GEOPHYSICAL RESEARCH LETTERS, VOL. 22, NO. 22, PAGES 3035-3038, NOVEMBER 15, 1995

The response of stratospheric ozone to volcanic eruptions: Sensitivity to atmospheric chlorine loading

XueXi Tie and Guy Brasseur
National Center for Atmospheric Research, Boulder, Colorado

Abstract. Model calculations suggest that the ozone decrease observed a few years after the eruptions of Mt. Pinatubo and El Chichon may have been unique in the Earth's history, and is directly linked to the emission in the atmosphere of industrially manufactured chlorofluorocarbons. For chlorine loadings typical of the pre-1980 period, the ozone column abundance should have increased after a large volcanic eruption. After 1980, as a result of growth in chlorine loading, the response of ozone became negative in winter at mid- and high latitudes. In the future, the response of ozone is expected to become positive again, if the production of chlorofluorocarbons is sufficiently reduced. The calculations also show that, under low chlorine loadings, the response of ozone is insensitive to the magnitude of the eruption, while, under present conditions (high chlorine loading), the ozone depletion increases with the amount of SO_2 injected in the stratosphere by the volcano.

Introduction

Abnormally low abundances of stratospheric ozone have been reported during the 2-3 years following the eruption of Mt Pinatubo (The Philippines, June 1991). The analysis of ozone column abundances measured by the Total Ozone Mapping Spectrometer (TOMS) has revealed ozone concentrations significantly below climatological values (ranging from approximately 8 to 10% at high-latitudes of the northern hemisphere during the 1991-1992 and 1992-1993 winters (Randel and Wu, 1995)). Numerical models which simulate the behavior of chemical constituents in the middle atmosphere and, specifically, account for the effects of the Mt Pinatubo eruption (Brasseur and Granier, 1992; Pitari and Rizi, 1993; Tie et al., 1994a; Rodriguez, et al., 1994; Bekki and Pyle, 1994) suggest that, in addition to dynamical and radiative perturbations which affected stratospheric ozone during a few months following the eruption, the reduction in the abundance of stratospheric ozone observed at mid- and high latitudes over a period of 2 to 3 years was of chemical origin. The mechanisms involved are the heterogeneous conversion of nitrogen oxides into nitric acid (HNO_3)

$$N_2O_5 + H_2O \text{ (aerosol)} \text{ ------> } 2\ HNO_3 \qquad (1)$$

and of chlorine nitrate ($ClONO_2$) into HOCl and HNO_3

$$ClONO_2 + H_2O \text{ (aerosol)} \text{ -> } HOCl + HNO_3 \qquad (2)$$

on the surface of sulfate aerosol particles. After large volcanic eruptions, the aerosol loading of the atmosphere is increased ten to a hundred-fold, and the surface area density available for these heterogeneous reactions to occur is also dramatically enhanced. The effect of reaction (1) is to reduce the abundance of ozone-destroying nitrogen oxides and, as a result, to enhance the level of ClO and OH radicals (Granier and Brasseur, 1992) which destroy ozone in the lower stratosphere (Hofmann and Solomon, 1989). Thus, if the rate of heterogeneous reaction (1) is increased as a result of volcanic eruptions, the ozone abundance is expected to be enhanced in the middle stratosphere (where its loss is dominated by NO_x) and reduced in the lower stratosphere (where ClO_x and HO_x radicals play a dominant role in its destruction). However, since the amount of N_2O_5 present in the atmosphere is limited by the rate at which it is produced, reaction (1) is rapidly "saturated" as the aerosol loading increases. In other words, the rate-limiting step for the NO_x -> HNO_3 conversion is the $NO_2 + NO_3$ -> N_2O_5 reaction rather than reaction (1) for sufficiently large aerosol loading. Such saturation does not occur as rapidly for reaction (2). This latter reaction is effective only in cold air masses, i.e., during winter in the polar lower stratosphere. As HOCl is photolyzed (e.g., at polar sunrise), chlorine radicals (Cl) are produced and destroy ozone catalytically in the lower stratosphere.

