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Decadal evolution of total ozone decline: Observations and model results

Kleareti Tourpali,[1] Xue Xi Tie,[2] Christos S. Zerefos[1] and Guy Brasseur[2]

Abstract. In this study we examine the rate of change in the total ozone decline observed during past years over both the northern and the southern hemisphere. This is studied from the analysis of the longest available reevaluated series of total ozone observations (1964-1993), with the aid of a two-dimensional chemical/transport model of the middle atmosphere, which takes into account microphysical formation of polar stratospheric clouds (PSCs) and heterogeneous mechanisms under different stratospheric chlorine-loading conditions. In our analysis the zonal mean total ozone decreases during the last two decades were compared to the corresponding mean ozone levels during the undisturbed period 1964-1973. The effects of quasi-cyclical and transient phenomena such as the quasi - biennial oscillation, the El Nino/Southern Oscillation and the solar cycle, which are known to significantly influence the ozone variability, have been filtered out from the observations, allowing a more straightforward comparison between model results and observations. These model results are in good agreement with the observed change in the rate of total ozone decline over the middle to high latitudes of both the northern and the southern hemisphere. These model calculations indicate that the ozone depletion at high latitudes in both hemispheres is mainly caused by heterogeneous reactions on the surface of PSCs. At northern midlatitudes, though, the ozone losses are caused by heterogeneous reactions on the surface of sulfate aerosols, especially after large volcanic eruptions. From a sensitivity study performed with the model, a 2° decrease in temperature was found to affect significantly the ozone field, especially in the northern hemisphere, by facilitating the heterogeneous conversion processes on PSC surfaces through enhancement of their concentration, and by accelerating the reactions on the surface of sulfate aerosols.

1. Introduction

Numerous scientific analyses on the trends and behavior of atmospheric ozone have been published, responding to the increasing interest in the observed stratospheric ozone decline [*Reinsel et al.*, 1987, 1994; *Bojkov et al.*, 1990, 1995; *Stolarski et al.*, 1992; *Harris et al.*, 1997]. These analyses, as well as the International Ozone Assessments [*World Meteorological Organization (WMO)*, 1988; 1992; 1995] have shown a downward trend in total column ozone that began in the late 1970s with significant decreases over the polar and high latitudes on both hemispheres, which cannot be explained solely by natural causes. It is now well established that man- made chemical compounds released into the atmosphere are responsible for the largest part of the observed ozone depletion through heterogeneous processes, not entirely limited to the polar regions, where the impact of chlorine and bromine compounds on ozone is strongly enhanced by the presence of polar stratospheric clouds (PSCs) [*Crutzen and Arnold*, 1986; *Solomon*, 1990]. Scientific evidence points to the existence of a threshold in the stratospheric chlorine-equivalent loading for the onset of ozone loss, estimated to be about 2 pbbv [*WMO*, 1995].

Under the present chlorine-equivalent loading conditions, volcanic eruptions are believed to have a strong influence on ozone [*Hoffman and Solomon*, 1989; *Brasseur and Granier*, 1992; *Tie et al.*, 1994a, 1994b; *Tie and Brasseur*, 1995; *Solomon et al.*, 1996]. In addition to the volcanic interference, the relative phase of quasi-cyclical phenomena such as the quasi-biennial oscillation (QBO), the longer-lasting El Nino/Southern Oscillation (ENSO) events and the solar cycle, may introduce additional variance and significantly modify the ozone field [*Zerefos et. al.*, 1992; *Randel and Cobb*, 1994]. Both El Chichon and Pinatubo erupted at solar maximum periods during ENSO events and were accompanied by the east phase of the QBO (beginning of the east phase in the case of Pinatubo) [*Zerefos et al.*, 1992; 1994]. The synergy of these natural phenomena has contributed to the observed extreme deficiencies in the ozone record [*Bojkov*, 1987; *Bojkov et al.*, 1993].

Using both satellite and ground based data, it appears that winter/spring ozone loss in the last decade has become consistently larger than that reported over a longer time period [*WMO*, 1995]. This indication of an acceleration in the ozone decline in recent years as compared to the trends in the 1970s, especially in the middle to high latitudes of the northern hemisphere is now well documented [*Bojkov et al.*, 1995; *Harris et al.*, 1997]. Moreover, recent model calculations from 2-D stratospheric models, show that models are able to reproduce in general these observed features of the ozone trends [*WMO*, 1995, chap. 6]. It should be noted that, at middle latitudes of both hemispheres, most of the models show an underestimation of the observed decline, even if PSC chemistry is included.

The purpose of this paper is to provide a new look at the total ozone decrease in the last decades, from both observations and from model results. The observation data used in this study come from the longest available ground-based reevaluated and satellite homogenized global total ozone record spanning from

[1]Laboratory of Atmospheric Physics, Aristotle University of Thessaloniki, Thessaloniki, Greece.
[2]National Center for Atmospheric Research, Boulder, Colorado

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1964 through 1994, kindly provided by *Bojkov and Fioletov* [1995].

As part of our study, the effect of natural long-term oscillations such as the QBO, ENSO, and the solar cycle on total column ozone is filtered out, in order to remove any interfering synergistic effects which can result in large ozone changes [e.g., *Bojkov*, 1987]. Using then the long-term filtered data, we examine, first, the different phases of the ozone decline and their connection to the stratospheric equivalent chlorine loading, confirming earlier findings on the existence of a threshold for the onset of ozone loss [e.g. *WMO*, 1992, 1995; *Solomon et al.*, 1992; *Daniel et al.*, 1995].

