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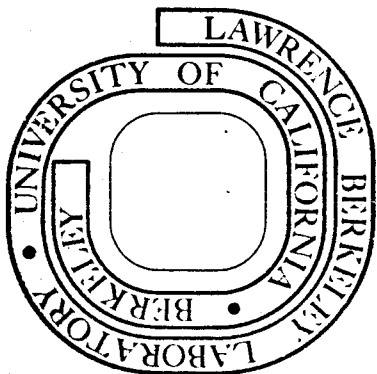
Harold Johnston

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# The Concorde, Oxides of Nitrogen, and Stratospheric Ozone

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As of the spring of 1971, the oxides of nitrogen were regarded as negligible so far as stratospheric photochemistry and supersonic transports were concerned. I have presented three separate lines of argument, each illustrating that the oxides of nitrogen are a very important variable. The conclusions from these three lines of argument are presented in this article, and a rebuttal is given to certain indirect attacks that have been made on my previous reports. I strongly adhere to my principal conclusion, namely, that the oxides of nitrogen are 'a highly important variable in this problem and must be given realistic consideration'.

During the past year I have published four reports and articles (Johnston, 1971a, b; 1972 a, b) on the probable environmental impact of supersonic transports (SST) operating in the stratosphere, with especial emphasis on the role of the oxides of nitrogen, NO and NO<sub>2</sub>. These reports have been rather technical and not easily understood by a general reader. In this report I review the points made in previous articles with an emphasis on the conclusions rather than on the derivations, which can be checked in the original articles. First, I review the state of knowledge as it existed in the spring of 1971.

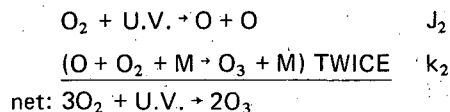
*Spring 1971* — In a fifty-seven page chapter on 'The Supersonic Transport' in *Technical Information for Congress* published in April 1971 (Committee of Science and Astronautics, 1971) there was a lengthy discussion of possible environmental impacts of the SST, but no mention was made of the role of the oxides of nitrogen in destroying stratospheric ozone. The effect was completely overlooked. The 'Study of Critical Environmental Problems' (SCEP) in the summer of 1970 made a calculation of the world-wide burden of NO<sub>x</sub> (NO and NO<sub>2</sub>) to be expected from five hundred SST. The value deduced was 7 parts per billion (ppb, 10<sup>-9</sup>) on a world-wide basis throughout the stratosphere, and they expected a 'possible peak concentration' of 70 ppb over regions of high traffic. The SCEP report stated that 'in stratospheric photochemistry . . . NO<sub>x</sub> . . . may be neglected'. A similar study in July 1971 by much the same group, reaffirmed this conclusion (SMIC, 1971). The statement by SCEP that 'NO<sub>x</sub> . . . may be neglected' was not based on a careful study of the question. As was brought out in a discussion in Boulder, Colorado (Dept of Commerce, 1971), this conclusion came from an off-the-cuff statement by one participant in the conference, based on a comparison between the known large mole fraction of NO in the ionosphere and the estimated increase of NO in the stratosphere.

Crutzen (1970) had proposed that the oxides of nitrogen were important in the natural ozone balance in the stratosphere. However, the SCEP report did not mention Crutzen's article.

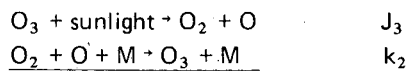
My Ph.D. thesis in 1948 was the first determination of the rate of reaction between ozone and nitrogen dioxide, and since that time my graduate students and I have studied many chemical and photochemical reactions of the oxides of nitrogen, nitric acid vapor, ozone, free radicals, etc. In 1966 I published a book on *Gas Phase Reaction Rate Theory* (Johnston, 1966) that featured reactions of the oxides of nitrogen. In 1968 I published a book on the rates of reaction of ozone, oxygen molecules, and oxygen atoms (Johnston, 1968), and in this book I discussed catalytic destruction of ozone by free radicals based on water and by the oxides of nitrogen. When in March 1971 I was presented (Dept of Commerce, 1971) with the SCEP estimate of 7 to 70 ppb NO<sub>x</sub> in the stratosphere and the statement that it 'may be neglected', I instantly knew that there was a contradiction in these two statements. Since then, I have demonstrated that the oxides of nitrogen are an important variable by three different methods; these three methods are reviewed in the following sections.

## (I) Purely chemical considerations

Ozone is formed in the stratosphere by the breaking down of molecular oxygen, O<sub>2</sub>, by solar ultra violet radiation to give two oxygen atoms, O, which combine with another oxygen molecule to form ozone, O<sub>3</sub> (Chapman; 1930a, b). These statements are compactly expressed by two chemical equations

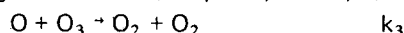


where M is either O<sub>2</sub> or N<sub>2</sub>. Ozone strongly absorbs ultraviolet radiation between 200 and 300 nanometers (nm), and it is the only effective shield of the earth's surface against the harsh ultraviolet radiation between 300 and 250 nm. This absorption of solar radiation breaks ozone apart, but it is instantly re-formed (Chapman, 1930a, b)

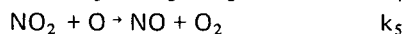
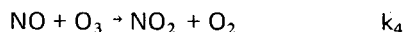


net: no chemical reaction

The entire atmosphere of oxygen would be converted to ozone if there were no natural processes to destroy ozone. In pure air the destruction process is the reaction of an oxygen atom with ozone to form two oxygen molecules (Chapman, 1930a, b)

