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Harold S. Johnston and Edward Quitevis

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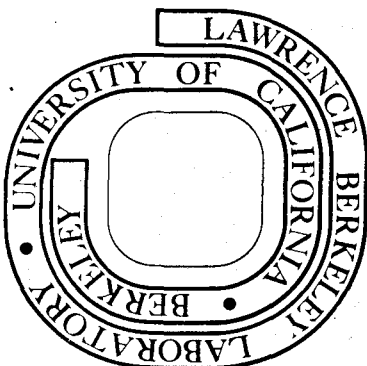
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The Oxides of Nitrogen with Respect to Urban Smog,
Supersonic Transports, and Global Methane

by

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Johnston, Harold S., and Quitevis, Edward-The Oxides of Nitrogen with Respect to Urban Smog, Supersonic Transports, and Global Methane.

Abstract

Nitrogen oxides and hydrocarbons produce ozone in the photochemical smog reactions in urban atmospheres, and the ozone so produced is deleterious to people, plants, and materials. Nitrogen oxides in the stratosphere destroy ozone in a catalytic cycle, and reduced stratospheric ozone would lead to increased biologically damaging ultraviolet radiation at the earth's surface. Large fleets of supersonic transports would significantly increase stratospheric oxides of nitrogen and significantly decrease stratospheric ozone. If nitrogen oxides form ozone in urban air and destroy ozone in the stratosphere, there must be a crossover between these two processes somewhere in the atmosphere. This article considers a realistic natural background distribution of ozone and the oxides of nitrogen and a single (large) set of reaction rate constants. A uniform calculation from the surface of the earth to the top of the stratosphere evaluates the role of natural methane in a global smog reaction, and it locates the height, 13 kilometers at 45° latitude, where, *an increase of* ~~increasing~~ nitrogen oxides forms ozone just as fast as it destroys it. With respect to ozone formation and destruction, the different role of nitrogen oxides in the lower troposphere and the stratosphere is the natural consequence of the different solar radiation fields in these two regions.

Introduction

By now it is well established that the oxides of nitrogen from the exhaust gases of large fleets of supersonic aircraft would seriously reduce stratospheric ozone⁽¹⁻⁹⁾ and admit extra, biologically damaging, ultraviolet radiation to the earth's surface⁽¹⁰⁾. For over 20 years it has been established that the oxides of nitrogen and hydrocarbons in urban areas form ozone through the photochemical smog reaction⁽¹¹⁾, and this ozone is toxic, damages materials, and kills plants⁽¹²⁾. When these two statements are put side by side, they seem to say that an increase of nitrogen oxides in the stratosphere would reduce ozone there but an increase of nitrogen oxides in cities would increase ozone - and both changes have deleterious effects. But then one asks, How can this be? How can nitrogen oxides destroy ozone in one part of the atmosphere and form ozone in another part? This article reviews the properties of urban photochemical smog, the role of nitrogen oxides in the stratospheric ozone balance, and the role of methane as a source of smog in the global troposphere. It is shown that a common set of chemical reactions with known rate constants, ^{which} gives reaction rates at all elevations, does predict a crossover between formation and destruction of ozone by nitrogen oxides at about 13 km.

Ozone Formation in Urban Smog

The photochemical nature of Los Angeles smog was established by Haagen-Smit and co-workers⁽¹¹⁾ in the early 1950's. By means of a simple specific test for ozone, Haagen-Smit showed that air containing trace amounts of hydrocarbons and nitrogen oxides react in sunlight to produce ozone. For the same initial concentrations of reactants, the rate of reaction depended strongly on the nature of the hydrocarbon; methane was found to be the least reactive of all hydrocarbons. It was shown that the role of nitrogen oxides was complex: with zero nitrogen oxides there was no smog; with a moderate amount there was strong, rapid production of smog; but with somewhat larger amounts of nitrogen oxides the production of smog was inhibited.

A number of aspects of photochemical smog can be shown from recent observations in the atmosphere at a number of sites in California. In five widely separated cities in the central valley of California⁽¹³⁾, oxidant (mostly ozone) builds up simultaneously during the morning, it reaches a broad maximum in the early afternoon, and it falls to low values at night, Figure 1. There is a strong seasonal effect with maximum smog during the summer and early fall and much less during the winter and spring months, Figure 1. Over almost a decade, 1963-1971, photochemical oxidant showed a pronounced decrease in downtown Los Angeles, but there was an equally pronounced increase 50 miles inland in the same basin at Riverside⁽¹⁴⁾, Figure 2. In the middle period covered by these trends at Los Angeles and Riverside (starting in 1966), new automobiles were required to reduce hydrocarbon and carbon monoxide emissions, but nitrogen oxides increased by 50 per cent as a result of the higher combustion temperatures used to reduce hydrocarbons. The decrease of ozone in Los Angeles, the increase of ozone in Riverside, and the simultaneous increase in nitrogen oxides is one of many examples of the

complex response of atmospheric ozone to nitrogen oxides and other factors.

The essential features of photochemical smog can be produced in the laboratory^(15,16). Light sources simulate sunlight by providing radiation above 300nm. Small amounts of hydrocarbons and nitrogen oxides are added to scrupulously purified air in a large chamber, typically made of glass. An example of such a "smog chamber" experiment is given by Figure 3, where initial reactants were 3 parts per million (ppm) of propylene, 1.3 ppm of nitric oxide (NO), and about 0.2 ppm of nitrogen dioxide (NO₂). When the light was turned on, propylene decreased, NO was converted to NO₂, and later ozone built up while NO₂ decreased. Many other products, such as formaldehyde, other aldehydes, peroxyacetyl nitrate (PAN), and nitric acid, were also formed.

The multi-faceted role of nitrogen oxides⁽¹⁷⁾ is illustrated by Figure 4. Three smog-chamber experiments are presented, in which the initial propylene was 3 ppm in each case but the initial NO_x (NO + NO₂, mostly NO in these cases) was 3, 1.5, and 0.5 ppm in the 3 cases. During the first half of the reaction, the rate of destruction of propylene was fastest for the least nitric oxide and slowest for the most nitric oxide. Nitrogen oxides above 0.5 ppm, in this case, acted to slow down or inhibit the initial rate of the smog reactions. However, in the second half of the destruction of propylene, the roles reversed. With 0.5 ppm and NO_x the rate became much slower and in five hours much propylene remained unconsumed. With 1.5 ppm of NO_x, the rate accelerated until the rate became much faster than for the other cases, and by five hours the propylene was virtually all consumed.

Similar data, but in this case focussing on the oxidant produced, are given by Figure 5. A series of experiments was carried out, each starting with 2 ppm propylene and with various initial concentrations of nitrogen

oxides. One set of experiments progressed for 6 hours, and one set of experiments was carried out for 2 hours. Maximum oxidant is plotted against initial nitrogen oxide concentration. The two-hour experiments show the classic "inhibition" of smog by NO_x ; low NO_x give low oxidant, 1 ppm of NO_x gave maximum oxidant, 2 ppm or higher gave very little oxidant. The experiments that went for 6 hours showed a similar qualitative pattern, but the quantities are quite different. The maximum oxidant occurred with 2 ppm initial NO_x for the 6 hour experiment, and the maximum amount of oxidant is greater than that for the 2 hour case. The "inhibition", for 6 hour runs, occurs at and above 3 ppm of NO_x .

The laboratory data shown in Figure 5 provide a possible explanation for the long-term trends in Los Angeles and Riverside shown in Figure 3. Sea-breezes take about 2 hours to reach downtown Los Angeles and 6 or 8 hours to reach Riverside, which is 50 miles inland. Picture both Los Angeles and Riverside as being situated in 1964 somewhat like the point at 1.0 ppm NO_x in Figure 5. In the next few years there was a large increase of NO_x at each station, both as population increased and as the automobile emission index for NO_x increased by 50%. Moving from 1.0 to 1.5 ppm NO_x in Figure 5 results in a large decrease in smog in the 2 hour experiment (Downtown Los Angeles) but in a large increase in smog in the 6 hour experiment (Riverside).

This example may reflect a general effect: increasing NO_x may cause little or no increase of smog in the traffic-heavy urban centers, but it may cause large increases in smog at suburban and rural areas up to hundreds of miles downwind. There have been many recent examples of newly-discovered, high concentrations of ozone in non-urban areas (18-21).

The broad aspects of the chemistry of photochemical smog are understood, and the major features can be reproduced by means of large scale computer programs.

Ozone Destruction in the Stratosphere (1-9)

The stratosphere is high, dry, cold, and penetrated by ultraviolet radiation with wave lengths down to 190nm. Radiation below 242nm dissociates oxygen to produce ozone. Ozone, in turn, strongly absorbs solar radiation below 300nm. The only effective shield of the surface of the earth against biologically damaging radiation between 300 and 250nm is ozone. An average world-wide vertical profile of ozone is given by Figure 6. The troposphere is typically 0 to 15 kilometers, and the stratosphere is 15 to 50 kilometers. The height of maximum ozone concentration is about 20 to 25 kilometers.

In the stratosphere ozone is formed almost exclusively by the photolysis of oxygen; curve A in Figure 7 shows a vertical profile of the rate of formation of ozone⁶. In the natural stratosphere, ozone is destroyed by a long list of reactions, the major ones of which are given in Figure 7: B. NO_x catalytic cycle; C, Ozone destruction by ozone ($O + O_3 \rightarrow O_2 + O_2$); D, E, F, G, H. Reactions of free radicals (H, HO, HOO) based on water. As can be seen from Figure 7, the NO_x catalytic cycle is far more important than all other mechanisms for ozone destruction. On a world-wide basis the balance sheet for ozone formation and destruction is given by Table 1.