The observational results are then compared during the different phases of the decline, to the results of a 2-D chemical/dynamical model study of the chemical effects on the ozone layer, associated with heterogeneous mechanisms under different-chlorine loading scenarios, which represent the three subperiods of observations mentioned above, namely the last three decades, 1964-1973, 1974-1983, and 1984-1993. The model, an updated version of the model *Brasseur et al.*, [1990] and *Brasseur and Granier* [1992], described in section 3, has included the representation of PSCs, sulfate aerosols calculated by microphysical processes, and the heterogeneous reactions on the surface of PSCs and sulfate aerosols. With the aid of the model, we examine the rate, the aspects, and the possible causes of the observed ozone deficiencies under the different chlorine and sulfate aerosol loading conditions of the subperiods chosen, providing also a validation of the model's sensitivity to the stratospheric temperature decrease.

2. Data and Method of Analysis

Time series of total ozone have been used as global zonal means derived from recently reevaluated ground-based total ozone data by *Bojkov and Fioletov* [1995]. In the present study the term "total ozone" refers to the total column of ozone in the atmosphere. The construction of the data set used here is based on the strong spatial correlation which exists between the long-term variations in the time series of observations of ground-based stations. As described in their paper, *Bojkov and Fioletov* [1995] used both ground-based and total ozone mapping spectrometer (TOMS) observations to calculate zonally averaged monthly mean deviations for 5° latitudinal belts for the entire total ozone observing period, before the satellite global coverage became available.

To filter out the effect of natural oscillations on total ozone, a simple statistical model is used for the total ozone variations at each latitude belt, described by the following equation:

$$OZ(i,j) = S(i,j) + Q(i,j) + SO(i,j) + SE(i,j) + Tr(i,j) + \text{residual}$$

where i denotes the month and j the year of total ozone (OZ) and its components, i.e., the seasonal (S), the QBO (Q), the ENSO (SO), the solar cycle effect (SE), and finally, the trend term (Tr). Total ozone data were deseasonalized by subtracting the long-term monthly mean (1964-1993) pertaining to the same calendar month. The QBO component in total ozone was filtered by using two variables to describe this fundamental equatorial oscillation: the monthly mean equatorial zonal winds at 25 hPa and at 50 hPa, as suggested by *Bojkov and Fioletov* [1996].

In the zonal means studied here, the ENSO signal appears significant mainly in the tropical region. At the extratropics and at higher latitudes it shows a strong longitudinal dependence [*Randel and Cobb*, 1994; *Zerefos et al.*, 1994]. The ENSO signal was filtered from the zonal monthly mean total ozone time series, using as an index of ENSO the Southern Oscillation Index (SOI) and by determining its effect and phase lag from an undisturbed-from-volcanic-eruption period (i.e., the period from January 1965 to December 1975).

Finally, the solar cycle signal appears to be stronger in the tropical and subtropical regions. It decays slowly as we move to higher latitudes in both hemispheres, where it is masked by the higher noise levels in the ozone field [Zerefos et al., 1997]. This effect has been examined and removed using as index the monthly averaged 10.7cm solar radio flux (in 10^{-22} W m^{-2} Hz^{-1}) from the World Data Center Space Test Program, Boulder, Colorado.

3. Model Description

The model used in the present study is an updated version of the 2-D (latitude/altitude) chemical/dynamical model of the stratosphere developed by *Brasseur et al.* [1990] and *Granier and Brasseur* [1992]. It extends from pole to pole with a latitudinal resolution of 5° and from the surface to the 85 km altitude with a vertical resolution of 1 km. Approximately 60 species and 110 chemical and photochemical reactions are included in the model.

The model used to simulate the formation and fate of PSCs is from *Larsen* [1991], *De Rudder et al.* [1996], and *Tie et al.* [1996]. In this microphysical model, the PSC particles are assumed to be spheres, which are distributed within 50 bins according to their size. Radii obey a geometric progression with a ratio of 2. Three types of particles are considered in the model. The first type is represented by diluted sulfuric acid particles, with a size distribution provided by the microphysical model of *Tie et al.* [1994a]. These sulfate aerosol particles serve as cloud condensation nuclei (CCN) for the PSC particles. When the atmospheric temperature decreases, nitric acid vapor becomes supersaturated with respect to nitric acid trihydrate [*Crutzen and Arnold*, 1986], and a second type of particle is formed. These particles, named type I PSC particles (PSC I), are composed of a nitric acid trihydrate shell surrounding a small sulfate core. When the temperature decreases further and reaches the frost point, PSC I act as condensation nuclei for a third type of particle named type II PSCs (PSC II), composed of an ice shell coating a PSC I core. The three microphysical processes which are considered in the present study, i.e., nucleation, condensation, and sedimentation, are described by *De Ruder et al.* [1996]. The formation of sulfate aerosol before and after the eruption of El Chichon and Pinatubo is simulated by a microphysical model of sulfate aerosols [*Tie et al.*, 1994a; 1994b]. The heterogeneous reactions on the surface of PSCs and sulfate aerosols included in the model are the following:

(R-1) $ClONO_2(g) + H_2O(a,p) = HOCl(g) + HNO_3(a,p)$

(R-2) $ClONO_2(g) + HCl(a,p) = Cl_2(g) + HNO_3(a,p)$

(R-3) $N_2O_5(g) + H_2O(a,p) = 2\ HNO_3(a,p)$

(R-4) $N_2O_5(g) + HCl(p) = ClNO_2(g) + HNO_3(p)$

(R-5) $HOCl(g) + HCl(a,p) = Cl_2(g) + H_2O(a,p)$

where (g) denotes the species in the gas phase, (p) species in the surface of PSCs, and (a) in the surface of sulfate aerosol. The kinetic rates of these seven reactions included in the model are described by *Tie et al.* [1996].

