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February 1992

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Stratospheric Aircraft: Impact on the Stratosphere?

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February 1992

STRATOSPHERIC AIRCRAFT: IMPACT ON THE STRATOSPHERE?

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Abstract

The steady-state distribution of natural stratospheric ozone is primarily maintained through production by ultraviolet photolysis of molecular oxygen, destruction by a catalytic cycle involving nitrogen oxides (NO_x), and relocation by air motions within the stratosphere. Nitrogen oxides from the exhausts of a commercially viable fleet of supersonic transports would exceed the natural source of stratospheric nitrogen oxides if the aircraft should be equipped with 1990 technology jet engines. This model-free comparison between a vital natural global ingredient and a proposed new industrial product shows that building a large fleet of passenger stratospheric aircraft poses a significant global problem. NASA and aircraft industries have recognized this problem and are studying the redesign of jet aircraft engines in order to reduce the nitrogen oxides emissions. In 1989 atmospheric models identified two other paths by which the ozone destroying effects of stratospheric aircraft might be reduced or eliminated: (1) Use relatively low supersonic Mach numbers and flight altitudes. For a given rate of nitrogen oxides injection into the stratosphere, the calculated reduction of total ozone is a strong function of altitude, and flight altitudes well below 20 kilometers give relatively low calculated ozone reductions. (2) Include heterogeneous chemistry in the two-dimensional model calculations. The first test of this suggestion, made in 1991, included a single heterogeneous reaction and gave results encouraging for the future of stratospheric aviation. Necessary conditions for answering the question on the title above are to improve the quality of our understanding of the lower stratosphere and to broaden our knowledge of heterogeneous stratospheric chemistry. This article reviews recently proposed new mechanisms for heterogeneous reactions on the global stratospheric sulfate aerosols.

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Review

Philosophy with respect to global change

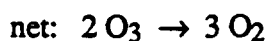
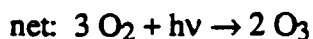
If a natural ingredient has a known effect on the global atmosphere, we should presume that an anthropogenic doubling of the natural ingredient will substantially increase the global effect unless a special nullifying mechanism can be demonstrated. Also, we should presume that a one-per-large-number increase of the natural ingredient will cause no more than a one-per-large-number global increase in the effect unless a special amplifying mechanism can be demonstrated. These statements imply a different burden of proof on those whose industrial process would, more or less, double and those who would cause a small increase of a significant global atmospheric ingredient. These statements also imply that it is scientifically and socially responsible to call attention to one industry's proposal to double a vital natural global atmospheric ingredient, and it is environmentally respectable to try to find if special nullifying mechanism exist.

Global ozone balance

Natural formation of stratospheric ozone

Figure 1 shows the major features of the natural ozone balance in the stratosphere. Ozone formation and destruction occur throughout the sunlit stratosphere, but the rates vary strongly with latitude, season, and altitude. The 24 hour average rate of ozone formation at half or more its maximum rate is shown by the gray area of Figure 1. The 24 hour average rate of ozone destruction by nitrogen oxides at half or more its maximum rate is the area enclosed by the heavy hatched line of Figure 1. Ozone occurs throughout the stratosphere and troposphere, but the concentration at half or more its maximum value parallels the tropopause as a relatively narrow band with the highest values at the winter pole.

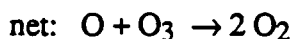
From the 1930s through the 1960s a small group of scholarly scientists studied stratospheric ozone. Chapman in 1930 worked out the basic mechanisms for the formation and destruction of stratospheric ozone from solar radiation and molecular oxygen



where rds stands for rate determining step. These scientists devised an ingenious ground-based optical method to measure the overhead column and vertical profile of ozone.

Natural destruction of stratospheric ozone

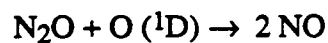
In the 1950s, new chemical laboratory data and rocket-based measurements of solar radiation above the atmosphere revealed that Chapman's mechanism predicted twice as much stratospheric ozone as that observed. Something else besides Chapman's mechanism destroys natural stratospheric ozone. During the 1960s efforts to identify 'something else' were unsuccessful until Paul Crutzen [1970] proposed a homogeneous catalytic cycle based on the nitrogen oxides, nitric oxide (NO) and nitrogen dioxide (NO₂), collectively known as NO_x.



Although ozone is over a hundred times as abundant as the nitrogen oxides in the stratosphere, this catalytic cycle destroys ozone with no loss of NO_x, and numerous cycles occur during the stratospheric residence time of NO_x. One year later Crutzen [1971] and Nicolet [1971] independently discovered the source of stratospheric nitrogen oxides,

Figure 2. Nitrous oxide (N₂O) is produced in soils and oceans as a by-product of nitrogen

fixation in the biological nitrogen cycle. Nitrous oxide is stable in the troposphere with over a hundred year atmospheric lifetime, is slowly transported into the stratosphere, is destroyed by far ultraviolet radiation there, and reacts in the middle stratosphere with electronically activated atomic oxygen to produce nitric oxide:



Since nitrous oxide has almost the same ultraviolet absorption spectrum as CF_2Cl_2 , Crutzen's mechanism for the nitrous oxide cycle provided Molina and Rowland [1974] with a 'hand-in-glove' analogy that made it certain that chlorofluorocarbons (CFC) are slowly transported up into the stratosphere and are broken down by ultraviolet radiation there.

Scientific knowledge of the stratosphere was in a very primitive state in 1970. A golden age of new concepts in stratospheric science was the period of 1970-1975. During 1972-1975 these developments were under the leadership of the Department of Transportation's Climatic Impact Assessment Program [CIAP, 1974; NAS, 1975] with strong interdisciplinary, interagency, and international support. The new methods of stratospheric measurements and photochemical modeling developed during this period confirmed Crutzen's proposed catalytic cycle for ozone destruction involving nitrogen oxides, confirmed the nitrous oxide source of stratospheric nitrogen oxides, and confirmed Crutzen's estimate of the magnitude of this source. Since 1976 the National Aeronautics and Space Agency (NASA) has carried out the Upper Atmosphere Research Program (UARP), continuing the work of the early 1970s, widely extending the laboratory data base and stratospheric measurements, and strongly improving the dynamic-radiative-photochemical models (for example, [WMO, 1986, 1990b]). Using the stratospheric distribution of nitrous oxide as measured by NASA satellites, Crutzen and Schmailzl [1983] integrated the global rate of NO_x production from nitrous oxide to find $(1.2 \pm 0.6) \times 10^{12}$ grams or 1.2 ± 0.6 Tg of NO per year, a value within the range of Crutzen's 1971 estimates. This nitric oxide production occurs primarily at 30 ± 5

kilometers. Both CIAP and NASA found that, in addition to NO_x and Chapman reactions, free radicals derived from water (HO and HOO) and chlorine radicals (ClO and Cl) are also natural ozone destroyers. Between the upper stratospheric region of maximum ozone production rate and the lower stratospheric region of maximum ozone concentration, the nitrogen oxides according to Crutzen's mechanism are by far the most important agency for natural ozone destruction, accounting for more than 60 percent of the total.