By now the sources and sinks of natural NO_x are recognized and evaluated. The artificial source of NO_x from 500 Boeing SST as projected in 1971 (fuel flow 60 metric tons of fuel per hour per SST, emission index 15 grams NO per kilogram of fuel, 7 hours per day at cruise height of about 20 km) would be about twice the natural source of NO_x; and 500 Concorde or Tupolevs (one third the rate of fuel consumption as the Boeing SST) would add about two-thirds as much NO_x to the stratosphere as the natural source. It is now widely recognized that these large perturbations of stratospheric nitrogen oxides would cause a large reduction of stratospheric ozone.

Table 1. Balance between ozone formation and destruction in the natural stratosphere (global averages).

<u>Mechanism</u>	<u>Relative ozone rate</u>
$O_2 + h\nu(\text{below } 242\text{nm})$	+ 100%
$O + O_3 \rightarrow O_2 + O_2$	- 17%
HO_x reactions	- 12%
Transport to earths surface	- 1%
$NO + O_3 \rightarrow NO_2 + O_2$	- 70%
$NO_2 + O \rightarrow NO + O_2$	
net: $O_3 + O \rightarrow O_2 + O_2$	

The magnitude of the expected reduction of ozone by supersonic transports has been estimated by a series of model calculations that have included various degrees of atmospheric motions. The percentage reduction of ozone as a function of the percentage increase of stratospheric nitrogen oxides, as calculated by several different groups, is given by Figure 8. The various modelers tend to agree that doubling the stratospheric column of NO_x would decrease the ozone column by about 20%. There is some disagreement as to how much a given fleet of SST would increase the stratospheric inventory of NO_x and decrease ozone, as shown in Table 2.

The calculation by Cunnold et al (1974) involved a three dimensional model⁹ of atmospheric motions and ozone photochemistry; the other calculations were primarily one dimensional (vertical, global average). The model involving three dimensional motions gives a result somewhat in the middle of the models including only one dimension. The reduction of ozone as a function of latitude as predicted by Cunnold et al is given by Figure 9. The world-wide average ozone reduction was 12%, that in the northern hemisphere (where all traffic was assumed to be) was 16%, and the maximum ozone reduction near the flight corridor was 25%.

The results of modelers of stratospheric motions and photochemistry, the considerations of the magnitude of natural versus artificial sources of NO_x , and the recognized importance of nitrogen oxides in the natural ozone balance strongly confirm the proposition that supersonic transports would seriously deplete ozone in the stratosphere. Quantitative considerations^(1b) of the effects on ozone of nitric oxide produced by cosmic rays and by nuclear bombs further support this thesis.

Table 2. Results of model calculations for worldwide average reduction of ozone by 500 large SST (see text for detailed properties), including maximum "corridor effect" in some cases.

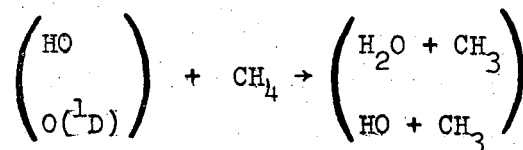
Calculated ozone reduction, per cents		Author	Ref.
<u>Global</u>	<u>Local maximum</u>		
23	50	Johnston 1971	(1)
8		Crutzen 1974	(2)
7		Chang 1973	(4)
11		McElroy <u>et al</u> 1974	(6)
21		Shimazaki <u>et al</u> 1974	(8)
12	25	Cunnold <u>et al</u> 1974	(9)

Continuity of Ozone Photochemistry from the Ground to the Top of the Stratosphere

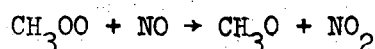
The two sections above reviewed the photochemistry of urban smog and stratospheric perturbation by supersonic transports. By examples and references these sections stated each horn of the dilemma posed in the Introduction: NO_x does form ozone in urban smog and destroy ozone in the stratosphere. This section considers where in the atmosphere the crossover occurs between these two opposing trends.

A series of calculations⁽²²⁾ was carried out with set of 23 species and 36 reactions from the ground to the top of the stratosphere. Standard temperature and concentration of air at mid-latitudes was used. Standard, observed profiles of ozone, water, and methane were used, Figure 10. A profile of total NO_x ($\text{NO} + \text{NO}_2 + \text{HNO}_3$) was deduced from calculations and observations, and the partitioning between NO , NO_2 , and HNO_3 at midday is shown in Figure 11. The calculated concentration of oxygen atoms is also included in Figure 11.

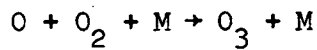
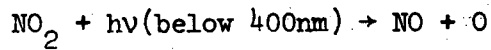
In urban situations methane is considered not to form smog in the few available hours per day, Figure 1. However, in the global troposphere (and stratosphere) some ozone is formed from air, methane, NO_x , and sunlight^(22,23). The reaction is initiated by an attack by hydroxyl radicals, HO , or singlet oxygen atoms, $\text{O}({}^1\text{D})$, on methane to form methyl radicals.



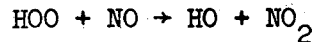
The methyl radicals add molecular oxygen to form a peroxy radical that converts NO to NO_2



Photolysis of nitrogen dioxide leads to ozone formation



Subsequent reactions of the radical CH_3O lead to one to three perhydroxyl radicals, which also can convert NO to NO_2



The net effect is that the slow, photochemical combustion of methane forms from one to four molecules of ozone. Starting with zero ozone, the rate of formation of ozone by the methane smog reaction is given by Figure 12 for two cases in terms of molecules cm^{-3} : (1) 10^9NO , 10^{11}NO_2 ; (2) 10^{11}NO , 10^9NO_2 . The initial rapid formation of ozone is simply the photolysis of NO_2 to form NO and O_3 . The subsequent rise in ozone with a doubling time of about one month is the methane-smog reaction. The final amount of ozone produced in each case is 2 or 3 x 10^{11} molecules cm^{-3} , comparable to observed, global, tropospheric ozone.

With the distributions of species given in Figures 10 and 11, a model calculation was made for a full set of reactions by a modified Gear routine^(4a). The calculation was run for 10^{14} seconds, long enough to attain a steady concentration of atomic and free radical species but short enough to avoid change of the background concentration of species. The relative rate of gross formation of ozone ($\text{HOO} + \text{NO}$ and $\text{CH}_3\text{OO} + \text{NO}$) from the methane-smog reaction is given by Figure 13. The rate of this reaction increases with O_3 , H_2O , CH_4 , and NO_x . As can be seen from Figures 10 and 11, the last 3 are relatively constant with height in the stratosphere, and thus the rate of ozone formation from the methane-smog reaction roughly parallels the ozone profile there. In the troposphere, water increases very rapidly as one moves

down from the tropopause to the ground, and the rate of the methane-smog reaction increases by a factor of 100 between 15 and 0 km, largely because of tropospheric water.

The rate of ozone destruction by NO_x increases simply as the product of concentration of NO_2 and oxygen atoms. Figure 12 shows that oxygen atoms rapidly increase with height. The rate of ozone destruction by NO_x , Figure 13, similarly shows a strong decrease as one moves from the troposphere to the ground.

In the stratosphere, the rate of ozone destruction by the NO_x catalytic cycle is more than 100 times faster than the rate of formation of ozone from the methane-smog reaction, Figure 13. At about 13 km these two rates become equal. Below 13 km, the methane-smog reaction is faster than the catalytic destruction of ozone by NO_x . (For hydrocarbons in urban areas that are much more active than methane in forming ozone and smog, the difference would be even greater than that shown for methane). Thus a given set of reactions directly predicts that NO_x has a net effect of destroying ozone in the stratosphere and of forming ozone in the lower troposphere. The distribution of species (Figures 11 and 12) and temperature is such that the relative effect of NO_x on ozone changes strongly with elevation.

Figure 13 shows a cross-over between ozone formation and destruction by NO_x at about 13 km with the standard NO_x profile given by Figure 12. Model calculations were carried out with twice as much and one-half as much as the standard NO_x profile. The cross-over points are shown in Figure 14 in an enlarged scale. It can be seen that the cross-over point is not sensitive to the NO_x concentration; an increase in NO_x increases both ozone formation and destruction and the cross-over is seen to be about 13.3 ± 0.2 km for all three cases.

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Acknowledgment

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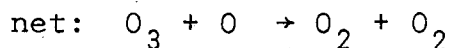
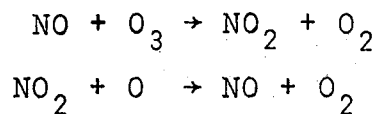
- Figure 1 - A. Photochemical oxidant (primarily ozone) as a function of hour of day in 5 cities in the California Central Valley up to 200 miles apart. The ozone forms and decays at approximately the same time at each site, indicating in situ photochemical formation. Average hourly oxidant concentration during the months July, August, and September. B. Maximum hourly oxidant concentration as a function of month of the year. Note the high concentrations in summer and early fall.
- Figure 2 - Long-term trends in photochemical smog (oxidant) at Downtown Los Angeles (close to the Pacific Ocean) and Riverside (50 miles downwind and inland). Three year moving average of daily one-hour maximum concentration for July-August, and September. Over the same period of time, oxidant decreased in Downtown Los Angeles and increased in Riverside.
- Figure 3 - A typical smog chamber experiment starting with 3 ppm propylene, 1.3 ppm NO, and 0.2 ppm NO₂ in air. The time scale is from turning on artificial sunlamps. Propylene decreases, NO is converted to NO₂, then ozone builds up and slowly decays. Other products such as aldehydes and nitrates are not shown.
- Figure 4 - Three smog-chamber runs with the same initial concentration of propylene (3 ppm) and with three different initial concentrations of nitrogen oxides. Note the rapid initial and slow long-term reaction with low initial (0.5 ppm) NO_x, and the slow initial and fast long-term reaction with high initial (1.5 ppm) NO_x.