4. Discussion and Results

4.1 Ozone Correlation With Chlorine Loading

CFCs, halons and hydrochlorofluorocarbons are able to derive active chlorine and bromine in the stratosphere, destroying stratospheric ozone [*Molina and Rowland*, 1974; *Stolarski and Cicerone*, 1974]. Even though the CFC release has decreased as a result of the Montreal Protocol and the subsequent amendments, the chlorine content of the stratosphere, which has been increasing in the past decades, is expected to change very little in the next years. Figure 1 shows the annual mean changes in the filtered total ozone data as described in section 2. Similar figures showing the changes in total ozone as zonal means over the past years have been presented in earlier studies [*WMO*, 1995; *Reinsel et al.*, 1994; *Bojkov and Fioletov*, 1995]. Nevertheless, our purpose here is to justify the choice of the subperiods used in the following sections of our observation and model study and also to examine in brief the total ozone connection to stratospheric chlorine loading, which is an essential input to the model.

The total ozone changes in Figure 1 are presented as area weighted averages over the northern (>35°N) and southern hemisphere (>35°S) extratropics, and the tropical region (35°S-35°N), as percent deviations from the 1964-1970 mean, a period

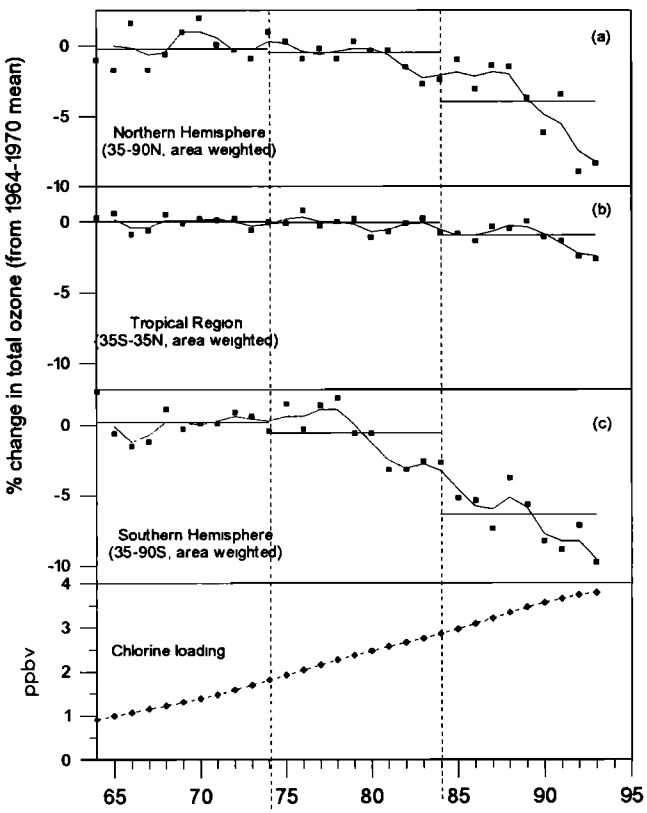

Figure 1. Deviations (in percent) from the 1964-1970 mean annual total ozone for the area weighted averages over (a) the northern hemisphere extratropics (>35°N), (b) the tropical region (35°S-35°N) and (c) the southern hemisphere extratropics (>35°S). QBO, ENSO and the solar cycle effects have been filtered from the total ozone data. The smoothed time series (1-2-1 weighting) are shown as solid lines, while the black squares represent the actual data points. Horizontal lines represent the mean of each subperiod. Figure 1d shows the time series of the estimated chlorine loading for comparison.

in which no ozone loss is observed. It should be stressed here that the tropical region, although all the prominent oscillations are filtered out (QBO, ENSO, and solar cycle), shows a very small change throughout the whole period of study. For both hemispheres, the total ozone correlation to the chlorine level, which is found insignificant before 1980, increases gradually with time and becomes highly significant if only the last 10 years are considered, excluding the years after the El Chichon and Pinatubo eruptions (linear correlation coefficients for the southern and the northern hemisphere extratropics are: -0.79(S) and -0.65(N) for 1974-1982, and -0.91(S) and -0.87(N) for 1984-1991).

Calculating the change of trend in the solid curves in Figure 1, the turning point in the ozone decline was found to be the year 1978 for the southern hemisphere, where the dynamical conditions favored the beginning of ozone loss. In the northern hemisphere the decrease shows a gentle slope from the mid-1970s, with the turning point around 1980. So, after filtering out the effects of natural oscillations from the total ozone record, the existence of a threshold for the onset of ozone loss that depends on the stratospheric chlorine abundance is supported, confirming earlier studies [*WMO* 1995; *Daniel et al.*, 1995]. In accordance with these earlier studies, for the area-weighted mean of the southern hemisphere, the timing of this onset corresponds to a chlorine level of approximately 2.5 ppbv.

