Title
SUPERSONIC AIRCRAFT AND THE OZONE LAYER

Permalink
https://escholarship.org/uc/item/9g5008tv

Author
Johnston, Harold S.

Publication Date
1974-05-01

LBL-2748 c 2
Environmental and
Earth Sciences
TID-4500-R62

SUPERSONIC AIRCRAFT AND THE OZONE LAYER

Harold S. Johnston

May 1974

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA BERKELEY

DISCLAIMER

Supersonic Aircraft and the Ozone Layer

Harold S. Johnston

Department of Chemistry
University of California and
Inorganic Materials Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

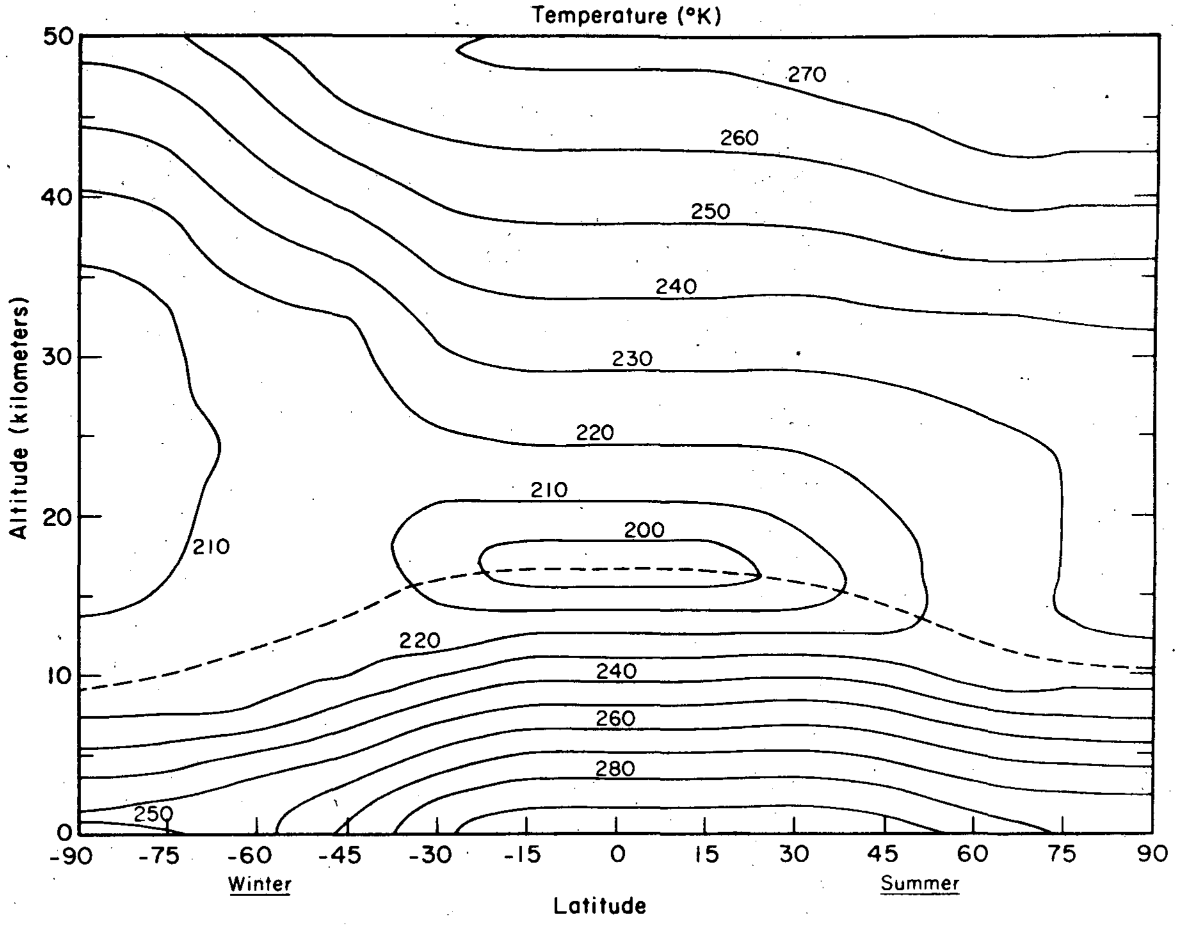
Abstract

Model calculations including atmospheric motions and the photochemistry of oxygen, water, and nitrogen oxides indicate that 500 supersonic transports would reduce the stratospheric ozone shield between 3 and 30 percent. Stratospheric ozone has been observed to change with solar-cycle modulated cosmic rays, presumably by virtue of the nitric oxide produced. The ozone data of 1960-70 are consistent with a small decrease and then increase of ozone associated with nitric oxide from nuclear-bomb tests. These observed changes of ozone with nitric oxide indicate a greater sensitivity of stratospheric ozone to nitric oxide than is given by most model calculations.

The atmosphere is discussed in terms of a series of shells. The lowest is called the "troposphere"; in it we live, have our weather, and fly subsonic aircraft. The stratosphere is next, it is a very stable body of air, and it is the region where supersonic aircraft fly. Above the stratosphere are the "mesosphere", "ionosphere", and the uppermost atmosphere that tapers off into interplanetary space. The stratosphere is defined primarily in terms of its temperature structure. The most important feature of the stratosphere, so far as life on earth is concerned, is its band of ozone, which is our only effective filter against ultraviolet radiation from 300 to 250 nm. The distribution of ozone in the natural stratosphere is determined by photochemistry and by air motions. The general features of the natural stratosphere are reviewed here, followed by considerations of how large fleets of commercial supersonic transports (SST) might perturb the stratosphere.

Temperature

At any instance, the temperature of the atmosphere varies with latitude, longitude, and elevation. It is different over continents and oceans; and it depends on the location and phase of storms. In spite of this great complexity, it is possible to define a "standard atmosphere", based on average temperatures. The temperature is averaged all around the world at one latitude ("zonal average") and it is averaged over a number of years. In this way the temperature of the globe can be represented by a two dimensional contour map. The standard temperature for January 15 is presented as Figure 1. The abscissa represents latitude from the north pole to the south pole (a distance of 20000 kilometers); and the ordinate represents altitude on