Figure 5 - Maximum oxidant produced with the same initial propylene (2 ppm) and various initial concentrations of nitrogen oxides. One series went for two hours and the other series for six hours. The "inhibition" of the smog reaction by NO_x occurred in each case but with quite different ratios and total effect between the two and six hour experiments.

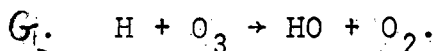
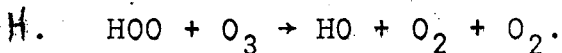
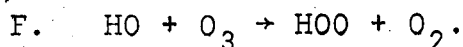
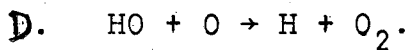
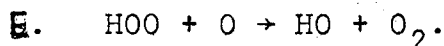
Figure 6 - An average world-wide vertical profile of ozone concentration as a function of height above sea level. The stratosphere is between about 15 and 50 km.

Figure 7 - Relative rates of photochemical formation of ozone (Curve A) and various mechanisms of destruction of ozone in the natural stratosphere:

B. The NO_2 catalytic cycle



C. The elementary reaction $\text{O} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2$.

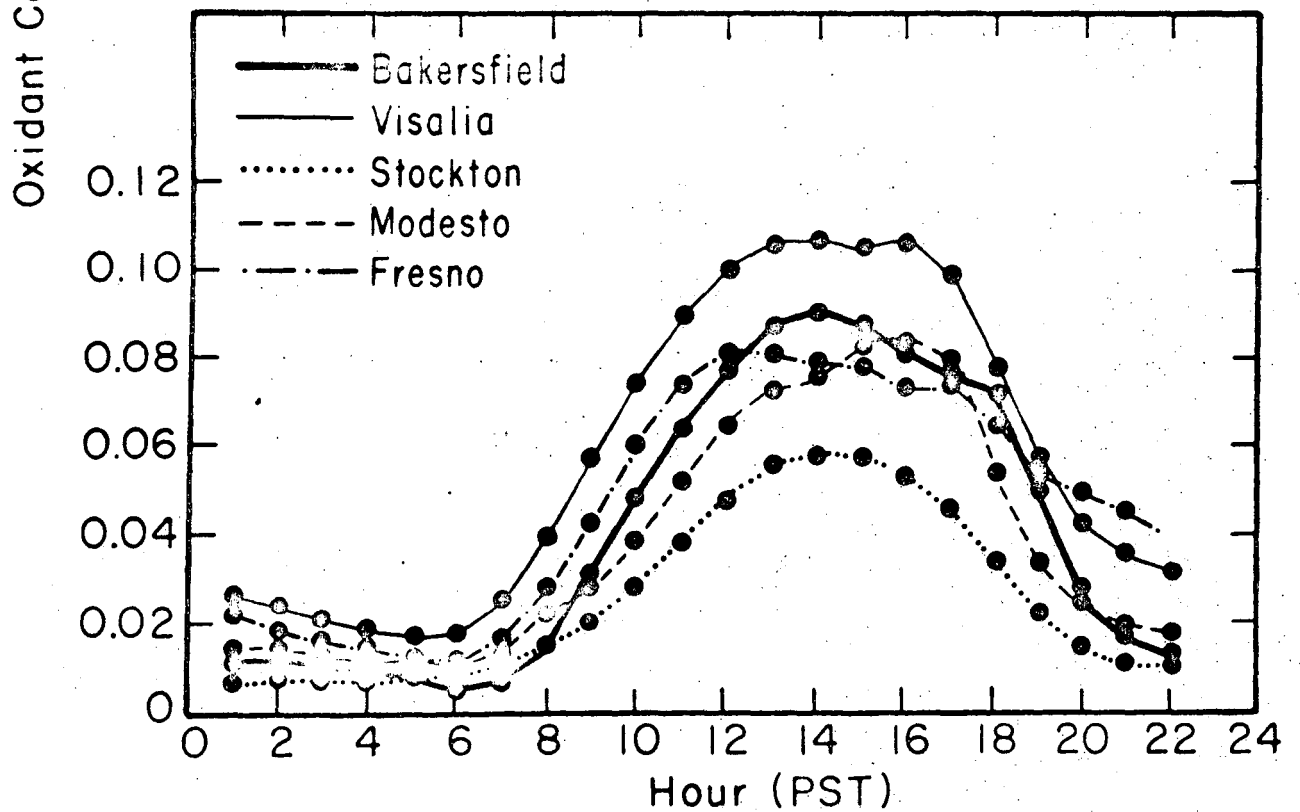
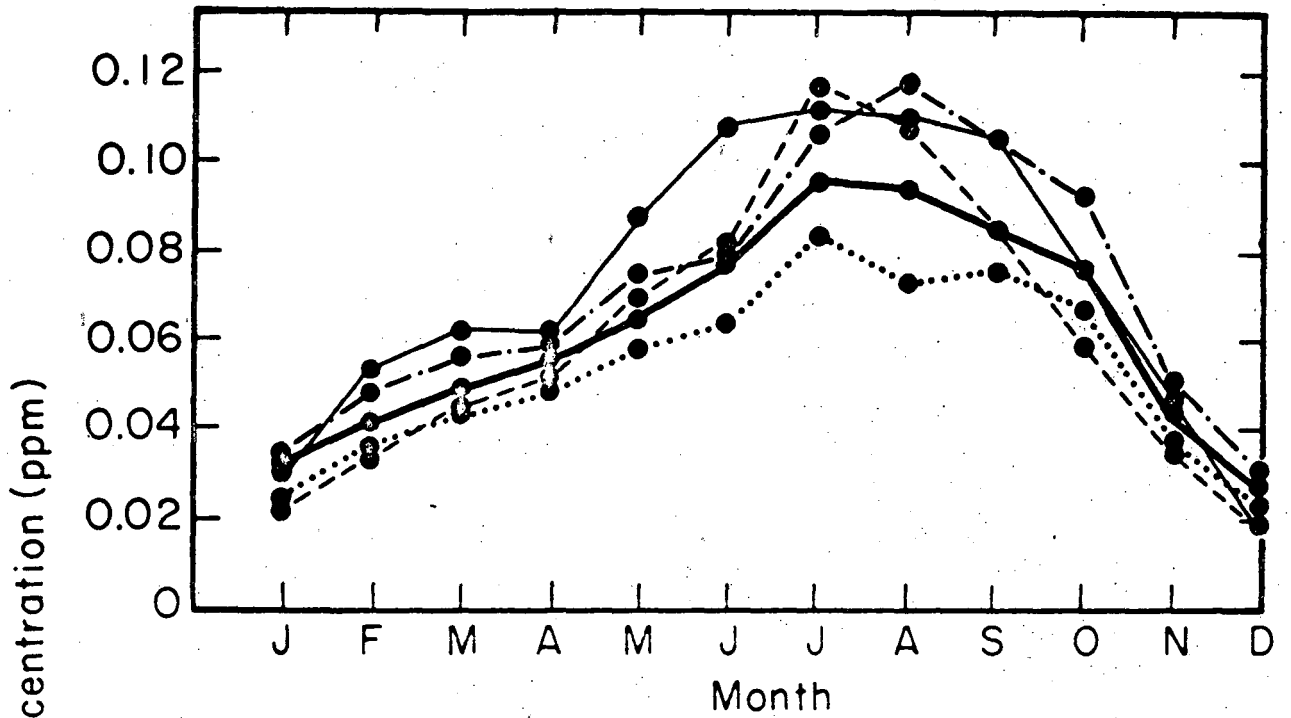


Curves D through H are the "water reactions."