In their earlier study, *Bojkov and Fioletov* [1995] compared two subsets of their reconstructed total column ozone means (1984-1994 versus the pre-1980 period), determining that the decline in the last decade during winter-spring over the northern hemisphere high latitudes can be as high as 6%, and over 20% in the antarctic spring. In our analysis, we go one step further, first, by filtering out the natural effects that can significantly affect the interannual ozone variability and, second, by examining the ozone data for three subperiods, each one presenting a different rate of decline. The first subperiod is chosen to be the undisturbed period 1964-1973, the first decade of our record, when the ozone change is small and the correlation to chlorine loading is insignificant. Second, is the onset of the ozone "hole" phenomenon (1974-1983), a period influenced partly by the eruption of the El Chichon. Finally, the last decade, is the period 1984-1993, when the declining phase of total ozone is accelerated and also influenced by the volcanic eruption of Mt. Pinatubo. The chlorine levels that are used as initial conditions for the model study, the results of which are discussed in the following sections, are the mean levels of the years 1968, 1978, and 1988, each year being representative of the average conditions pertaining to each subperiod under study.

Even though the CFC release has decreased as a result of the Montreal Protocol and its subsequent amendments, the chlorine content of the stratosphere, which has been increasing in the past decades, is expected to change very little in the next years. Based on the correlation of chlorine loading and the observed ozone trend, one can estimate the further ozone trend. According to the Intergovernmental Panel on Climate Change scenario C [*Houghton et al.*, 1990], the chlorine-loading will reduce to 2.4 ppbv in the year 2030, so that the ozone depletion attributed to this effect is expected to reduce significantly.

4.2 Evolution of Ozone Changes in the Last Two Decades

To examine the consistency of the total ozone change in the past two decades and also the consistency of the rate of this change, we have used the first decade of the record, 1964-1973,

as a base-level period for the calculations and comparisons. As discussed above, this period appears undisturbed, showing practically no ozone decline, or a small and insignificant change in some latitude belts. The effect of known natural signals such as the QBO, ENSO, and the solar cycle has been removed from the record, to avoid any synergistic interference in the calculation of the changes. The role and effect of the volcanic eruptions will be discussed below in more detail.

Figure 2 shows the total ozone change as percentage change from the level base period, for the period 1974-1983. The differences between the monthly means are presented as a latitude - month plot, for each month of the year and for each latitude belt. The shading indicates areas where this difference is significant over the 95% confidence level (determined by a t-test of the difference between means). As seen in Figure 2a, which presents results from the observational data, during the decade 1974-1983, total ozone is already much lower in the southern hemisphere, where low values appear persistent and significant in the whole winter-spring season, reaching as far as 60°S. The area and timing of the ozone hole are evident, with ozone decline from the undisturbed period reaching 10% at polar latitudes in austral spring. In the northern hemisphere, a decline in total ozone is already seen in the winter-spring season and at high latitudes over 50°N. Even though it appears significant only over a small area near the pole, it is a strong indication of total ozone depletion starting already in the northern hemisphere. Figure 2b presents the model calculations of the decline in total ozone for the period 1974-1983. The chlorine levels of 1978 (2.5 ppbv) were used as initial conditions. For the level base period, to which the model simulations are compared, we used the levels of 1968 (1.3 ppbv). The simulation includes the representation of heterogeneous reactions on the surfaces of PSCs and background sulfate aerosol. The calculated distributions of PSCs in the Arctic and in Antarctica are very different. Over Antarctica, nitric acid trihydrate particles (type I PSCs) are formed from early June to late September with a maximum surface area of 25 m^2/cm^3, while in the Arctic, type I PSCs are formed only in January with a maximum surface area of 5 m^2/cm^3. The ice crystal clouds (type II PSCs) are present over Antarctica in August but are not seen in the Arctic. The results from the model simulations are consistent overall with the calculations from the observations. The model simulation shows that ozone loss over the whole year has started already in the southern hemisphere, with the lowest values, and thus the highest ozone depletion in the southern spring period, in polar regions, in close agreement in magnitude of change with the observations. Little change is shown for the rest of the globe and for all seasons, with the exception of the high latitudes of the northern hemisphere in winter-spring where a change of -2% from the mean is calculated, suggesting that heterogeneous chemistry on PSCs has already started. This result is in very good agreement with the observations.

