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Photochemistry in the Stratosphere —
with Applications to Supersonic Transports

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Abstract

Two years ago it was pointed out that the oxides of nitrogen from the exhaust gases of 500 American SST would probably reduce the earth's ozone shield by about 20 percent on an average worldwide basis and up to 50 percent in zones of high traffic. These calculations depended on extensive assumptions about the natural background of nitrogen oxides in the stratosphere and the expected distribution of exhaust gases from SST. Also, this model involved steady-state photochemistry with explicit neglect of atmospheric motions.

Recent studies by many investigators have made some measurements of nitrogen oxides in the stratosphere, calculated the expected distribution of exhaust gases on the basis of an almost-realistic model of three dimensional motion, calculated the expected reduction of ozone in models that explicitly include one or two dimensional motions, and interpreted past historical events as constituting significant
injections of nitric oxide into the stratosphere. The model calculations, including atmospheric motions, give a worldwide reduction of ozone by 500 SST between 7 and 28 percent, and for a 3 to 6 fold "local maximum" between 20 and 50 percent ozone reduction. Some of these 1973 calculations, including motions, give results comparable to the 1971 steady-state calculations.

Recent studies indicate that the nuclear bomb tests of 1952-62 injected significant quantities of nitric oxide into the stratosphere; the observed increase of ozone in the northern hemisphere during the 1960s may, in part, be the atmosphere returning to normal after the end of large scale nuclear tests. Also, a recent interpretation of the sunspot modulation of cosmic rays gives a quantitative measure of the response of stratospheric ozone to an injection of nitric oxide; translated into terms of SST, these results indicate that 75 Concorde operating in one flight corridor for 11 months would decrease the local ozone column between 2 and 5 percent. Some biologists regard even this small reduction of ozone as a matter for serious concern.
Introduction

Two years ago it was pointed out that 500 American type supersonic transports (SST) operating at 20 km in the stratosphere would release so much oxides of nitrogen (NOx) in their exhaust that there would probably be a serious reduction of the earth's ozone shield. The estimated magnitude of ozone reduction was about 20 percent on a worldwide basis and up to 50 percent if there was a long-term, ten-fold, local maximum of the exhaust products. Natural atmospheric ozone is the only effective shield of the surface of the earth against solar radiation between 300 and 250 nm. Both DNA and proteins have a maximum absorption coefficient for radiation between 300 and 250 nm. The long wavelength "toe" of these absorption spectra extends to just above 300 nm. The ultraviolet damage to skin (sunburn, skin aging, skin cancer, etc.), to eyes (snow blindness), and to plants (inhibition of photosynthesis, stunted growth, death) is brought about by the small amount of solar radiation near 300 nm that now reaches the surface of the earth. Some biologists state that a systematic 5 percent reduction of ozone, which would cause a large increase in harmful ultraviolet radiation, would have serious biological consequences.

When these questions of a possible 20 to 50 percent reduction of ozone by SST were first posed two years ago, it was found that there were many aspects about the stratosphere...
that were very poorly understood.\textsuperscript{6,7} There had been a large number of determinations of ozone in the stratosphere, but the concentrations of trace species such as water, nitrogen oxides, methane, etc. was unknown or poorly known. From the persistence of radioactive debris following atmospheric nuclear bomb tests,\textsuperscript{8} for example, it was known that the stratosphere is exceedingly stable with tracer halftimes of one to five years; however, there remained many gaps in knowledge about the detailed motions and mixing processes in the stratosphere.

This full problem involves highly complex considerations of three dimensional atmospheric motions, absorption and emission of radiation (from the far ultraviolet to the far infrared), and the chemical reactions of a large number of species, including trace gases at very low concentrations. There are important couplings and feedback mechanisms between radiation balance, chemical reactions, and atmospheric motions. It appears that a realistic model of the atmosphere including coupled chemistry and radiation is far beyond the capacity of our largest computers, and significant results from such a realistic model is probably at least ten years in the future. When one is faced with an urgent practical problem involving a very complex situation, one should not postpone all decision until an "exact" solution is obtained. Also, one should not abandon all scientific analysis and
decide what to do strictly on the basis of judgment and intuition. Many intermediate approaches are possible: meaningful approximate scientific analyses can be carried out, and action decisions should be based both on the approximate scientific treatments and on judgment. The goal should be to provide for an informed judgment, not necessarily an "exact" solution.

In seeking a significant approximate treatment of this problem, I omitted all specific considerations of atmospheric motions, assumed a wide range of plausible distributions of natural and artificial oxides of nitrogen, and solved for the effect on ozone of an increase in oxides of nitrogen. Atmospheric motions were omitted both from the unperturbed and perturbed atmosphere, and the change to be expected from a change in NO$_x$ was examined over an extensive range of variables. One analysis considered only the terms in the differential equations for ozone. It was found that increases in the oxides of nitrogen from the SST would increase the destruction rate of ozone in some localities by a very large factor, more than 100. However, a reduction of ozone at one level permits the passage of ultraviolet radiation to a lower level with some increased ozone production there. To assess the effect of this buffering action, a series of steady-state calculations was made with the model of a static atmosphere. When this buffering action is included
the worst case of ozone reduction for a plausible NO$_x$ source from the SST was changed from a factor of 6 to a factor of 2. The expected reduction of the ozone column from 500 SST with a uniform worldwide distribution of NO$_x$ in the stratosphere was about 20 percent. The approximation of explicit neglect of atmospheric motions (atmospheric motions enter implicitly in that these would be the mechanism for setting up the assumed NO$_x$ distributions) permitted consideration of a large body of chemical reactions.