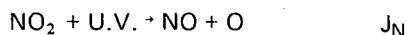


The oxides of nitrogen destroy ozone by a catalytic cycle



net:  $\text{O} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2$

where NO and NO<sub>2</sub> are regenerated and may be used over and over again (Johnston, 1971a, b; 1972a, b; Crutzen 1970, 1971a). Reaction 4 is not always followed by reaction 5, but rather it is usually followed by the photolysis of nitrogen dioxide



Thus, reaction 5 is the rate-limiting step in the catalytic destruction of ozone by NO and NO<sub>2</sub>. The ratio of the rate of destruction of ozone with and without oxides of nitrogen is simply given as follows:

$$\text{catalytic ratio} = \frac{\text{rate of 3 plus rate of 5}}{\text{rate of 3}}$$

If we let square brackets represent the concentration of a gaseous substance in units of molecules per cubic centimeter, the catalytic ratio can be simply expressed in conventional chemical form as follows:

$$\begin{aligned} \text{catalytic ratio} &= \frac{k_3 [\text{O}][\text{O}_3] + k_5 [\text{O}][\text{NO}_2]}{k_3 [\text{O}][\text{O}_3]} \\ &= 1 + \frac{k_5 [\text{NO}_2]}{k_3 [\text{O}_3]} \end{aligned} \quad (1)$$

At a typical stratospheric temperature, say 220°K, rate constant (Davis, 1972)  $k_5$  is  $9.2 \times 10^{-12}$  and the rate constant  $k_3$  is  $8.9 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ . Thus the catalytic ratio  $\rho$  may be rewritten

$$\rho = \text{catalytic ratio} = 1 + 10,300[\text{NO}_2]/[\text{O}_3] \quad (2)$$

A given amount of nitrogen dioxide is ten thousand times as effective in destroying ozone as the same amount of ozone itself. If NO<sub>2</sub> is 0.01 per cent of O<sub>3</sub>, then the rate of catalytic destruction of ozone by NO<sub>x</sub> is equal to the rate of destruction of ozone by pure air.

In the stratosphere the nitric oxide concentration, NO, is simply related to that for nitrogen dioxide, NO<sub>2</sub>; and likewise there is a straightforward relation between oxygen atom concentration and ozone concentration. The catalytic ratio may be re-expressed as follows (Johnston, 1971a):

$$\rho = 1 + \frac{[\text{NO}](k_4 k_5 / k_3 J_N)}{1 + [\text{O}](k_5 / J_N)} \quad (3)$$

The independent variables in this expression are nitric oxide and oxygen atoms. In these variables the time  $\tau$  to destroy half the ozone by reactions 3 and 5 is given by the expression

$$\tau = \ln 2 / (2k_3 [\text{O}]\rho) \quad (4)$$

The catalytic ratio  $\rho$  is a measure of the relative rate of destruction

of ozone in the presence and absence of NO<sub>x</sub>. The half-time  $\tau$  for ozone destruction is a measure of the absolute rate of ozone destruction. Both  $\rho$  and  $\tau$  may be expressed in terms of the independent variables: temperature, nitric oxide concentration, and oxygen atom concentration; compare equations (3) and (4). From a convenient monograph (Rawer, 1968), and the SCEP (1970) report, I deduced the total range of these independent variables in a sun-lit stratosphere with SST operation

Elevation	15 to 45 kilometers
T	217 to 260 °K
[O]	10 <sup>5</sup> to 10 <sup>10</sup> atoms cm <sup>-3</sup>
[NO <sub>x</sub> ]	10 <sup>8</sup> to 10 <sup>11</sup> molecules cm <sup>-3</sup>

[The SCEP report probably overestimated the amount of NO<sub>x</sub> to be expected from the SST; it used the value of 42 grams of NO per kilogram of fuel; in my reports I used 15 grams of NO per kilogram of fuel; and recent measurements on large jet engines give 20 to 30 grams of NO per kilogram of fuel (McAdams, 1971)]. For each temperature, 220, 240 and 260 °K, I prepared a complete table of the catalytic ratio  $\rho$  and the ozone half-time  $\tau$  for the full range of oxygen atoms between 10<sup>5</sup> and 10<sup>10</sup> per cm<sup>3</sup> and for nitric oxide concentrations between 10<sup>8</sup> and 10<sup>11</sup> per cm<sup>3</sup>. If the catalytic ratios  $\rho$  had been much greater than one for all values of the independent variables and if also the half-times  $\tau$  had all been equal to or less than 2 years (a stratospheric mean residence time), then I could have insisted that the oxides of nitrogen are certainly an important stratospheric variable, regardless of air motions, turbulence, or SST cruise height. In this case, an air motion would merely have transported a large chemical effect from one location to another. If the catalytic effect and its rate were large for all values of the independent variables, then it is proven, I think, that NO<sub>x</sub> is an important variable in this problem.