Supersonic passenger aircraft

During the late 1960's and into 1971, the United States government was financing the design and construction of two prototype supersonic transports (SST), which were to cruise at about 20 kilometer altitude, and the cost of these prototypes was to be repaid by the airframe manufacturers from profits from the sale of a planned fleet of about 500 aircraft [CIAP,1974]. The amount of fuel expected to be consumed by 500 of these SST was 7.7×10^{10} kg per year, and the amount of nitrogen oxides in the engine exhaust was estimated to be 12 grams of nitric oxide per kilogram of fuel. These estimates amount to 1.2 Tg of nitric oxide or 2.4×10^{34} molecules per year. Atmospheric modelers during this period calculated more or less 10% global average ozone reductions from such an artificial input of NO_x [Johnston, 1971; Crutzen, 1971; CIAP, 1974; NAS, 1975].

During the late 1980s and into the 1990s there is again a strong interest in building supersonic or hypersonic stratospheric aircraft. NASA, with input from the airframe industry, is conducting a research program on the possible effects of commercial stratospheric aviation [NASA, 1991]. Boeing representatives [Boeing, 1989] say that a commercially interesting mature fleet of supersonic aircraft would burn about 7×10^{10} kg fuel per year, the consensus in the NASA program is that supersonic aircraft fitted with engines based on 1990 technology would emit about 30 grams of nitric oxide per kilogram of fuel, and thus the amount emitted into the stratosphere would be about 2.1 Tg per year, which is 4.2×10^{34} molecules NO_x per year.

Model-free identification of a global problem

To bring together the discussion of stratospheric features up to this point, note the natural rate of nitric oxide production is about 1.2 Tg yr^{-1} , the rate of nitric oxide production by the formerly proposed (1971) American SSTs was 1.2 Tg yr^{-1} , and the rate of nitric oxide production by future stratospheric aircraft would be 2.1 Tg yr^{-1} if they were fitted with engines based on 1990 jet engine technology. One industry proposes to introduce a new product that, according to present knowledge, would more or less double the global rate of production of a vital natural ingredient, stratospheric nitrogen oxides. According to the first paragraph of this article, this projected more or less doubling a vital natural global stratospheric ingredient makes the consideration of this problem scientifically and socially responsible, and efforts looking for special mechanisms that would nullify the ozone reducing effect of these industrial nitrogen oxides are environmentally respectable. NASA [1991] and the aircraft industry are now working on the development of a new type of jet aircraft engine that would emit much less NO_x while maintaining present degrees of performance and efficiency.

Model calculations using only homogeneous chemical reactions

Atmospheric models help to identify other possible 'nullifying mechanisms' in this context. Using the Lawrence Livermore National Laboratory (LLNL) atmospheric models, Johnston, Kinnison and Wuebbles [1989] carried out 276 model runs, considering large variations in NO_x injection rate, flight altitude, and the stratospheric background amount of chlorine, water vapor, and methane. This wide range of conditions was designed to help understand the independent variables in the problem, not an attempt to be give realistic scenarios. A small fraction of the model results is presented here.

The calculated ozone reduction is, obviously, a strong function of the rate of injection of nitrogen oxides into the stratosphere. Assuming an average flight altitude of 22.5 kilometers, the LLNL modelers calculated global-average ozone reductions for the

following three rates of NO_x output from the aircraft exhaust on the basis of the two-dimensional (2D) model:

Injection of NO/Tg yr ⁻¹	Calculated global ozone change/%
4	-2.8
12 (equal to natural rate)	-8.6
32	-19

Another important variable in the calculated ozone reduction by SSTs is the altitude of NO_x injection. Figure 3 presents the calculated (LLNL 1-D) ozone reductions as a function of altitude of injection at each kilometer from 11 to 26 kilometers, where the step function illustrates the vertical grid height of the model. The rate of injection of nitrogen oxides is 1.2 Tg (NO) or 24×10^{33} molecules per year, that is the rate of natural NO_x formation in the stratosphere. The crossover altitude between ozone production by methane-NO_x smog reactions and ozone destruction by added NO_x (compare Johnston and Quitevis, 1975) is 13.5 kilometers. Figure 3 presents calculated globally averaged ozone reductions at average altitudes of 16.5, 19.5, 22.5, 25.5, and 28.5 kilometers, according to the LLNL two-dimensional model, where the step function illustrates the three kilometer vertical grid height of the model. The top of Figure 3 is the altitude of maximum NO_x natural formation from nitrous oxide. At this altitude a 100% increase of NO_x is calculated to give a 10 to 15% global ozone reduction, so the model already includes negative feedback mechanisms. The injection altitude that gives the maximum reduction of ozone is about 28 kilometers. The calculated global ozone reduction decreases rapidly as the NO_x injection altitude is assigned to lower altitudes, it is 7% for injection in the model cell between 18 and 21 kilometers, and it is 0.7% for injection in the next lower cell between 15 and 18 kilometers. The three kilometer vertical grid of the 2-D model is too coarse to track the changes in the 15 to 21 kilometer altitude range. Accurately to model the effect of aircraft in the 12 to 21 kilometer flight range, a necessary (but not sufficient) condition is that the model have a vertical grid height no greater than one kilometer.

Figure 4 shows the calculated ozone reduction, according to the LLNL 2-D model, as a function of latitude and at 3 altitudes for an NO_x injection of 2.4×10^{34} molecules per year. With the assumed flight corridor between 37 and 49 degrees north, the maximum local ozone column reduction is at the north pole, being about twice that of the global average value. Note the factor-of-ten drop in predicted ozone reduction between adjacent vertical cells, 15-18 and 18-21 kilometers, of the 2-D model.

The Atmospheric Effects of Stratospheric Aircraft component of NASA's High-Speed Research Program sponsored intercomparison of six 2-D atmospheric models, including that of LLNL [NASA 1992]. The modelers were given predicted future aircraft fuel usage as a function of latitude, based on studies by the aircraft industry. They considered three flight altitudes and three rates of NO_x production as a function of altitude. The six models were in general agreement in calculating large ozone reductions for SST altitudes above 20 kilometers and less ozone reductions for lower cruise altitudes, but they differed substantially in quantitative results for cruise altitudes below 18 kilometers. The LLNL model calculations shown in Figures 3 and 4 are typical of the current atmospheric models using homogeneous chemistry.