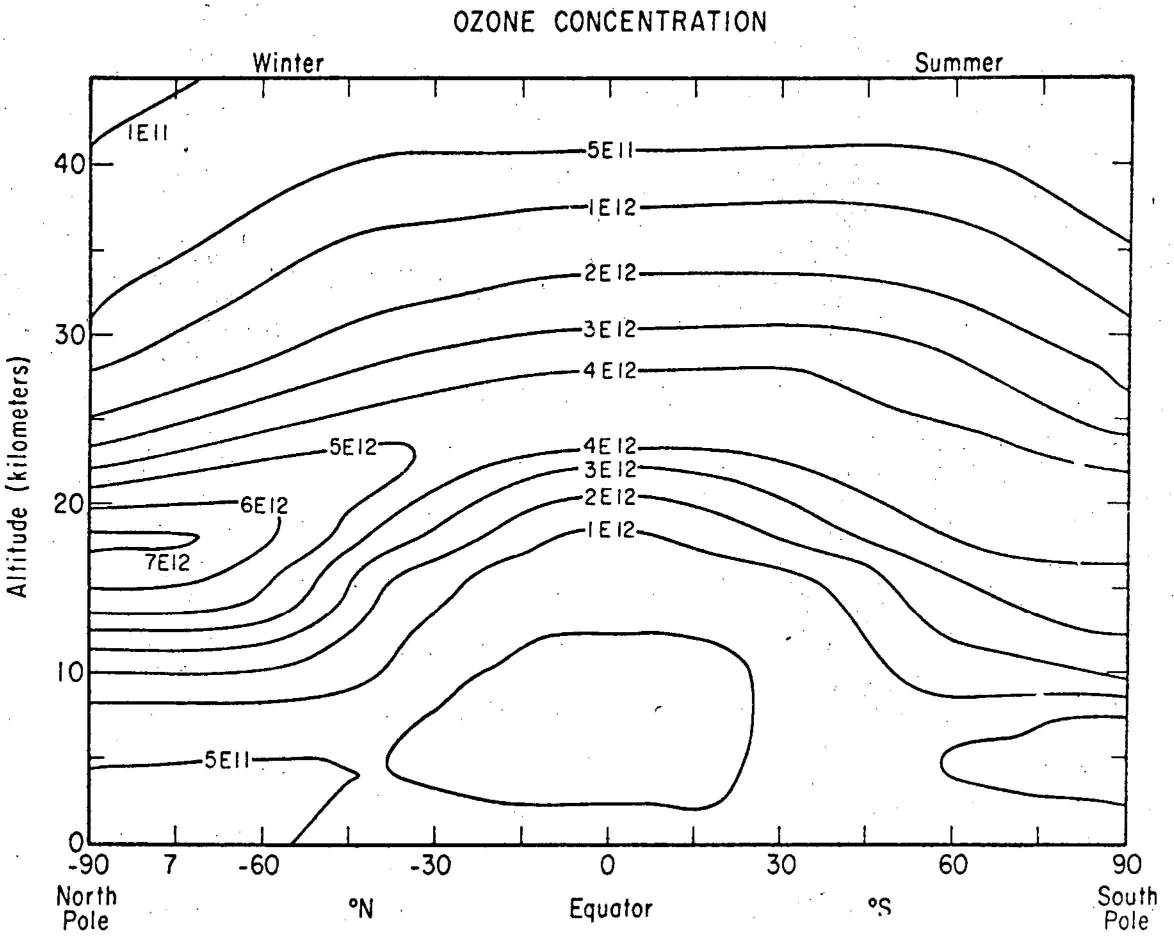
XBL 728-6734

Fig. 1.

a greatly expanded scale from 0 to 50 kilometers. The left half of the figure is the Northern Hemisphere, and the right half is the Southern Hemisphere. The region from 70°N to 90°N is in the polar night, and low temperatures extend to great heights. The lowest temperature is above the equitorial region at an elevation of about 17 kilometers. The dashed line represents the "tropopause", the separation between the troposphere and stratosphere. The temperature decreases from the surface of the earth to the tropopause and increases above the tropopause. An increase of temperature with altitude is called a "temperature inversion", and it confers great stability to air against vertical mixing.

Ozone[1]

Total ozone has been measured from ground based stations since 1925 at Arosa, Switzerland, since 1925 (with several gaps in the data) at Oxford, England, and since 1936 at Tromso, Norway. Measurements were made at almost 40 stations spaced over the globe during the International Geophysical Year, 1957-58. The data were so interesting that an extensive network of permanent stations was set up numbering about 40 in 1960 and over 100 in 1970. The data have been published regularly as <u>Ozone Data for the World</u>[2] since 1960. At a number of these ground-based stations, measurements of the approximate vertical distribution of ozone have been made by the "umkehr" method. Vertical profiles have been obtained by rockets[3]. In recent years, orbiting satellites have made detailed measurements of total ozone and its vertical distribution[4]. On the basis of 10 years (1960-69) of ground based observation, supplemented by rocket profiles, a zonal-average, standard



XBL 7310-5540

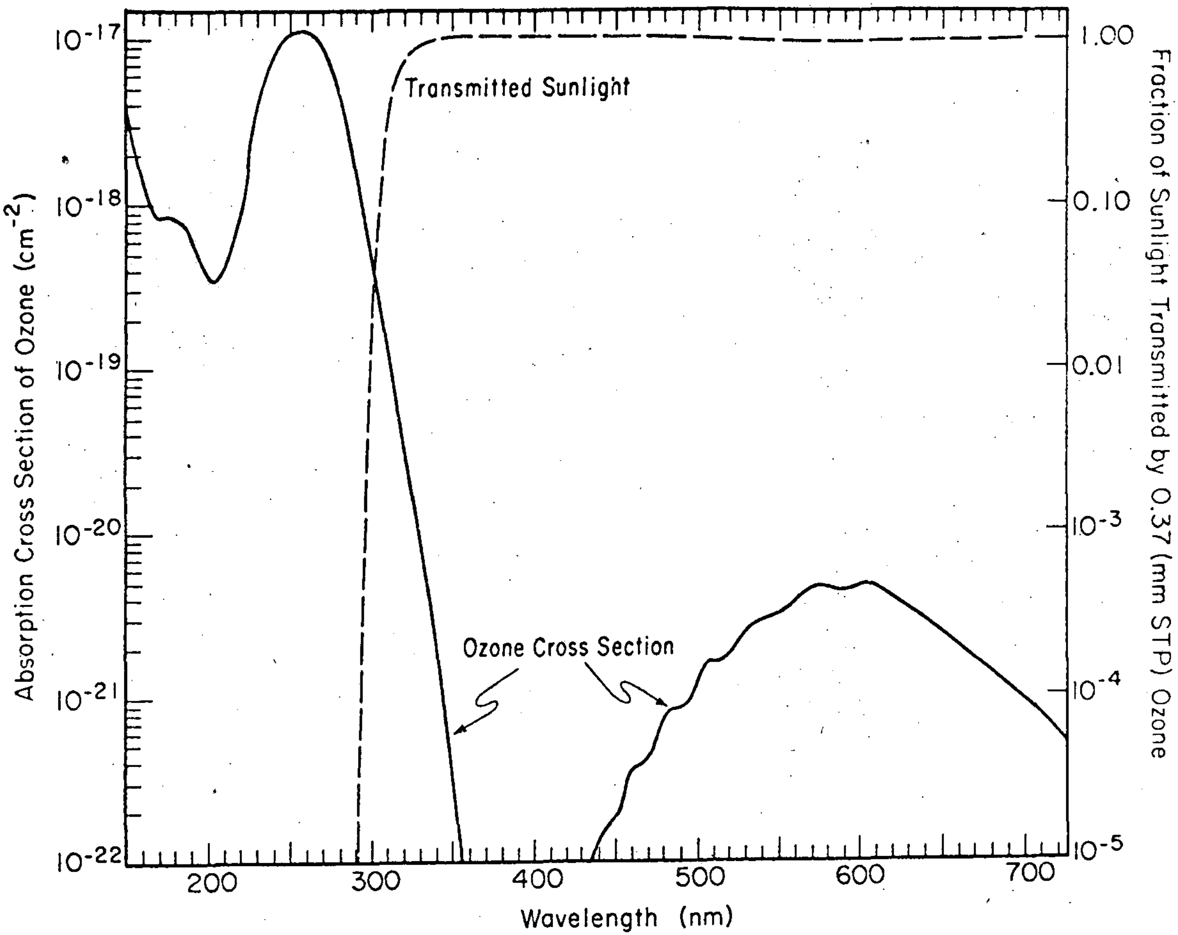
Fig. 2.

(January 15) distribution of ozone is presented as Figure 2. The elevation of maximum ozone is about 25 kilometers in the equatorial region, about 20 kilometers at 45 degree latitude, and about 18 kilometers at the poles.

Photochemistry

By the time sunlight reaches the top of the stratosphere, almost all radiation below 190 nm has been absorbed by nitrogen and oxygen molecules. In the stratosphere molecular oxygen absorbs radiation below 242 nm to form oxygen atoms, Reaction 1 in Table 1. Each of these oxygen atoms adds to an oxygen molecule to form ozone, O_3, Reaction 2. Ozone absorbs sunlight over a broad range of wavelengths, Figure 3. By the time solar radiation reaches the top of the troposphere, almost all radiation below 300 nm has been absorbed: 300 to 250 nm by ozone alone, 250 to 190 nm by both ozone and oxygen. When ozone absorbs visible or ultraviolet radiation, it is broken down to an oxygen atom and an oxygen molecule, Reaction 3. This reaction does not destroy ozone; it is immediately reformed by Reaction 2. If there were no reactions other than 1, 2, and 3, eventually all oxygen of the atmosphere would be converted to ozone. Even in totally pure air, ozone is destroyed by oxygen atoms, Reaction 4. Ozone is removed by transport to the troposphere and collision with the ground. As will be shown below, ozone is also destroyed in the stratosphere by other photochemical reactions.