The impact of volcanic eruptions on stratospheric ozone via reactions (1) and (2) thus depends directly on the chlorine loading of the stratosphere. This loading has increased over the last decades as a result of the growing production of industrially manufactured chlorofluorocarbons (CFCs), and is expected to decrease gradually as the production of CFCs is reduced as a result of the Montreal Protocol and subsequent amendments (Houghton et al., 1990). In this paper, we assess how the response of ozone to a specified volcanic eruption (of the magnitude of the Pinatubo eruption) would have changed under different atmospheric chlorine contents. To address this question, we use our 2-D chemical dynamical radiative model (Brasseur et al., 1990; Granier and Brasseur, 1992), with coupled microphysics (Tie et al., 1994a,b), and estimate the potential impact of such an eruption for chlorine loadings representative of different periods (pre-industrial conditions, present time, and the year 2015). We will also assess the sensitivity of the ozone response to the magnitude of the volcanic eruption under different loadings. In this study, we focus on the long-term (1-2 years) chemical effects of the volcanic eruptions, and ignore the transient radiative and dynamical effects which are significant during the few months following the injection in the stratosphere of sulfate aerosols. We also neglect the potential impacts of volcanic particles on the microphysical processes leading to the formation and fate of polar stratospheric clouds.

Paper number 95GL03057
0094-8534/95/95GL-03057$03.00

Model Simulations

Figure 1 a-f shows the changes in the ozone column abundance of the northern hemisphere calculated by our 2-D model in response to a volcanic eruption for 6 stratospheric chlorine loadings representative of the year 1850 (0.6 ppb), the year 1975 (1.9 ppb), the years following the eruptions of El Chichon (3.0 ppb), and Mt. Pinatubo (3.3 ppb), the year 2015 (2.93 ppb, corresponding to IPCC scenario C), and the year 2015 (3.7 ppb, corresponding to IPCC scenario B), respectively. The concentrations of CH_4, N_2O, and CO_2 are also changing with time according to IPCC scenarios (Houghton et al., 1990). The amount of SO_2 injected into the atmosphere is identical in the 6 cases, and is intended to reproduce conditions (intensity, location, season of eruption) encountered after the Mt. Pinatubo eruption. The conversion of SO_2 into sulfate aerosols and the transport of the volcanic material from the tropics into higher latitudes over a period of 3 years is treated as in the study of Tie et al. (1994a).

For chlorine loadings typical of the pre-industrial era (figure 1a), the ozone column abundance increases after the volcanic eruption, with the largest response (7%) occurring at high latitudes during the spring and fall seasons. The calculated increase in tropical ozone is less than 2%. For conditions representative of 1975, the impact of the Mt. Pinatubo-like volcano is significantly reduced at high latitudes (see Figure 1b), suggesting that the "ClO_x effect" counterbalances to a large extent the "NO_x effect". IN 1982-1984 (corresponding approximately to the period during which the impact of the eruption of El Chichon should have been the most pronounced, see Figure 1c), the response of ozone has become negative in the winter time at latitudes higher than 30°N. Ozone concentrations observed during the winter 1982-1983 were below normal (Mantis et al., 1985), coincident with enhanced aerosol mass density (Dutsch, 1985; Bais et al, 1985), suggesting a volcanic effect of approximately 3-6% at mid-latitudes (WMO, 1995). In 1992-1993 (after the eruption of Mt. Pinatubo), the calculated reduction in the ozone column (Figure 1d) reaches 8% in the northern polar regions (6% at mid-latitudes) in late winter/early spring. The change in the tropical column is insignificant. Reductions of at least this magnitude were reported over the United States (Hofmann et al., 1994) and Canada (Kerr et al., 1993), while an analysis of TOMS data shows that the total ozone abundance in 1992 was 2 to 3% below normal on the average (Gleason et al., 1993) and 8-15% below climatological values at high latitudes in winter (Randel and Wu, 1995). In 2015, assuming that the release in the atmosphere of chlorofluorocarbons is reduced according to IPCC scenario C (chlorine loading of 2.9 ppb), the ozone response to the volcanic eruption becomes positive again, except during a limited period (winter) when slightly negative values are predicted at high latitudes (Figure 1e). The ozone response is different in year, 2015 than in 1983 in spite of the fact that the chlorine load is almost identical in both cases. This results from the higher methane concentration predicted for 2015, which leads to convert additional reactive chlorine (Cl and ClO) into stable chlorine reservoirs (HCl), and hence to reduce the ozone destruction. If IPCC scenario B is adopted, the CFC production is not sufficiently reduced (chlorine loading of 3.7 ppb), and the ozone response to volcanic eruption remains negative and large (8 to 10%) at high latitudes in winter/spring (Figure 1f).