History of Model Calculations, 1974-1988

Scientists at the Lawrence Livermore National Laboratory (LLNL) have maintained a baseline of the calculated effects of two global perturbations through the years of the maturing of stratospheric science, Figure 5 (This figure covering various periods of time has appeared in several places and in several forms, in its present form by Johnston [1984], [WMO. 1986], and Johnston et al. [1991]). One curve shows the calculated future, steady-state, ozone-column change for the continuous usage of chlorofluorocarbons at the 1974 rate, where the time to reach steady state is 50 to 100 years. The other curve shows the calculated future, steady-state, ozone-column change for an assumed continuous world-wide injection of 3.0×10^{34} NO_x molecules per year, spread over a one kilometer band centered at 20 kilometer altitude, where the time to reach steady state for this aircraft

model is about 10 years. For these constant assumed perturbations, the calculated future ozone changes vary with the date of calculation, each of which used its current knowledge of the stratosphere. The variations of the results between the years of 1976 to 1981 were largely caused by new laboratory measurements of rate coefficients of 11 reactions in the HO_x family and the discovery of new species to include in the models [Johnston, 1984]. High calculated hydroxyl radical concentrations in the lower stratosphere resulted in high HNO₃/NO₂ ratios ($\text{HO} + \text{NO}_2 = \text{HNO}_3$) and low rates of ozone destruction by NO_x. High calculated hydroxyl radical concentrations in the lower stratosphere resulted in low calculated HCl / Cl ratios ($\text{HO} + \text{HCl} = \text{H}_2\text{O} + \text{Cl}$) and fast ozone destruction by chlorine reactions. For about two years, 1978-1979, the models calculated that NO_x from stratospheric aircraft increased the ozone column, and at the same time they calculated that chlorine reactions reduced global ozone by 20 %. Calculations using this model gave ozone reduction by NO_x in the middle stratosphere but gave even larger ozone production by the methane-NO_x smog reactions in the upper troposphere and lower stratosphere. After all HO_x reactions were redone by modern direct methods, the models calculated that NO_x injected at 20 kilometers reduces the ozone column. Since 1981, the calculated ozone reduction by supersonic aircraft is greater than that calculated for CFCs.

The Problem and possible solutions to it

Both the model-free considerations of the global ozone balance and calculations based on current atmospheric models pose a Problem for introduction of large fleets of stratospheric aircraft. As stated above, NASA and the aircraft industry have major programs underway to use 'advanced emission reduction technology' greatly to reduce NO_x emissions. The models indicate other possible solutions to this problem [Johnston, Prather, and Watson, 1991] : (1) LLNL (1989) and other model calculations find that for a given injection of nitrogen oxides, the calculated effect on total ozone is a strong function of altitude, Figures 3 and 4. A possible solution to the problem may be to accept lower

speed, but still in the supersonic range, so that the aircraft can fly at lower altitudes where ozone is calculated to be less affected by added NO_x :

Mach number	Altitude / km	Type
0.8	up to 12	Current passenger aircraft)
1.6	14-17	Passenger supersonic aircraft
2.4	17-20	
3.2	21-24	
>5	>28	'Hypersonic'

Models indicate, Figures 3 and 4, that there is some cruise altitude between 13 and 20 kilometers where supersonic aircraft would not reduce the ozone column. However, this altitude range is the most complicated and poorest understood part of the stratosphere. The current models agree fairly well for NO_x injection above 21 kilometers, but disagree substantially for such injections below 18 kilometers [NASA, 1992]. The models need an order of magnitude improvement to make credible predictions about the altitude at which it is safe to inject large amounts of NO_x into the stratosphere. Strong efforts are underway to make the atmospheric observations that will greatly improve our understanding of this part of the stratosphere [NASA, 1992]. (2) The models do not include the recently discovered heterogeneous chemistry associated with the Antarctic ozone hole. Considerations of heterogeneous chemistry may lead to less or greater calculated ozone reduction [Johnston et al, 1991].

Two recent developments

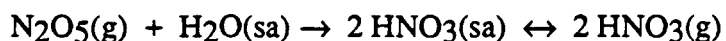
Satellite observations of surprisingly high ozone reductions at summer midlatitude

Using recently improved methods of calibrating the total ozone measuring channel on the Nimbus 7 satellite [WMO, 1990a], Stolarski et al [1991] found ozone column reductions up to five percent over the summer midlatitudes. This ozone reduction is much bigger than that expected from the Molina-Rowland [1974] model (Figure 5), which is

about four percent ozone reduction at the steady state to be reached about a half century from now. There is intense interest whether this observed ozone reduction might be caused by heterogeneous chemical reactions that activate CFC produced chlorine, and if so, by which reactions. So far, it has not been established that this observed ozone decrease is caused by CFCs.

Model calculations for supersonic aircraft using heterogeneous chemistry

To their 2-D model calculation of the aircraft perturbation, Weisenstein et al [1991] added one heterogeneous reaction, the conversion of nitrogen pentoxide to nitric acid in the global sulfuric acid stratospheric aerosol:



where (sa) refers to solvation in sulfuric acid. This calculation used the aircraft industry's model of SST fleet size and fuel consumption for the year 2015, assumed a three-fold reduction in engine NO_x emissions relative to 1990 technology, assumed a doubling of the present fleet of subsonic aircraft, and considered the flight altitude to be 17 to 20 kilometers, corresponding to Mach 2.4. The addition of this single heterogeneous reaction changed the calculated result from about 2 percent global ozone reduction to about 0.2 percent global ozone increase. The largest local effect on the ozone column was at 60 degrees North, a calculated 6 percent ozone decrease with homogeneous chemistry and a calculated 0.4 percent ozone increase with addition of this one heterogeneous reaction. The effect of this reaction is to convert fast reacting oxides of nitrogen, NO , NO_2 , NO_3 , N_2O_5 , into the inactive slowly reacting form of nitric acid, which is the same effect as that causing the 1978-1979 calculated ozone column increase, Figure 5. The calculated increase of ozone, which mostly occurred below 15 kilometers, is probably caused by ozone formation by the methane- NO_x smog reactions.

Figure 6 is a qualitative graphical expression of the two surprising situations discussed above and is a continuation of Figure 5, except the NO_x inputs are different

between the homogeneous and homogeneous models: (1) Model calculations state that a heterogeneous reaction changes the predicted effect of subsonic and supersonic aircraft in the lower stratosphere from an ozone decrease to an ozone increase, which is symbolized by the large upturn in the calculated ozone change. (2) The large ozone reductions in the spring Antarctic stratosphere have been unambiguously shown to be caused by heterogeneous reactions that activate chlorine in the lower stratosphere [Anderson et al, 1991]. Recent observations at midlatitudes show that the ozone column is decreasing [Stolarski et al 1991] much faster than that predicted by models considering CFCs and using homogeneous chemistry, and there is strong suspicion that heterogeneous reactions on sulfuric aerosols regenerate active chlorine species and contribute to this situation. This hypothesis, not the proven case in the Antarctic spring, is symbolized by the large downturn of the CFC line and question mark in Figure 6. The large ellipses of uncertainty shown in Figure 6 suggest that we do not know yet what the quantitative predictions will be when the full body of pertinent heterogeneous reactions are included in the models. There are many laboratories now actively working on heterogeneous atmospheric chemistry, and great activity and progress in this area is to be expected in the next few years.

Figure 6 shows that 1991 was a watershed year with respect to modeling stratospheric ozone. All stratospheric ozone models in the future must include physically and chemically soundly based heterogeneous reactions if they are to be pertinent.

Species and mechanisms in sulfuric acid solutions

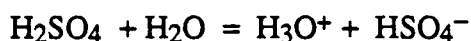
Species in H₂SO₄ / H₂O / HNO₃ solutions

There is a large literature on the species present in H₂SO₄ / H₂O / HNO₃ solutions [Ingold et al., 1950; Marziano et al., 1978; Sampoli et al., 1985; Ross et al., 1983]; Deno et al., 1961; Bayliss and Watts, 1963; Marziano et al., 1978; Burley and Johnston, 1992].