For most of the range of the independent variables, the catalytic ratio was larger than 2 and the half time for ozone destruction was shorter than one year. However, the catalytic ratio was less than 1.10 for about 3% of the domain of the independent variables [O], [NO], T. It was small for high [O], low [NO], and high T, which corresponds to the uppermost stratosphere. Also, the rate of ozone destruction was slow for about 10% of the domain of independent variables; the slow rates correlated with low [O], low [NO], and low T, which corresponds to the lowest stratosphere. This analysis is given in Figure 1 for one temperature, 220 °K (compare Tables 5 and 6 of Johnston, 1971a). The factor by which the oxides of nitrogen increase the rate of ozone destruction in pure air is given by the dashed lines for the values 2, 10, 100, and 1000. The time for [O] and [NO] to destroy half of the ozone at 220 °K is given by the solid slanting lines, and these times vary from less than one hour to more than ten years. The excluded region marked 'slow' in Figure 1 is for half times of two years or longer.

It is important to find where on Figure 1 the SST flights would be. The Concorde flies at a variable height, usually increasing as fuel is consumed. A typical figure may be taken as 17.5 kilometers, at which elevation the logarithm of the oxygen atom concentration is about 5.5. The Australian Academy of Science (1972) estimated the world-wide NO emission from the Concorde in 1985 to be  $102 \times 10^4$  kilograms per day. In this case a two year burden of NO<sub>x</sub> spread uniformly over the globe in a shell one kilometer thick (admittedly a rather arbitrary and unrealistic distribution, but it serves to set the order of magnitude) would have an NO<sub>x</sub> concentration of  $3 \times 10^{10}$  and an NO concentration of  $1.5 \times 10^{10}$  ( $\log[\text{NO}]$  would be 10.2). The point,  $\log[\text{O}] = 5.5$  and  $\log[\text{NO}] = 10.2$ , has a catalytic ratio of 100 (NO<sub>x</sub> destroys ozone 100 times

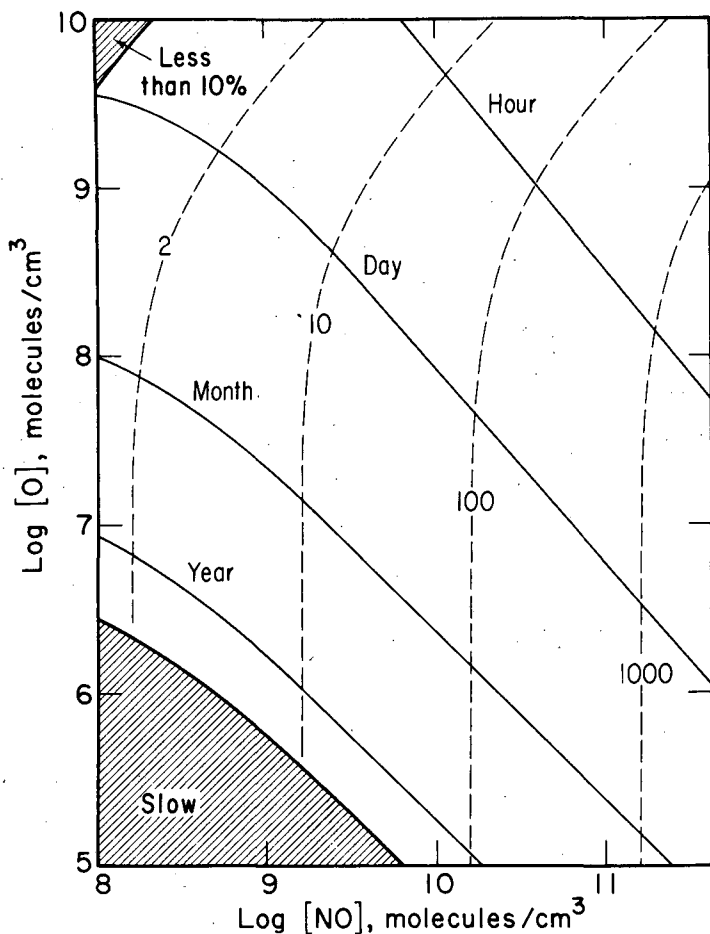


FIGURE 1

The catalytic ratio and the ozone half-life for the complete range of concentration of NO from the SST and of O in a sunlit stratosphere. --- catalytic ratio. — ozone half-life.

faster than ozone is destroyed in pure air) and an ozone destruction half-time of 5 months. If this quantity of  $\text{NO}_x$  was spread uniformly between 15 and 25 kilometers ( $\log[\text{O}]$  from 5 to 7,  $\log[\text{NO}] = 9.2$ ) the catalytic ratio would be 10 and the time to destroy half the ozone would vary with elevation between 50 days and 10 years. These effects are not negligible. If the engine exhausts accumulated in regions of high traffic to produce a local maximum, the catalytic ratios would be higher and the ozone destruction rates faster than these figures, which are for uniform, world-wide spread of the  $\text{NO}_x$ .

Although for most of the range of variables the effect of  $\text{NO}_x$  is both large and fast, a portion of the region gives a large catalytic ratio but a slow rate. This feature demands that the problem be treated more realistically in terms of the actual stratosphere. The first step in that direction is to calculate the steady-state ozone profile in an assumed static atmosphere. On the basis of results obtained from the simple, static model, we can identify some of the important variables that will need to be considered in more realistic, more complicated treatments of the problem.

## (2) Calculation of ozone profiles in the stratosphere

**Uniform distributions of  $\text{NO}_x$**  — I calculated ozone profiles in the stratosphere on the basis a photochemical steady state and a static atmosphere. The purpose of these calculations was to identify important chemical and physical variables, not to solve meteorological problems (that comes later and by others). These calculations are the logical next step beyond the purely chemical considerations of

catalytic ratio and ozone destruction rates. I used a fine wavelength grid of one nanometer, an elevation grid of one kilometer, and I averaged the solar intensity for every 5 degrees of solar angle over a 24 hour period. At each kilometer of the elevation grid, corrections were made for the absorption of sunlight by all overhead species. These calculations used the observed solar spectrum above the atmosphere and observed photochemical and chemical quantities. They involved no adjustable parameters.