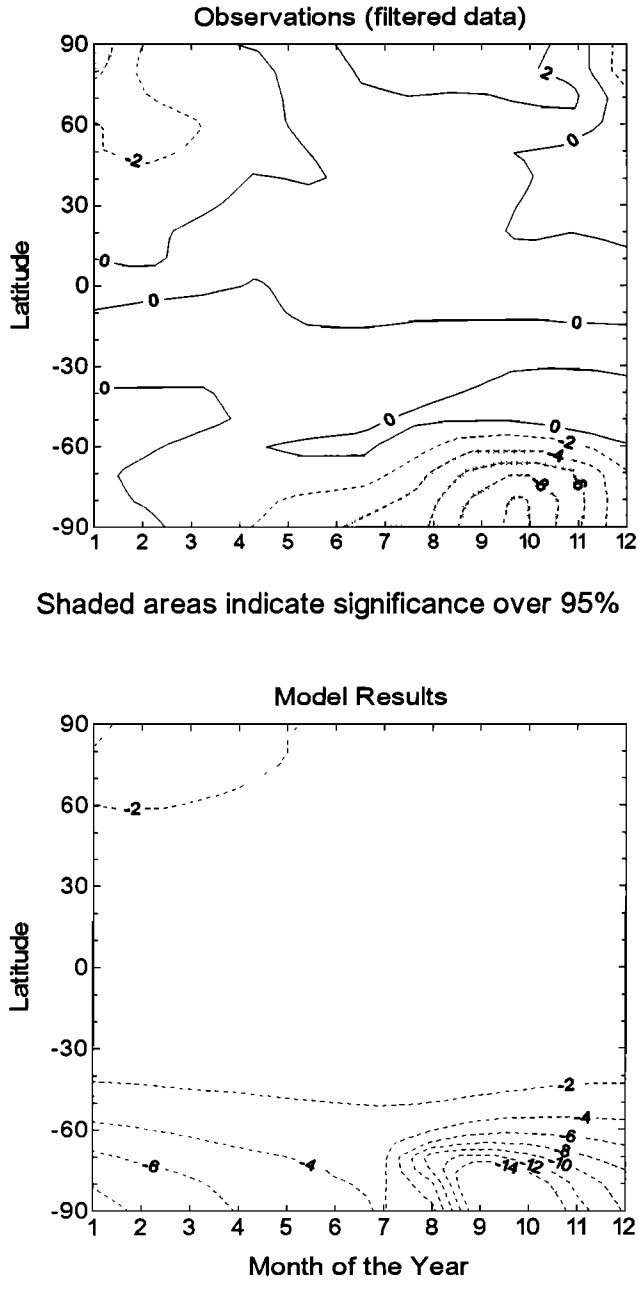

Figure 2. (a) Difference (in percent) between total ozone values for the periods 1964-1973 and 1974-1983. QBO, ENSO, and the solar cycle effects have been filtered from the total ozone data. Shading indicates significance over the 95% level. (b) Model calculated changes in total ozone (%) for the same period with heterogeneous reactions on the surface of PSCs and background aerosols.

Figure 3 shows the results for both observations (Figure 3a) and the model simulation (Figure 3b) for the period 1984-1993. The difference from the level base period becomes higher, and the changes in total ozone become much stronger. The observational results in Figure 3a show that in the southern hemisphere, highly significant total ozone changes dominate over all months, even at lower southern latitudes reaching into the tropical region, with the lowest values found in the middle to high latitudes in the southern spring, exceeding a change of 30% from the base-level period. The decline of total ozone in this period is found to be significant at middle to high latitudes in the northern hemisphere, during the whole winter-spring season, when the change from the undisturbed period exceeds -6%. In both cases (Figures 2 and 3) the differences in the equatorial belt and in most of the tropical region remain very low (below -1%), showing that in the time periods examined here, practically no change, and thus no ozone decline has occurred over these regions.

The observational results of Figure 3a are in extremely close agreement with the ones shown already by *Bojkov and Fioletov* [1995], even though they have compared the last decade to the pre-1980 period. This is expected because the period before 1980 shows the same characteristics as our base-level period.

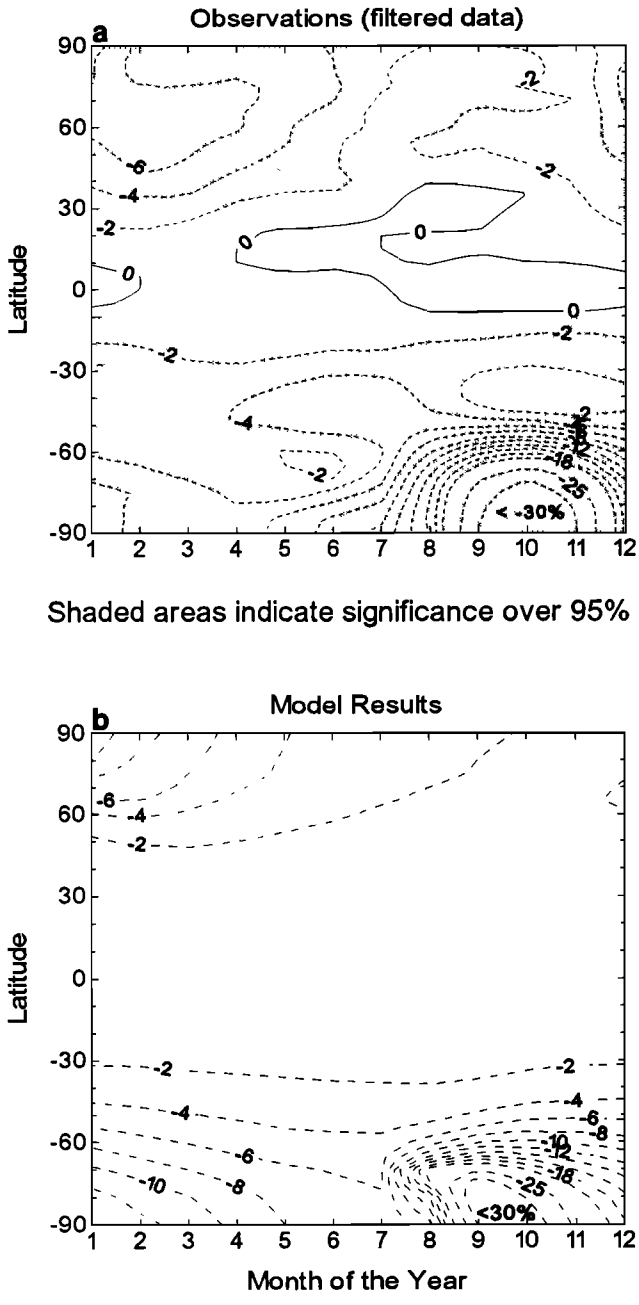

Figure 3. (a) Difference (in percent) between total ozone values for the periods 1964-1973 and 1984-1993. QBO, ENSO, and the solar cycle effects have been filtered from the total ozone data. Shading indicates significance over the 95% level. (b) Model calculated changes in total ozone (%) for the same period with heterogeneous reactions on the surface of PSCs and background aerosols.