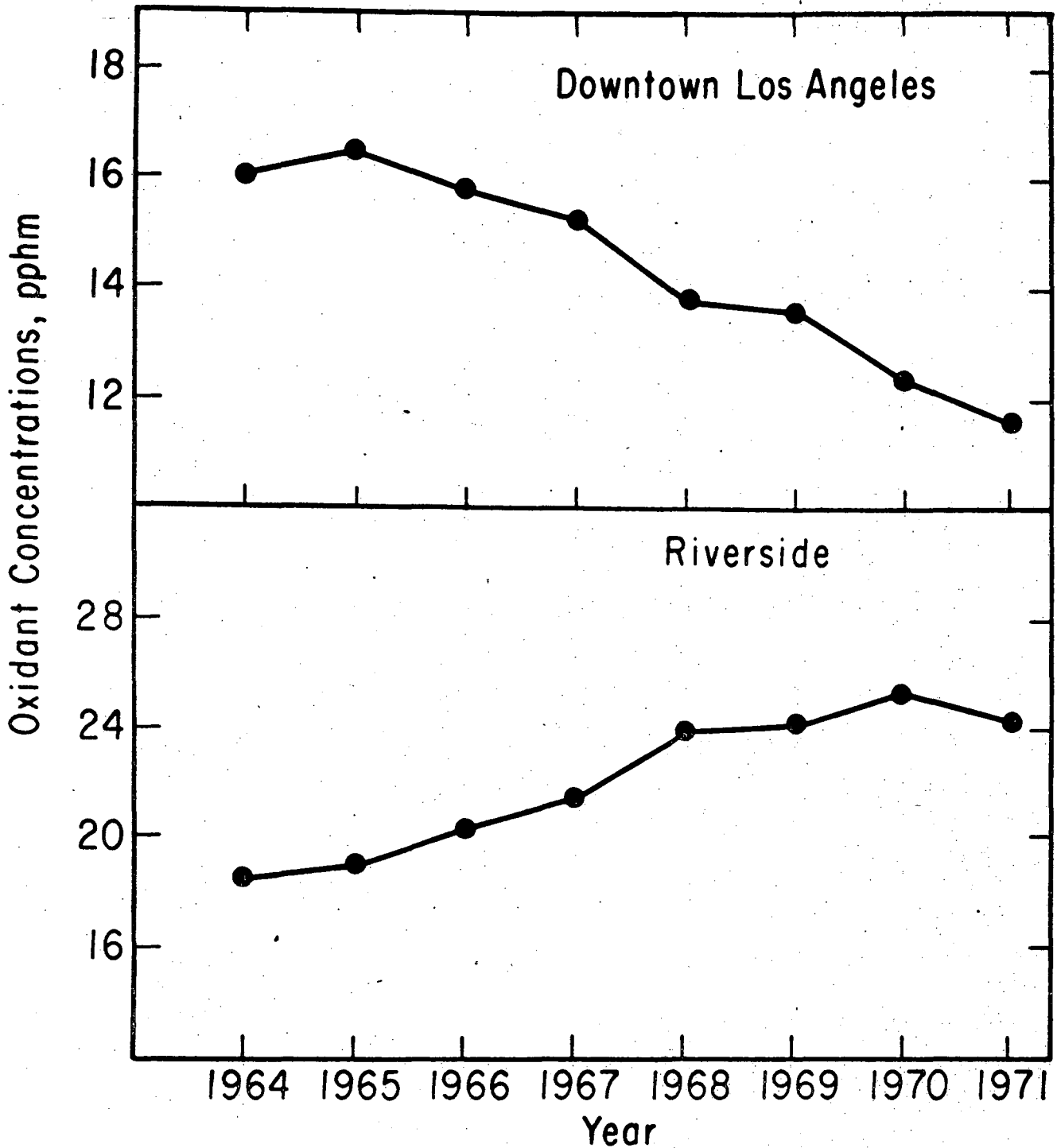
- Figure 8 - Model calculations of percentage ozone reduction as a function of percentage NO_x increase according to various investigators, reference numbers are enclosed in triangles or squares (more recent work by squares when one author has two or more reports).
Lines, ref. 1.
- Figure 9 - Latitude dependence of ozone reduction when all SST flights occurred between 40 and 50° North, according to MIT three dimensional model, reference 9. The rate of injection corresponds to 500 Boeing SST as projected in 1971 (but with reduced NO_x emission index, 15 g NO per kg fuel). The world-wide average ozone reduction is 12%; the local maximum near the flight corridor is 25%. One Dobson unit is 2.68×10^{16} molecules cm^{-2} .
- Figure 10 - Vertical profiles of ozone, water, and methane.
- Figure 11 - Vertical profile of natural NO , NO_2 , HNO_3 and oxygen atoms.
- Figure 12 - The rate of formation of ozone by the methane - NO_x - smog reaction for two initial cases: (1) 10^9 NO , 10^{11} NO_2 molecules cm^{-3} ; (2) 10^{11} NO , 10^9 NO_2 molecules cm^{-3} .

Figure 13 - Vertical profiles of the rate of formation of ozone from the methane - NO_x - smog reaction and of rate of ozone destruction from the NO_2 catalytic cycle. The former reaction increases with background O_3 , CH_4 , H_2O (Figure 10) and the latter reaction is proportional to the concentration of oxygen atoms (Figure 11) and NO_2 (Figure 11). For a given set of 36 reactions and the profiles shown in Figures 10 and 11, there is a crossover at about 13 km between ozone destruction and ozone formation so far as NO_x is concerned.

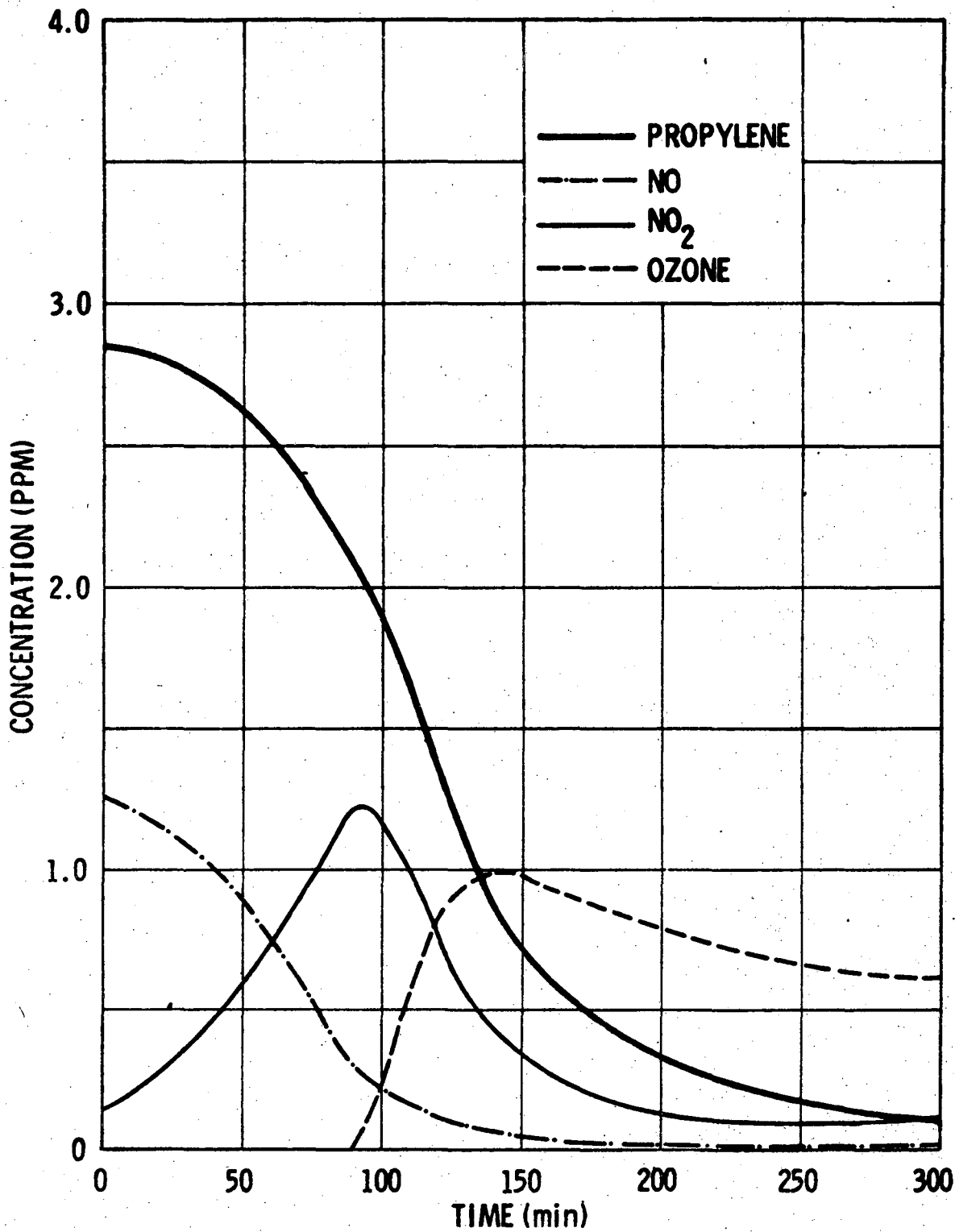
Figure 14 - Similar to Figure 13 except for an enlarged scale between 10 and 20 km. Curve 1. NO_x as in Figure 11. Curve 1/2. NO_x as in Figure 11 reduced by a factor of 2. Curve 2. NO_x in Figure 11 multiplied by a factor of 2. Note that the elevation of the crossover point is almost the same for these three widely different NO_x profiles.