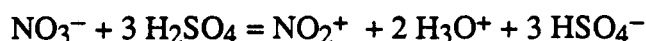
Pure sulfuric acid is strongly interlinked by hydrogen bonds, and to a limited degree it reacts reversibly with itself through a proton transfer:



The principal driving force for this reaction is the solvation energy of the two ions, approximately given by the Born equation [Atkins, 1990, p. 248]. Similarly, sulfuric acid donates a proton to water to form two solvated ions:



Sulfuric acid, above 80% by mass, reacts reversibly with nitrate ion to form nitronium ion:



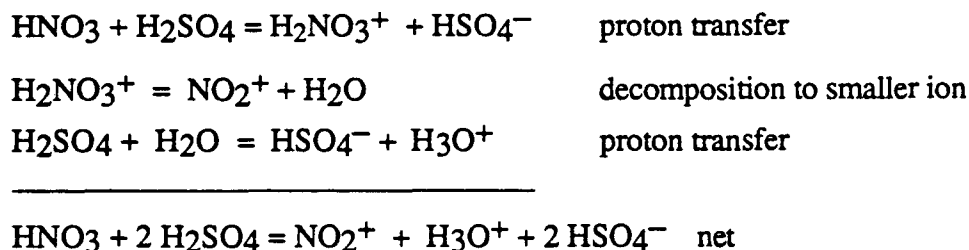
and this process approaches completion at about 95% by mass of sulfuric acid.

In solutions consisting primarily of sulfuric acid and water but with small amounts of nitric acid or nitrogen pentoxide, there are three sets of products with continuous gradations between them as given by Table 1. In strong sulfuric acid, nitric acid exists as nitronium hydronium di-bisulfate, $\text{NO}_2^+ + \text{H}_3\text{O}^+ + 2 \text{HSO}_4^-$. Solid nitrogen pentoxide is nitronium nitrate, and gaseous nitrogen pentoxide probably goes into solution as these ions. In solution, nitrogen pentoxide becomes di-nitronium hydronium tri-bisulfate, $2\text{NO}_2^+ + \text{H}_3\text{O}^+ + 3 \text{HSO}_4^-$. At about 80% sulfuric acid by mass, nitrate ions or nitrogen pentoxide or nitric acid exist primarily as molecular nitric acid. There are few nitronium ion in solutions with less than 80% sulfuric acid. Nitric acid or nitrogen pentoxide exist as hydronium and nitrate ions in dilute sulfuric acid or aqueous solutions.

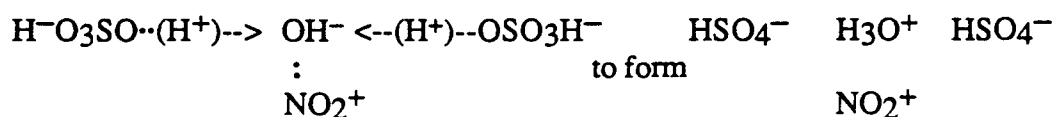
Dissolved nitrogen pentoxide produces 6 ions in concentrated sulfuric acid, no ions in about 80% sulfuric acid by mass, and 4 ions in dilute aqueous solutions, which are different from the 6 ions existing in strong sulfuric acid. The ionic composition of sulfuric acid-water solutions changes very rapidly with sulfuric acid percentage. The structures of nitrogen species are almost totally different at 0%, at 80%, and at 95% sulfuric acid.

Step-wise and concerted mechanisms

The reaction of nitric acid with sulfuric acid may be regarded as a series of elementary steps with two intermediate species:



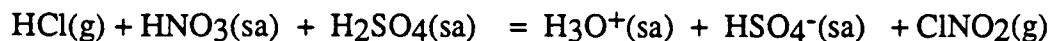
The reaction may also be regarded as a single concerted mechanism with no H_2NO_3^+ or H_2O intermediates being required.



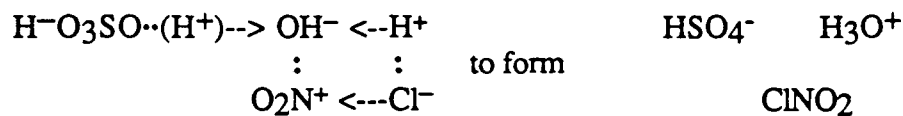
Two sulfuric acid molecules more or less simultaneously donate two protons to the hydroxyl group on nitric acid, splitting out and neutralizing a hydroxyl ion and producing two positive ions and two negative ions at once. Since sulfuric acid and nitric acid form strong hydrogen bonds to each other, this concerted reaction could occur with motion primarily by protons and electrons, followed by separation of the reaction products.

Reactions of Hydrogen Chloride with $\text{HNO}_3/\text{H}_2\text{O}/\text{H}_2\text{SO}_4$

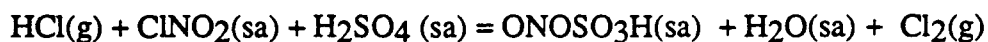
Burley and Johnston [1992] give several ionic and concerted mechanisms in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}/\text{HNO}_3/\text{HCl}$ systems. The overall reactions are given here but not all the detailed ionic and concerted mechanisms. In the laboratory preparation of nitryl chloride ClNO_2 , we bubble gaseous HCl through a solution 0.75 mol fraction sulfuric acid and 0.25 mol fraction nitric acid [Volpe and Johnston, 1956]. The overall reaction is



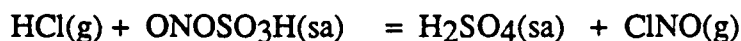
The concerted mechanism is



As the reaction progresses, two unwanted side products, chlorine and nitrosyl sulfuric acid, form:

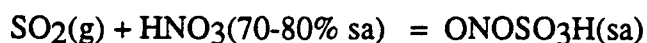
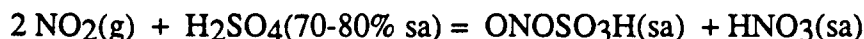
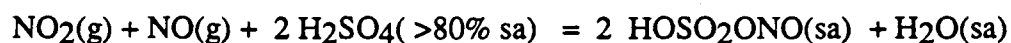


At still later stages of the reaction, nitrosyl chloride forms, which is very difficult to remove from the desired nitryl chloride:



Nitrosyl sulfuric acid

According to Steele et al. [1983], the composition of stratospheric sulfuric acid aerosols is largely in the range 60-80% H₂SO₄ by mass. At these sulfuric acid concentrations nitryl chloride would not form at room temperature, requiring higher concentrations of sulfuric acid. However, there are other processes that produce nitrosyl sulfuric acid in sulfuric acid as dilute as 70% by mass [Yost and Russell, 1944] :

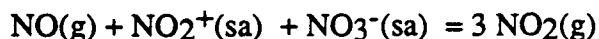
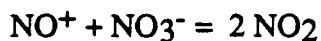
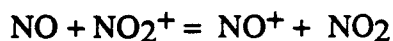


Nitrosyl sulfuric acid has been observed in stratospheric aerosols [Farlow et al. 1978]. It is a non-volatile solid that may precipitate out of sulfuric acid solution, but it is moderately soluble in sulfuric acid solutions (about 5%, depending on temperature and sulfuric acid concentration). Nitrosyl sulfuric acid is potentially an important stratospheric species [Burley and Johnston, 1992].

