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PREPRINT

CONF-8308134--2

TROPOSPHERIC RESPONSE TO A NUCLEAR EXCHANGE

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This paper was presented at the Third International Conference on Nuclear War, Erice, Sicily, August 19-23, 1983.

October 1983

Lawrence Livermore National Laboratory

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INTRODUCTION

The immediate effects of a full-scale nuclear war would be large and severe. The number of prompt fatalities alone that might occur in the U.S. and U.S.S.R. has been estimated at between 130 and 270 million (U.S. Office of Technology Assessment, 1979).

The survivors of such a war would have many hardships to endure, including global-scale changes that may affect people in nations other than those directly involved in the conflict. One such global-scale effect relates to possible changes in the chemical structure of the atmosphere. These changes may come about as a result of changes caused by the nuclear explosions themselves (direct effects) or as a result of changes caused by fires that may start after the explosions (indirect effects). This paper focuses on the expected global-scale changes in the chemical structure of the atmosphere from both direct and indirect effects after a full-scale nuclear exchange.

The immediate effects of a nuclear explosion include the creation of a hot mass of air or fireball which rises in the atmosphere to a level that depends on the yield of the explosion. Because the fireball is hot, it is able to dissociate atmospheric nitrogen, N_2. As the fireball cools, nitrogen atoms recombine with oxygen to form nitrogen oxides, NO and NO_2. In addition,

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* The work reported here was the result of a collaborative effort of the author with following persons: P. S. Connell, F. M. Luther, R. F. Perret and D. J. Wuebbles. This work was performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

dust and recondensed gases are swept up through the stem of the fireball and deposited at the same level to which the fireball rises. The deposition of nitrogen oxides and dust in the atmosphere constitutes the immediate, direct effect of the explosion. Indirect effects on the atmosphere occur because of the many fires which may start after the explosion. The fires will emit smoke and other gases into the atmosphere which can change the concentrations of important trace constituents.

This paper focuses on the response of atmospheric ozone to a nuclear war. Figure 1 shows a profile of ozone as a function of altitude. The location of the stratosphere and troposphere is indicated in the figure. As shown in the figure, most of the earth's ozone resides in the stratosphere. In the stratosphere,

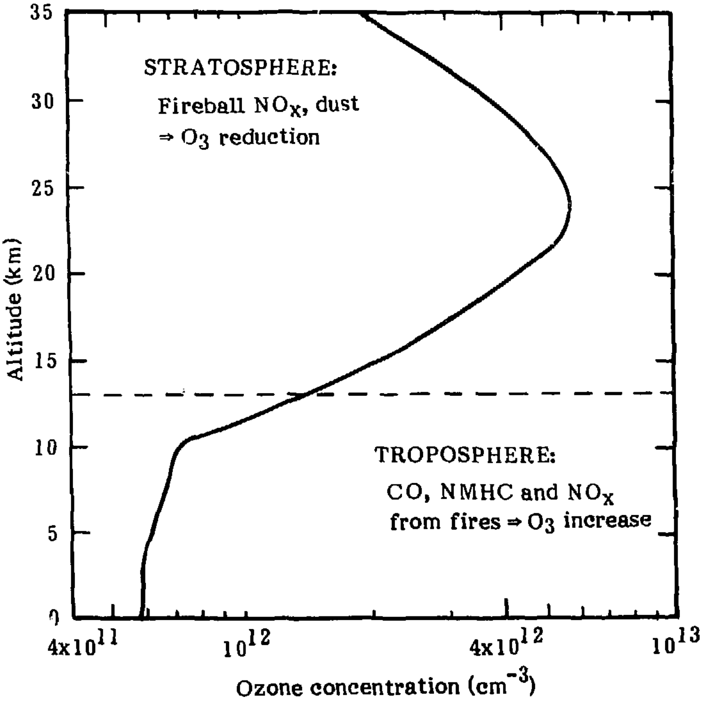

Fig. 1. Ambient ozone concentration as a function of altitude. Most of the total column of ozone in the ambient atmosphere resides in the stratosphere. Nitrogen oxides deposited in the stratosphere by the rising fireball tend to reduce O_3. Gases produced by fires in the troposphere tend to increase O_3.

the nitrogen oxides produced in the fireball are able to participate in a catalytic reaction cycle which leads to a decrease in ozone. This decrease allows biologically damaging ultraviolet radiation to penetrate to the surface of the Earth. In the troposphere, the smoke and gases from fires cause a different ozone response. In the troposphere, we expect an increase in ozone. Significantly increased ozone levels at the earth's surface would cause the same deleterious effects as severe urban smog. Because the study of the tropospheric response to fires is relatively new, we give particular attention to this aspect of the problem.