The rate with which ultraviolet light breaks molecular oxygen into oxygen atoms, Reaction 1, can readily be calculated from the observed solar radiation above the atmosphere and the measured optical properties of oxygen and of ozone. This rate can be calculated at any



XBL 7311-6740

Fig. 3.

Table 1. Elementary chemical reactions discussed in this article.

A. Pure-air reactions; the Chapman mechanism for stratospheric ozone; the O_x family

1. O_2 + sunlight → O + O
2. $O + O_2 + M \rightarrow O_3 + M$
3. O_3 + sunlight → O_2 + O
4. $O_3 + O \rightarrow O_2$ to O_2

B. Water reactions; the HO_x family (a)

5. $HO + O_3 \rightarrow HOO + O_2$
6. $HOO + O_3 \rightarrow HO + O_2 + O_2$

C. Odd nitrogen reactions; the NO_x family (b)

7. $NO + O_3 \rightarrow NO_2 + O_2$
8. $NO_2 + O \rightarrow NO + O_2$
9. NO_2 + sunlight → NO + O

D. Nitric acid reactions (a, b)

10. $HO + NO_2 \overset{M}{\rightarrow} HNO_3$
11. HNO_3 + sunlight → $HO + NO_2$
12. $HO + HNO_3 \rightarrow H_2O + NO_3$

(a) There are more than a score of other reactions in the HO_x family; several of the rate constants were observed for the first time in 1973.

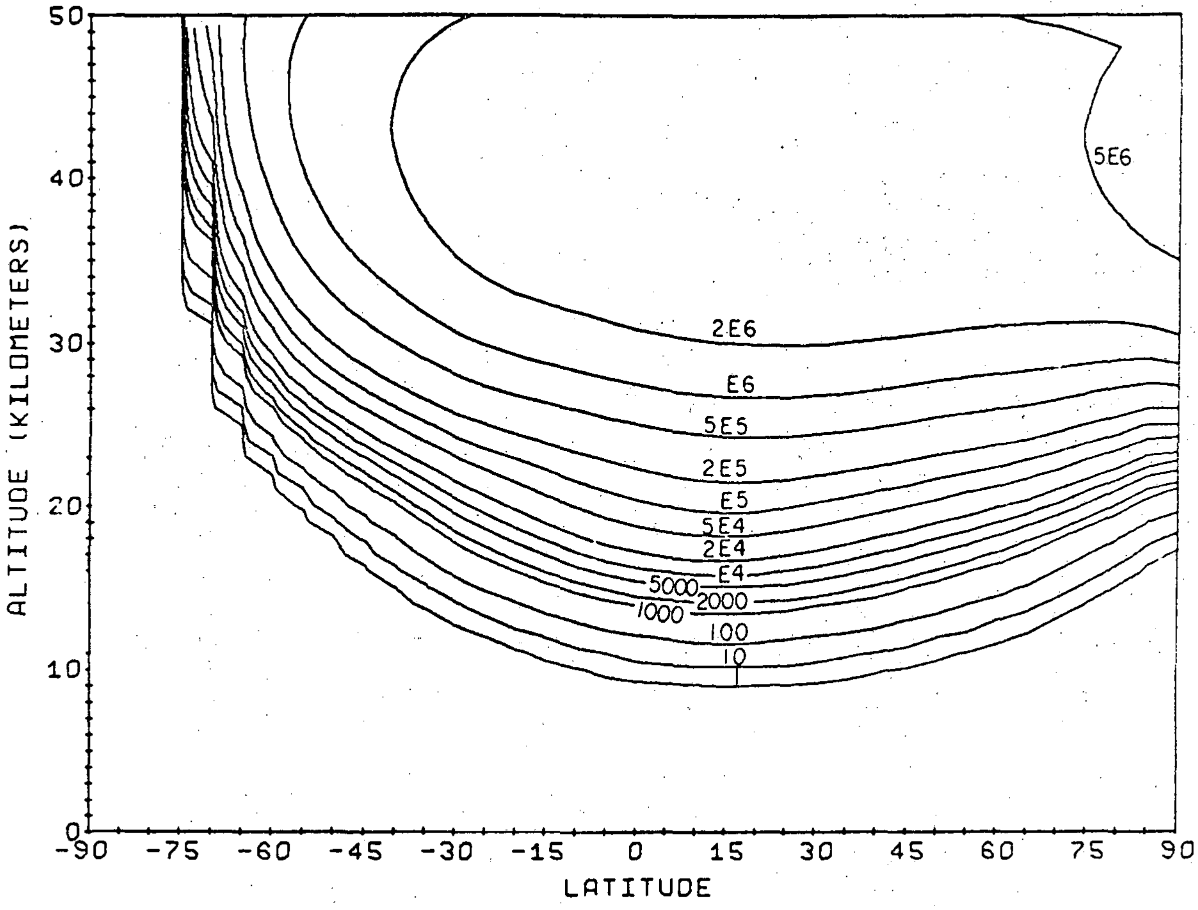
(b) There are more than a score of other reactions in the NO_x family.

latitude, longitude, and elevation. The zonal average rate of photolysis of oxygen (Reaction 1) for a standard January 15 is given by Figure 4. From 45°N to the south pole and above 30 kilometers, there is a broad band of fast, almost uniform rate of oxygen photolysis.

The rate of formation of ozone is twice the rate of photolysis of oxygen (Reactions 1 and 2). If the local concentration of ozone (Figure 2) is divided, point by point, by the local rate of formation of ozone, then one has calculated the photochemical "ozone replacement time". Such ozone replacement times were calculated for a standard January 15, Figure 5. These photochemical replacement times cover a very wide range; contours are given for periods from one day to 10 years. The ozone replacement times give a measure of instantaneous rates (compare the use of 4.5 billion year half time to characterize the rate of radioactive decay of uranium). In order to evaluate the significance of these wide-ranging ozone-replacement times, one must compare these periods with the time scale of horizontal and vertical stratospheric motions.