In the stratosphere, the free radicals H, HO, and HOO are formed indirectly from water. These radicals also destroy ozone; however, in the stratosphere the degree and rate of ozone destruction by these radicals are far less than by  $\text{NO}_x$  or by  $\text{O}_3$  itself. After a detailed analysis of these reactions, they were omitted from the reaction scheme that I used to calculate ozone profiles [recent experimental data by Langley and McGrath (1971) abundantly confirm that these reactions are indeed negligible].

Although the rate constants for the  $\text{NO}_x$  reactions discussed above are fairly well known, the background concentration of NO and  $\text{NO}_2$  has not been measured in the stratosphere. Thus a primary purpose of these calculations was to explore the effect of assumed  $\text{NO}_x$  backgrounds on the calculated ozone profiles. A large number of uniform distributions of  $\text{NO}_x$  was explored. The basic condition was  $45^\circ$  latitude and the solar equinox. Other calculations were made from the equator to  $75^\circ$  latitude. Various temperature profiles were used.

For these wide ranges of variables it was found, without exception, that the ozone vertical column is extremely sensitive to  $\text{NO}_x$  above one part per billion (ppb) (Note: one ppb is  $10^{-9}$ ).

Four calculated ozone profiles at the equator (solar equinox, 24 hour average solar intensity) are shown in Figure 2, together with a recently observed (Randhawa, 1971) ozone profile over Panama ( $9^\circ\text{N}$ ). One calculated profile is for pure air, and it is far greater than the observed ozone. Three curves are given for various amounts of  $\text{NO}_x$  uniformly spread throughout the stratosphere, at 3, 10, and 100 ppb. The ozone column is sensitive to added  $\text{NO}_x$ . About 3 ppb of  $\text{NO}_x$  reduces the ozone column by more than a factor of two below the value calculated for zero  $\text{NO}_x$ , and it agrees fairly well with the observed ozone column.  $\text{NO}_x$  at 10 or 100 ppb reduces the ozone column to exceedingly low values (recall the SCEP statement that 70 ppb of  $\text{NO}_x$  'may be neglected').

These profiles include the partial self-healing effect of reformation of ozone at lower elevations. The reduction of ozone by  $\text{NO}_x$  is still a very large effect. The ozone half-time is much shorter (less than three months) than north-south transport times above about 27 kilometers, and thus the upper halves of these profiles should be fairly realistic. Atmospheric motions undoubtedly are important over the lower half of these profiles. Some models of atmospheric motion make the effect of  $\text{NO}_x$  from the SST less serious than in a static atmosphere, but some models (Crutzen, 1971b) of atmospheric motion indicate a much larger ozone destruction by the SST than the corresponding static model.

**Non-uniform distributions of  $\text{NO}_x$**  — A uniform distribution of  $\text{NO}_x$  in the natural stratosphere is highly improbable as can be seen from consideration of the natural sources and sinks. A uniform distribution of  $\text{NO}_x$  throughout the stratosphere from the SST is even more improbable. The exhaust gases are laid down over a relatively narrow range of elevations, and vertical mixing is a slow process in the stratosphere. I made a large number of steady-state calculations with non-uniform  $\text{NO}_x$  backgrounds and with a fixed quantity of  $\text{NO}_x$  spread uniformly, world-wide, over shells of various thickness. When the shell of exhaust gases is one

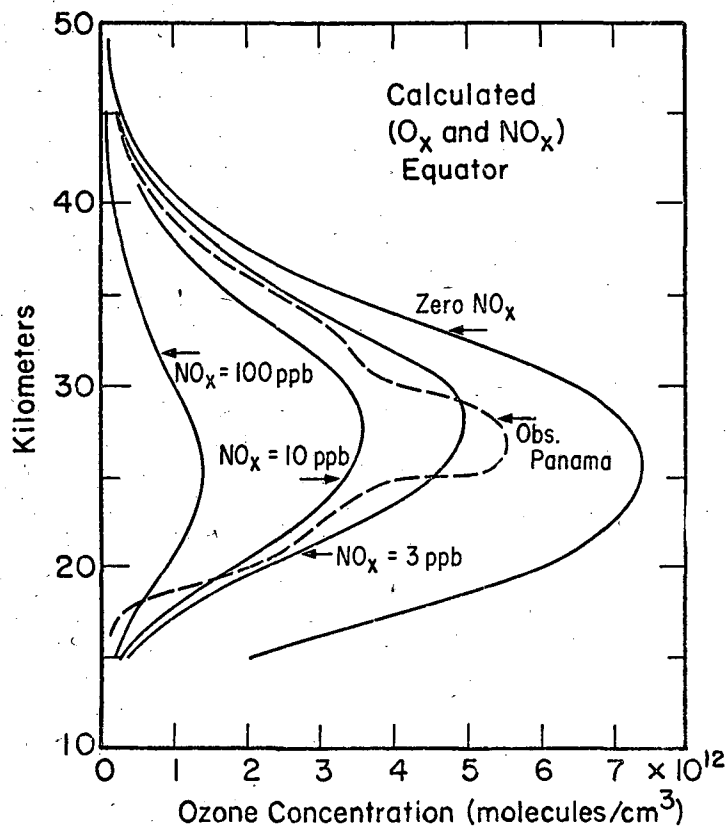


FIGURE 2

Observed and calculated ozone profiles at the equator. Calculations based on a static atmosphere and the steady-state. The discrepancy between the curve calculated with zero  $\text{NO}_x$  and the observed curve is called the 'ozone deficit'.