CHEMISTRY OF ATMOSPHERIC OZONE

In the stratosphere, nitrogen oxides formed in the fireball react with O_3 according to the reactions

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + O \rightarrow NO + O_2$$

$$\text{Net:}\quad O + O_3 \rightarrow O_2 + O_2 \quad .$$

The net result of these two reactions is a destruction of O_3. Since these reactions do not decrease the total amount of nitrogen oxides, this cycle may be repeated many times. Nuclear explosions must be greater than about 0.5 megatons in order for the fireball to rise into the stratosphere and have this type of effect.

In the troposphere, chemical effects are caused by gases and smoke emitted by fires as well as by nitrogen oxides produced in the fireballs of weapons smaller than about 0.5 megatons. The gases which are emitted in fires (and which are of concern to us) are the nonmethane hydrocarbons, carbon monoxide, and nitrogen oxides. These gases can participate in chemical reactions which produce ozone.

In the clean troposphere, where low nitrogen oxide concentrations are found, carbon monoxide and nonmethane hydrocarbons react with hydroxyl, HO, initiating chemical chains whose net effect is to destroy ozone. For example, for CO the reaction cycle is:

$$CO + HO \rightarrow CO_2 + H \tag{1}$$

$$H + O_2 \xrightarrow{M} HO_2 \tag{2}$$

$$HO_2 + O_3 \rightarrow HO + 2O_2 \tag{3}$$

$$\text{Net:}\quad CO + O_3 \xrightarrow{M} CO_2 + O_2$$

As nitrogen oxides become more abundant, the hydroperoxyl radical, HO_2, preferentially reacts with NO, creating the following cycle (for CO):

$$CO + HO \rightarrow CO_2 + H \tag{4}$$

$$H + O_2 \xrightarrow{M} HO_2 \tag{5}$$

$$HO_2 + NO \rightarrow HO + NO_2 \tag{6}$$

$$NO_2 + h\nu \rightarrow NO + O \tag{7}$$

$$O + O_2 \xrightarrow{M} O_3 \tag{8}$$

$$\text{Net:} \quad CO + 2O_2 \rightarrow CO_2 + O_3$$

Similar, though more complicated cycles, are initiated by the reaction of fire-produced nonmethane hydrocarbons with HO.

When smoke is present in this chemical system, it absorbs sunlight. The cycle that produces O_3 may therefore be stopped at reaction (7), which depends on the amount of light that is present. Thus, photolysis of NO_2 will not occur if the smoke decreases the light level far enough. Since the hydroxyl radical, which appears in reactions (1) and (4), is also ultimately formed by photochemical reactions, the initiation of both the ozone formation cycle and the ozone destruction cycle can be decreased by the presence of smoke. The purpose of the study that I am reporting here was to find out whether tropospheric ozone is increased or decreased in the coupled system that includes smoke, nitrogen oxides, methane, nonmethane hydrocarbons, and carbon monoxide.

Figure 2 shows the NO_2 photolysis rate as a function of time in the troposphere at two different levels: the surface and 9 km. Smoke loadings above the surface are initially very thick, so that the photolysis rate at ground level is far below the ambient value. As the atmosphere is cleansed of smoke, the surface nitrogen dioxide photolysis rate starts to recover and reaches its previous value after 2 to 4 months. The strong effect of the smoke on NO_2 photolysis does not take place in the upper troposphere. At 9 km the NO_2 photolysis rate remains close to the ambient value. Therefore we can expect ozone to be created in the upper troposphere but not near the surface where there is shielding by smoke.