The opposite approximation to this problem has been carried out by Mahlman. He has a three dimensional model of the atmosphere with 11 layers between 0 and 31 km. He includes oceans and continents, evaporation and condensation of moisture, seasonally varying radiation, and both absorption and emission of radiant energy. The atmosphere is driven by solar heating, and the physical model is essentially the laws of physics. It requires very great computer capacity and computer time to run this model, even with no chemical reactions. At present it appears infeasible to add chemical reactions to this model. This three dimensional model successfully predicts the distribution of ozone in the stratosphere on the basis of a formation function at 31 km and destruction at the ground. Mahlman, then, regarded the exhaust from SST as an inert tracer and calculated the spread and distribution of the exhaust gases as a function of time. The calculation
was run for a simulated time of 11 months. A graphical solution was presented giving the global distribution of exhaust gases (regarded as an inert tracer) after simulated 11 month operation of SST. Results were presented for the distribution of water vapor and of NO\textsubscript{x} from 500 SST. This calculation gives the distribution of exhaust gases with no considerations of chemistry; my previous calculations\textsuperscript{1} gave the chemical effect of prescribed distributions. Although these approaches are exactly supplementary, the sum of the two approaches is far from complete because interactions and feedback mechanisms are important.

Intermediate approaches are possible and are being carried out. One dimensional (vertical) models consider turbulent diffusion, in some cases a vertical wind, and large sets of chemical reactions. Two dimensional models are also being developed which can include a substantial set of chemical reactions and both horizontal and vertical motions. Such models can be partially calibrated against observed stratospheric data following atmospheric nuclear bomb testing, 1952-62. These models readily permit the simulation of exhaust gases from the SST, including chemical and photochemical reactions. Results from these one dimensional and two dimensional models are beginning to come in (late 1972 and mid-1973).
It was recognized two years ago\textsuperscript{6,7} that there was an inadequate data base for satisfactory model calculations of the stratosphere. To reduce our ignorance about the composition and dynamics of the stratosphere, there has been an organized, interdisciplinary research effort, the Climatic Impact Assessment Program (CIAP) of the U.S. Department of Transportation. Several other nations, other governmental agencies, and other groups are cooperating with this program. The goal of CIAP is to assess by the end of 1974 the probable effect of SST exhaust gases on the ozone shield, of the effect of particulates on the global radiation balance, of the effect of water from the exhaust gases on stratospheric cloudiness, and to seek to identify any other possible effects. Much new information has been obtained by August 1973, and much more is expected during the next year. It is premature to pretend to a final assessment at this time. However, it is possible and timely to make a progress report comparing the new findings with the proposals of two years ago.
Ozone in the Natural Stratosphere

Ozone is produced in the stratosphere from oxygen ($O_2$) and ultraviolet radiation below 242 nm. In terms of elementary chemical reactions, this formation of ozone occurs in two steps:

$$O_2 + hv \ (\text{below } 242 \ \text{nm}) \rightarrow O + O$$

$$ (O + O_2 + M \rightarrow O_3 + M) \ \text{TWICE}$$

Net: $$3 \ O_2 \overset{242 \ \text{nm}}{\rightarrow} 2 \ O_3$$

This production of ozone is balanced by several different removal or destruction processes: (1) transport to the lower troposphere with destruction at the ground; (2) chemical destruction by oxygen atoms (the $O_x$ system); (3) chemical destruction by free radicals based on water, H, HO, HOO (the $HO_x$ system); and (4) catalytic destruction by the oxides of nitrogen (the $NO_x$ system). These destruction processes are illustrated by the most important examples in terms of chemical reactions, as follows:
\[ \text{O}_x \text{ system: } \quad 0 + 0_3 \rightarrow O_2 + O_2 \]

\[ \text{HO}_x \text{ system: } \quad \text{HO} + 0_3 \rightarrow \text{HOO} + O_2 \]
\[ \text{HOO} + 0_3 \rightarrow \text{HO} + O_2 + O_2 \]
\[ \text{Net: } 2 \, 0_3 \rightarrow 3 \, O_2 \]

\[ \text{NO}_x \text{ system: } \]
\[ (A) \quad \text{NO} + 0_3 \rightarrow \text{NO}_2 + O_2 \]
\[ \text{NO}_2 + 0 \rightarrow \text{NO} + O_2 \]
\[ \text{Net: } 0 + 0_3 \rightarrow O_2 + O_2 \]

\[ (B) \quad \text{NO}_2 + 0_3 \rightarrow \text{NO}_3 + O_2 \]
\[ \text{NO}_3 + h\nu(\text{visible}) \rightarrow \text{NO} + O_2 \]
\[ \text{NO} + 0_3 \rightarrow \text{NO}_2 + O_2 \]
\[ \text{Net: } 2 \, 0_3 \rightarrow 3 \, O_2 \]

At present it appears that the relative contributions of the four ozone destruction processes are: 15

(1) Transport \hspace{1cm} 1\%
(2) \text{O}_x \hspace{1cm} 15 \text{ to } 20\%
(3) \text{HO}_x \hspace{1cm} 10 \text{ to } 20\%
(4) \text{NO}_x \hspace{1cm} 60 \text{ to } 74\%
The vertical profiles of ozone have been observed by sounding rockets, and examples of such data above 20 km are given by Figure 1. The total overhead ozone column can be fairly easily obtained by optical measurements made on the ground, and broad features of the vertical profile can likewise be obtained. Before 1950, the only extensive records of ozone data were those taken at Arosa (Switzerland), Tromso (Norway), and Oxford (England). Starting with the International Geophysical year 1957-58, numerous stations have made regular observations of total ozone, and now there are more than 100 such stations. Since 1960 the detailed records of these stations have been published as Ozone Data for the World. In recent years total ozone data (and some aspects of its vertical distribution) have been obtained by satellites. Contour lines of total ozone (in units of milliatmosphere - cm, STP) as seen by satellite for the northern hemisphere are illustrated by Figure 2.

The contour lines of total ozone column in Figure 2 are not precisely parallel to the latitude lines, but there is a very strong correlation with latitude. The variation of ozone around the world at a given latitude is less than the variation from one latitude to another, for example, 15° away. This fact suggests a convenient, approximate representation ("zonal average") of the global ozone distribution on one flat diagram, as illustrated by the heavy lines of
Figure 3. The abscissa goes from the north pole through the equator to the south pole, and the ordinate gives elevation from zero to 50 km. The zonally averaged ozone concentration is given by contour lines.