Other possible heterogeneous mechanisms

Acid catalyzed analogy to reaction of NO with N₂O₅

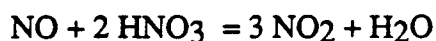
The gas-phase reaction between nitric oxide and N₂O₅ has been extensively studied: NO + N₂O₅ = 3 NO₂. The analogous reaction of nitric oxide with nitronium nitrate in sulfuric acid solution has an ionic mechanism:



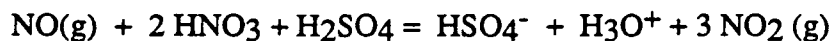
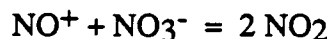
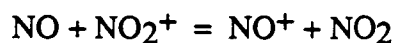
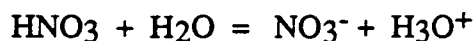
The overall reaction is exothermic, but it is not known whether the component steps are exothermic or endothermic.

Oxidation of nitric oxide by nitric acid.

In attempting to study the gas phase reaction



Smith [1947] found the reaction to occur only heterogeneously on the walls of the apparatus, and its rate increased with a decrease of temperature. A plausible ionic mechanism in sulfuric acid is



Heterogeneous reactions of nitric oxide gas on $\text{H}_2\text{SO}_4 / \text{H}_2\text{O} / \text{HNO}_3$ systems at stratospheric temperatures should be studied.

Reaction with hydrogen peroxide

In our laboratory, we have prepared peroxy nitric acid HOONO_2 by the reaction of nitrogen pentoxide and concentrated hydrogen peroxide on metal surfaces. Sulfuric acid forms mono-peroxy sulfuric acid H_2SO_5 and di-peroxy sulfuric acid $\text{H}_4\text{S}_2\text{O}_8$.

Heterogeneous reactions in $\text{H}_2\text{SO}_4 / \text{H}_2\text{O} / \text{HNO}_3 / \text{H}_2\text{O}_2$ systems at stratospheric temperatures should be investigated.

Conclusions

(1) Using two-dimensional atmospheric models with only homogeneous chemistry, modelers calculate large ozone reductions from a fleet of supersonic aircraft operating above 20 kilometers altitude. (2) A small calculated ozone increase is found upon adding one heterogeneous reaction (occurring on global stratospheric sulfuric acid aerosols) to such models for a fleet of supersonic aircraft operating between 17 and 20 kilometers. (3) It is possible that the surprisingly large ozone reduction observed at summer mid-latitudes is caused by some unidentified, world-wide heterogeneous process that converts inactive chlorine to photochemically active chlorine in the lower stratosphere. (4) The subject of heterogeneous catalysis on the global sulfate layer is at an early stage of development. To answer the question in the title of this article, we must vastly improve the quality of our understanding of the lower stratosphere, including all important heterogeneous processes that affect NO_x , HO_x , Cl_x , and ozone in the global stratosphere. Additional possible heterogeneous reactions in the stratosphere are presented in this article. (5) All stratospheric ozone models in the future must include soundly based heterogeneous reactions if they are to be pertinent.

Acknowledgement

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Titles to figures

- (1) Principal features of the natural global ozone balance.
- (2) Nitrous oxide, a by-product of the nitrogen cycle, as the principal source of stratospheric nitrogen oxides.
- (3) Percentage change of the ozone vertical column as calculated for each kilometer from 11 to 26 kilometers by the LLNL one-dimensional model, and percentage change of the ozone vertical column as calculated for each kilometer from 15 to 30 kilometers by the LLNL two-dimensional model, where the rate of NO_x input is 1.2 Tg NO per year. The step-function figures give the vertical grid scale of the LLNL models .

(4) Percentage change of the ozone vertical column as calculated by the LLNL two-dimensional model, as a function of latitude from pole to pole and at three altitudes. The NO_x injection is the same as that of Figure 3.

(5) Calculated ozone-column change to steady state for two standard assumed perturbations: (a) 2000 molecules cm⁻³s⁻¹ over one kilometer interval centered at 20 km; (b) CFC-11 and CFC-12 emitted continuously at 1974 rate. These calculations were made at LLNL over this 14 year period using then current photochemical parameters, eddy diffusion functions, and boundary conditions (Source: numerous LLNL reports, articles, and communications; this form by Johnston [1984] and WMO [1986], updated to 1988). These calculations used only use homogeneous chemistry.

(6) Qualitative effect of heterogeneous chemistry on observed CFC perturbations [Stolarski et al. 1991] and on calculated supersonic stratospheric aircraft effects [Weisenstein et al, 1991].

Table 1. Ionic Reactions of HNO₃ and N₂O₅ in Three Concentration Regions of H₂SO₄/H₂O Solutions

H ₂ SO ₄ > 80% by mass	
	N ₂ O ₅ = NO ₂ ⁺ + NO ₃ ⁻
	NO ₃ ⁻ + H ₂ SO ₄ = HNO ₃ + HSO ₄ ⁻
HNO ₃ + H ₂ SO ₄ = NO ₂ ⁺ + H ₂ O + HSO ₄ ⁻	HNO ₃ + H ₂ SO ₄ = NO ₂ ⁺ + H ₂ O + HSO ₄ ⁻
H ₂ O + H ₂ SO ₄ = H ₃ O ⁺ + HSO ₄ ⁻	H ₂ O + H ₂ SO ₄ = H ₃ O ⁺ + HSO ₄ ⁻
HNO ₃ + 2 H ₂ SO ₄ = NO ₂ ⁺ + H ₃ O ⁺ + 2 HSO ₄ ⁻	N ₂ O ₅ + 3 H ₂ SO ₄ = 2 NO ₂ ⁺ + H ₃ O ⁺ + 3 HSO ₄ ⁻
H ₂ SO ₄ ≅ 80% by mass	
	N ₂ O ₅ = NO ₂ ⁺ + NO ₃ ⁻
	NO ₂ ⁺ + 2 H ₂ O = HNO ₃ + H ₃ O ⁺
	NO ₃ ⁻ + H ₂ SO ₄ = HNO ₃ + HSO ₄ ⁻
	H ₃ O ⁺ + HSO ₄ ⁻ = H ₂ SO ₄ + H ₂ O
HNO ₃ (g) = HNO ₃ (sa)	N ₂ O ₅ + H ₂ O = 2 HNO ₃
H ₂ SO ₄ < 80% by mass	
	N ₂ O ₅ = NO ₂ ⁺ + NO ₃ ⁻
	NO ₂ ⁺ + 2 H ₂ O = HNO ₃ + H ₃ O ⁺
	HNO ₃ + H ₂ O = H ₃ O ⁺ + NO ₃ ⁻
HNO ₃ + H ₂ O = H ₃ O ⁺ + NO ₃ ⁻	N ₂ O ₅ + 3 H ₂ O = 2 H ₃ O ⁺ + 2 NO ₃ ⁻