RESULTS

In the calculations I am reporting here, a number of assumptions were made which should be made explicit. The first assump-

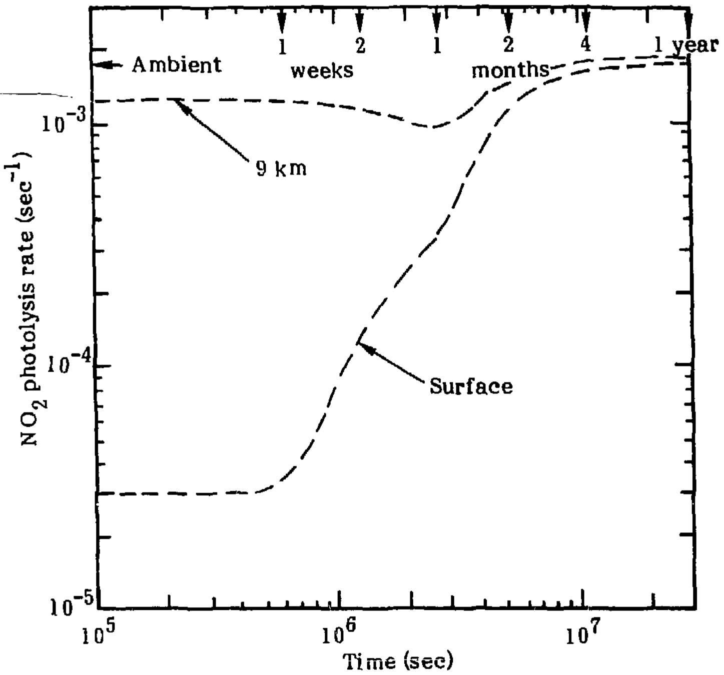

Fig. 2. Photolysis rate for nitrogen dioxide as a function of time at the surface and at 9 km in the troposphere. As the smoke from fires clears, the photolysis rate returns to its ambient value.

tion is the particular scenario that we have assumed for the war itself and for the emissions. In these calculations, we considered a 5300 megaton exchange. The choice for the exchange was based on published estimates of the superpower arsenals and our estimate of what we consider to be a realistic exchange. Even though the total megatonnage available in the superpower arsenals is close to 13,000 megatons, not all of these weapons are exploded in our scenario. Some of the weapons are assumed to be destroyed in silos before they can be used. Others may not be exploded at all, because once the damage becomes large enough, it is unlikely that the exchange would continue. Figure 3 shows the deposition of nitrogen oxides produced in this exchange as a function of altitude. A total of 8.3 tg N is deposited in the stratosphere and troposphere. As shown there, most of the fireball nitrogen is deposited in the stratosphere and will lead to a decrease in stratospheric ozone. A small amount is deposited below 13 km and will contribute to an increase of ozone in the troposphere.

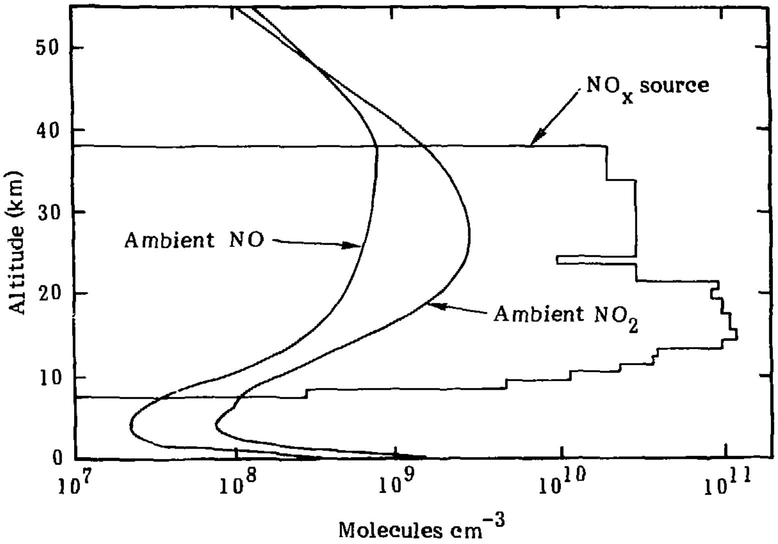

Fig. 3. Direct source of fireball-produced nitrogen oxides for our reference scenario. The source has been averaged over the Northern Hemisphere. The total megatonnage assumed in this scenario was 5308 mt.