The separation between the troposphere and stratosphere, the "tropopause," occurs at about 10 km at the poles and at about 16 km at the equator. The contour lines of ozone in the lower stratosphere more or less parallel the tropopause. The height where the maximum concentration of ozone occurs is about 26 km at the equator, about 20 km at 45° latitude, and about 16 km at the poles. As can be seen from Figure 3, the maximum concentration of ozone in March is between 60°N and the north pole, not over the equator, which receives maximum irradiation.

The global rates of chemical and photochemical reactions can also be expressed as zonal average contour maps. The rate of formation of ozone (twice the rate of photolysis of O₂) is given by the light lines in Figure 3. If there were no destruction of ozone, it would require an ozone production rate of 3 x 10⁴ molecules cm⁻³ sec⁻¹ to form 10¹² molecules cm⁻³ of ozone in one year. To produce in one year the maximum concentration of ozone, 7 x 10¹², it would require a rate of 2 x 10⁵ of ozone formation. In the north polar region at 16 to 18 km, the concentration of ozone is 7 x 10¹² molecules cm⁻³ but one must go to 23 km in the temperate zone or to
20 km in the tropical zone to find ozone formation rates as great as $2 \times 10^5$ molecules cm$^{-3}$ sec$^{-1}$. This superposition of global maps of ozone concentration and ozone formation rate clearly shows the importance of air motions in shaping the vertical and horizontal distribution of ozone. Insofar as polar ozone is concerned, the "ozone formation region" in Figure 3 is that where the rate is greater than $2 \times 10^5$ molecules cm$^{-3}$ sec$^{-1}$.

It is not the purpose of this paper to go into the vast details of stratospheric photochemistry, but some of the problems will be briefly stated here. In its act of shielding the surface of the earth against short wavelength radiation, ozone is photodissociated

$$0_3 + \text{hv} \ (\text{below } 310 \text{ nm}) \rightarrow O_2 + 0 \ (^{1}\text{D})$$

$$0_3 + \text{hv} \ (\text{above } 310 \text{ nm}) \rightarrow O_2 + 0 \ (^{3}\text{P})$$

The excited singlet oxygen atom is typically deactivated to the triplet ground state atom, which adds to $O_2$ to reform $O_3$; there is no net reaction:

$$0_3 + \text{hv} \rightarrow O_2 + 0$$

$$0 + O_2 + M + O_3 + M$$

Net: no reaction
However, O (\(^1\)D) is very important in both HO\(_x\) and NO\(_x\) chemistry. Hydroxyl radicals are formed from singlet oxygen atoms and water

\[ O (\(^1\)D) + H\(_2\)O \rightarrow 2 \text{HO} \]

The active oxides of nitrogen (NO, NO\(_2\)) are formed in the stratosphere from inert nitrous oxide by means of singlet oxygen

\[ O (\(^1\)D) + N\(_2\)O \rightarrow 2 \text{NO} \]

Nitrogen dioxide, like ozone, is photolyzed in a "do-nothing cycle"

\[ \text{NO}_2 + h\nu (\text{below 400 nm}) \rightarrow \text{NO} + \text{O} \]
\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \]
\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]

Net: no reaction

There are numerous other reactions involving the O\(_x\) system, the HO\(_x\) system, and the NO\(_x\) system, and there is an important interaction between the HO\(_x\) and NO\(_x\) systems involving nitric acid vapor. Nitric acid is formed from hydroxyl radicals and nitrogen dioxide

\[ \text{HO} + \text{NO}_2 \xrightarrow{\text{M}} \text{HNO}_3 \]
This process is reversed by ultraviolet radiation and by hydroxyl radicals

\[ \text{HNO}_3 + \text{hv (below 320 nm)} \rightarrow \text{HO} + \text{NO}_2 \]
\[ \text{HNO}_3 + \text{HO} \rightarrow \text{H}_2\text{O} + \text{NO}_3 \]

Recent measurements of NO, NO\(_2\), and HNO\(_3\) in the stratosphere are given by Figure 4. In the stratosphere between 15 and 25 km the observed NO is between 0.1 and 3 \(\times\) \(10^9\) molecules cm\(^{-3}\); NO + NO\(_2\) (observed as NO\(_2\) at night) is 1 to 8 \(\times\) \(10^9\) molecules cm\(^{-3}\); and nitric acid is between 1 and 10 \(\times\) \(10^9\) molecules cm\(^{-3}\). The total vertical column of NO + NO\(_2\) + HNO\(_3\) is about \(10^{16}\) molecules cm\(^{-2}\).

The rate of formation of oxides of nitrogen in the stratosphere has been estimated by several authors.\(^{14b,24,25}\) The principal source appears to be the reaction of singlet oxygen atoms with nitrous oxide, which is formed in the soil and which diffuses up into the stratosphere. This source strength appears to be about 1 \(\times\) \(10^8\) molecules cm\(^{-2}\) sec\(^{-1}\). Cosmic rays at latitudes greater than 60° are a significant source of ions and then NO in polar regions; the rate is 0.4 \(\times\) \(10^8\) molecules cm\(^{-2}\) sec\(^{-1}\) at the pole and very small below 60° latitude.\(^{26}\) Ammonia may survive rainout and penetrate the stratosphere to a small extent, but whether ammonia would form or destroy NO\(_x\) in the stratosphere is uncertain.\(^{23}\) Nitric oxide produced in the ionosphere may\(^{23}\) or may not\(^{22}\)
be transported down into the stratosphere, but if it is, the source is about $0.1 \times 10^8$ molecules cm$^{-2}$ sec$^{-1}$. The net effect of all these processes is a natural source of NO$_x$ of about $(1.5 \pm 0.5) \times 10^8$ molecules cm$^{-2}$ sec$^{-1}$. 
Perturbation of Ozone by Supersonic Transports

Estimates of the amount of nitric oxide expected to be injected into the stratosphere by supersonic transports have covered a wide range. It is important to identify the source of this wide range of estimate.