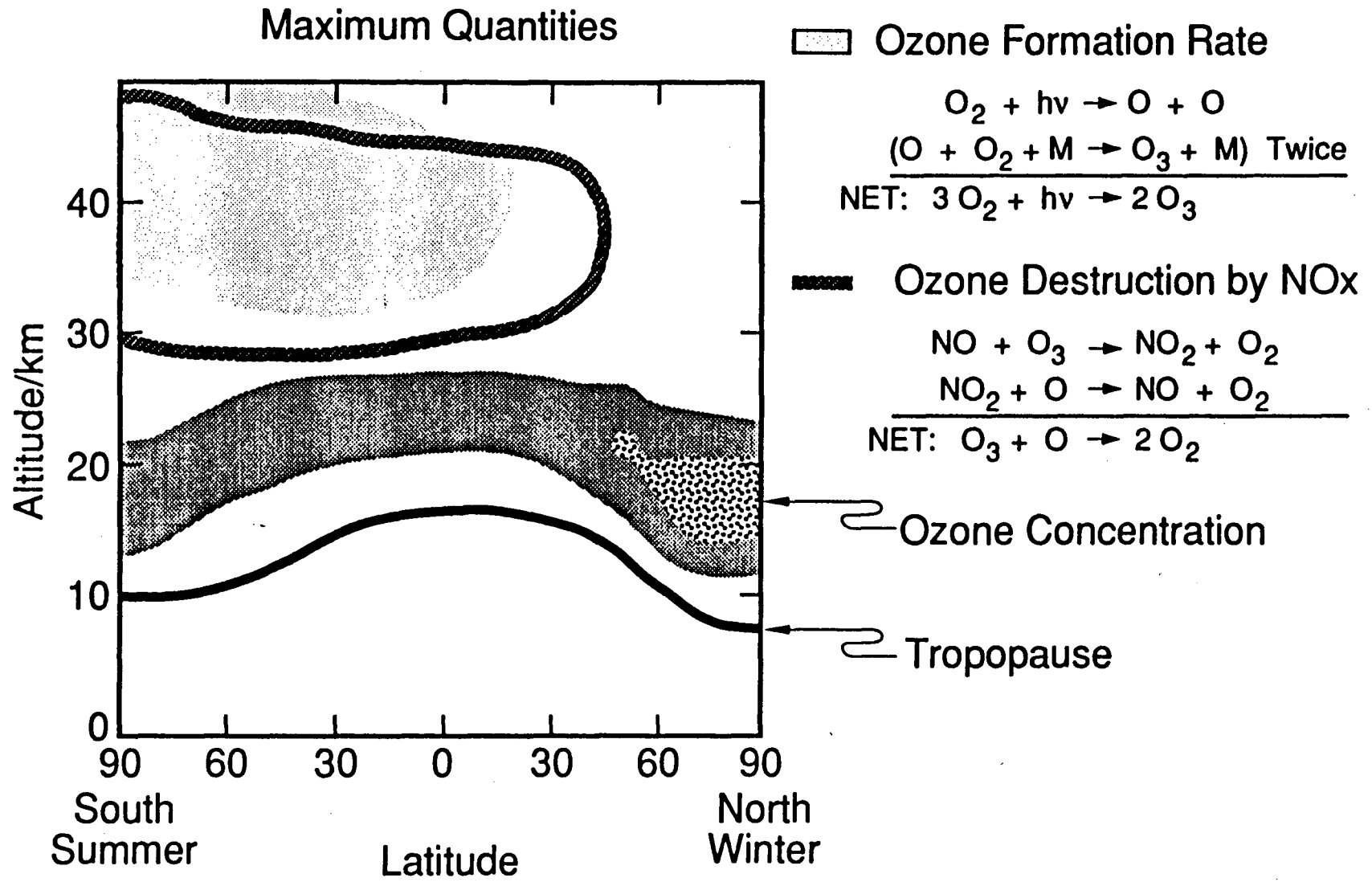


Figure 1

NATURAL SOURCE OF STRATOSPHERIC NITROGEN OXIDES

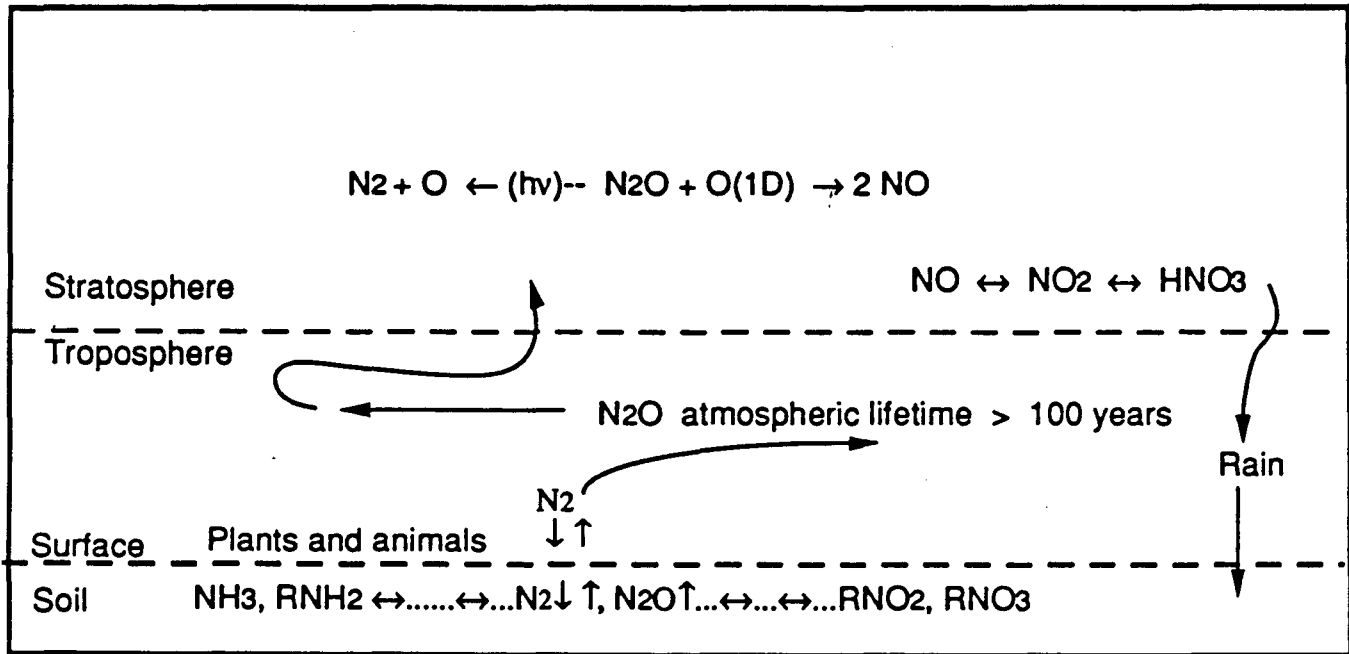


Figure 2

AIRCRAFT CRUISE ALTITUDE