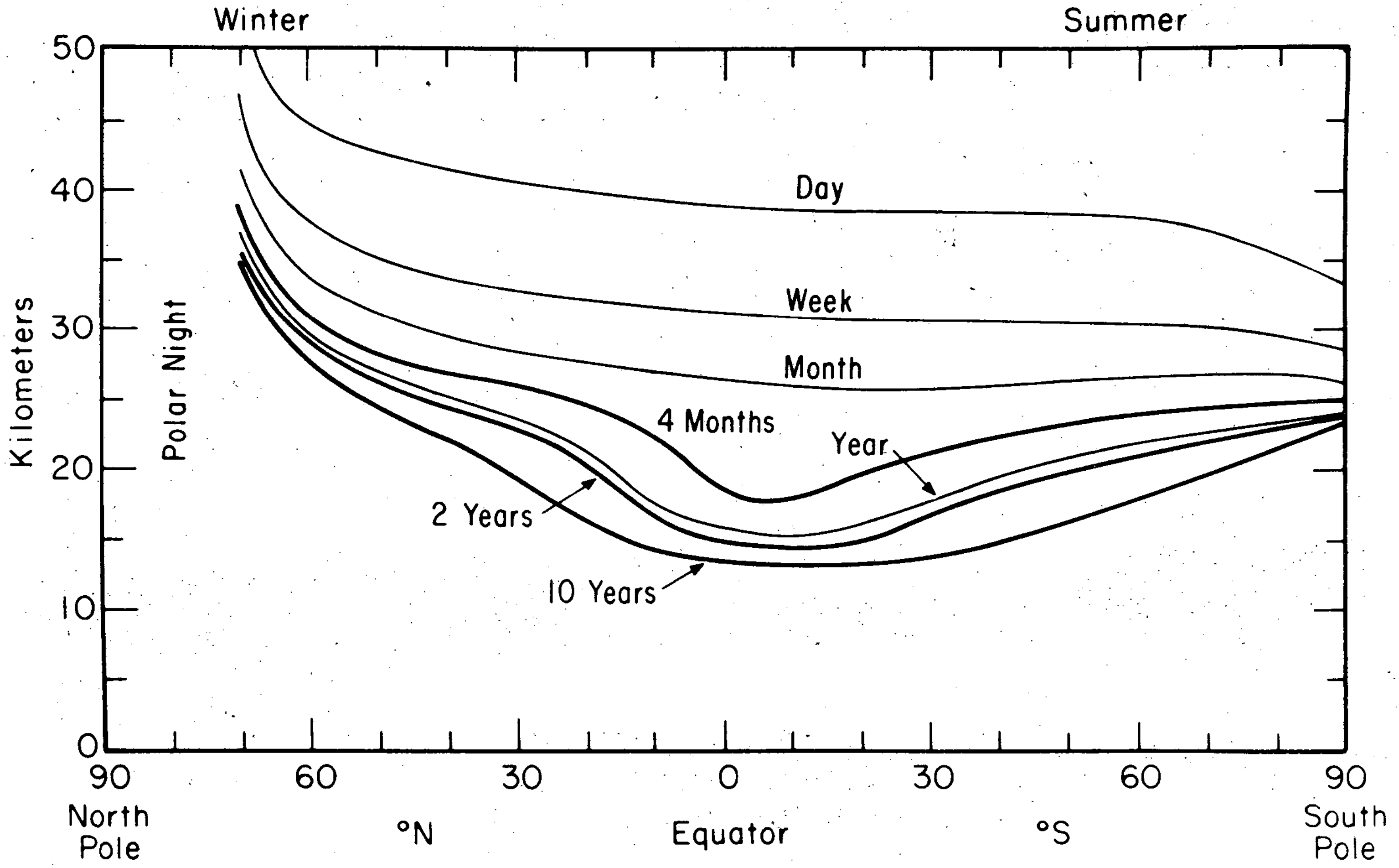
Motions

The dominant effect of horizontal motions in determining the distribution of stratospheric ozone is illustrated by Figure 6, where contours for the concentration of ozone (Figure 2) are superimposed on contours for ozone-replacement time (Figure 5). Above the dashed line, the ozone-replacement time is 4 months or less; below the heavy solid line, the ozone-replacement time is 10 years or more. In Figure 6 and in several subsequent figures, the ozone formation region is regarded



XBL 746-6537

Fig. 4.

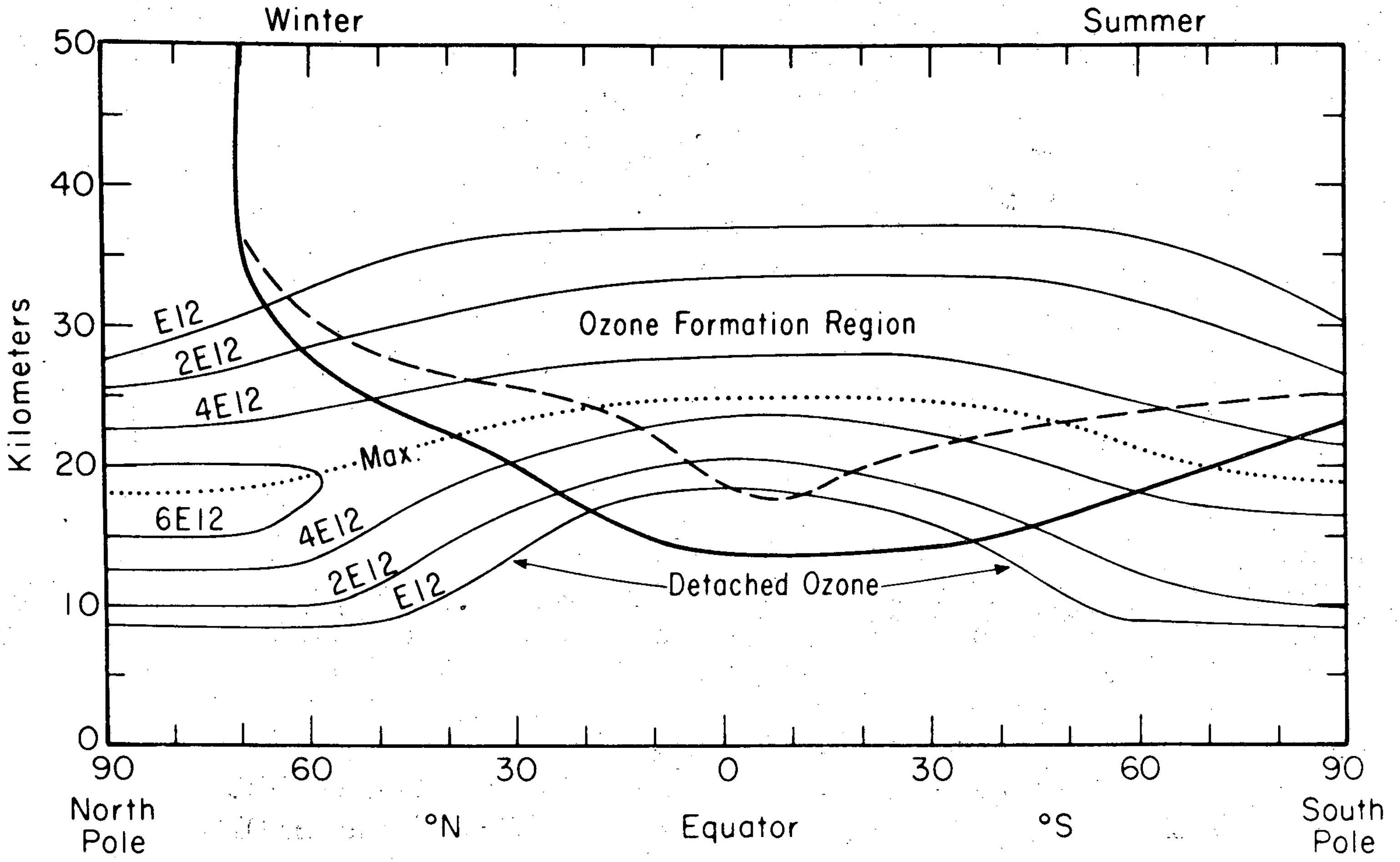


OZONE REPLACEMENT TIME, JANUARY 15 (LOCAL OZONE CONCENTRATION DIVIDED BY LOCAL OZONE FORMATION RATE)

XBL 7310-5506

Fig. 5.