The variables in the problem are: (1) the number of SST, (2) the rate of fuel consumption, (3) the emission index (EI) or grams of NO emitted per kilogram of fuel burned, and (4) whether emissions are calculated on the basis of a uniform worldwide average or of a "local maximum" tenfold (or some other factor) the worldwide average.

The projected number of SST for the period 1990-2000 is several hundred, sometimes predictions are as low as 200 and sometimes as high as 1000. The number 500 has been widely used, both for economic justification and for model calculations of environmental hazards. The number 500 is taken as the standard, reference case here.

The amount of fuel consumed per hour by the abandoned American SST is about three times as great as for the Concorde. The American SST is taken as the standard case. An average operation period of 7 hours per day per SST is taken as standard.
Recent measurements\textsuperscript{27} of the amount of nitric oxide emitted per unit weight of fuel burned give an "emission index" of $15 \pm 5$ grams NO per kilogram of fuel. The Study of Critical Environmental Problems (SCEP)\textsuperscript{28} was given an emission index of 42 by General Electric engineers, and this high figure has been used in several calculations. My calculations\textsuperscript{1} in 1971 used an emission index of 14.8 g NO per kg fuel. Although Goldburg\textsuperscript{29} said the value 14.8 was a factor of five too high, the wind tunnel data on SST-type engines under simulated stratospheric conditions do not support an emission index anywhere near as low as Goldburg's 3 grams NO per kilogram of fuel, and modelers have not used such numbers. In this paper 14 g/kg is taken as the reference emission index.

The North Atlantic traffic corridor between Europe and North America will be more heavily traveled than the rest of the world. By what factor should the worldwide average rate of SST exhaust emission be multiplied to account for this high traffic corridor? The "local maximum" traffic density has been given a factor up to 20 times the world average, but some argue that atmospheric motions will average it out to one. In the stratosphere, flow between the northern and southern hemisphere is slow, and at least a factor of two is indicated for the "local maximum." Mahlman's calculation of the spread of an inert tracer in
a three dimensional global model (when continued for several years of simulated time) should provide a good answer to this problem.

With a fivefold spread in the projected number of SST (200 to 1000), with a threefold difference in rate of fuel consumption by the Concorde and the Boeing SST, and with a threefold range in emission index (14 to 42), one can see that there is a forty-fivefold spread in the estimated, worldwide-average, emission rate of nitric oxide from SST's. Between the lowest estimate (200 Concorde, worldwide average) and the highest estimate (1000 Boeing SST, 42 EI, twentyfold "local maximum") there is almost a thousandfold spread in estimated zonal emission rates. Model calculations have been made on this full range of cases, and in comparing one calculation with another it is important to be explicit about where along this factor of 1000 each calculation stands.

Table 1 and Figure 5 give 13 calculations by 6 investigators of the percent reduction of the vertical ozone column by the operation of supersonic transports. These cases are scaled by a relative factor that is one for 500 Boeing SST, 14 emission index, worldwide average. The cases vary on this relative scale from 0.13 to 120. The calculated reductions of ozone vary from 0.4 to 70 percent. My calculations made in 1971 were steady-state calculations,
Table 1. Calculated percentage reductions of ozone column for various models

<table>
<thead>
<tr>
<th>Supersonic Transports Number</th>
<th>Type</th>
<th>Emitting Index</th>
<th>Local max.</th>
<th>Relative factor</th>
<th>Reduction of ozone column</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>C</td>
<td>14</td>
<td>1</td>
<td>0.13</td>
<td>0.4-2.4</td>
<td>Hesstvedt (1973)</td>
</tr>
<tr>
<td>300</td>
<td>C</td>
<td>14</td>
<td>1</td>
<td>0.20</td>
<td>8</td>
<td>LLL (1973)</td>
</tr>
<tr>
<td>600</td>
<td>C</td>
<td>14</td>
<td>1</td>
<td>0.40</td>
<td>16</td>
<td>LLL (1973)</td>
</tr>
<tr>
<td>500</td>
<td>B</td>
<td>14</td>
<td>1</td>
<td>1.0</td>
<td>28</td>
<td>LLL (1973)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>26</td>
<td>Crutzen (1972)</td>
</tr>
<tr>
<td>500</td>
<td>B</td>
<td>14</td>
<td>1</td>
<td>1.0</td>
<td>23</td>
<td>Johnston (1971)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>18</td>
<td>Hesstvedt (1972)</td>
</tr>
<tr>
<td>500</td>
<td>B</td>
<td>42</td>
<td>1</td>
<td>3.0</td>
<td>47</td>
<td>LLL (1973)</td>
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<td></td>
<td>4.0</td>
<td>50</td>
<td>Crutzen (1972)</td>
</tr>
<tr>
<td>1000</td>
<td>B</td>
<td>42</td>
<td>1</td>
<td>6.0</td>
<td>25</td>
<td>Stewart (1973)</td>
</tr>
<tr>
<td>500</td>
<td>B</td>
<td>14</td>
<td>10</td>
<td>10</td>
<td>50</td>
<td>Johnston (1971)</td>
</tr>
<tr>
<td>1000</td>
<td>B</td>
<td>42</td>
<td>20</td>
<td>120</td>
<td>70</td>
<td>Stewart (1973)</td>
</tr>
</tbody>
</table>

a. Emission index, grams NO in exhaust per kilogram of fuel burned.

b. This factor taken from continuous curve of added NOx without specific mention of number of SST, etc.

c. C, Concorde; B, Boeing.
assuming a stationary atmosphere. All of the other calculations include one or two dimensional atmospheric motions. For given assumptions about relative emission rate, some 1973 calculations give equal or greater ozone reduction as the 1971 "static" calculations. The spread in results for equal emissions arises from different assumptions about motion fields, boundary conditions, NO\textsubscript{x} background, choice of sets of reactions, elevation at which the SST is assumed to fly, etc. For the reference case of worldwide spread of 500 Boeing SST, the calculated reduction of the ozone column varies between 7 and 28 percent (both extremes reported in 1973), whereas the static (1971) model gave 23 percent. Three models, all including atmospheric motions, used relative emission factors between 3 and 6, and the calculated ozone reductions vary between 25 and 50 percent. The static (1971) model required a tenfold "local maximum" to give a 50 percent ozone reduction. The 70 percent ozone reduction given by Stewart\textsuperscript{33} (1973) involves an extreme case: 1000 Boeing SST, 42 emission index, twentyfold local maximum.