As part of the indirect effects of the nuclear exchange, we assumed a situation in which about 13,000 tg of fuel is burned. This leads to an emission of 640 tg C carbon monoxide, 80 tg C nonmethane hydrocarbons and 26 tg N NO_x. These emissions were assumed to be released at the surface and mixed upward by diffusion. The chemical response of the atmosphere was calculated with a one-dimensional model. The emissions were averaged over the Northern Hemisphere and we calculated the vertical distribution of ozone and other species, averaged over the hemisphere. Our calculated changes are therefore smaller than they would be, for example, in the plume of a particular fire or if the emissions from the fire were concentrated over a smaller range of latitudes. Another assumption we made concerns the emissions after the war. Species like carbon monoxide have a source in today's atmosphere from fossil fuel combustion. We have chosen to consider the emissions after the war from fossil fuel combustion to be essentially zero (10% of present emissions). Finally, as discussed in other papers from this conference, the smoke that is contributed to the atmosphere may have a large effect on the temperature structure of the atmosphere. This temperature change will contribute to a change of the vertical mixing rates and chemical reaction rates in the atmosphere. We have not yet considered how these changes would affect our model calculations.

Figure 4 shows the calculated tropospheric column abundance of nonmethane hydrocarbons, carbon monoxide, smoke and nitrogen oxides as a function of time. In the ambient atmosphere smoke is removed primarily by rain. Nitrogen oxides are removed by rain and dry deposition. As shown in Figure 4, they are removed much more rapidly than CO and nonmethane hydrocarbons. As discussed above, nitrogen oxides play a key role in forming ozone, while smoke can inhibit the ozone forming potential of NO_x. Therefore the relative abundance of these two contaminants is an important factor for the determination of how much ozone is formed. Because the extent and frequency of rain in the post-war atmosphere is poorly determined, the lifetimes for nitrogen oxides and smoke are poorly determined. We can therefore expect some uncertainty in the amount of ozone formed due to this uncertain factor.

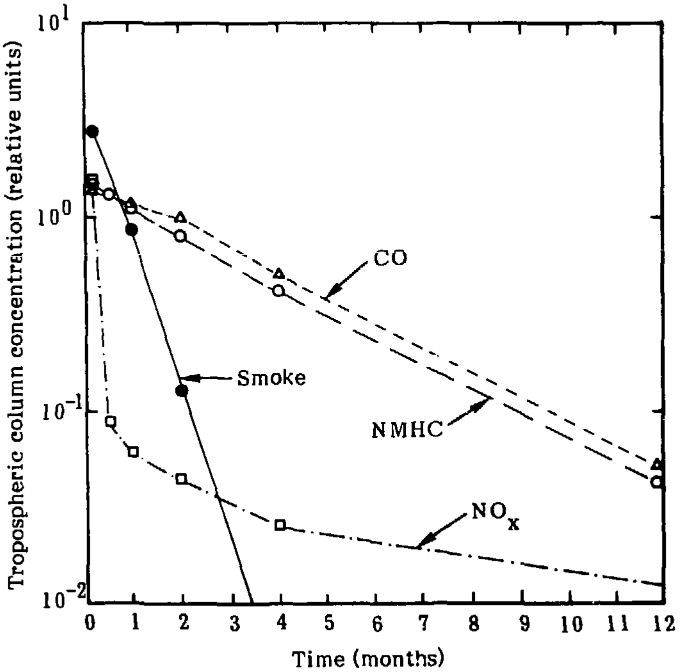

Fig. 4. Time history of nonmethane hydrocarbon, carbon monoxide, nitrogen oxides and smoke column abundances. The relative abundance units are: NO_x (10^{17} cm^{-2}), NMHC (10^{18} cm^{-2}), CO (10^{19} cm^{-2}), and smoke (10^{14} gm). The figure illustrates the short lifetime for NO_x relative to NMHC and CO.

Figure 5 shows the percentage change in tropospheric ozone as a function of altitude. The solid and dashed lines show the increase in ozone with and without the effects of smoke, respectively. Without smoke, there is a large increase in O_3 in the lower troposphere. The photolysis of NO_2 is not obstructed (without smoke) and, therefore, the total tropospheric column abundance of O_3 is largest at early times when NO_2 is a maximum. The column abundance of O_3 decreases from an increase of 55% at one week to a 36% increase at two weeks and a 24% increase at two months. With smoke in the atmosphere, the buildup in O_3 takes much longer. At two weeks time the column abundance of ozone is increased by about 10% and builds up to a 20% increase after two months. Smoke therefore delays the buildup of ozone, and, because the nitrogen oxide level has decreased by the time the smoke clears, smoke limits the amount of ozone that is formed.