The evolution as a function of time of the volcanic effects on global ozone (entire northern hemisphere and latitudes north of 45°N, respectively) is given in Figure 2. The evolution with time of the chlorine loading is also shown; the values for the future are taken from Scenario A (2.9 ppb Cl_x in 2015 and 1.8 ppb in 2050)

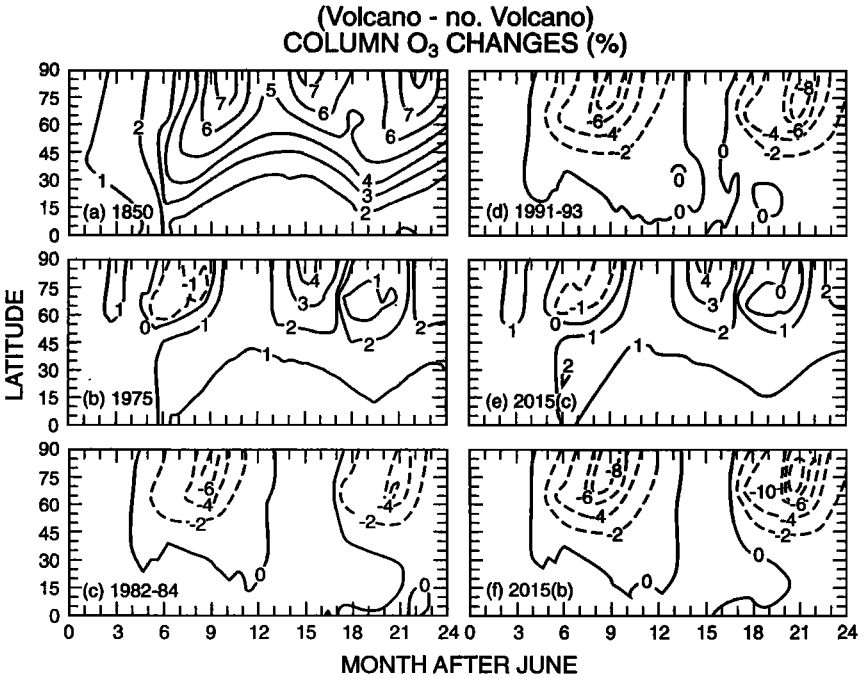

Figure 1. Changes (percent) in the column ozone abundance of the northern hemisphere in response to a Mt. Pinatubo-like volcanic eruption calculated as function of latitude and time (month) for different chlorine loadings corresponding to; (a) 1850 (0.6 ppb); (b) 1975 (1.9 ppb); (c) El Chichon period (3.0 ppb); (d) Pinatubo period (3.3 ppb); (e) 2015 (2.9 ppb, IPCC scenario C); (f) 2015 (3.7 ppb, IPCC scenario B). The abundance of CO_2 and CH_4 increases with time according to IPCC scenarios (CO_2=290 ppm; CH_4=0.9 ppm in 1850; CO_2=350 ppm; CH_4=1.7 ppm in 1990).