All model calculations reported in Table 1 and Figure 5 are stated by the authors as being tentative. In each case, further work is to be done. A minimum criterion for these one dimensional and two dimensional models is that they adequately predict the present, natural distribution
of ozone and of the oxides of nitrogen. In addition they should be consistent with the history of radioactive gases in the stratosphere. Once they are verified in this way, then the results of artificial input of exhaust gases from the SST can be seriously considered. Meanwhile, it appears that models including atmospheric motions do not give results drastically different from the static, steady-state model, when the two approaches make comparable assumptions about rate of input of exhaust gases and concerning the NO\textsubscript{x} natural background.
Injection Experiments

Although very valuable information can be obtained from computer models of the stratosphere, one always must worry about completeness. Has some important chemical reaction been left out? Has some important feedback mechanism been overlooked? It would be desirable to inject a known amount of nitric oxide in the stratosphere and to measure the effect on ozone. Certain thoughts of this kind are now reviewed.

The straightforward concept is to release nitric oxide from a balloon or other platform and to follow NO, NO\textsubscript{2}, HNO\textsubscript{3}, and O\textsubscript{3} as a function of time. However, at realistic stratospheric values of NO\textsubscript{x}, the half time to destroy ozone is many months. Such an injection experiment would have to be followed for about 6 months to give significant data on the effect of NO\textsubscript{x} on ozone. The quantity of NO required to make such an experiment is exceedingly great. 500 American SST would emit about a million tons of NO per year in the stratosphere, and a useful injection experiment would require perhaps one percent of that. So far, no one appears to have devised an experiment that will meet all of these requirements.

It would be very convenient if some past action, natural or artificial, had injected known large amounts of oxides of nitrogen into the atmosphere. Three such possibilities are discussed here: (1) combustion in the troposphere,
(2) atmospheric tests of nuclear bombs, and (3) the sunspot 
modulated influx of cosmic rays in the polar regions.

Combustion in the troposphere. In recent decades the 
amount of combustion in the troposphere, including regular 
aircraft as well as ground-based activities, has increased. 
However, NO$_2$ and HNO$_3$ are so rapidly washed out by rain 
that the ambient mole fraction of NO$_x$ in the middle or upper 
troposphere is only one to three ppb.$^{34}$ The mole fraction 
of NO$_x$ (including HNO$_3$) is higher than this in the strato-
sphere. Thus the gradient of NO$_x$ is from the stratosphere 
toward the ground. Random diffusion processes (turbulent 
and molecular) would transport NO$_x$ down, not up. A bodily 
mixing of tropospheric air with stratospheric air would 
reduce the mole fraction of NO$_x$ in the stratosphere. Thus 
it does not appear that this historical trend can be inter-
preted as an injection experiment of NO$_x$ into the stratosphere.

Nuclear Bomb Tests. Foley and Ruderman$^{35}$ in 1972 calcu-
lated the amount of nitric oxide that would be produced by 
nuclear bombs exploded in the atmosphere. This work was 
extended in 1973 by Johnston et al.$^{36}$ and by Gilmore.$^{37}$ 
The high temperature in the nuclear explosion fixes large 
amounts of nitric oxide from air, and the rising mushroom 
cloud transports much of it into the stratosphere, if the 
energy of the bomb is one megaton or more. There is a linear 
relation (with about a factor of three uncertainty) between
bomb energy and molecules of nitric oxide formed. Also, there is a linear relation between strontium-90 or excess carbon-14 and bomb energy. Although nitric oxide from the bombs was not measured, $^{90}\text{Sr}$, $^{14}\text{C}$ and other radioactive nuclides were measured in the stratosphere for many years after the termination of large scale tests in 1962. An example of observed $^{90}\text{Sr}$ in the stratosphere is illustrated by Figure 6. The linear relationship between nitric oxide produced and $^{90}\text{Sr}$, as measured, permits the construction of profiles of bomb-added nitric oxide at various times and latitudes, for example, Figure 7. Large nuclear bombs were tested at irregular intervals between 1952 and 1962, and then (except for relatively small tests by France and by China) stopped. There was an extremely active period of testing between the fall of 1961 and the end of 1962, mostly by USSR above the Arctic Circle. From data such as Figures 6 and 7, one finds that the maximum amount of artificial nitric oxide in the northern hemisphere occurred in early 1963, and the hemisphere average was between 1 and $3 \times 10^{15}$ molecules cm$^{-2}$. The nitric oxide added to the southern hemisphere entered there over a long period of time, and it was about an order of magnitude less than the northern hemisphere.

The bomb-produced increment of nitric oxide, as measured by the observed distribution of $^{90}\text{Sr}$, is about one-third to one-tenth of that expected as the worldwide
average from 500 American SST. The calculated reduction of ozone by the bomb-produced nitric oxide is approximately 5 or 10 percent in the northern hemisphere, and much less in the southern hemisphere. If the 100 or so ozone observing stations now in operation had uninterrupted data extending back for 30 years, then one could sharply answer the question as to how much the global ozone was affected by nuclear bomb tests; one would, in that case, have a reference period before the tests started in 1952, the period of large scale testing from 1952-62, and the decade following the cessation of large scale testing after 1962. Unfortunately, there are only two stations, Tromso and Arosa, with continuous records of total ozone covering this full period. At a given ozone-observing station, there is a fairly large daily noise pattern, well-understood annual cycles, less well-understood "quasi-biennial" cycles, eleven year sunspot cycles, and possible long term secular trends. With these variations, it is very difficult to spot at one or two stations the expected 5 or 10 percent decrease of ozone by 1963, followed by an approximately 10 year restoration period. However, a proper statistical analysis of all the ozone data of the world since the installation of a large number of stations (1957-1963) should detect a 5 or 10 percent change of total ozone.
Komhyr et al. (1971) analyzed the total ozone data from about a dozen selected stations for the period 1961-70, and they found a statistically significant increase of ozone at most of the stations, averaging about 5 percent. Johnston et al. (1973) applied Komhyr's method to all the stations of the world for the period 1960-70, inclusive. The stations were averaged with proper weight given to number of days of observation at each station and weighted as the inverse square of the standard deviation of observations at each station. No significant trends were found in the southern hemisphere, but a statistically significant increase of ozone of 5 ± 1.2 (twice the standard deviation) percent was found for the northern hemisphere for the period 1963-70 inclusive. A marginally significant decrease of ozone -3 ± 3 percent was found for the three years 1960-62 inclusive; however, the phase of the quasi-biennial cycle was such that this decrease would have been larger if the biennial cycle had not been present.