OZONE CONCENTRATION, JANUARY 15, RELATIVE TO OZONE FORMATION REGION, TRANSITION REGION, AND DETACHED OZONE REGION

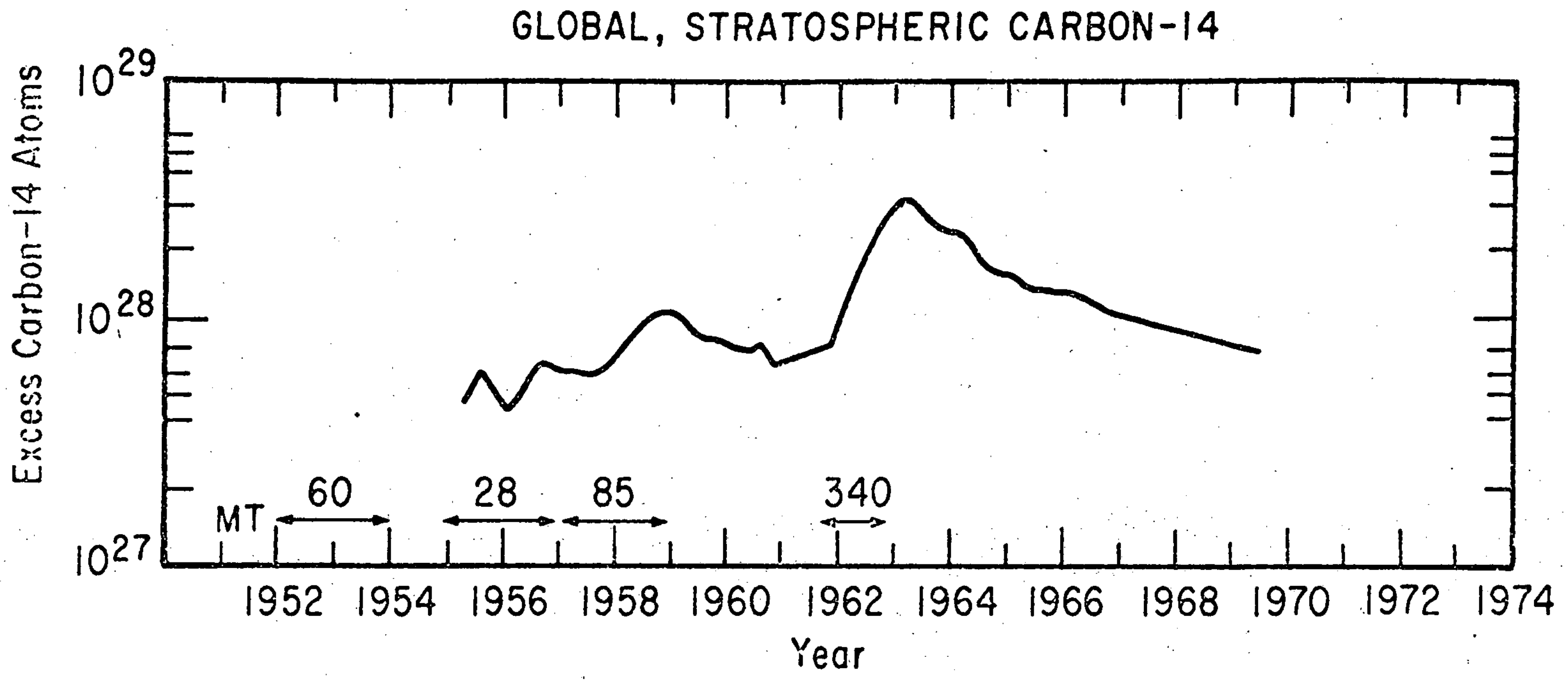


XBL 7310-5507

Fig. 6.

as that where the ozone replacement time is 4 months or less; and any ozone in a region where the replacement time is 10 years or more is regarded as being "detached" from its source. About half the global ozone is outside the formation region. The maximum concentration of ozone is at the winter pole, and the concentration is much less at the summer pole (6 months later). These observations show that air motions are a major factor in the natural ozone distribution. East-west winds circle the globe, often in a few days. Horizontal eddy diffusion transports ozone and other trace gases in a north-south direction with a typical time scale of a few months.

The time scale for vertical mixing in the stratosphere and for net loss from the stratosphere to the troposphere can be estimated from the history of radioactive, nuclear-bomb debris in the stratosphere. The rising, cooling mushroom cloud following the detonation of large nuclear bombs (one megaton or more), stabilizes and flattens out in the stratosphere. One radioactive by-product is carbon-14, presumably in the form of gaseous carbon monoxide or carbon dioxide. Carbon-14 was extensively sampled by high flying aircraft and by balloons, and the results have been recorded in a series of reports[5]. The total amount of carbon-14 in the stratosphere between 1955 and 1969 is plotted in Figure 7. Between 1952 and the end of 1962, there were four periods of testing large nuclear bombs in the atmosphere. The duration of these test periods and the total bomb yields in megatons (MT) are indicated on Figure 7. After the conclusion of the large-scale tests in December 1962, the total stratospheric burden of carbon-14 decreased



XBL 7311-6741

Fig. 7.

with time. The quantity in the stratosphere on January 1, 1963 was reduced by one half in 1.6 years; the quantity on January 1, 1964 was reduced by one half in 2.4 years; the quantity on January 1, 1965 was reduced by one half in 4 years. If one examines the history of carbon-14 in the stratosphere, the explanation for the increasing half-time with time is apparent. Immediately after the bomb tests, the radioactive debris was spread between 10 to 22 kilometers in the polar stratosphere and from 15 to 25 kilometers in the tropical stratosphere. The carbon-14 low in the stratosphere (around 15 kilometers) came out much faster than that somewhat higher (20 kilometers). Within 2 years a substantial amount of carbon-14 had spread up to almost 30 kilometers. The short half lives (1.6 to 2.4 years) apply to the carbon-14 at relatively low elevations (15 to 20 km), and the longer half lives (4 years) apply to the carbon-14 above 20 kilometers.

The carbon-14 data indicate very slow vertical mixing and long (1.6 to 4 years) half-residence times of gases in the stratosphere. On the basis of these data, one conservatively assigns 2 years as the half-residence time of SST exhaust gases that are deposited at 20 kilometers. SST exhaust gases deposited between 17 and 19 kilometers (a typical cruise pattern for the Concorde) have a somewhat shorter half-residence time, perhaps about 1.5 years.

Global ozone balance[6]

With the actual, standard distribution of temperature (Figure 1) and ozone (Figure 2), one can calculate the distribution of solar radiation throughout the global atmosphere, and thus one can evaluate the local rate of elementary chemical and photochemical reactions.

With the atmosphere of the world as it was prepared by photochemistry and by air motions, one can ask and answer several important questions in a relatively straight forward way. The rates per seconds can be evaluated throughout the atmosphere, and these instantaneous local rates can be integrated to examine balances or imbalances for the global stratosphere. The effect of air motions inside the stratosphere cancel out in such a calculation. The integral of the transport of ozone over the volume of the stratosphere is simply the flux of ozone across the boundaries of the stratosphere, and these fluxes have been determined experimentally[1b].

With this method of evaluating instantaneous rates, the balance sheet between ozone formation and ozone destruction by "pure air reactions", by "water reactions", and by transport to the troposphere is given in Table 2. According to this analysis, ozone is produced 352×10^{29} molecules per second faster than it is being destroyed. At this rate the global inventory of ozone would double in less than two weeks. Clearly there is "something else" besides pure air and water involved in the natural ozone balance.

The oxides of nitrogen are rapidly interconverted from one form to another; the important species are nitric oxide (NO), nitrogen dioxide (NO_2), and nitric acid (HNO_3). Ozone converts nitric oxide to nitrogen dioxide. Hydroxyl radicals (HO) convert nitrogen dioxide to nitric acid. Ultraviolet radiation reverses both of these processes. Although the ratios vary with elevation, these three forms of NO_x occur roughly in the proportions one to two to three when summed over the entire stratosphere.

Table 2. Global ozone balance sheet for instantaneous formation and destruction of ozone for standard January 15.