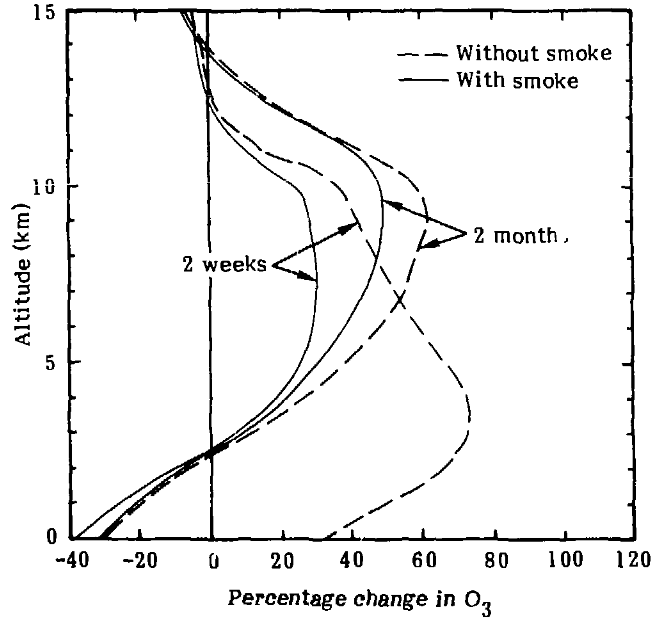

Fig. 5. Percentage change in tropospheric O_3 as a function of altitude at 2 weeks and 2 months with and without smoke. Without smoke, total tropospheric column O_3 is increased by 55% after 1 week. The increase drops to 36% after 2 weeks and 24% after 2 months. With smoke, the early time production of O_3 is inhibited, but it builds up to an increase of 19% after two months.

As discussed above, nitrogen oxides are removed from the atmosphere by rain and surface deposition. Figure 6 shows the calculated NO_x (NO plus NO_2) concentration at one month and two months after the exchange, with and without rainout processes included in the model. When rainout processes are neglected, there is a large increase in NO_x in the middle troposphere. We expect, therefore, that ozone should increase to larger levels in this region of the atmosphere when rain is excluded from the model. Figure 7 shows the percentage change in ozone as a function of altitude with and without the effect of rain. At two months time the tropospheric ozone column is increased by 55% when rainout is neglected; whereas the increase is only 20% when rainout processes continue at their ambient, present-day rates.

Figure 8 summarizes the effects of some of the uncertainties described previously. It shows tropospheric ozone as a function of altitude two months after the nuclear exchange. The curve labled Standard Case includes all of the emissions from fires and assumes that rainout processes continue at ambient, present-day rates. For this case, tropospheric ozone is increased by about 20%

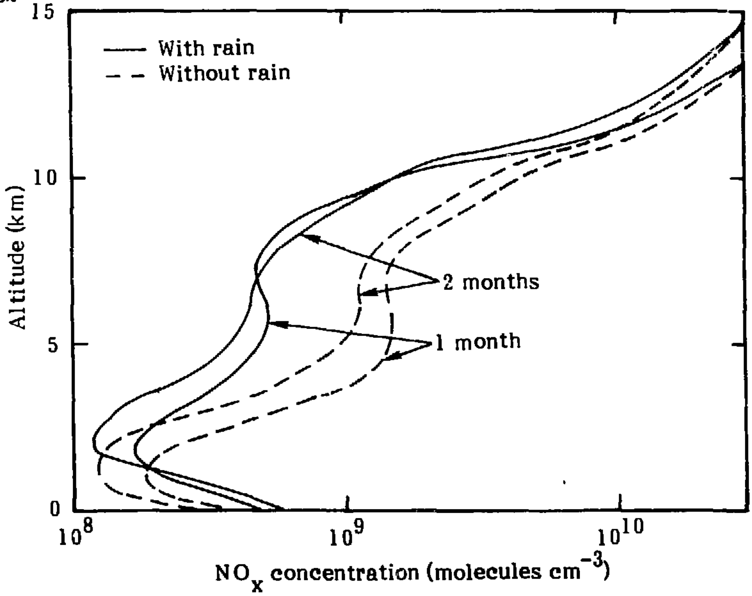

Fig. 6. Vertical distribution of nitrogen oxides at 1 month and at 2 months with and without rain as a removal mechanism in the model. Without rain, NO_x remains elevated for a much longer period of time allowing O_3 levels to build up (see Fig. 7).