London and Kelley (1973) analyzed all data for total ozone from 1957 through 1970. They used the data to assign an average monthly value of ozone to zones of the earth. In this way they have an estimate of the total ozone of the world and of each hemisphere for each month from 1957 to 1971. These total-ozone data corrected for seasonal variation and expressed as deviations from the
average are shown by Figure 8. There was no significant trend in the southern hemisphere. In the northern hemisphere London and Kelley report a decrease of $-2.4 \pm 0.8$ (mean deviation) percent over the period 1957-1961 and an increase of $11 \pm 2.3$ percent over the decade 1961-1970. The minimum ozone occurred (Figure 8) in the spring of 1961, but the quasi-biennial cycle also went through a minimum there, and thus the time of the minimum should not be taken literally. The decreasing slope of the early years plus and minus its mean deviation intersects the increasing slope through the later years plus and minus its mean deviation somewhere between 1960 and 1963. The analyses by Johnston et al. and by London and Kelley agree in three major respect: no significant trends in the southern hemisphere, a decrease in the northern hemisphere of total ozone in the late 1950s and early 1960s and a large increase of ozone in the middle and late 1960s. The increase of ozone in the 1960s may be interpreted as stratospheric ozone returning to normal after the perturbation by nitric oxide from the nuclear bomb tests of 1952-62. If this interpretation is accepted, one has a calibration point for the sensitivity of the stratosphere to added oxides of nitrogen: an increase of $\text{NO}_x$ (including HNO$_3$) by $(1$ to $3) \times 10^{15}$ molecules cm$^{-2}$ reduces the ozone column between 5 and 10 percent (references 36 and 40, respectively).
Modulated Cosmic Rays as Nitric Oxide Source. Ruderman and Chamberlain \(^2^6\) (1973) pointed out that a natural cycle with respect to cosmic rays may be interpreted in terms of the effect of nitrogen oxides on ozone. Low energy cosmic rays are steered by the earth's magnetic field, they are deflected in equatorial and temperate zones, but they are guided into the atmosphere in polar regions. The cosmic rays produce atoms and ions in the stratosphere, and ion production as a function of latitude and elevation has been extensively measured for several decades.\(^4^1\) It is straightforward to calculate how much nitric oxide is produced from the stopping of cosmic rays in the stratosphere. The earth's magnetic field is affected by the stream of ions from the sun which varied with the eleven year sunspot cycle. This varying magnetic field strongly changes the intensity of cosmic rays in polar regions. The production of nitric oxide should thus be modulated in polar regions by the eleven year sunspot cycle, and this modulated effect should spread with an increasing phase shift and decreasing amplitude from the poles to the equator.

This problem was analyzed in depth by Ruderman and Chamberlain.\(^2^6\) They were able to evaluate the magnitude of the change of nitric oxide and the phase shift between sunspot cycle change of ozone at Tromso, Arosa, and as a hemispheric average. Only Tromso and Arosa have
total ozone data that go back continually to the 1940s. Angell and Korshover (1973) analyzed these data and found a pronounced correlation of total ozone (smoothed with a 30 month running mean) with the sunspot cycle, Figure 9. There was a phase shift of 32 months at Tromso (70°N) and 38 months at Arosa (48°N) in close agreement with Ruderman and Chamberlain's calculations. The amplitude of the ozone change is greater at Tromso (close to the polar source) than at Arosa. The coherence between the sunspot cycle and the ozone response is largely destroyed in the early 1960s, presumably as an effect of nuclear bombs. In the southern hemisphere the nuclear bomb effect was small and a correlation of total hemispherical ozone and sunspot cycle is apparent.

Ruderman and Chamberlain obtained the magnitude of the change in nitric oxide vertical column at Tromso, at Arosa, and for the southern hemisphere, and the amplitude of the ozone modulations shown in Figure 9 gives the change of ozone as a function of change of nitric oxide. Their results are summarized in Table 2, together with the point based on nuclear bomb tests.
Table 2. The observed response of stratospheric ozone to injections of nitric oxide by nuclear bombs and by cosmic rays.

<table>
<thead>
<tr>
<th>Example</th>
<th>Location</th>
<th>Change in $\text{NO}_x$ molecules cm$^{-2}$</th>
<th>Observed change of $O_3$ percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bombs</td>
<td>No. Hemi.</td>
<td>$(1-3) \times 10^{15}$</td>
<td>$5 - 10$</td>
</tr>
<tr>
<td>Cosmic rays</td>
<td>Tromso</td>
<td>$2 \times 10^{14}$</td>
<td>$2 - 5$</td>
</tr>
<tr>
<td></td>
<td>Arosa</td>
<td>$1 \times 10^{14}$</td>
<td>$1 - 2$</td>
</tr>
<tr>
<td></td>
<td>So. Hemi.</td>
<td>$4 \times 10^{13}$</td>
<td>$0.3 - 0.7$</td>
</tr>
</tbody>
</table>