OXIDANT TRENDS

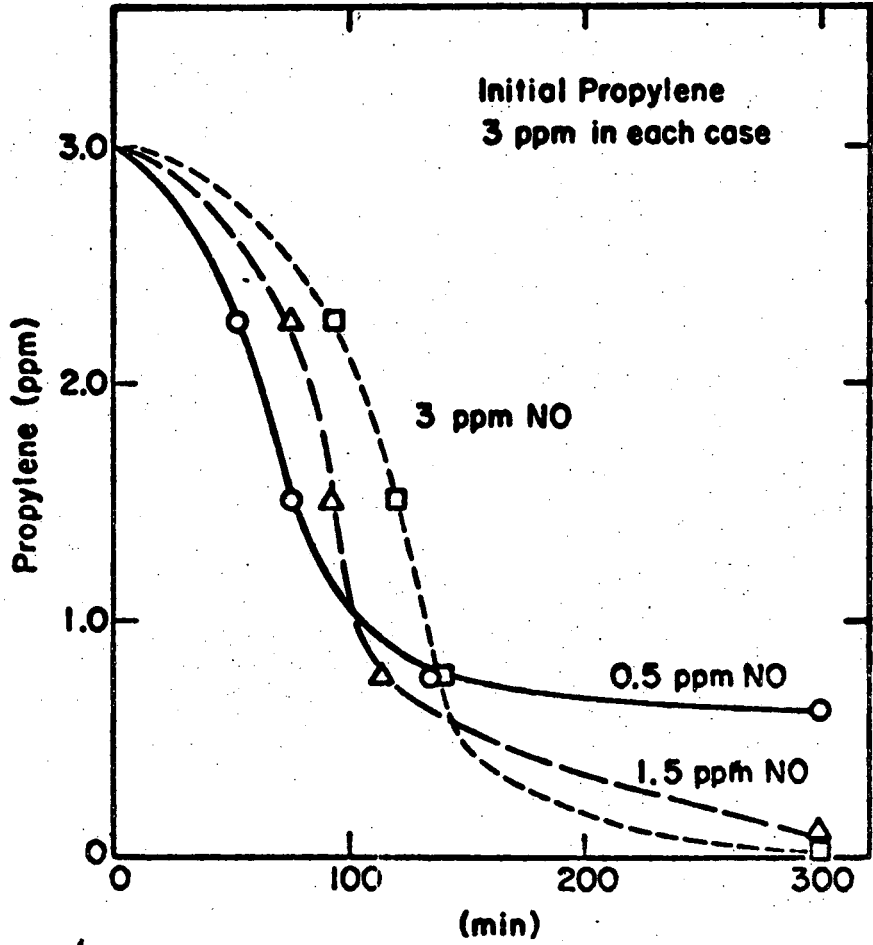


Three-Year Moving Averages of Daily Maximum One-Hour Concentrations for July, August, and September

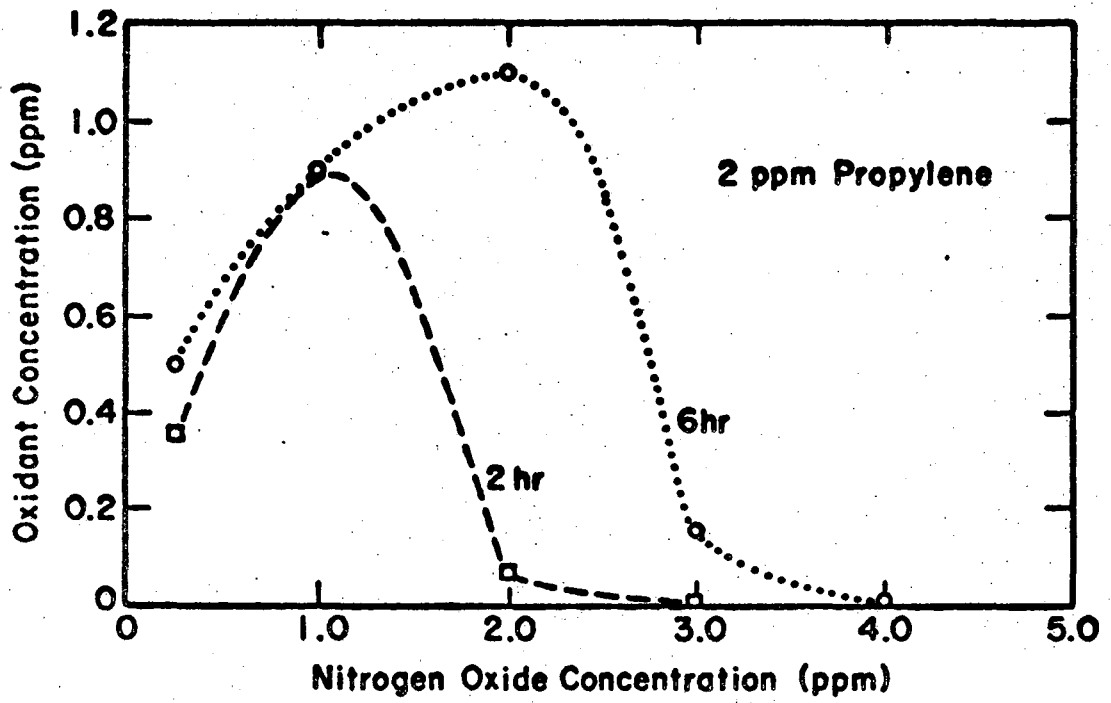


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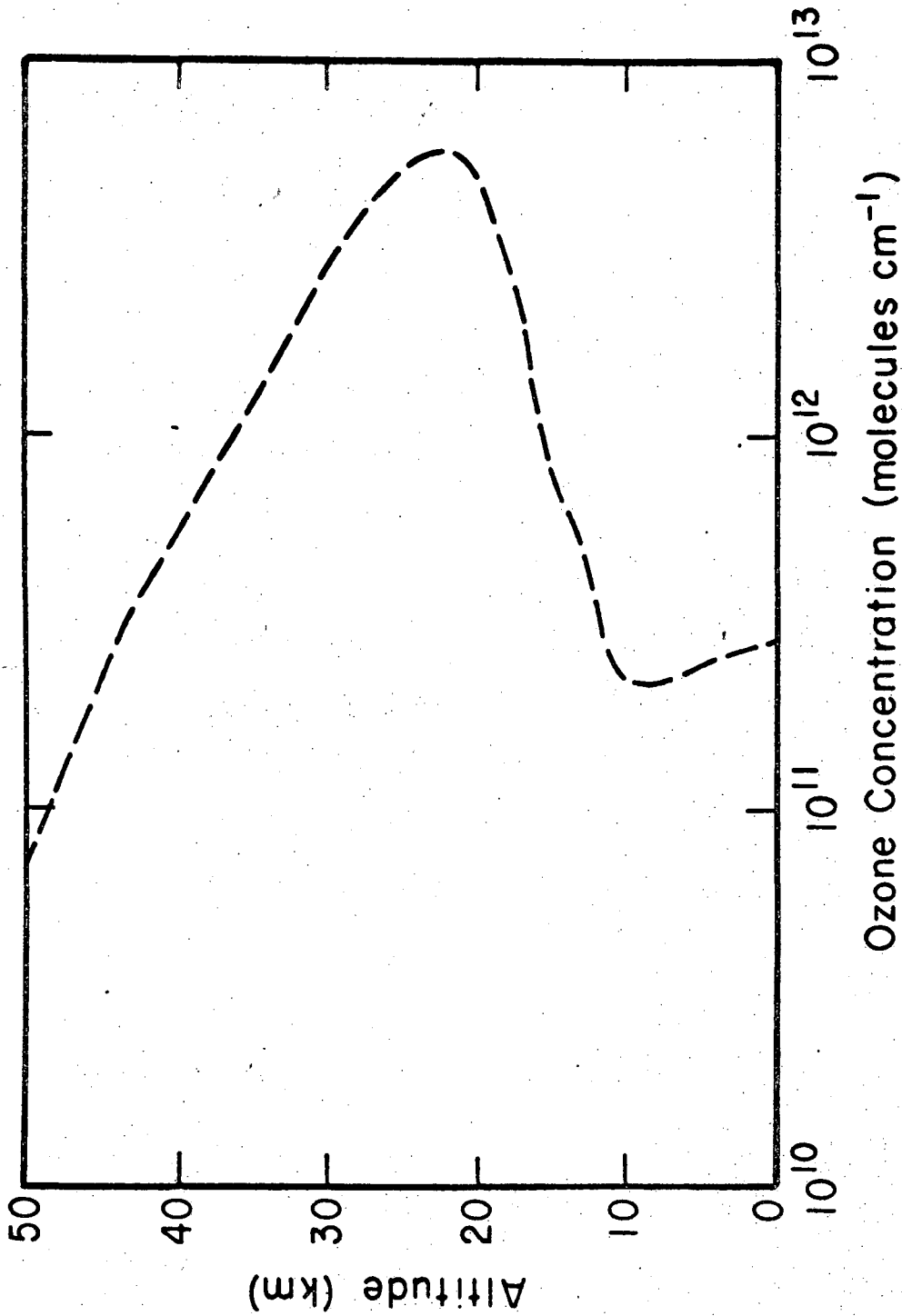