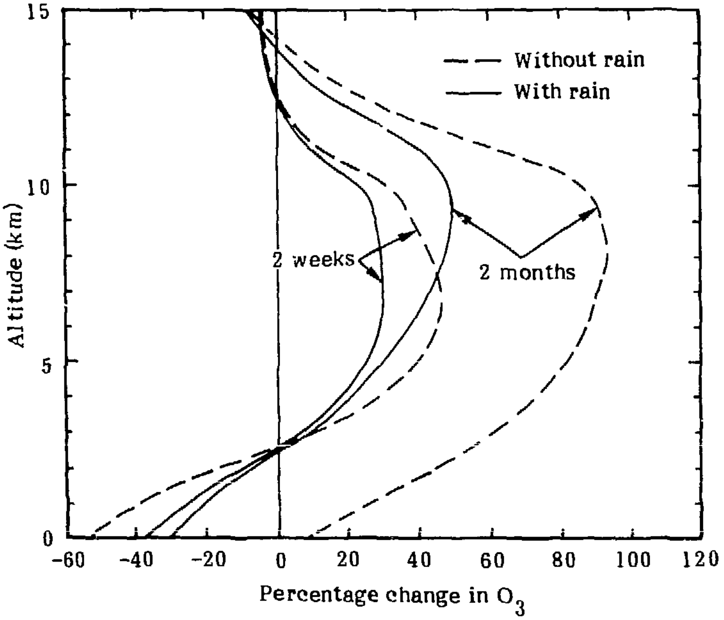

Fig. 7. Percentage change in O_3 as a function of altitude at 2 weeks and 2 months with and without rain as a removal process for smoke and soluble gases. Without rain, nitrogen oxides remain elevated allowing O_3 to increase more in the upper troposphere where smoke is not shielding the photolysis of NO_2.

at two months. The dotted line shows the effect of omitting the smoke, carbon monoxide, nitrogen oxides, and hydrocarbons from fires. In this case tropospheric ozone is increased by 9%. The dashed-dot line shows the effect of neglecting smoke in the calculation. Without smoke after two months time, tropospheric ozone is increased by 25%. At earlier times in the problem, the increase was much larger, of course. The long-dashed line shows the effect of decreased rainout processes. Without rain, ozone is increased by 55% after two months.

Despite these increases in ozone in the troposphere, total column ozone is still decreased due to the large deposition of NO_x in the stratosphere. Figure 9 shows the change in total ozone as a function of time. The calculated maximum hemispheric average decrease in total O_3 in our standard case is about 30%. After 4 years time, total O_3 has only recovered to 90% of its previous value. It returns to ambient levels after about 10 years time. Of course, the recovery rate depends entirely on the mixing rates

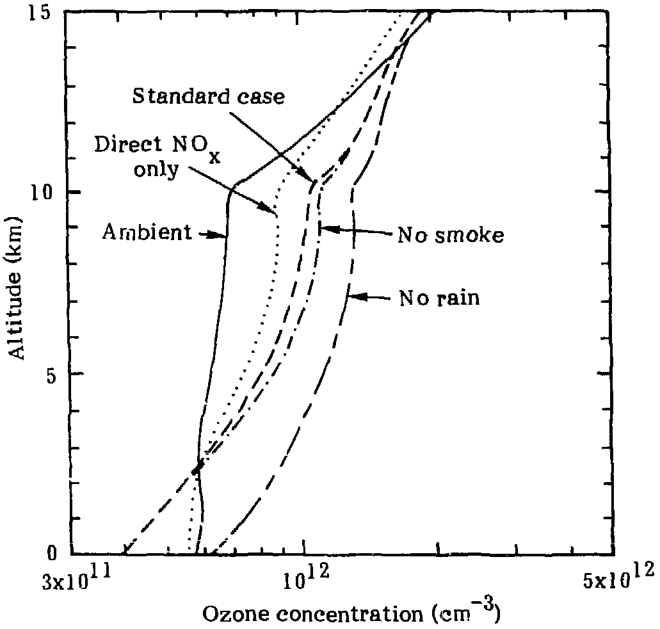

Fig. 8. Ozone concentration as a function of altitude in the troposphere at 2 months time for 4 different model assumptions: Direct NO_x only (no smoke or gases from fires), Standard Case (direct NO_x plus smoke and gases from fires, see text), No smoke (standard case, neglecting smoke), and No rain (standard case, with rainout processes for smoke and soluble gases neglected). The case with no smoke produced much more O_3 at earlier model times.

in the atmosphere. If the atmospheric mixing rates and dynamics change because of the smoke loading, the recovery rate could be quite different.