The four points in Table 2 constitute a calibration curve for the effect of nitric oxide on stratospheric ozone, and model calculations should be checked against these relatively direct experimental results. The cosmic rays are particularly direct involving observed atmospheric ionization and observed total-ozone data; the only calculation is that relating rate of ion formation to rate of nitric oxide formation. A comparison of a model calculation and these new interpretations of cosmic ray and nuclear bomb data in terms of ozone depletion by nitric oxide is given by Figure 10. The calculations are based on the photochemical steady-state, $45^\circ$ latitude, solar equinox, static atmosphere, various uniform $\text{NO}_x$ backgrounds (0.3, 1.0, and...
3.0 ppb), and added NO\textsubscript{x} spread over a band about 10 km wide above and below 20 km (a model for SST injection). These calculations were made before the paper by Ruderman and Chamberlain appeared, and the assumed added NO\textsubscript{x} column only goes down to 1 \times 10^{14}. The four "calibration" points from Table 2 are entered on Figure 10. Within the experimental error, these four calibration points follow the nonlinear calculated curve associated with an NO\textsubscript{x} background between 0.3 and 1 ppb in the lower stratosphere. If the 10 percent increase in ozone between the early 1960s and 1970 as given by London and Kelley can be assigned to the return to normal after the end of the nuclear bomb tests, then all four points lie on the curve of highest sensitivity of ozone to NO\textsubscript{x}.

In Mahlman's analysis\textsuperscript{9} of the spread of (inert) exhaust gases by means of a three dimensional global circulation model, he specifically solved for the case of 500 American SST with an emission index of 42. His computation only went for 11 months, and he estimated that the peak distribution would be perhaps a factor of two higher if allowed to run for an indefinitely long time. His emission index is about three times too high, his value is about two times too low of nitrogen oxides because of inadequate time, and thus his estimate is about 50 percent too high. The vertical profile associated with Mahlman's calculation is indicated by an arrow in Figure 10.
My (1971) estimate of the worldwide average NOx column from 500 American SST with 14.8 emission index is also indicated on the figure, and it is somewhat less than that of Mahlman. If Mahlman's estimate is divided by 3 to correct for emission index and multiplied by 2 to correct for insufficient model simulation time, then it is very close to the 1971 estimate. If the calculated curves are regarded as being calibrated by the cosmic ray modulation and by the nuclear bomb response, then the indicated reduction of the ozone shield by 500 American SST (emission index 14) is between 17 and 28 percent. The indicated ozone reduction by 500 Concordes is between 8 and 17 percent.

The results of the nuclear bomb tests seem to lie somewhat lower than one would expect from extrapolation of the data for cosmic ray modulation. It could be that the results for 500 SST would be somewhat lower than indicated by the calculated curves in Figure 10.

On the other hand, the modulation amplitude of NOx at Tromso corresponds to only 75 Concorde SST (emission index of 14) after flying regular schedules for only 11 months (Mahlman model). The data for Tromso in Figure 9 between 1936 and 1954 (negligible perturbation by nuclear bomb tests) appear to correspond to the effect of only 25 American SST or 75 Concordes. The ozone perturbation at Arosa corresponds to only 13 SST or to 40 Concordes. In each case, there is a noticeable change of ozone.
Conclusions

The calculated ozone reductions by nitrogen oxides according to 1973 models of the stratosphere including one and two dimensional motions are in fairly good agreement with 1971 models of the stratosphere based on the photochemical steady-state and a static atmosphere (Figure 5). Of course, a static model of the atmosphere will not predict the distribution of species in the atmosphere, but starting with an observed or assumed distribution, the static model does a useful job in predicting the changes to be expected from more or less NO\textsubscript{x} (or other additive).

A recent analysis of the modulation of cosmic rays in the polar regions by the eleven year solar cycle (Ruderman and Chamberlain) indicates that the NO\textsubscript{x} increment from 75 Concorde SST operating for 11 months would produce a 2 to 5 percent reduction in the vertical ozone column. This analysis does not depend on photochemical model calculations, it depends on a logically close-coupled relation between observed\textsuperscript{41} ionization by cosmic rays, inferred\textsuperscript{37} nitric oxide production from these ionization processes, and correlations\textsuperscript{18} observed of total ozone with the sunspot cycle. To the extent that Ruderman and Chamberlain's analysis is confirmed, there is direct evidence that stratospheric ozone is highly sensitive to added nitric oxide.
Acknowledgement

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REFERENCES


6. Friedman, H., Chairman, ad hoc panel of National Academy of Sciences, NO\textsubscript{x} and the ozone layer, News Report, National Academy of Sciences, October 1972, 2-3.


20. Lovill, J. E., Characteristics of the general circulation of the atmosphere and the global distribution of total ozone as determined by the Nimbus III satellite infrared interferometer spectrometer, *Atmospheric Science Paper* No. 180,
Department of Atmospheric Science, Colorado State University, Fort Collins, Colorado (Dec. 1972).


30. Hesstvedt, E., (a) Effect of supersonic transport upon the ozone layer, studied in a two-dimensional photochemical model with transport, AGARD Conference on Atmospheric Pollution by Aircraft Engines (April 1973). (b) Effect of water vapor and nitrogen oxides upon the ozone layer, Symposium on Atmospheric Ozone, Arosa, Switzerland (August 1972).


Figure 1. Vertical profiles of ozone between 20 and 50 km as measured by rockets.  
   a. Duplicate profiles at one latitude and at approximately the same season.  
   b. Effect of latitude.  

Figure 2. Total ozone in the northern hemisphere as measured from Nimbus IV satellite, May 1969. Contour lines are in units of milli-atmosphere-cm STP (Dobson units).  

Figure 3. Zonal average ozone concentration (heavy lines) in units of molecules cm$^{-3}$ (6E12 = 6x10$^{12}$) and zonal average production rate (light lines) in units of molecules cm$^{-3}$ sec$^{-1}$. Note: 3x10$^4$ molecules cm$^{-3}$ sec$^{-1}$ produces 1x10$^{12}$ molecules cm$^{-3}$ in one year.  

Figure 4. Recent observation of oxides of nitrogen in the stratosphere, including HNO$_3$, NO, and NO$_x$ (NO + NO$_2$).  