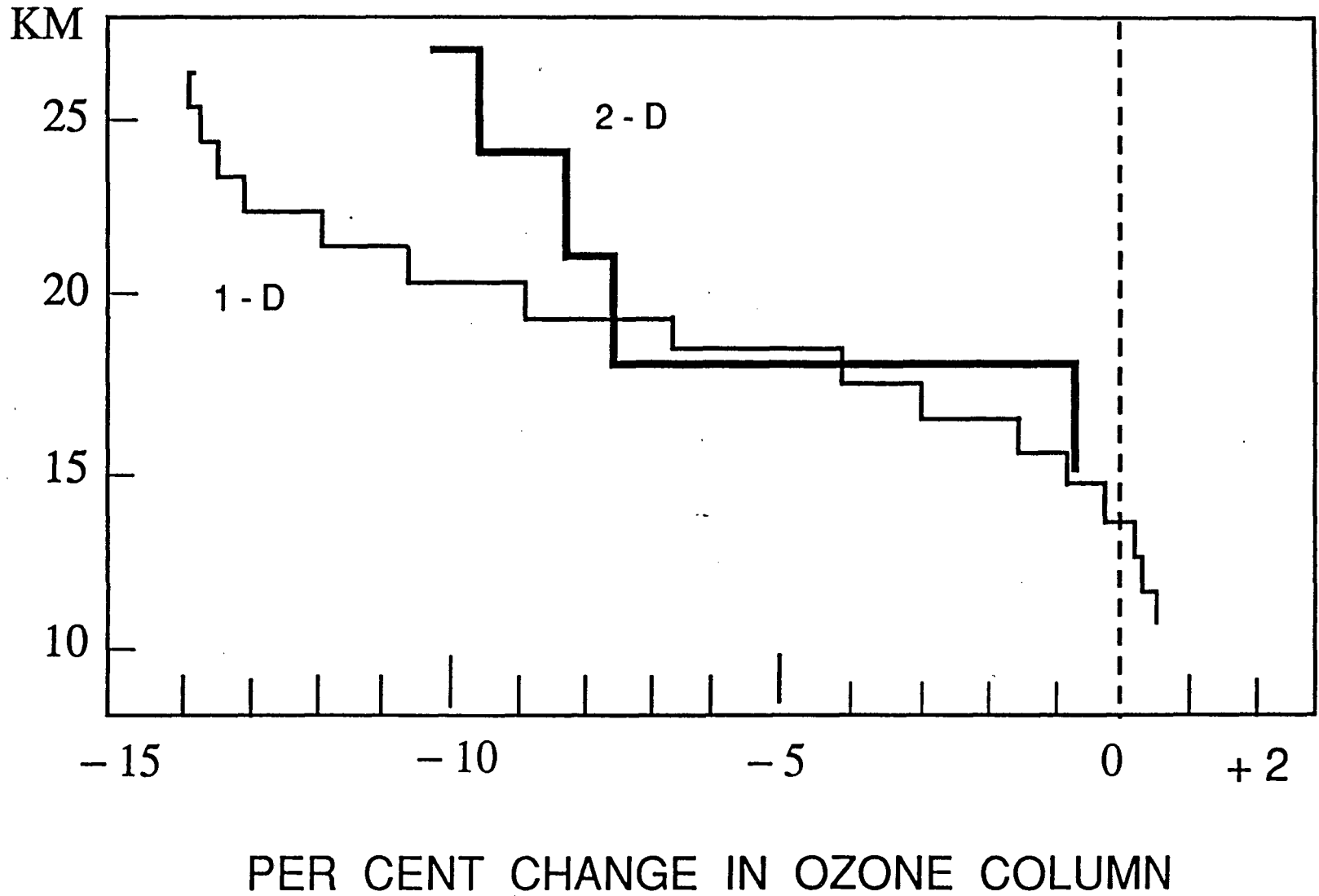


Figure 3

REDUCTION OF OZONE COLUMN AS FUNCTION OF LATITUDE FOR 3 FLIGHT ALTITUDES

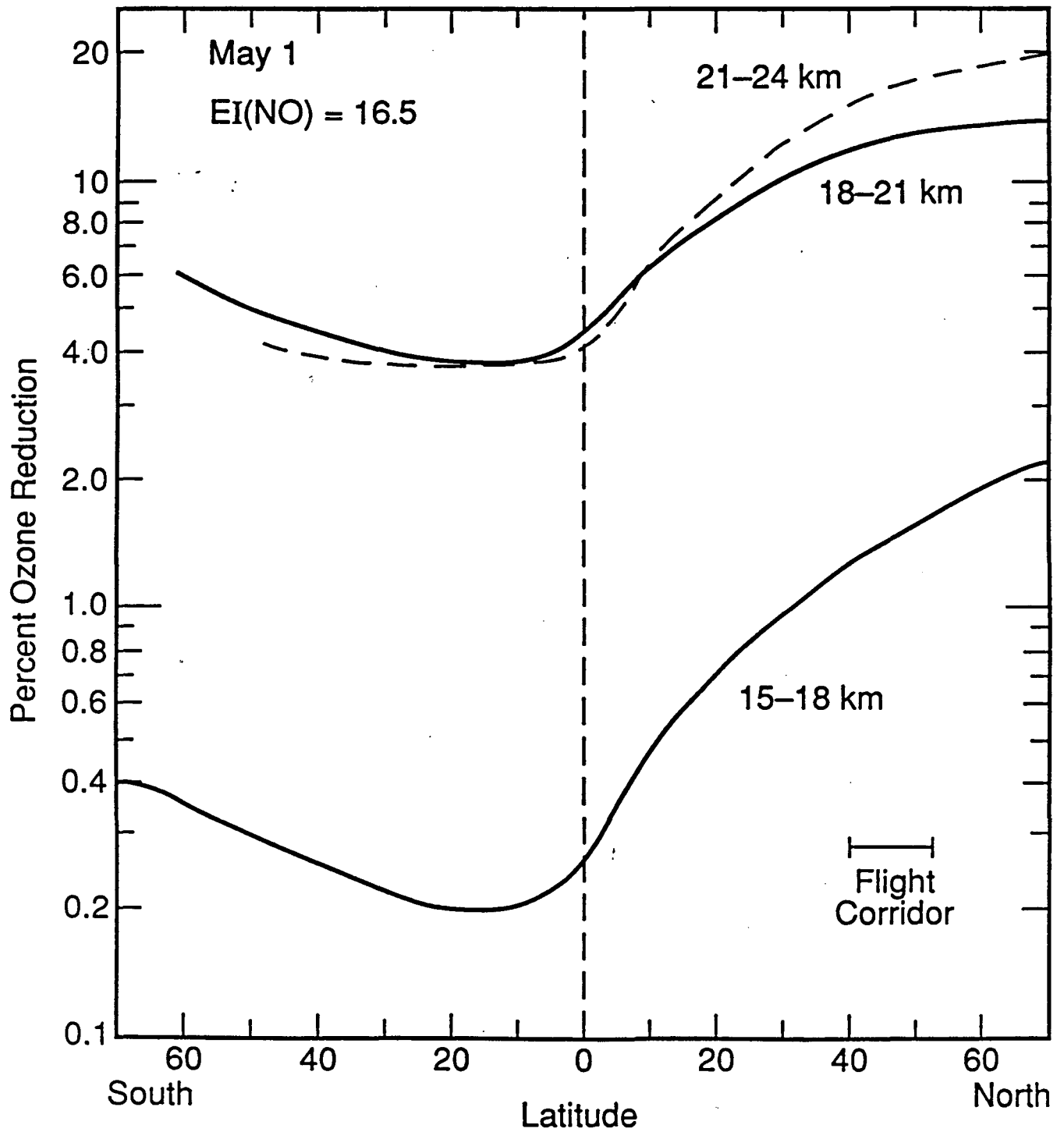


Figure 4