kilometer thick, the ozone contained therein is rapidly reduced almost to zero, but ozone outside this shell is untouched. The resultant steady-state ozone reduction is only 3% of the total column. If the same quantity of  $\text{NO}_x$  is spread over a shell 4 kilometers thick, the degree of reduction per unit volume is less, but the reduction of the total column is much greater, 12%. For the given added quantity of  $\text{NO}_x$ , the maximum ozone reduction of 23% occurred at a spread of 10 kilometers. Further spread covering 16 kilometers resulted in a 20% ozone reduction. For a small degree of vertical spread of the  $\text{NO}_x$  the reduction of the ozone column is small; for a moderate degree of vertical spread the reduction of the ozone column is large; and for a further vertical spread of the same material the reduction of the ozone column is less than for a moderate spread.

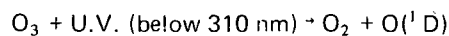
These calculations involved a large non-uniform background of  $\text{NO}_x$ . The model of a uniform world-wide distribution of SST exhaust gases throughout a fixed shell is, of course, unrealistic. A critic is being rather unsophisticated to make a point of this, however. These square corners and arbitrary thicknesses point out to any thoughtful reader that I am making model calculations to identify important variables; I make no pretence of depicting all the complexities and realities of the stratosphere. From several hundred steady-state, static-air calculations covering the globe and a wide range of uniform and non-uniform  $\text{NO}_x$  backgrounds, I concluded that the following variables are important in this problem:

1. The amount of  $\text{NO}_x$  in the stratosphere as a natural background.

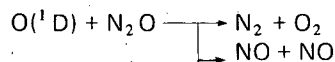
2. The distribution both in elevation and latitude of the  $\text{NO}_x$  in the stratosphere as a natural background.
3. The amount of  $\text{NO}_x$  released by the Concorde or other SST exhaust.
4. The distribution, both in latitude and in the vertical direction, of the artificial  $\text{NO}_x$  after long-term SST operation.
5. The formation and destruction (photochemical and chemical) of nitric acid in the stratosphere; the eddy diffusion (up and down) of nitric acid.
6. The time required for atmospheric motions to sweep SST exhaust gases out of the stratosphere.
7. Other known chemical reactions between stratospheric species number well over 100, and a precise consideration (getting down to the last 5%) will require consideration of these reactions. Also, we must keep on the look-out for new reactions or newly observed rates for familiar reactions.

### (3) Comparison of natural and artificial source strengths of $\text{NO}_x$ in the stratosphere

In recent months the principal source of natural  $\text{NO}_x$  in the stratosphere has been identified. Nitrous oxide,  $\text{N}_2\text{O}$ , is produced in small amounts from soil bacteria under anaerobic conditions. This gas is rather inert in the troposphere; it resembles carbon dioxide in several respects. It penetrates the stratosphere by eddy diffusion, and nitrous oxide is decomposed directly by solar ultraviolet radiation to give nitrogen and oxygen (Bates and Hayes, 1967), and it is indirectly destroyed by sunlight to form some nitric oxide in the stratosphere:



$\text{O}(\text{}^1\text{D})$  deactivated and destroyed in many ways



This source of stratospheric NO appears to have been discovered by Crutzen (1971a) and confirmed by Nicolet and Vergison (1971) and by McElroy and McConnell (1971). The estimates of NO formation from this mechanism vary because of uncertainties in rate constants and in effective vertical eddy transport rates. The range of estimated NO formation rates for each author is given in Table 1. The average minimum and average maximum rate of natural NO formation is  $(0.34 \text{ to } 1.55) \times 10^8 \text{ molecules cm}^{-2} \text{ sec}^{-1}$ . The average world-wide input of NO into the stratosphere by the Concorde as of 1985 as estimated by the Australian Academy of Science (1972), gives a source strength of  $0.47 \times 10^8 \text{ molecules cm}^{-2} \text{ sec}^{-1}$ . The Concorde flux is between 30% and 138% of the natural background source of  $\text{NO}_x$ .

TABLE 1 Natural and artificial fluxes of  $\text{NO}_x$  into the stratosphere in units of  $10^8 \text{ molecules cm}^{-2} \text{ sec}^{-1}$  on a world-wide basis

Calculated natural flux	Author	Reference
0.29 to 1.5	Crutzen	1971a
0.5 to 2.5	Nicolet	1971
0.25 to 0.65	McElroy	1971
ave. 0.34 to 1.55		
Estimated Concorde flux (1985)		
0.47	AAS	1972

The  $\text{NO}_x$  from the exhaust of the Concorde will be subject to many complicated photochemical and meteorological effects in the stratosphere. At present it appears that no one understands what all these complications entail. However, the natural nitric

oxide from nitrous oxide and soil bacteria is subject to this same photochemical and meteorological environment, and the natural  $\text{NO}_x$  now reduces ozone by about a factor of two below the value it would otherwise have (Figure 2). Since a source  $(0.34 \text{ to } 1.55) \times 10^8 \text{ molecules cm}^{-2} \text{ sec}^{-1}$  of natural  $\text{NO}_x$  is now the dominant factor in balancing stratospheric ozone, an artificial increment of  $0.47 \times 10^8 \text{ molecules cm}^{-2} \text{ sec}^{-1}$  from the Concorde will very probably have a significant effect in reducing stratospheric ozone below its natural value. This safe qualitative statement is converted to a rather speculative quantitative estimate in the next paragraph.