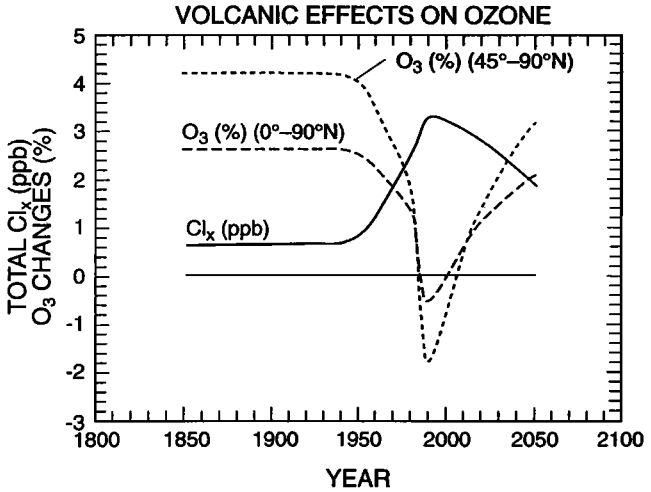

Figure 2. Effect of a Mt. Pinatubo-like volcanic eruption on total ozone (percent) calculated as a function of time (year) of the potential eruption between year 1850 and year 2050 (averaged column in the northern hemisphere and north of 45°N, respectively). The corresponding chlorine loading is also represented.

of the 1994 UNEP/WMO assessment (WMO, 1994). What is striking in this figure is that negative ozone responses are predicted only during a very limited period (30 years) of the Earth's history (from approximately year 1980 to year 2010) with a maximum effect in the 1990's. Thus, the observed ozone depletion recorded after the eruption of Mt. Pinatubo appear to have been exceptional, and a direct result of human activities. The change at 65°N (March) in the vertical distribution of ozone (in percent) and in the rates (molecules/cm^3/s) associated with the NO_x, HO_x, and ClO_x catalytical cycles of ozone destruction are shown in Figure 3 for 2 specific time periods (1850 and post Pinatubo conditions). For the pre-industrial era, the impact of the hypothetical Pinatubo eruption is largest near 25-30 km, with a 25% increase in the ozone density resulting from a significant decrease in the ozone loss rate by NO_x. For conditions representative of the early 1990's the same effect is predicted by the model above 25km, but in addition, a large increase in the ClOx destruction rate between 10 and 20km leads to a 25% reduction in the ozone density near 15km altitude.

Similar model calculations were repeated for an eruption injecting a larger amount of SO_2 into the stratosphere, and producing a surface area density 5 times larger than calculated in the case of Mt. Pinatubo's eruption. The results shown in Figure 4 suggest that the ozone response under pre-industrial conditions is not significantly affected by the intensity of the eruption. This is a direct consequence of the saturation affecting heterogeneous reaction (1). With high (present-day) chlorine loadings, however, the ozone response is very sensitive to the intensity of the eruption. In this case, it is reaction (2), which is not subject to saturation, that plays the major role at high latitudes, and a reduction in the ozone column of more than 40% is calculated north of 60°N in winter/spring. Near 15km altitude, the ozone density calculated at 65°N in February with the 1992 chlorine loading is reduced by a factor that is 5 times larger than in the case representative of the Pinatubo's eruption.

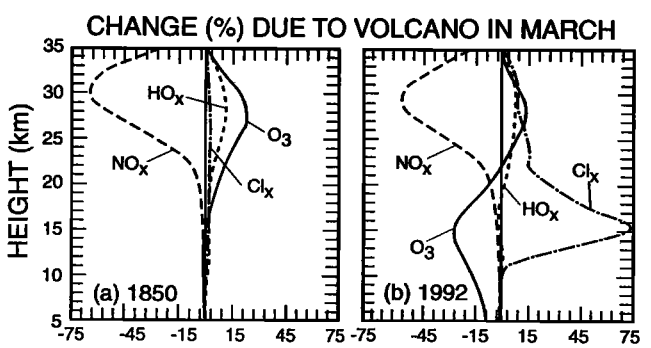

Figure 3. Changes (percent) in the vertical profiles of ozone density (O_3) and in the ozone destruction rates associated with NO_x, HO_x, and ClO_x catalytical cycles at 65°N in March for different conditions; (a) year 1850 with chlorine loading of 0.6 ppb; (b) year 1992 with chlorine loading of 3.3 ppb.