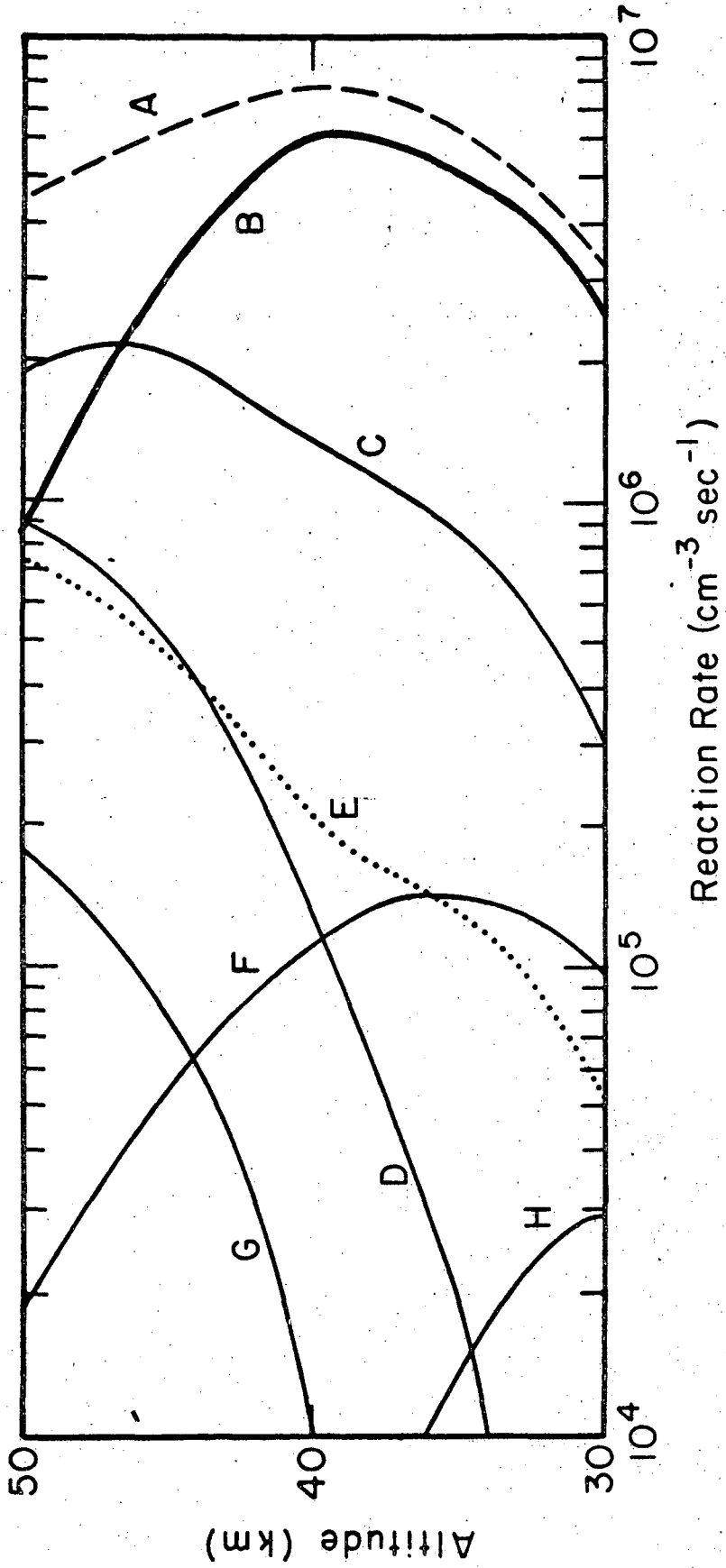
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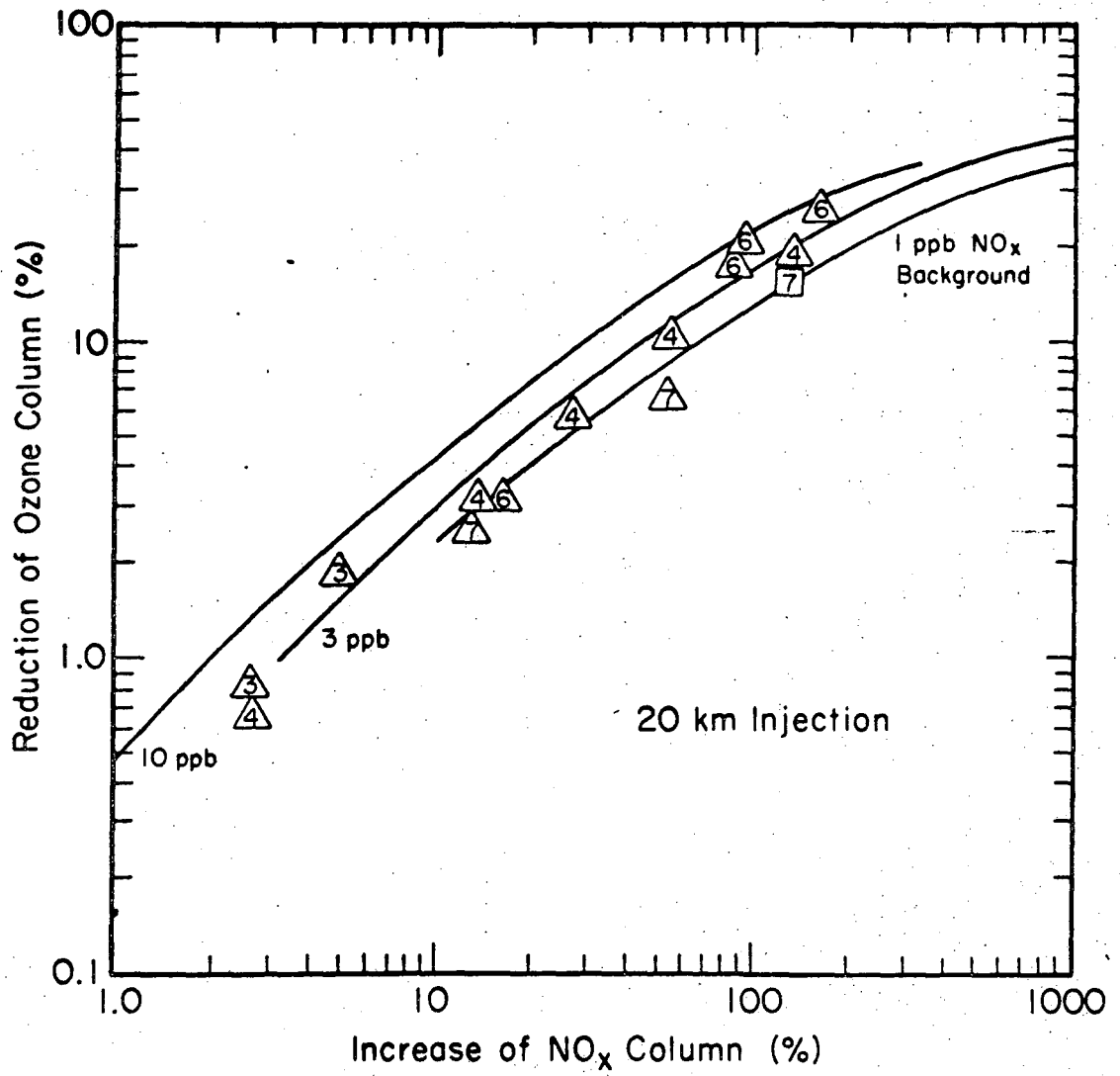
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GLOBAL MEAN OZONE CONCENTRATION PROFILE