A very crude estimate of the magnitude of the effect of the Concorde on the ozone column can be made by comparing the natural and artificial source strengths of  $\text{NO}_x$ . The reduction of ozone at any one position varies as the square root of the catalytic ratio, and the dependence on  $\text{NO}_x$  thus has the form  $(1 + \beta[\text{NO}_x])^{1/2}$ . If the present reduction of ozone by the natural oxides of nitrogen,  $[\text{NO}_x]_0$ , is a factor of 2, then  $\beta[\text{NO}_x]_0$  is 3. If  $\text{NO}_x$  is increased by 30% (the ratio of 0.47 and 1.55 in Table 1), the reduction of ozone below the present level is  $(4/4.9)^{1/2} = 0.90$  or a 10% decrease. If the artificial  $\text{NO}_x$  is 1.38 times the natural value (the ratio of 0.47 and 0.34 in Table 1), the ozone column is changed by  $(4/8.2)^{1/2} = 0.66$  or a 34% decrease. These calculations are suggestive only. The Concorde injects high concentrations of  $\text{NO}_x$  over a narrow range of elevation (about 17 to 19 km) and it spreads horizontally and vertically, becoming more dilute as it does so. The natural  $\text{NO}_x$  is formed at low concentrations over a wide range of elevation (about 15 to 35 km). I can think of models of air motions that would indicate the Concorde pattern to be less deleterious to ozone (either very high or extremely low vertical mixing) or more deleterious to ozone (more or less uniform spatial spread between 15 and 25 km) than the simple comparison given here.

### Some counter arguments

As of 1 May 1972, I have seen no case where someone has read my reports, found a substantive mistake, and spoken up to correct the mistake. Even though I have seen no direct engagement with my printed arguments, I have seen several examples of flanking attacks, some of which are discussed here.

I have been accused of using inflated figures of  $\text{NO}_x$  emission relative to the Concorde. My reports were based on the expected performance of the American SST, not the Concorde. The proposed American SST would burn considerably more fuel than the Concorde and fly at a somewhat higher elevation. In this report I have used emission data as given by the Australian Academy of Science (1972) to translate some of the earlier discussion to the Concorde (also I used up-dated (Davis, 1972) values for photochemical and chemical rate constants).

A recurrent criticism is, in effect, that I did not solve the problem of global air circulation including interacting photochemistry. Indeed, I did not solve this problem, nor does it appear that anyone else will be able to do so for several years and further generations of bigger and faster computers. I never attempted to solve meteorological problems of any sort; that is for the meteorologists to do; but they should put the correct chemistry in their models. A year ago it was said ' $\text{NO}_x$  . . . may be neglected', whereas  $\text{NO}_x$  is clearly the biggest chemical problem of the stratosphere — beyond the Chapman (1930a, b) reactions.

A specific criticism is that I made some of my calculations on the basis of a photochemical steady state in a static atmosphere. For one of my three lines of argument, I did indeed use this method,

and I said so all the time. Even though it is an approximate, not exact, method, it is a very valuable and valid tool in identifying important variables in the problem. The effect of  $\text{NO}_x$  on stratospheric ozone is so great that even the simple steady-state calculation with a static atmosphere is sufficient to demonstrate some features of the problem.

Another criticism sometimes made is that I overlooked the 'water reactions'. In fact, I thoroughly considered the water reactions (Johnston, 1968, 1971a) and found them to be negligible compared to reactions of the oxides of nitrogen. There is quite a difference between overlooking an effect and in quantitatively considering the effect and then rejecting it because it is found to be small. On the other hand, I object to the way the water reactions have been handled by others. In explaining the ozone deficit (compare the calculated and observed ozone profiles in Figure 2), two water reactions that have never been observed were postulated and their rate constants were used as adjustable parameters to force calculated ozone columns to agree with observations. Chemical kinetics is a powerful predictive science if one transfers observed, established, elementary rate constants from one environment to another. It is an abuse of chemical kinetics to use the rate constants of hypothetical reactions as adjustable parameters.

Some people carefully assert that any change in stratospheric ozone caused by the Concorde would be well within the existing range of natural fluctuations. When it comes from a knowledgeable person, this argument is a very cynical one, as can be seen by an examination of the range of natural fluctuations. Figure 3, derived from Dobson's (1968) analysis of data taken during the International Geophysical Year, indicates the natural trends of ozone with season and latitude in the northern hemisphere. In sub-polar regions, the ozone shield is the thickest in the world, the sun is rarely at a high overhead angle, and the ozone shield varies by about 40% between spring and fall. In tropical and lower temperate regions, between  $30^\circ\text{N}$  and  $30^\circ\text{S}$ , the ozone shield is the thinnest in the world, the sun is often at a high overhead angle, and the natural ozone shield varies very little throughout the year. A 40% systematic reduction of ozone (the range of annual polar fluctuations) in tropical regions would be a major disaster (Smith, 1972). It is totally unacceptable to justify a large *systematic* reduction of ozone on the basis of the large fluctuations that naturally occur in sub-polar regions.