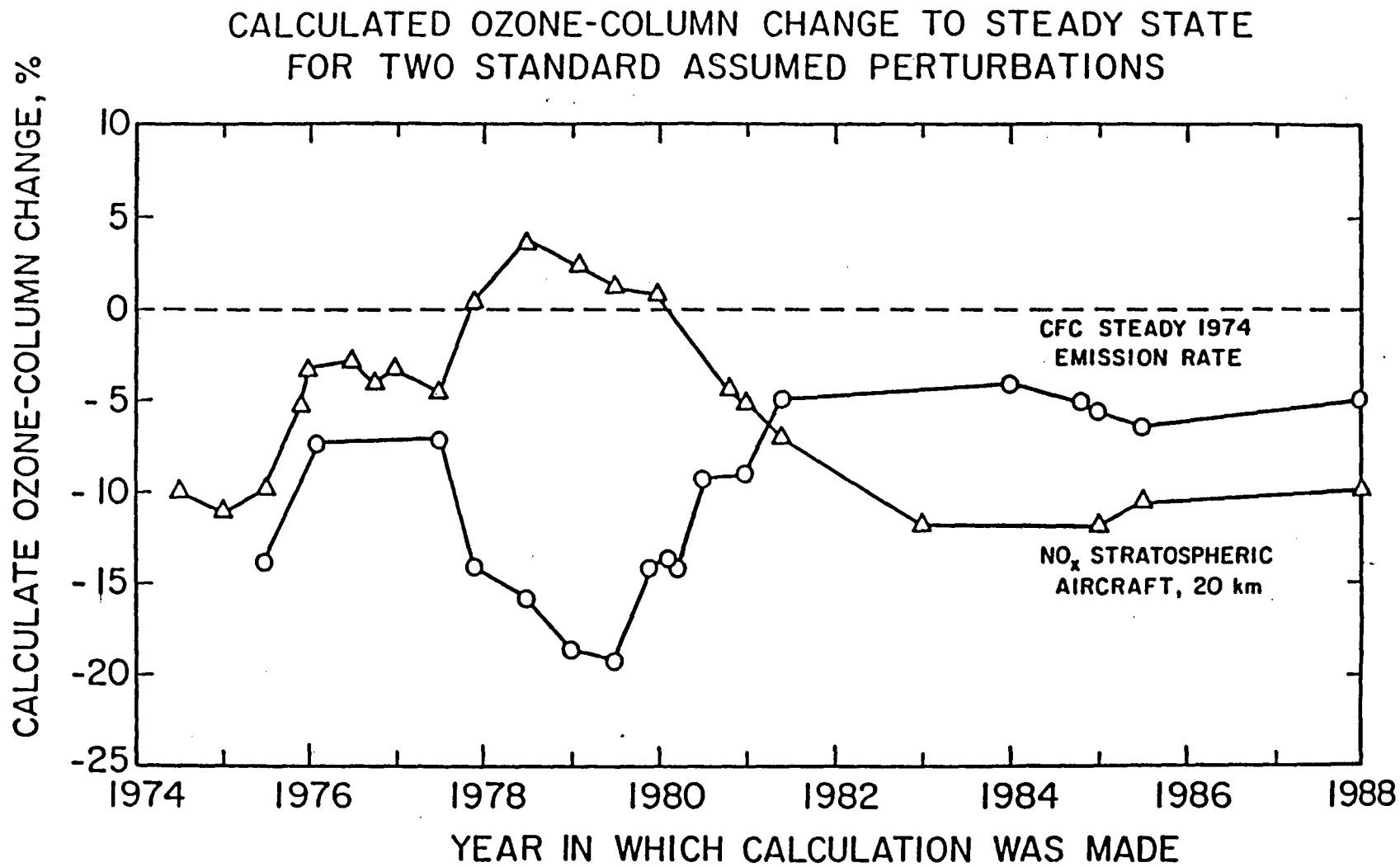
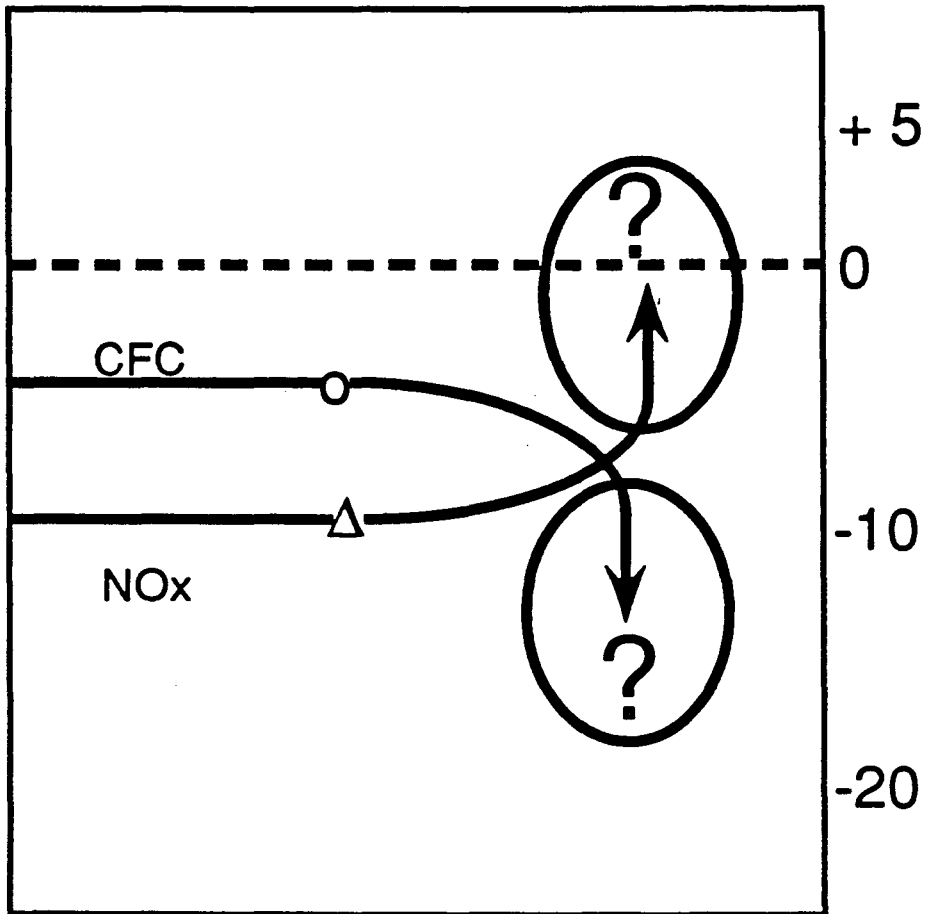


Figure 5



HOMOGENEOUS 1991 HETEROGENEOUS 1991

Figure 6

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