Reaction	Rate in units of 10^{29} molecules sec^{-1}
Ozone formation (reactions 1 and 2)	+500
Ozone transport to troposphere	-6
O_x reactions (reaction 4)	-86
HO_x reactions (reactions 5, 6, and others)	-56
Unbalanced ozone production	352

It has been proposed that the primary agents in the natural ozone balance are the oxides of nitrogen (Reactions 7, 8, and 9 in Table 1 and approximately 20 other reactions not listed there).[7,8] The catalytic cycles involved in these reactions will be discussed in some detail. There are two competing cycles, one destroys ozone

NO_2 catalytic cycle

$$\begin{array}{ll} (7) & NO + O_3 \rightarrow NO_2 + O_2 \\ (8) & NO_2 + O \rightarrow NO + O_2 \\ \hline \text{net:} & O_3 + O \rightarrow O_2 + O_2 \end{array}$$

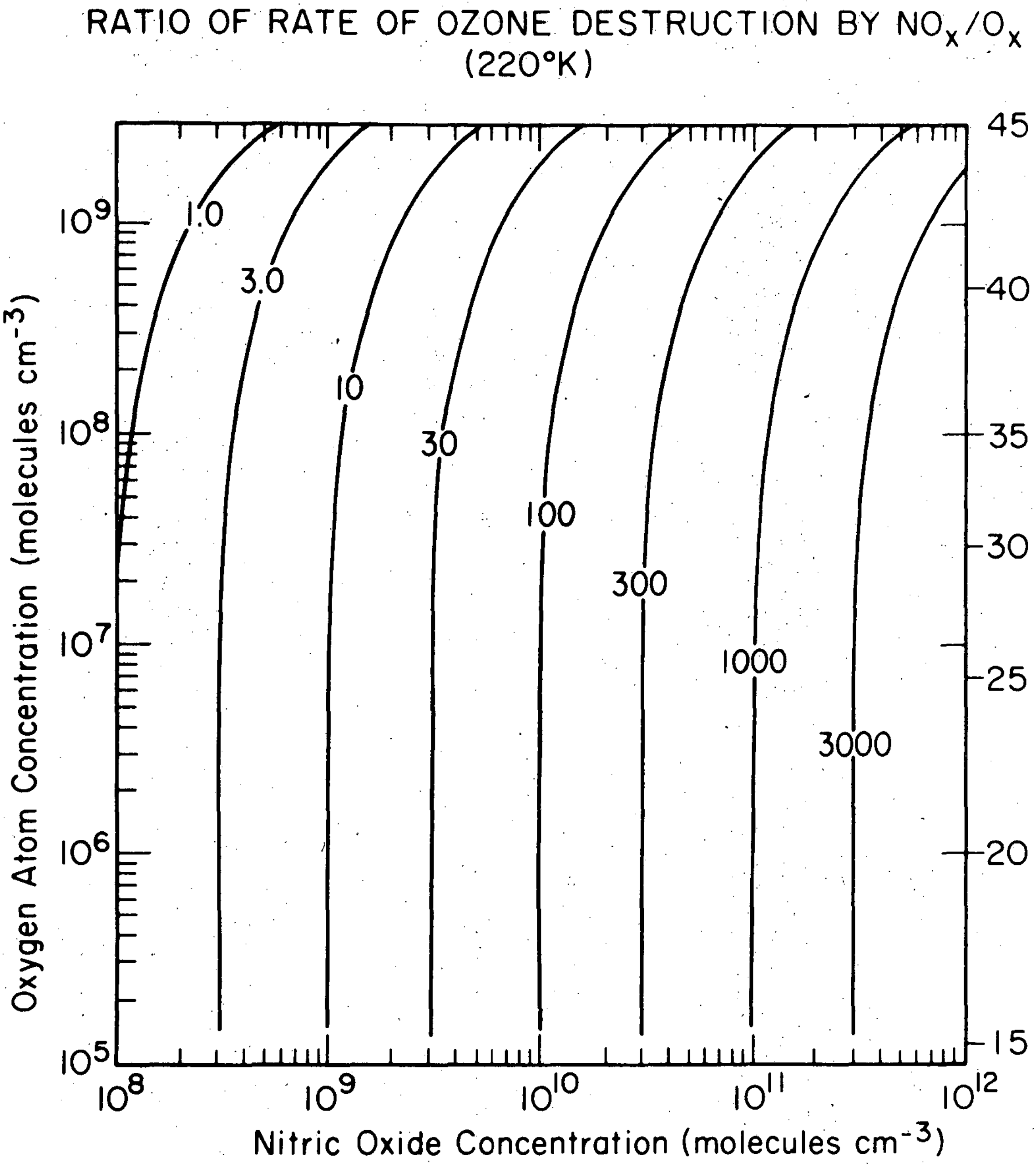
and one is neutral with respect to ozone

$$\begin{array}{ll} (7) & NO + O_3 \rightarrow NO_2 + O_2 \\ (9) & NO_2 + \text{sunlight} \rightarrow NO + O \\ (2) & O + O_2 + M \rightarrow O_3 + M \\ \hline \text{net:} & \text{no reaction} \end{array}$$

The NO_2 cycle is a prime example of homogeneous, gas-phase catalysis: nitric oxide is consumed in the first step and reformed in the second; ozone is destroyed in the cycle but the oxides of nitrogen are not destroyed. The second, "do nothing" cycle competes with the catalytic cycle, and the relative rate of destruction of ozone by NO_x and by the pure air mechanism (Reaction 4) is

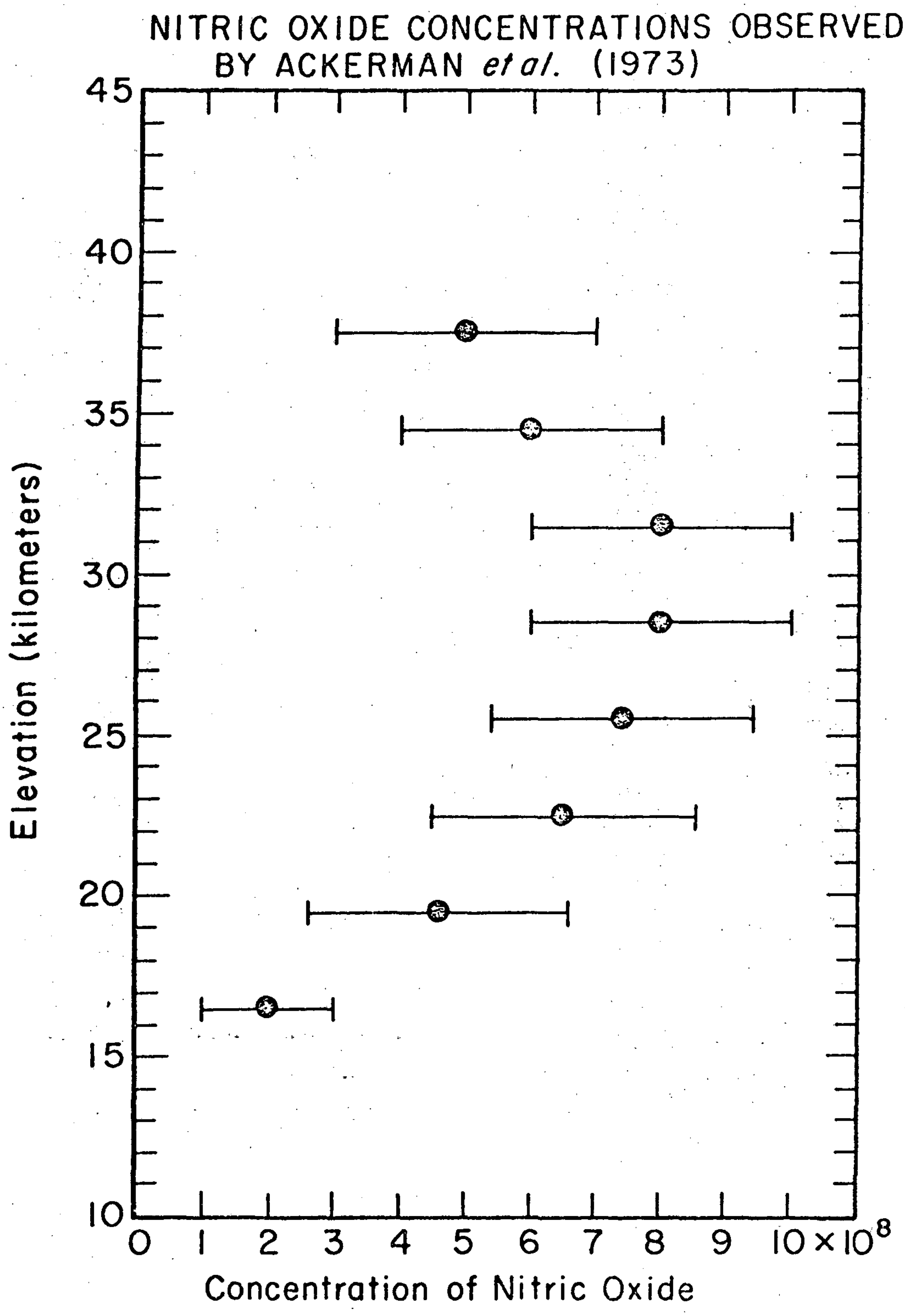
$$\frac{\text{catalytic rate}}{\text{rate of reaction 4}} = \frac{k_7 k_8}{k_4 j_9} \frac{[NO]}{(1 + k_8[O]/j_9)} \qquad (I)$$

This ratio of rates depends only on the temperature and the concentrations of nitric oxide [NO] and of oxygen atoms [O]. At 220°K (compare Figure 1)



XBL 7310-5508

Fig. 8.