Summary

Model calculations show that the response of ozone to a volcanic eruption similar to that of Mt. Pinatubo is very sensitive to the atmospheric chlorine loading. For chlorine loadings typical of the pre-industrial era, the ozone column abundance increases after the eruption, with the largest response occurring at high latitudes during the winter season. For chlorine loading representative of the 1980's, the response of ozone becomes negative in winter at mid to high latitudes. This transition in the ozone response suggests that, as a result of CFC production and emission, the "NO_x effect" associated with volcanic eruptions (which tends to enhance stratospheric ozone) is counterbalanced by a "ClO_x effect" (which tends to deplete ozone). In the future (year 2015), the response of ozone is expected to become positive again, if the CFC production is sufficiently reduced. Thus, the observed ozone depletion recorded during 2-3 years following the eruptions of El Chichon and Mt. Pinatubo may have been unique in the Earth's history, and is a direct result of human activities.

The response of ozone under pre-industrial conditions is not significantly affected by the intensity of the eruption, since the

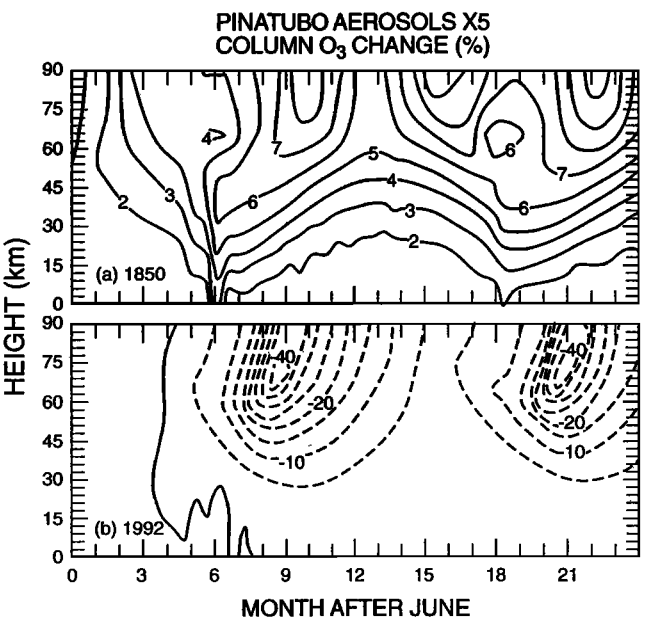

Figure 4. Same as Figure 1, but for a surface area density of volcanic aerosols increased by a factor 5; (a) in 1850 with chlorine loading of 0.6 ppb; (d) in 1992 with chlorine loading of 3.3 ppb.

heterogeneous conversion of nitrogen oxides to nitric acid is saturated. However, for chlorine loadings representative of current conditions (3.3 ppb in 1990) the ozone response is expected to increase with the intensity of the eruption, since the heterogeneous conversion of chlorine reservoirs ($ClONO_2$) to reactive chlorine (Cl) is not saturated.

Acknowledgments. The authors are grateful to S. Solomon who made helpful suggestions concerning this study, and to R. Garcia, W. Randel, G. Tyndall, and two anonymous reviewers for useful comments on the manuscript. X. Tie and G. Brasseur are supported in part by DOE Atmospheric Chemistry Program under contract number DE-AI05-94ER619877. The National Center for Atmospheric Research is sponsored by the National Science Foundation.

References

Bekki, S., and J. A. Pyle, A two-dimensional modelling study of the volcanic eruption of Mount Pinatubo, *J. Geophy. Res.*, 99, 18861, 1994.

Bais, A. F., C. S. Zerefos, I. C. Ziomas, N. Zoumakis, H. T. Mantis, D. J. Hofmann, and G. Fiocco, Decreases in the ozone and SO_2 columns following the appearance of the El Chichon aerosol cloud at mid-latitude, in atmospheric ozone, *Proceedings of the Quadrennial Ozone Symposium, Halkidiki, Greece,* pp353-356, D. Reidel, Hingham, Mass., 1985.