During the past ten years, military aircraft have operated in the stratosphere for the first time. Komhyr *et al.* (1971) analysed the ozone data from a few of the hundred ozone-observing stations over the world (Meteorological Branch, 1960-69), and for seven cases, Komhyr found ozone to increase between 2% and 10% during the last ten years. The juxtaposition of these two statements is sometimes regarded as a 'disproof of the  $\text{NO}_x$  hypothesis'. It is implied that if  $\text{NO}_x$  does indeed catalyse the destruction of ozone, then the military planes should have caused ozone to decrease, whereas the observations indicate an increase. However, US military planes for the last ten years burned fuel in the stratosphere at an average rate 2000 fold less than would be the case for 500 American SST, and this amount of  $\text{NO}_x$  would be expected to have an undetectable effect. The facts about the increase of ozone over the world are not entirely clear. I find that some stations (Meteorological Branch, 1960-69) showed a decrease of ozone, and many stations showed no significant increase or decrease. Table 2 lists the all-year average ozone columns for several stations: two that Komhyr reported as showing the largest increase (Kodaikanal, India, +10% and Oxford, England, +8.9%); two



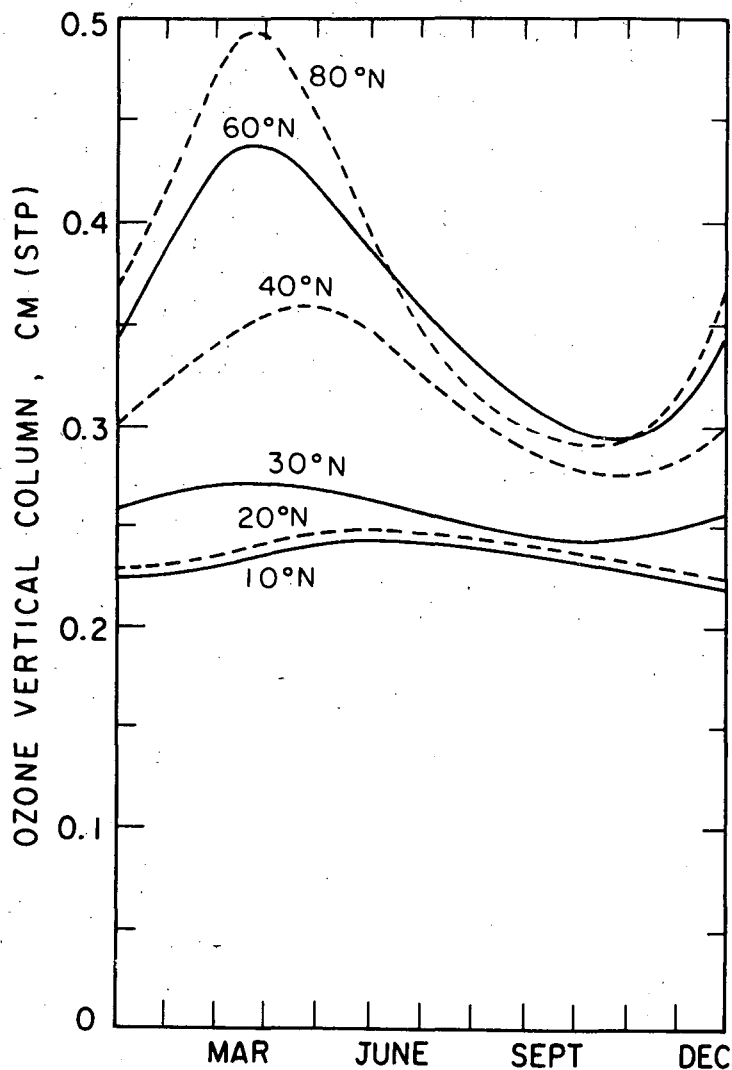


FIGURE 3

Ozone vertical column in the northern hemisphere for the year 1958 as a function of latitude and season.

stations, not discussed by Komhyr, that showed a decrease (Val Joyeux, France and Aarhus, Denmark); and two main Australian stations (Darwin to which Komhyr assigned a 6% increase and Aspendale to which Komhyr assigned a  $1 \pm 1\%$  decrease). Also given in Table 2 are the results from Aspendale by another method. The case for an ozone increase is suggestive but not compelling. At Arosa, Switzerland, ozone vertical profiles have been observed over a long period of time, and Dütsch (1969) noted a correlation of total ozone with the sunspot cycle, especially in the upper stratosphere. Dütsch observed a pronounced maximum of ozone at Arosa in 1958-61, following the sunspot maximum in 1957-58, and a decrease of ozone out to the sunspot minimum about 1963-64. If the upper stratospheric ozone is related to solar flare activity, as Dütsch's one set of long-term observations suggests, then some increase in ozone over the period 1963-1969 would be expected. In summary of this point, the factual situation is not entirely clear; there is an hypothesis for natural long term fluctuations of ozone, and the small amount of military traffic in the stratosphere is not expected to have had an effect on ozone in any case.