Figure 5. Calculated reductions of total ozone as a function of added NO$_x$:  
   a. Ozone profiles at the equator calculated (1971) from photochemical steady state and a static atmosphere.  
   b. Effect of uniform mole fractions of NO$_x$ on total ozone column. Lower curve neglects the buffering action of partial reformation of ozone at lower elevations after it is destroyed by NO$_x$; upper curve includes this radiation-transfer, buffering action (Steady state, 1971).  
   c. NO and O$_3$ vertical columns as a function respectively
of 300 Concordes, 600 Concordes, 500 American SST, 1500 American SST (worldwide average, 14 g NO/kg fuel emission index), including one-dimensional atmospheric motions (1973).

d. Decrease in ozone vertical column for various numbers of SST given in Figure 5c.

e. Decrease of stratospheric ozone after initiation of flight by 1000 American SST (42 g/kg emission index). Minimum injection is based on world-wide average; maximum injection assumes 20-fold local maximum. This model includes one dimensional atmospheric motions (1973).

f. Calculated reduction of vertical ozone column from SST exhaust according to different models from static 1971 model to models with one or two dimensional motions in 1972 and 1973.

Figure 6. Stratospheric distribution of strontium-90 as observed from atmospheric sampling program: May-Aug., 1963; Jan.-Apr., 1964.

Figure 7. Maximum bomb produced NO\textsubscript{x} as inferred from observed distribution of strontium-90 (Fig. 6), including the linear relationships: nuclear bomb yield and nitric oxide; nuclear bomb yield and strontium-90.

Figure 8. Trends in total ozone following the large scale nuclear bomb tests of 1952-62.

a. Increase in ozone at various individual stations,
in terms of monthly deviations from monthly normals.
b. Change in hemispheric ozone in terms of monthly deviations from monthly normals: there is no significant trend in the southern hemisphere; there appears to be a decrease of $-4.7 \pm 1.5$ percent per decade before 1961 and an increase of $11.3 \pm 2.3$ percent per decade after 1961 in the northern hemisphere.

Figure 9. The effect of sunspot cycles on cosmic rays, ionization of the atmosphere, production of nitric oxide in the atmosphere, and the total ozone response.

a. Ionization at various elevations as a function of sunspot number, Thule, Greenland.
b. Oscillating amplitude of rate of ionization as a function of altitude, Thule, Greenland.
c. Total ozone variation (percent) as a function of sunspot number. Note phase shift at Tromso and at Arosa, relative amplitude at Tromso and Arosa, and destruction of coherence between sunspot cycle and ozone during the period of large scale atmospheric nuclear bombs.

Figure 10. Calibration of sensitivity of stratospheric ozone to increases in nitrogen oxides on the basis of cosmic ray modulation (Fig. 9c) and nuclear bomb tests (Figs. 7 and 8b). The three curves are calculated (steady-state model) on the basis of uniform NO$_x$ backgrounds of 0.3, 1.0, or 3.0 parts per billion. Estimates of the nitric
oxide increments from 500 American SST are given on the basis of two year accumulation (1971) and three-dimensional global atmosphere model for 11 month flight time.
OZONE PROFILES FROM ROCKET SOUNDINGS
Krueger (1973)

Fig. 1a

Ozone Concentration (log scale)

Kilometers

3.8 x 10^{12}
Aug.
64°N

5.8 x 10^{12}
Feb.
38°N

4.3 x 10^{12}
March
22°N

4.5 x 10^{12}
March
4°N

XBL 738-1685
OZONE PROFILES FROM ROCKET SOUNDINGS, HAWAII, 22°N
A. J. Krueger, Goddard Space Flight Center (1973)

Fig. 1b
TOTAL OZONE, NORTHERN HEMISPHERE
NIMBUS IV SATELITE, MAY, 1969

East

West


XBL 738-1679

Fig. 2
OZONE PRODUCTION RATE, MOLECULES cm\(^{-3}\) sec\(^{-1}\)
and
OZONE CONCENTRATION, MOLECULES cm\(^{-3}\)

Fig. 3
Ozone at the Equator (Calculated)

Fig. 5a
Fig. B5. Unperturbed and perturbed NO and O$_3$ vertical profiles from one-dimensional vertical kinetics transport model.

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FIRST ANNUAL REPORT,
DOT-CIAP PROGRAM

M. C. MacCracken
Principal Investigator

MS. date: February 13, 1973

LAWRENCE LIVERMORE LABORATORY
University of California/Livermore, California/94550

Fig. 5c
Fig. B6. Estimated perturbations in O₃ column density from one-dimensional vertical kinetics transport model.

Fig. 5d
Fig. 7: Calculated percentage decrease in total ozone subsequent to injection of nitric oxide into the stratosphere.

STRATOSPHERIC CONTAMINATION EXPERIMENTS WITH A ONE-DIMENSIONAL ATMOSPHERIC MODEL

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CALCULATED REDUCTION OF VERTICAL OZONE COLUMN
ACCORDING TO DIFFERENT MODELS

Fig. 5f
STRATOSPHERIC DISTRIBUTION OF STRONTIUM-90 (dpm/1000 SCF)

Fig. 6
Atmospheric Total Ozone Increase during the 1960s

Fig. 1 Plots of mean monthly total ozone deviations from monthly normals for selected stations. Linear trend lines have been fitted to the data.

W. D. Komhyr
E. W. Barrett
G. Slocum
H. K. Weickmann

Fig. 8a
3-MONTH RUNNING MEAN (TOTAL O₃ DEPARTURE FROM MEAN)

- Northern Hemisphere
- Southern Hemisphere

Year


m atm cm (10⁻³ cm STP)

Fig. 8b
Fig. 9a
OSCILLATING AMPLITUDE OF STRATOSPHERIC IONIZATION

Fig. 9b
Sunspot Number

Tromso
70°N
32 Mos.

Arosa
47°N
38 Mos.

Southern Hemisphere

Fig. 9c
NATURAL AND ARTIFICIAL ALTERATION OF OZONE BY NO\textsubscript{x}

Fig. 10
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