The comparison between Figures 2a and 3a, both observational results, shows that the changes in the last decade appear intensified (i.e., more negative) by 3 or more times. This result, revealing an acceleration in the ozone decline in the last decade, is seen better in the southern hemisphere, at latitudes higher than 30°S, over the whole year. The higher rate of change is seen clearly in midlatitudes of the northern hemisphere, starting already in the early winter months and persisting until late northern spring. Although the ozone levels are lower in the northern polar region, the rate of ozone loss is following the same course as in the previous period. These results are in agreement with recent findings from ground-based Dobson stations, mainly located in the northern hemisphere, which point to an acceleration of total ozone trends in the last years, as compared to trends calculated over the whole period of the stations observations. [*WMO*, 1995; *Bojkov et al.*, 1995; *Harris et al.*, 1997].

In Figure 3b, results are presented from the model simulation that includes heterogeneous reactions on the surfaces of background aerosol and PSCs. The chlorine levels of 1988 (3.5 ppbv) were used as initial conditions. The higher changes in total ozone in the southern hemisphere are reproduced, reaching also the southern tropical region, at the same levels as the decline calculated from the observations. The region with the lowest values is, as expected, the polar area in spring, the model showing in this case a somewhat smaller decline (31%) than the one calculated from the observations (38%). In the northern hemisphere, and especially at midlatitudes, the model simulated ozone loss is less and is not seen as far south as in the observations. Nevertheless, the lowest values appear in the same region and during the same months of the year, following the same pattern as the observations. Consistent with the observations, the model simulation shows very little change in the tropical region.

4.3 Effect of Volcanic Aerosols

In both decades, the comparison between model and observational results, reveals an underestimation of the ozone loss at midlatitudes in the model, mainly in the northern hemisphere. One of the reasons for this underestimation is considered to be the increase of sulfate aerosol loading by the eruptions of El Chichon in 1982 and Pinatubo in 1991 [*Tie et al.*, 1994a,b; *Tie and Brasseur*, 1995; *Solomon et al.*, 1996], an effect that is not included in the model runs presented in the previous section but is present in the observational results. This is better seen during the period of the Mt. Pinatubo eruption and at a lesser degree in the changes during the first decade, as presented in Figures 2a and 3a.

In order to examine the interference of volcanic aerosol particles, we performed a model simulation for the case of the Pinatubo eruption. The very large aerosol loading at middle and high latitudes due to large volcanic eruptions, normally remains in the stratosphere for a period of about 2 years. For this reason, we have assumed for the model simulation that from 1984 to 1993, the sulfate loading is in the volcanic condition for a total of 4 years (the year 1984 and from the Pinatubo eruption through 1993), and in the background condition for the remaining 6 years of the decade. Figure 4 shows the changes of ozone between 1984 and 1993, a period when the averaged sulfate aerosol loading represents both volcanic and background conditions, and 1964/1973, our level base period. The comparison of these two periods shows a consistent result with the observations, seen in Figure 3a. Figure 4 shows larger calculated negative departures of total ozone over the northern hemisphere middle and high latitudes during the winter - spring season, i.e., improvement of the model results as compared to the observations.

The model simulation was not performed for the case of the El Chichon eruption, because as shown in Figure 2, the differences between model and observations are not as significant, and the overall comparison is much better even without the effect of the volcanic eruption. This can be partly due to the lower aerosol loading from this eruption and partly to the lower chlorine loading at that time, factors that can significantly alter the effect in a quantitative and qualitative sense. Also, the period of high aerosol loading that is included in the analysis is only 1.5 years

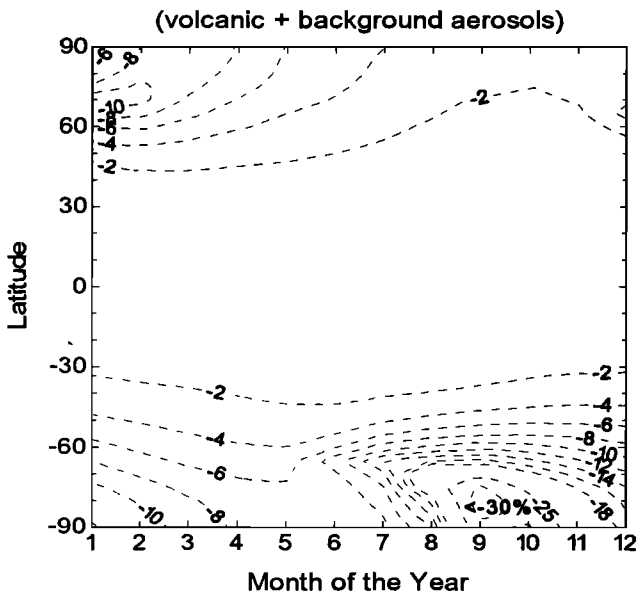

Figure 4. Model calculated changes in total ozone (%) between 1964-1973 and 1984-1993 with heterogeneous reactions on the surface of PSCs and weighted sulfate aerosols for the period 1984-1993 (4 years in enhanced aerosols and 6 years in background aerosols).

(April 1982 to December 1983) as compared to the 4 years in the case of the 1984-1993 period. However, at least part of the underestimation (about 2% of total ozone loss) at midlatitudes around 50°N, might be attributed to the effects of the eruption.

The model results indicate that the ozone depletion at high latitudes of both the northern and southern hemispheres is mainly caused by the heterogeneous reactions on the surface of PSCs, while at northern midlatitudes, the heterogeneous reactions on the surface of sulfate aerosols, especially after large volcanic eruptions, are greatly responsible for the ozone loss.