Brasseur, G., M. H. Hitchman, S. Walters, M. Dymek, E. Falise, and M. Pirre, An interactive chemical dynamical radiative two-dimensional model of the middle atmosphere, *J. Geophys. Res., 95,* 5639-5655, 1990.

Brasseur, G., and C. Granier, Mount Pinatubo aerosols, chlorofluorocabons, and ozone depletion, *Sciences, 257,* 1239-1242, 1992.
Dutsch, H. U., Total ozone trend in the light of ozone soundings, the impact ofEl Chichon, *Proceedings of the Quadrennial Ozone Symposium, Halkidiki, Greece, pp353-356, D. Reidel, Hingham, Mass., 1985.*

Gleason, J. F., P. K. Bhartia, J. R. Herman, R. McPeters, P. Newman, R. S. Stolarski, L. Flynn, G. Labow, D. Larko, C. Seftor, C. Wellemeyer, W. D. Komhyr, A. J. Miller, and W. Planet, Record low global ozone in 1992, *Science, 260,* 523-526, 1993.

Granier, C. and G. Brasseur, Impact of heterogeneous chemistry on model predictions of ozone changes, *J. Geophys. Res., 97,* 18015-18033, 1992.

Hofmann, D. J. and S. Solomon, Ozone destruction through heterogeneous chemistry following the eruption of El Chichon, *J. Geophys. Res., 94, 5029-5041, 1989.*

Hofmann, D. J., S. J. Oltmans, W. D. Komhyr, J. M. Harries, J. A. Lathrop, A. O. Langford, T. Deshler, B. J. Johnson, A. Torres, and W. A. Matthews, Ozone loss in the lower stratosphere over the United States in 1992-1993: Evidence for heterogeneous chemistry on
Pinatubo aerosol, *Geophys. Res. Lett., 21,* 65-68, 1994.

Houghton, J. T., G. J. Jenkins, and J. J. Ephraums, Climate change, *The IPCC Scientific Assessment, Cambridge University Press, Cambridge UK, 1990.*

Kerr J. B., D. I. Wardle, and D. W. Tarasick, Record low ozone values over Canada in early 1993, *Geophy. Res. Lett., 20,* 1979-1982, 1993.

Mantis, H. T., C. S. Zerefos, A. Bais, I Ziomass, and A. Kelessis, The northern hemisphere ozone minimum in 1982-1983, *Arch. Meteorol. Geophys. Bioclimat. Sec. B., 36, 135-145, 1986.*

Pitari, G., and V. Rizi, An estimate of the chemical and radiative perturbation of stratospheric ozone following the eruption of Mt. Pinatubo, *J. Atmos. Sci., 50,* 3260-3276, 1993.

Randel, W. J., and F. Wu, Ozone and temperature changes in the stratosphere following the eruption of Mt. Pinatubo, *J. Geophys. Res.*, accepted, 1995.

Rodriguez, J. M., K. M. W. Ko, and N.-D. Sze, C. E. Heisey, G. K. Yue, and M. P. McCormick, Ozone response to enhanced heterogeneous processing after the eruption of Mt. Pinatubo, *Geophys. Res. Lett., 21, 209-212, 1994.*

Tie, X., G. Brasseur, B. Briegleb, and C. Granier, Two-dimensional simulation of Pinatubo aerosol and its effect on stratospheric ozone, *J. Geophy. Res., 99,* 20545-20562, 1994a.

Tie X., X. Lin, and G. Brasseur, Two-dimensional coupled dynamical/chemical/microphysical simulation of global distribution of El Chichon volcanic aerosols, *J. Geophy. Res., 99,* 16779-16792, 1994b.

WMO, *Scientific Assessment of Ozone Depletion: 1994,* 1995.

(Received June 20, 1995; revised September 5, 1995; accepted September 28, 1995.)