The effect of the decrease in total ozone is to increase the solar ultraviolet flux to the surface. Figure 10 shows the ratio of the perturbed to ambient UV flux as a function of time. The flux ratio at 300 nm and the integrated flux ratio from 280-320 nm are shown. The more damaging shorter wavelengths are increased relatively more than the integrated total, which is dominated by the greater solar fluxes at longer wavelengths. Without smoke in the atmosphere, the flux at 300 nm is increased by a factor of 3 to 5. With smoke included in the calculation, as long as the smoke is present, there is a protection from the increased UV flux. In the calculation shown in Fig. 10, this protection dis-

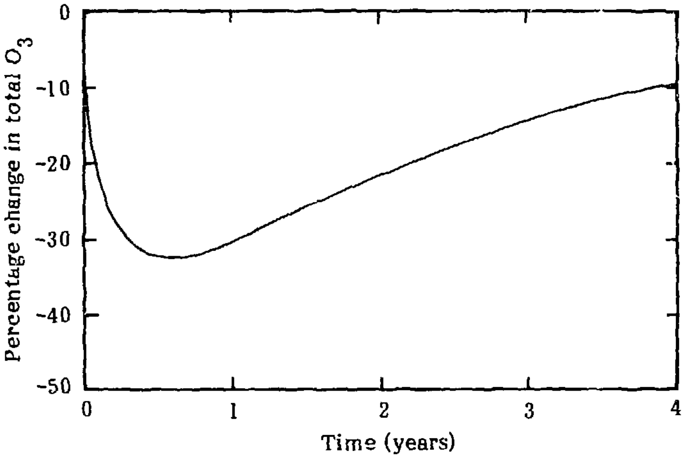

Fig. 9. Percentage change in total column ozone as a function of time for the standard case described in the text. Even though tropospheric ozone is increased, column ozone is decreased due to the deposition of fireball produced nitrogen oxides in the stratosphere.

appears on the time scale of a few months, as rainout processes remove the smoke. If rainout processes were diminished, the protection would last longer.

CONCLUSION

The main conclusions from this study are that tropospheric ozone does increase as a result of carbon monoxide, nonmethane hydrocarbons and NO_x emitted in fires. The range we calculated in this study varied from 20 to 55%. That range of uncertainty is primarily due to an uncertainty in the amount of rain. The amount of rain is an important and, as yet, undetermined factor. Without smoke in the problem we would have calculated a much larger increase in tropospheric ozone equivalent to values calculated previously by *Crutzen and Birks* (1982). In our model, smoke inhibits the amount of ozone that is able to build up and, in fact, surface ozone does not increase above ambient values. In addition, the presence of smoke inhibits UV penetration to the surface.

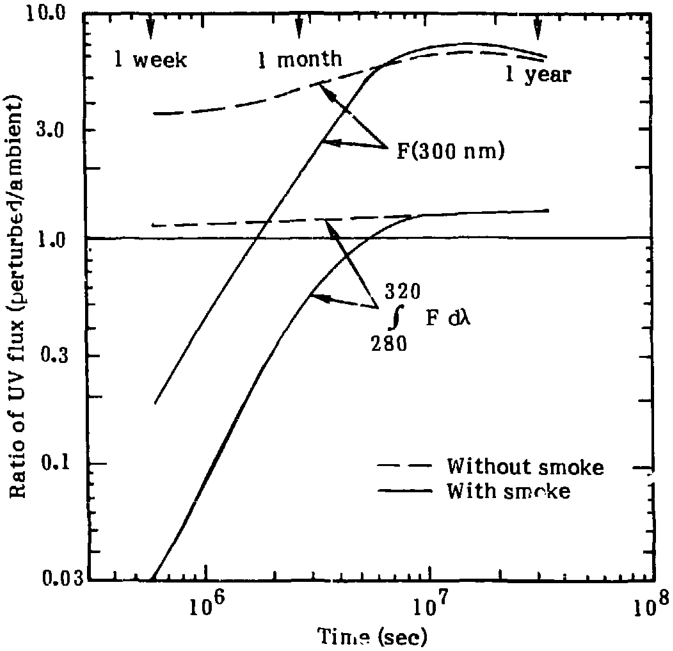

Fig. 10. The ratio of ultraviolet flux at the surface of the earth in the perturbed and ambient atmospheres with and without smoke. Smoke inhibits the penetration of UV to the surface as long as it is present.

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