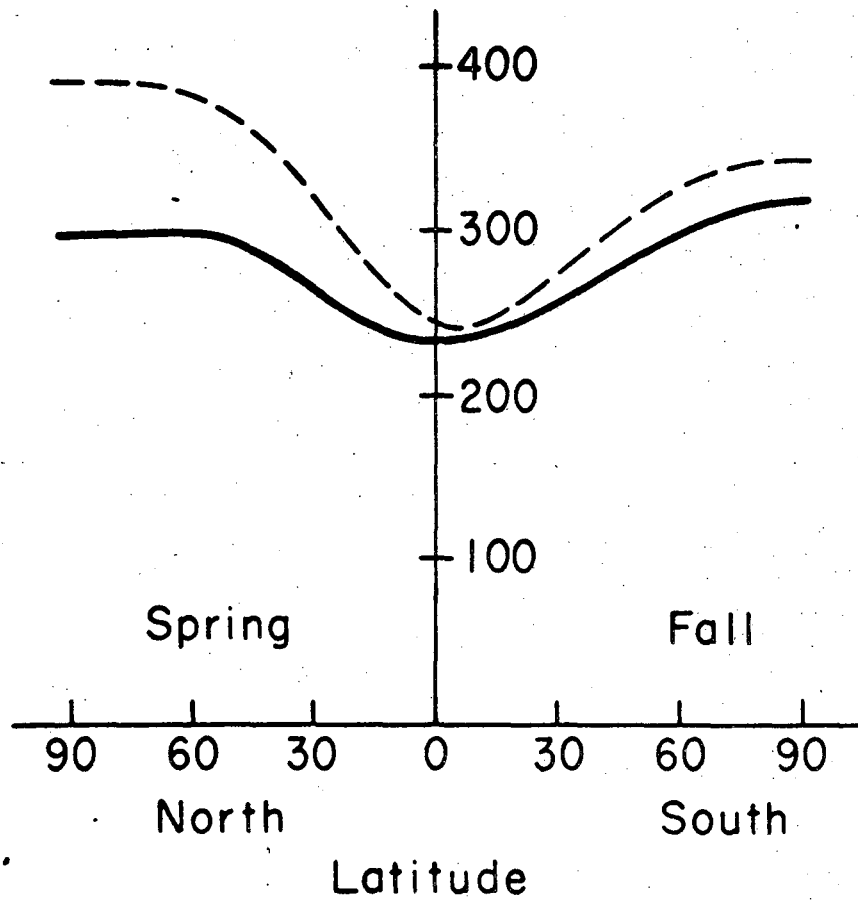


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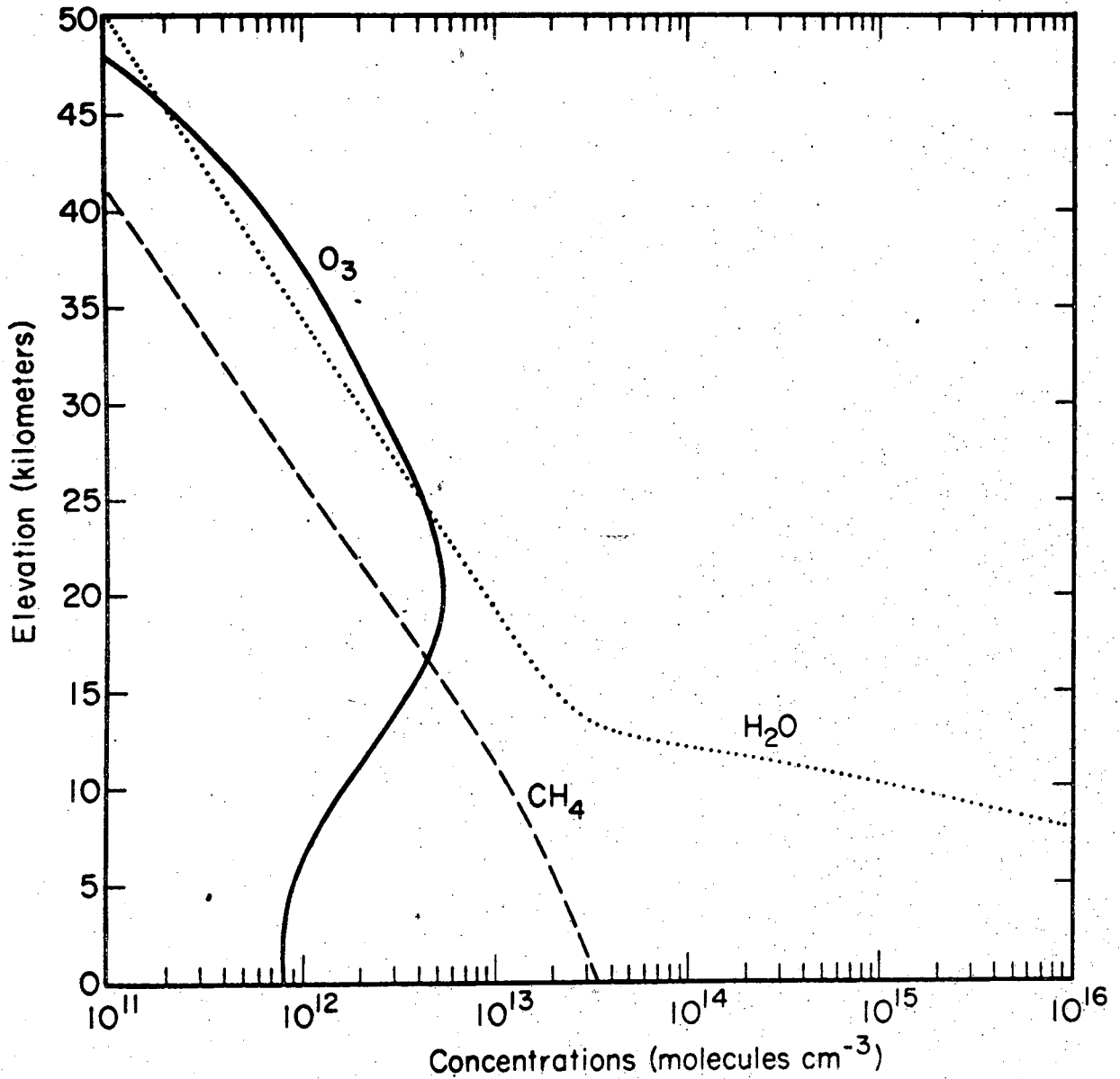
TOTAL OZONE DISTRIBUTION (DOBSON UNITS)



--- Natural Ozone
— Perturbed Ozone

0 0 0 0 4 2 0 6 7 9 1

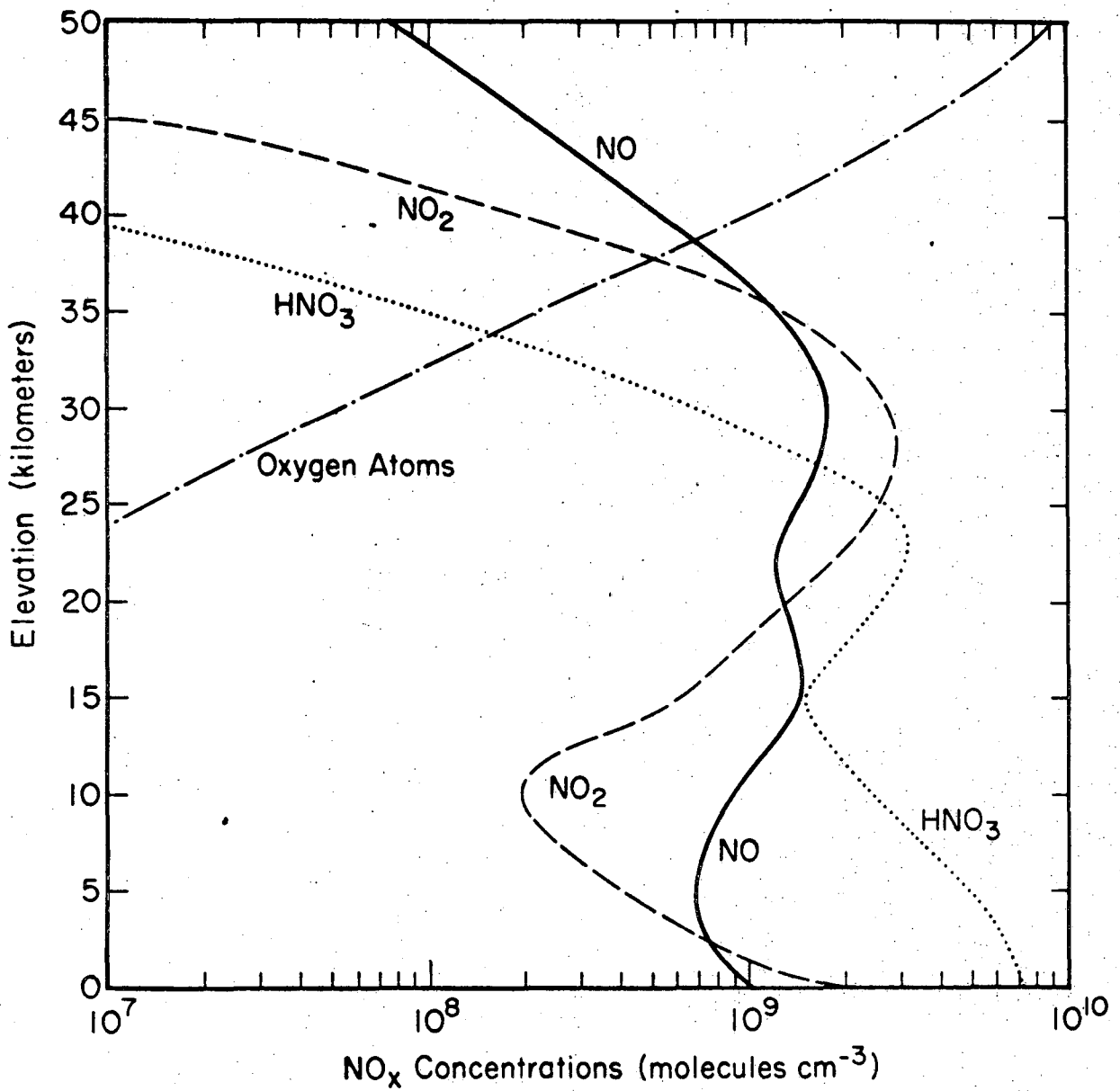
STANDARD VERTICAL PROFILES OF OZONE, METHANE, AND WATER (45° N LATITUDE, SPRING)



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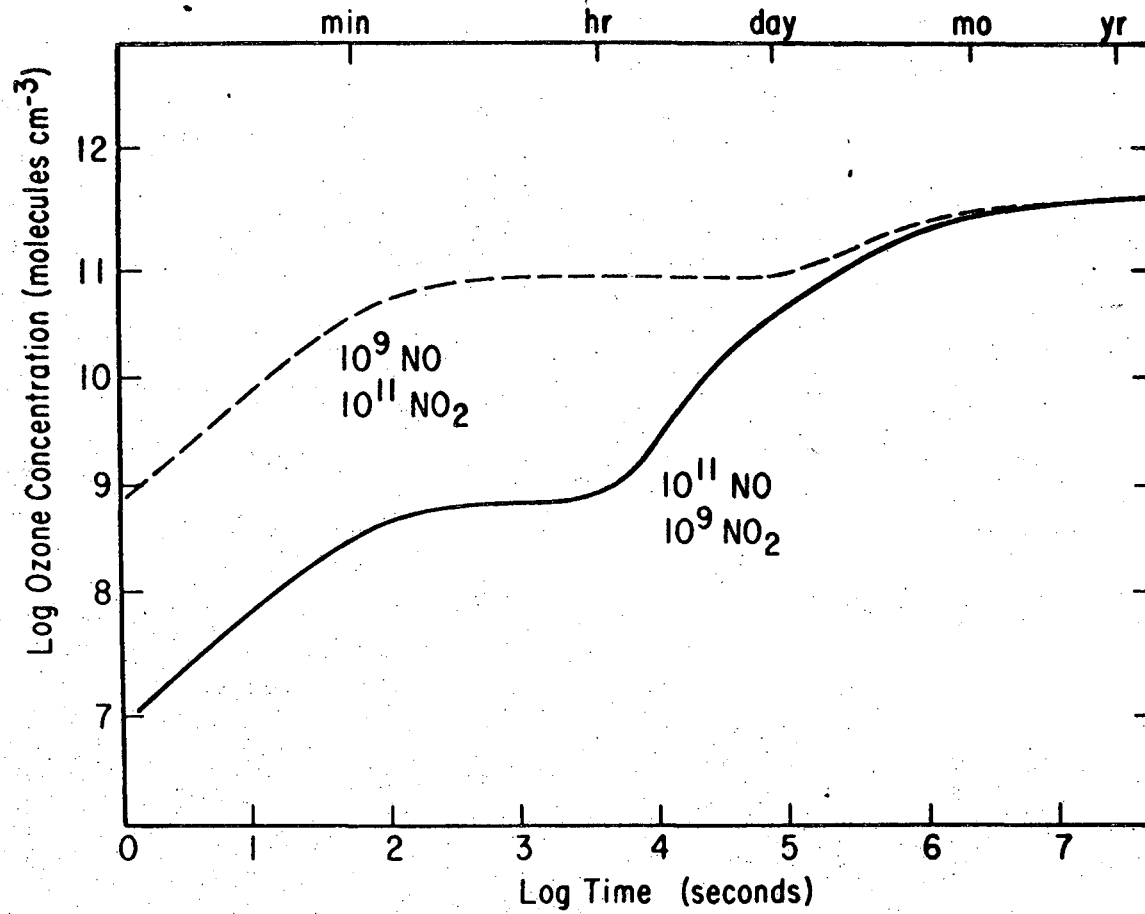
VERTICAL PROFILES OF OXIDES OF NITROGEN AND OF OXYGEN ATOMS (45°, SPRING, NOON)