4.4 Effects of the Stratospheric Temperature Decrease

The stratospheric temperature has been known for some years now to decrease [*WMO*, 1988; *Labitzke and van Loon*, 1994a & b], considered as a consequence of the greenhouse gases increase (such as CO_2, CH_4 etc.). This decrease, as studied in long-term stratospheric data of the northern hemisphere [*Labitzke and van Loon*, 1994a & b], is most prominent in the months of early spring, coinciding with the time of the observed large change in ozone. Even though the stratospheric ozone decrease would, in turn, lead to temperature decreases, in this study we do not consider this feedback, focusing on the response of total column ozone to a stratospheric temperature decrease.

The decrease in stratospheric temperature has two effects on the ozone depletion. First, lower temperatures will enhance the formations in the concentration of PSCs, which lead to increases in the heterogeneous conversion on the surface of PSCs. Second, the decrease of temperature will enhance the reaction coefficients on the surface of sulfate aerosols [*Hanson et al.*, 1994]. Both effects will lead to the increase in active chlorine (ClO), and thus to a decrease in ozone concentration. In the model, as a sensitivity study, we have decreased the temperature by 2°. In the first simulation (Figure 5a), both effects (i.e., the increase in the concentration of PSCs and the reaction coefficients on the surface of sulfate aerosols) are included in the model. The result (Figure 5a) shows that the decrease in stratospheric temperature increases significantly the ozone loss at middle to high latitudes of the northern hemisphere. Comparing this to Figure 3b, the decrease in total ozone between 1984-1993 and 1964-1973 changes from 6% to 20% at high latitudes, and from 2% to 10% at mid-

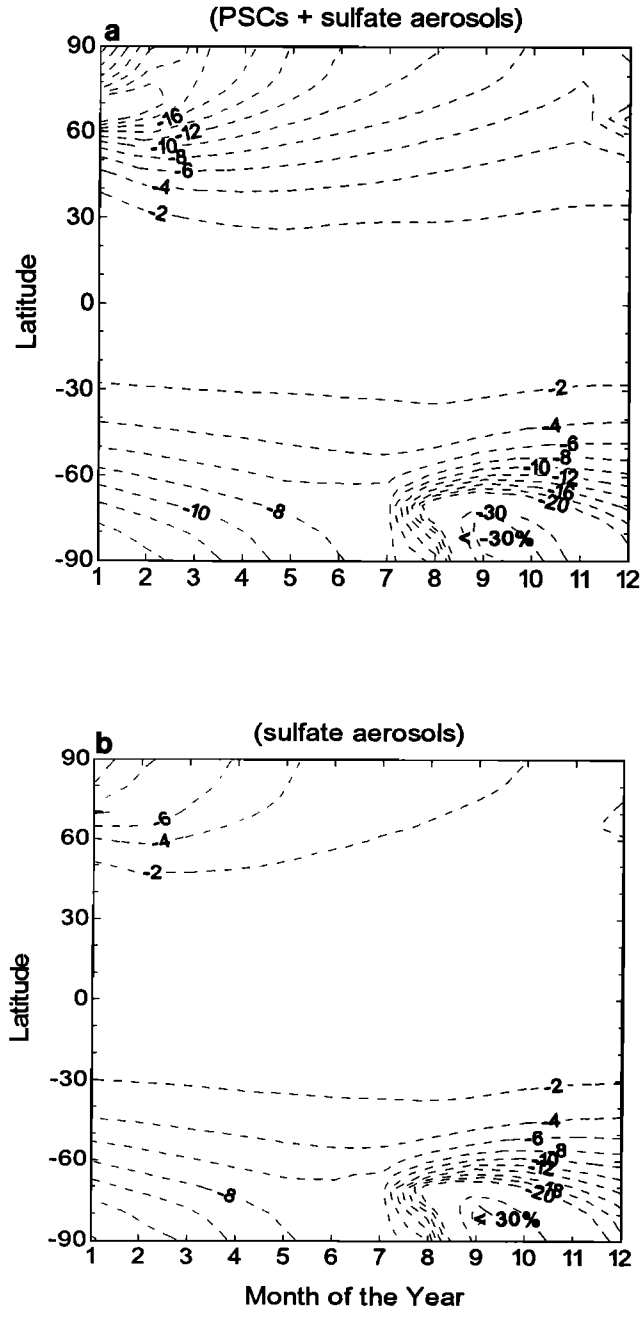

Figure 5. (a) Model calculated changes in total ozone (%) between 1984-1993 and 1964-1973 with heterogeneous reactions on the surface of PSCs and background aerosols. The stratospheric temperature is decreased by 2° to allow the increase in the concentration of PSCs and the reaction coefficient on the surface of sulfate aerosol in the model. (b) Model calculated changes in total ozone (%) between 1984-1993 and 1964-1973 with heterogeneous reactions on the surface of PSCs and background aerosols. The stratospheric temperature is decreased by 2° to allow only the increase in the reaction coefficient on the surface of sulfate aerosol in the model.

latitudes of the northern hemisphere during winter and spring. As a second run, we have included in the model only the effect of the increase in reaction coefficients on the surface of sulfate aerosols. The result (Figure 5b) shows insignificant difference as compared to the results in Figure 3b. The contrast of values between Figure 5a and 5b indicates that the decrease in stratospheric temperature (by 2°) could lead to a potential increase in the concentration of PSCs in the northern hemisphere. As a result, the ozone depletion could be significantly enhanced.

