozone observed at different latitudes (costal and high latitude stations). SP: South Pole, CP: Cape Point, AS: American Samoa, MLO: Mauna Loa, WFM: Whiteface Mountain, HPB: Hohenpeissenberg, ZS: Zugspitze, B: Barrow.](image-url)
TIME DEPENDANT CALCULATIONS OF OZONE CHANGES

Changes in ozone column densities

The 2-D chemistry/transport model which has been developed at the Institute of Geophysics, University of Oslo (Stordal et al., 1985; Isaksen et al., 1990) is used to calculate long term variations in stratospheric ozone. It has previously been used for time dependent model studies of the chemical distribution and the man made impact on the ozone layer. In the present study we will show calculated development of ozone over the last 6 years. The calculations are continued 20 years into the future (to year 2004). Two sets of time dependent model studies are performed. One study which has a standard PSC impact, without the impact of Mt. Pinatubo eruption (base run), and one run where the year to year variation in PSC is taken into account, and with the impact of Mt. Pinatubo. Both runs have solar cycle variations included.

Figures 4 a) and 4 b) show calculated ozone variations between 1998 and 2004 for the month of April at 40°N and at the Equator respectively.

Figure 4. a) Model calculated variation in ozone column density at 60°N for April. Filled out squares represent calculations with a standard PSC impact and no impact from the Mt. Pinatubo volcanic eruption. Open squares represent calculations with actual year to year variations in PSCs in the Arctic for 1992 through 1995, and with the impact from the Mt Pinatubo volcanic eruption included.
First of all, the variations in ozone over a time scale of the solar cycle (11 years) is strongly modified by the solar cycle variation. The calculations also show a significant decrease on top of the solar cycle variation at 40°N which is due to the long term man made impact from chlorine and bromine compounds. The impact is less at low latitudes, which is in agreement with observations.

The calculations demonstrate that the excess amounts of particles after the Mt. Pinatubo eruption and the variation in PSC occurrence in the Arctic have a significant impact on the northern hemispheric ozone column densities, and that the sulfate particles affect low latitude ozone column densities.

The calculations also show that it is likely that we could expect an increase in ozone column densities toward the next solar maximum after the turn of the century due to the dominating effect of the solar cycle variation.

Figure 4.b. Same as Figure 4.a for the Equator.

Changes in tropospheric ozone

The observed change in Norther Hemispheric ozone in the troposphere shown in Figure 3 is most likely a result of increases in emission of ozone precursors (NOx, CO and hydrocarbons) from different pollution sources. It is, however, possible that changes in
stratospheric ozone of the magnitude we have discussed above could affect tropospheric chemistry and thereby ozone significantly. These changes could have climatic implications in that they affect ozone and methane which are climate gases.

Changes in tropospheric chemistry is initiated through ozone photo dissociation by UV-B radiation:

\[ \text{O}_3 + h\nu \rightarrow \text{O}^{(1\text{D})} + \text{O}_2 \]

followed by the reaction:

\[ \text{O}^{(1\text{D})} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH} \]

Since OH is a key compound in tropospheric chemistry, changes in its distribution will affect a large number of compounds. In particular it controls the distribution of methane.

Reduction in stratospheric ozone will lead to more penetration of UV-B radiation and enhanced OH production, and thereby to changes in the tropospheric climate gases CH\textsubscript{4} and O\textsubscript{3}. Model studies of the changes in tropospheric ozone from enhanced photo dissociation due to the observed changes in stratospheric ozone is shown in Figure 5.

Figure 5. Calculated percentage change in tropospheric ozone due to increased UV-B fluxes between 1980 and 1993 for the month of December.
Ozone is reduced in most of the troposphere, and the reductions are particularly large at high southern latitudes where stratospheric ozone reductions are largest. It seems likely that the marked reductions in ozone observed during the last two decades in the Southern Hemisphere troposphere is a result of stratospheric ozone reductions. It is also likely that the reduced growth in free tropospheric ozone in the Northern Hemisphere since the late 1980s is caused by the enhanced UV-B fluxes.

The strong linkage between stratospheric ozone reduction, UV-B increases, and changes in tropospheric compounds are demonstrated in Figure 6. The figure shows result from a model calculation where changes in stratospheric ozone between 1970 and 2050 is calculated based on past and predicted future emissions of CFC and bromine compounds. The calculations are made with the global 2-D model refered to above, and yearly average global values are depicted in the figure. Key tropospheric compounds like OH, O₃, and CH₄ show significant changes in response to changes in stratospheric ozone and UV-B fluxes. Tropospheric OH increases while O₃ and CH₄ increases when stratospheric ozone is reduced. The change in trends which occur around the turn of the century reflects the reduction in emissions since the late 1980s.

![Figure 6. Relative changes in photo dissociation rate for O(1D) production, OH concentration, O₃ concentration, and CH₄ concentration due to the relative change given in the figure from the adopted changes in the emission of CFCs and bromine compounds.](image_url)
CLIMATE IMPACT DUE TO OZONE CHANGES

Ozone is a greenhouse gas, and changes in its distribution in the height regions (lower stratosphere and upper troposphere, Wang et al., 1980) could have significant impacts on the climate. Two conditions are of importance when we discuss ozone-climate interactions, which are different compared to other greenhouse gases: a) ozone is a secondary greenhouse gas formed and destroyed by chemical reactions in the atmosphere, and therefore connected to the emission of other gases (NOx, hydrocarbons, methane, CFCs. etc.), b) it has sufficient short lifetime to undergo large regional variations.

Reductions in stratospheric ozone which is connected to the release of CFCs will lead to enhanced cooling. Due to the large latitudinal variation in ozone reductions, the climate impact will be largest at high latitudes where stratospheric ozone reductions are largest (IPCC, 1995). The global average radiative forcing from the observed ozone reductions between 1970 and 1990 is approximately -0.2 W/m² (Hansen et al., 1993). The combined positive forcing from all greenhouse gases between 1980 and 1990 is estimated to be 0.45 W/m². Since a large fraction of the ozone reduction is believed to come from increases in CFCs which have a direct positive forcing. Taking the indirect negative forcing from ozone into account the net forcing from CFCs are strongly reduced (approx. by 50 %).

The changes in tropospheric distribution of CH₄ and O₃, due to stratospheric ozone reductions, discussed above, will also have a climate impact. Since both compounds are reduced in the troposphere, the change in radiative forcing is negative. Based on the ozone and metane changes calculated above, Bekki et al. (1994) calculate the negative forcing from tropospheric changes to be 30 to 50 % of the negative stratospheric forcing from ozone. This adds to the compensating effects from indirect radiative forcing from CFC changes.

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