11

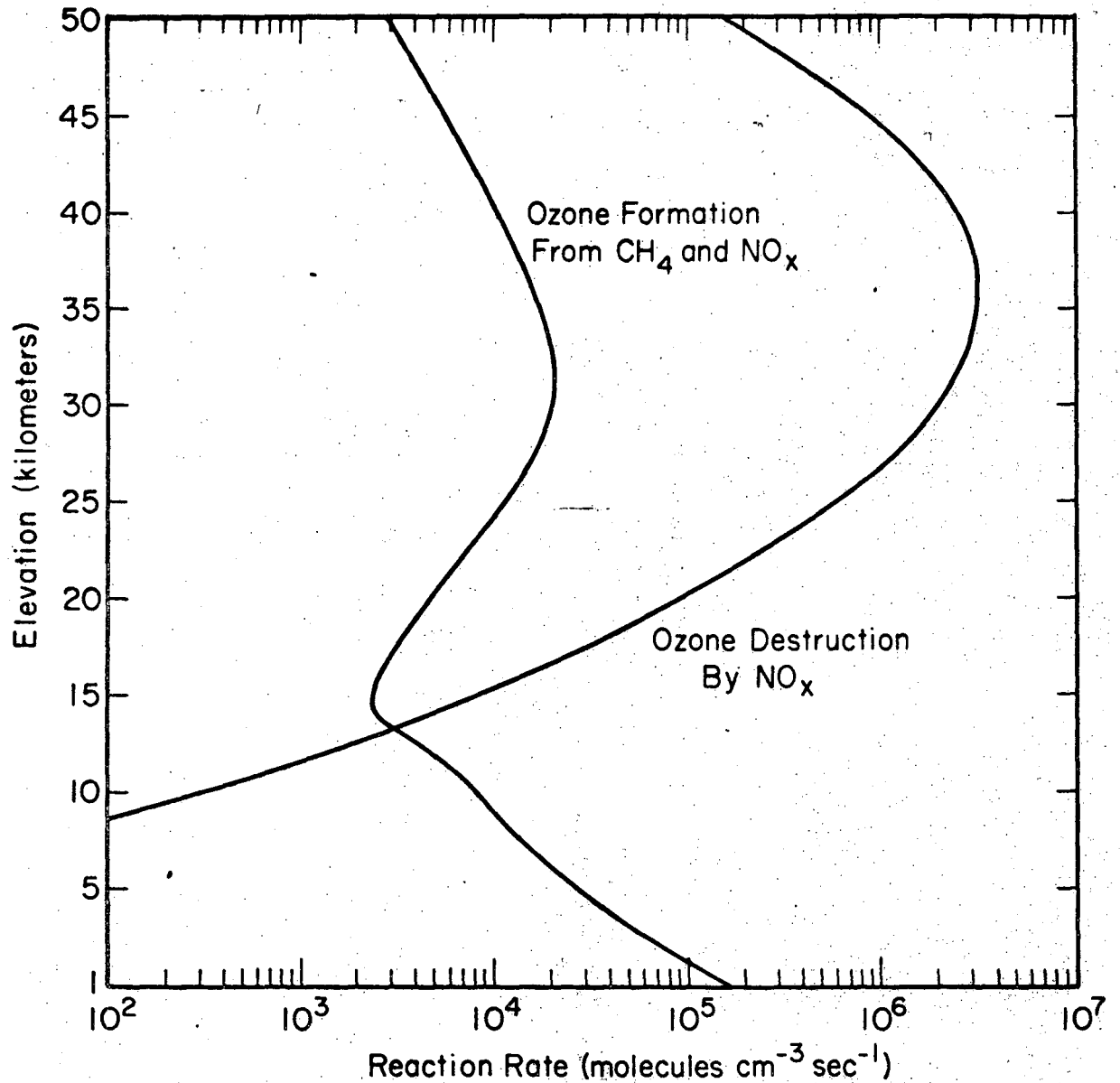
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RATE OF FORMATION OF OZONE FROM METHANE-SMOG REACTION



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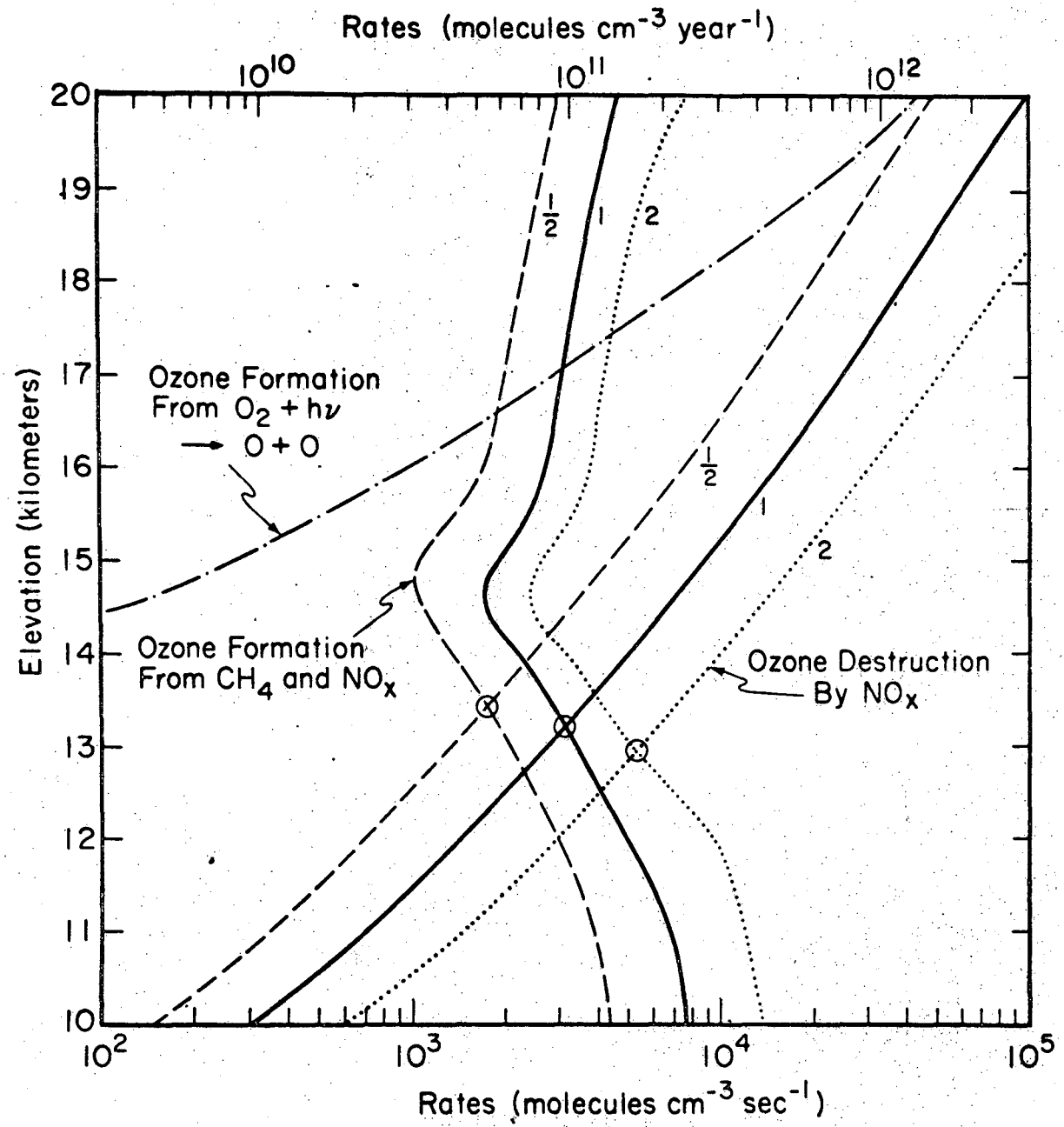
OZONE FORMATION FROM THE SMOG REACTIONS BASED
ON METHANE AND NITROGEN OXIDES
(45° LATITUDE, SPRING)



XBL 747-6687

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OZONE FORMATION AND DESTRUCTION FOR STANDARD NO_x PROFILES AND FOR ONE-HALF, AND FOR TWICE THE STANDARD PROFILES



XBL 747-6688

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