XBL 7311-6743

Fig. 9.

this ratio of rates is plotted in Figure 8.

In the problem of unbalanced ozone production, the pure air reactions destroy 17 percent of the ozone formed and 70 percent is unaccounted for, even after considering the water reactions. To account for the natural ozone balance, we need some agents that destroy ozone about four times faster than oxygen atoms destroy ozone. From Figure 8 it can be seen that 4×10^8 molecules of NO per cubic centimeter destroy ozone about 4 times faster than the O_x reactions destroy ozone. Thus if nitric oxide, <u>as such</u>, averages about 4×10^8 molecules cm^{-3}, then the oxides of nitrogen are sufficient to account for the natural ozone balance.

A recent measurement[9] of nitric oxide as a function of elevation is given by Figure 9. The observed values vary from 2×10^8 at 16.5 km, to 8×10^8 at 28 to 32 km, and 5×10^8 at the highest observed elevation of 37.5 km. A comparison of Figures 8 and 9 shows that this observed nitric oxide distribution is sufficient to give a global ozone balance. It is sufficient to destroy about 70 percent of the ozone that is formed - per second, any second of the year. More measurements of NO_x in the stratosphere are needed to see if this observed profile of nitric oxide is typical or not.

Perturbed stratosphere

The natural stratosphere is estimated to have about $(3 \pm 1.5) \times 10^{34}$ molecules of NO_x ($NO + NO_2 + HNO_3$). Assuming a 1.5 year half-residence time for exhaust gases from the Concorde (16 to 19 kilometer flight level), one estimates 500 Concordes to increase the amount of NO_x in the stratosphere by 1.2×10^{34} molecules. Assuming a 2 year half-residence time for exhaust gases from the Boeing SST (20 to 21 kilometer flight level) and recognizing that it burns about 3 times as much fuel per hour as the Concorde, one estimates 500 Boeing SST to increase the amount of NO_x in the stratosphere by $4.5x10^{34}$. Thus 500 SST of either type promise more or less to double the natural quantity of NO_x in the stratosphere. The effect of this perturbation on the ozone shield is the subject of a series of model calculations.

Model calculations

The results of model calculations from seven different investigators are summarized in Table 3. The table is given in terms of elevation of SST flight, average NO_x emission rate in units of 10^8 molecules per square centimeter per second, and the calculated percentage reduction of the vertical ozone column. Part A gives results of early models that did not include nitric acid chemistry or that used older, incorrect values for nitric acid rate constants. Part B gives results from models that include nitric acid chemistry. The models indicate that about half the NO_x of the stratosphere is reversibly tied up as nitric acid. The seven investigators all found that oxides of nitrogen inserted in the stratosphere by supersonic transports reduce ozone. The calculations without consideration of nitric acid indicate about twice as great an ozone reduction as the calculations that include nitric acid. The modelers agree that for a given rate of input of NO_x, the ozone reduction increases with elevation of insertion. For example, for an insertion rate of $2.3x10^8$ molecules NO_x cm^{-2} sec^{-1} at 17, 20, and 25 kilometers, McElroy _et al_ found ozone to be reduced respectively 9, 18, and 26 percent.

Many calculations were made with a model of 500 Boeing SST, emitting 14 grams of NO per kilogram of fuel, and uniform world-wide spread of

Table 3. Summary of Results of Model Calculations

Injection Altitude km	Source Strength 10^8 molecules cm^{-2} sec^{-1}	Ozone Reduction %	References
	A. Early models without HNO_3 chemistry		
20	1.5	22	(8) Johnston, 1971
20	15	50	
20	1.5a	27	(10) Crutzen, 1972
20	6.2a	50	
20	0.31	8	(11) Chang et al, 1973a
20	0.62	17	
20	1.5	30	
20	4.6	46	
20	1.5a	18	(12) Hesstvedt, 1972
27	9.1	22	(13) Stewart et al, 1973
27	108	70	
	B. Models including HNO_3 chemistry		
20	0.31	2	(11) Chang et al, 1973b
	0.62	4	
	1.5	8	
	4.6	17	
17	0.31	0.9	
	0.62	1.8	
	1.5	3.7	
	4.6	9	
25	0.42	5.3	(14) McElroy et al, 1974
	2.3	26	
	4.3	40	
20	0.42	3.6	
	2.3	18	
	4.3	28	
17	0.42	1.8	
	2.3	9	
	4.3	14	
20	1.6	24	(15) Shimazaki, 1973
17	4.0	27	
17	4.0	37	

Table 3. Summary of Results of Model Calculations

Injection Altitude	Source Strength	Ozone Reduction	References
	10^8 molecules cm^{-2} sec^{-1}	%	
	C. Two dimensional models, including HNO_3 chemistry		
18	0.22	0.3	(12)Hesstvedt, 1973
23	0.22	1.7	45° summer
28	0.22	4.3	
18	0.22	<<0.1	45° winter
23	0.22	0.1	(12)Hesstvedt, 1974
28	0.22	0.6	Luther's K
17	0.40	1.0	values
17	0.65	1.7	
17	1.50	3.7	
17	4.0	9.0	
20	0.40	3.7	
20	0.65	5.8	
20	1.50	12	
20	4.0	27	

a. Emissions were not given in these units but the original NO_x increments were estimated to be approximately these values.

the exhaust; this model corresponds to 1.5×10^8 molecules NO_x cm^{-2} sec^{-1}. The models without nitric acid gave ozone reductions between 18 and 30 percent for this case, and models with nitric acid indicate ozone reductions of 7 to 15 percent. Some calculations have been made assuming a "local maximum" several times greater than the uniform world-wide average. Such a local maximum presumably occurs at the latitude of the North Atlantic and North Pacific flight routes. In 1971 it was felt that a ten-fold local maximum was possible[16], but in 1973 it is felt that a long-term, local maximum would be no greater than a factor of three higher than the global average. The models without nitric acid indicate a 50 percent reduction of ozone for the local maximum zone with 500 Boeing SST; the models with nitric acid indicate an ozone reduction of 17 to 30 percent.

The Concorde burns only about one-third as much fuel per hour as the proposed Boeing SST. Thus 500 Concerdes give a world-wide emission rate of about 0.5×10^8 and a three-fold local maximum rate of about 1.5×10^8 molecules NO_x cm^{-2} sec^{-1}. For insertions at 17 kilometers, current models indicate ozone reductions of about 1 to 3 percent on a world-wide basis or 3 to 7 percent for a three-fold local maximum. The models reported in 1972 and afterwards included both atmospheric motions and photochemistry. The disagreement between one model and another can largely be traced to the different assumptions made about motions and turbulence in the stratosphere.