5. Summary and Conclusions

The longest reevaluated available time series of total ozone, with global coverage as zonal means, has been used to study the consistency of total ozone decline observed during the last two decades. A 2-D chemical/dynamical model has been used to examine the relation of this decline to the stratospheric chlorine loading, sulfate background, and volcanic aerosol loading and temperature decrease.

The total ozone data used have been filtered in order to remove the natural quasi-periodic oscillations such as the QBO, ENSO, and the 11-year solar cycle effect, which are already known to significantly affect the variability of the ozone layer. The observed total ozone decline and its acceleration are studied on decadal timescales, calculating the differences from the first decade of the record (1964-1973), a period that shows no ozone trend, and can be thus considered as unaffected from the increase of the stratospheric chlorine-equivalent loading. Also, only a very small change is seen in the filtered total ozone in the tropics, a region where all the natural quasi-periodic oscillations peak.

A 2-D chemical-dynamical model of the middle atmosphere has been used in this study to simulate qualitatively and quantitatively the evolution and changes of total ozone under different stratospheric chlorine-loading conditions, representing the mean conditions for the decades 1964-1973, 1974-1983 and 1984-1993, the same time periods used in the analysis of the observations. The representation of PSCs at high latitudes of both hemispheres, of sulfate aerosols, calculated by microphysical processes, and the heterogeneous reactions on the surface of PSCs and sulfate aerosols has been taken into account in the model simulations.

Our study confirms some of the well-known features of ozone depletion, showing that in the periods 1974-1983 and 1984-1993, low ozone values dominate at high latitudes of both hemispheres, being lower in the last decade by more than 3 times in certain areas and seasons. In our analysis of the filtered total ozone data, this is seen at the high latitudes of the southern hemisphere but is more striking at middle to high latitudes of the northern hemisphere, revealing an acceleration in the total ozone decline in the last decade. The differences in the equatorial belt and in most of the tropical region remain very low (below 1%), in both decades, showing that practically no change, and thus no ozone decline, has occurred over these regions. Even though a somewhat different approach is used here, the results are found to match those of other studies covering the issue of observed total ozone trends [*WMO*, 1994; *Bojkov et al.*, 1995; *Harris et al.*, 1997].

The observation results were then compared to results of model simulation, which in the first place included only the representation of heterogeneous reactions on the surfaces of PSCs and background sulfate aerosol, using different calculated distributions of PSCs in the Arctic and the Antarctic regions. The acceleration in total ozone decline is evident also in the model simulations. The model results are in good agreement with the observations, especially at high latitudes throughout the year, and during the first decade. This comparison supports the notion that at southern and northern high latitudes, total ozone variability is strongly affected by heterogeneous processes inside PSCs. In the middle to high latitudes of both hemispheres, though, this simulation of the model, which incorporates only background aerosols, underestimates the ozone decline. Although evident in the first decade, this is much clearer in the last decade and in the northern hemisphere middle to high latitudes.

This pronounced underestimation was considered here to be linked to the effect of the volcanic eruptions of El Chichon and Pinatubo, which occurred in the first and second decade of analysis. Even though the natural oscillations affecting the ozone layer were filtered from the data, the volcanic effects are still included. In order to examine further this effect on a decadal time period, a model simulation was performed for the case of the Mount Pinatubo eruption. In this simulation the sulfate aerosol loading was averaged to represent both the enhanced aerosol loading of volcanic origin and the background conditions. This resulted in an improvement of the comparison with the observations at northern midlatitudes in a quantitative as well as in a qualitative sense.

The good agreement between the model and observation results, if both simulations are considered, shows the model's capability, within some limitations, to parameterize the PSC and sulfate aerosol chemistry and its effect on total ozone. The model results indicate that at high latitudes, in both the northern and southern hemispheres the ozone depletion is mainly associated to the heterogeneous reactions on the surface of PSCs, while at northern midlatitudes the heterogeneous reactions on the surface of sulfate aerosols, especially after large volcanic eruptions, can contribute up to 5% or more to the observed ozone losses, as suggested by both theory and observations [e.g., *Zerefos et al.*, 1994; *Randel and Wu*, 1995; *Tie and Brasseur*, 1995; *Solomon et al.*, 1996].

Stratospheric temperature changes can facilitate the heterogeneous conversion processes on PSC surfaces, by enhancing the formations in their concentration. Another important effect of the temperature decrease is the increase of the reaction coefficients on the surface of sulfate aerosols. In a sensitivity study performed with the model, in an attempt to address the question of temperature feedback on ozone responses to perturbations, both these factors are taken into account. It was found that a 2° change in stratospheric temperature can lead to a potential increase in the concentration of PSCs, mostly in the northern hemisphere, resulting in a significant increase in ozone depletion.

The consistent rate of the ozone decline as seen in this study, and the apparent relation to the stratospheric chlorine loading, as studied with the aid of the model, shows that even larger decline would have been highly likely without reductions in the human emissions of ozone-depleting substances. Dynamical changes in the atmosphere may enhance the observed acceleration in the ozone decrease, also by altering the ozone transport to higher latitudes, an issue that is not addressed in this study. Model simulation validations are needed to investigate the large-scale transport in the lower stratosphere and the response of total ozone to temperature perturbations from lower atmospheric levels, also through feedback between the stratosphere and troposphere.

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G. Brasseur and X. X. Tie, National Center for Atmospheric Research., P. O. Box 3000, Boulder, CO, 80307-3000

K. Tourpali and C. S. Zerefos, Laboratory of Atmospheric Physics, Aristotle University of Thessaloniki, Physics Department, P. O. Box 149, 54006 Thessaloniki, Greece. (e-mail: tourpali@ccf auth gr)

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