The report of the Australian Academy of Science (1972) said: 'The source of ozone (ultra violet radiation acting on atmospheric oxygen) is strongest in summer and at low latitudes, yet the resulting ozone concentration is greater in high than in low latitudes and reaches a maximum in spring. The natural ozone distribution predicted by a static approach would thus be completely false in both time and space. It is to be regretted that overseas scientists whose warnings have received much publicity have neglected the dynamic nature of the phenomenon; in consequence of this neglect, though their warnings should be heeded, their detailed conclusions can carry little weight.' Contrary to this statement, the geographical variation mentioned in this quotation and the problems of air motions were discussed at considerable length in my report UCRL-20568, June 1971 (Johnston, 1971a), pages 94-103, including figure 12. I believe that my discussion there is balanced and reasonable. From the quotation above, it can be seen that the authors did not read my principal 1971 report on this problem, even though it was repeatedly referred to in my *Science* article (Johnston, 1971b). By not reading my report, the authors put

TABLE 2 Ten-year records of annual average ozone column in units of milli-atmosphere centimeters from Meteorological Branch (1960-69)

Station	Increase (a)	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969
Kodaikanal 10°N	+10	246	254	246	247	258	255	257	261	266	
Oxford 52°N	+8.9	356	341	340	360	343	352	361	349	361	361
Aarhus 45°N	(b)	373	362	361	383	355	339	346	321	341	350
Val Joyeux 48°N	(b)				327	314	335	323	290	279	262
Brisbane 27°S	+6.6	289	275	286	288	286	297	291	295	297	288
Aspendale 38°S	+1.1	329	307	326	326	328	328	314	321	324	314
Aspendale (Umkehr Method)					318	322	325	301	316	313	

(a) Increase in units of per cent per decade as given by Komhyr *et al.*, 1971.

(b) Not reported in Komhyr *et al.*, 1971.

together an argument that my conclusions carry little weight. However, by not reading my report, the authors never discovered what my conclusions were; the principal conclusion was that 'NO<sub>x</sub> is a highly important variable in this problem and it must be given realistic consideration' (Johnston, 1971a, p.114). If this conclusion carries 'little weight' with the Concorde sponsors, then there is great need for a wide body of neutral scientists to take an interest in this problem.

The Australian Academy of Science stated: 'The two most thorough attempts to estimate nitric oxide amounts that are compatible with the observed ozone concentrations give results differing by approximately an order of magnitude. . . . this seems to be attributable to different choices of values of the rate constants'. As a matter of fact, the integrated column of NO<sub>x</sub> as found by Crutzen was 12 ppb (10<sup>-9</sup>) of the total stratosphere above 15 kilometers, and my integrated column of NO<sub>x</sub> was 6.6 ppb, a factor of 2, not an order of magnitude. Furthermore, Crutzen included nitric acid HNO<sub>3</sub> in his inventory of NO<sub>x</sub>, whereas I omitted nitric acid from what I called NO<sub>x</sub>. I estimate the column of nitric acid to be about 5 ppb of the stratosphere above 15 kilometers. Our supposed difference is not based on 'different choices of the rate constants' but rather on a different method of labelling nitric acid.

Again, 'neither calculation adequately allowed for transport processes in the stratosphere, and these will ameliorate the impact of the supersonic aircraft on the ozone layer'. So far as I can tell, it is a matter of blind faith and unlimited optimism to say that all considerations of atmospheric motions and transport processes will *ameliorate* the impact of the SST. Crutzen (1971b) made parallel calculations for a static atmosphere and for an atmosphere in motion. In some cases he found the effect of atmospheric motions to lead to a much bigger reduction of ozone by the SST than for a static atmosphere. In one case he found ozone reduction to be twice as sensitive to NO<sub>x</sub> in the case of air motions as for my worst case with a static atmosphere. To be sure, Crutzen has not yet solved the total problem of global air circulation with interacting photochemistry. However, he has shown that one may not blindly trust air motions to reduce the impact of the SST on the ozone layer.

Several other indirect criticisms of the case against the importance of NO<sub>x</sub> to stratospheric photochemistry are discussed in Johnson, 1972a.

**Conclusions** — I have developed three independent lines of argument concerning the importance of NO<sub>x</sub> in the stratosphere:

(1) A purely chemical analysis compared the rate of destruction of ozone by NO<sub>x</sub> to the rate of destruction of ozone in pure, sunlit air. The catalytic rate constant is 10,000 times larger than the uncatalysed rate constant, and thus trace amounts of nitrogen dioxide can be very important. (2) Photochemical steady-state calculations in the static atmosphere were made for several hundred different situations: NO<sub>x</sub> backgrounds, latitude, solar angles, temperature, etc. In all cases, it was found that stratospheric ozone is highly sensitive to changes in NO<sub>x</sub> mole fractions of 10<sup>-9</sup> or higher. (3) The natural source strength of NO<sub>x</sub> in the stratosphere was compared with the artificial source strength based on the Australian Academy of Science estimate for the Concorde in 1985. These two source strengths are about equal. At present NO<sub>x</sub> is the most important factor in the natural destruction of ozone and thus the ozone balance. The Concorde thus promises more or less to double a very active natural ingredient.

These analyses prove, I think, that NO<sub>x</sub> from SST exhaust may not 'be neglected'. (Recall that one year ago it was the almost

universal judgment that NO<sub>x</sub> was negligible.) The problem may not be dismissed with a clever quip or a qualitative statement of opinion or preference. Furthermore, the strength of the basic argument and the degree of damage (Smith, 1972) that could be done to the world if stratospheric ozone were reduced by a large amount are such that the burden of proof should be on those who would add NO<sub>x</sub> to the stratosphere, not on those who warn against such pollution.

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