Some cases in Table 3 fall far outside the range indicated by other models. Stewart <u>et</u> <u>al</u>[13] find a 70 percent ozone reduction, but their rate of NO_x insertion is very large. For an insertion rate of

0.22×10^8 at 23 km and 45°, Hesstvedt[12a] found a 1.7 percent reduction of ozone in the summer, but this went down to an 0.1 percent reduction in the winter. Radioactive debris in the stratosphere at 23 kilometers has a half time for removal of several years; and it is difficult to accept Hesstvedt's 17 fold change in ozone reduction by NO_x between summer and winter. Hesstvedt's winter stratosphere must have an unrealistic pattern of motions. Both the very large ozone reductions by Stewart *et al* and the very small ozone reductions by Hesstvedt appear to be in logical difficulty. Aside from these extreme cases, there is a concensus in 1973 among modelers that 500 SST would reduce ozone between 3 and 30 percent.

Injection experiments

One must always be worried about the completeness of any model calculation. Has some chemical reaction been omitted? How well is the rich spectrum of turbulence represented by the approximations used by the modelers? Has some important interaction mechanism been overlooked? Direct injection experiments where large amounts of nitrogen oxides are inserted in the stratosphere and followed for a year or more appear to be hopelessly complicated and expensive. It would be convenient if some past action, natural or artificial, had injected known amounts of nitric oxide into the stratosphere. Two such possibilities have recently been proposed.

Nuclear bombs

Foley and Ruderman[17] calculated the amount of nitric oxide that would be produced by nuclear bombs exploded in the atmosphere. This work was extended by Johnston, Whitten, and Birks[18], by Goldsmith *et al*[19], and by Gilmore[20]. There is agreement as to the amount of nitric oxide produced in the atmosphere

$$N_{NO} = (1.0 \pm 0.5) \times 10^{32}\ Y_{MT} \qquad \text{(II)}$$

where N_{NO} is the number molecules of nitric oxide and Y is the bomb yield in megatons. Nuclear bombs also produce carbon-14 which becomes a gas (CO or CO_2) similar in transport properties to NO or NO_2.

$$N_{C14} = 2.0 \times 10^{26}\ Y_{MT} \qquad \text{(III)}$$

Thus the observed carbon-14 is directly proportional to the nitrogen oxides produced by the bombs

$$N_{NO} = (0.5 \pm 0.25) \times 10^{6}\ N_{C14} \qquad \text{(IV)}$$

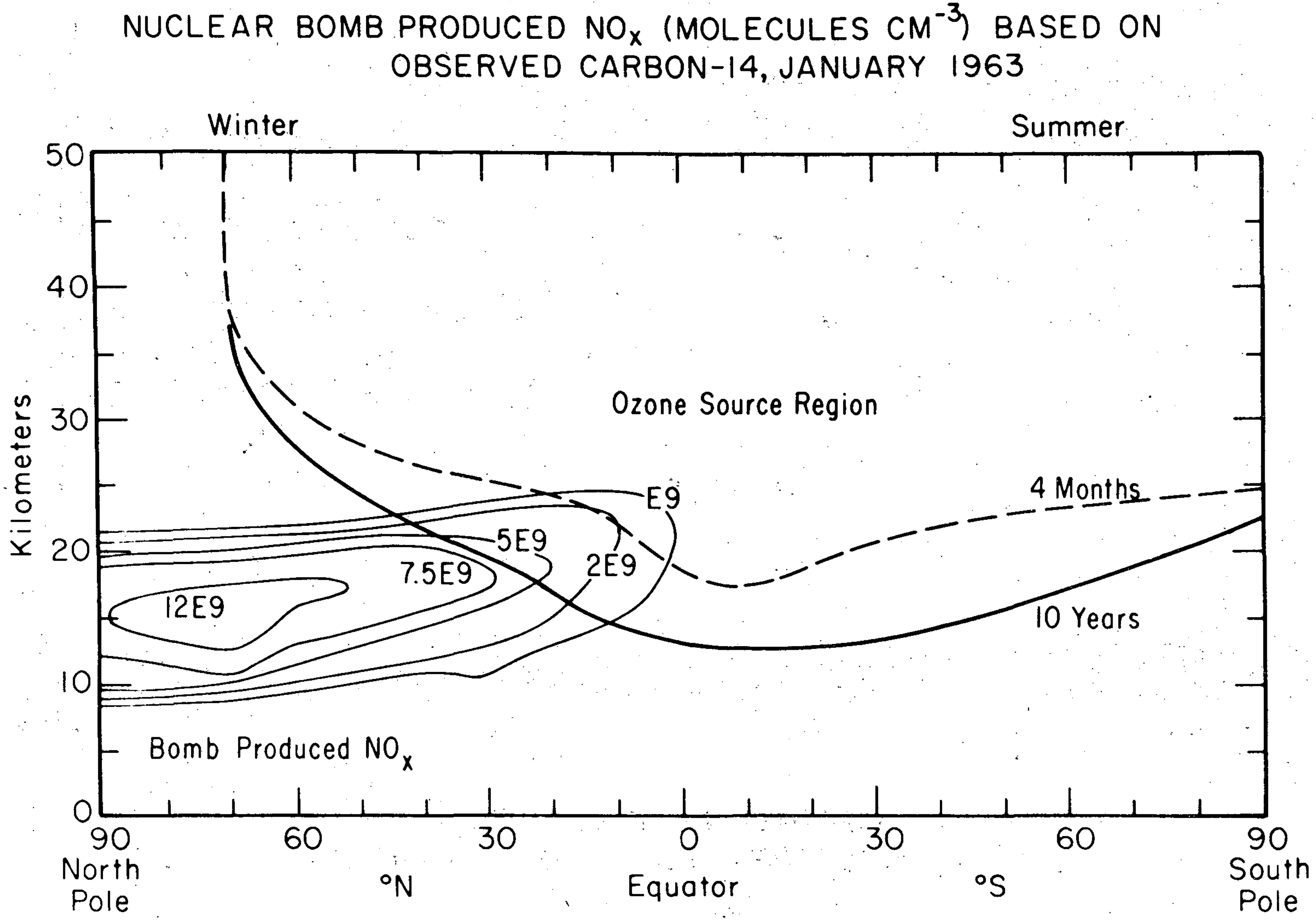
The records[5] of carbon-14 show that in January 1963, at the conclusion of the large-scale bomb tests of 1952-62, about two-thirds of the carbon-14 was in the stratosphere and one-third was in the troposphere.

The quantity of artificial NO_x in the stratosphere in January 1963 was $(1.8 \pm 0.6) \times 10^{34}$, as calculated from observed carbon-14. As noted above, the natural stratosphere is believed to have about $(3 \pm 1.5) \times 10^{34}$ molecules of NO_x, 500 Concordes are expected to increase stratospheric NO_x by about 1.2×10^{34} molecules, and 500 Boeing-type SST are expected to add about 4.5×10^{34} molecules of NO_x to the stratosphere. By any comparison, the quantity of NO_x injected into the stratosphere by nuclear bomb tests was large.

Casual inspection of the historical ozone data by Goldsmith _et al_[19] revealed no large or conspicious changes of ozone during the large-scale nuclear tests of 1952-62. However, Johnston[8] in 1971 showed that 4.2×10^{34} molecules of NO_x could reduce the ozone column anywhere between 3 and 50 percent depending on the distribution of NO_x in the stratosphere. Atmospheric motions determine the distribution of NO_x in the stratosphere, and Goldsmith *et al* gave no consideration to air motions and the actual distribution of artificial NO_x. As can be seen from Figure 6, atmospheric motions are very important in the ozone problem. One must consider atmospheric motions in this problem, either implicitly[8] by assuming a wide range of possible distributions or explicitly[10-15] by solving the coupled differential equations for air motions and photochemistry.

It is not necessary to resort to model calculations to determine the distribution of NO_x in the stratosphere following the nuclear bomb tests of 1952-62. These distributions may be reconstructed from the observed distribution of carbon-14. The global distributions of the artificial NO_x clouds in the stratosphere (based on the central number in Equation IV) for January 1963, January 1964, and January 1965 are given by Figures 10A, B, C.

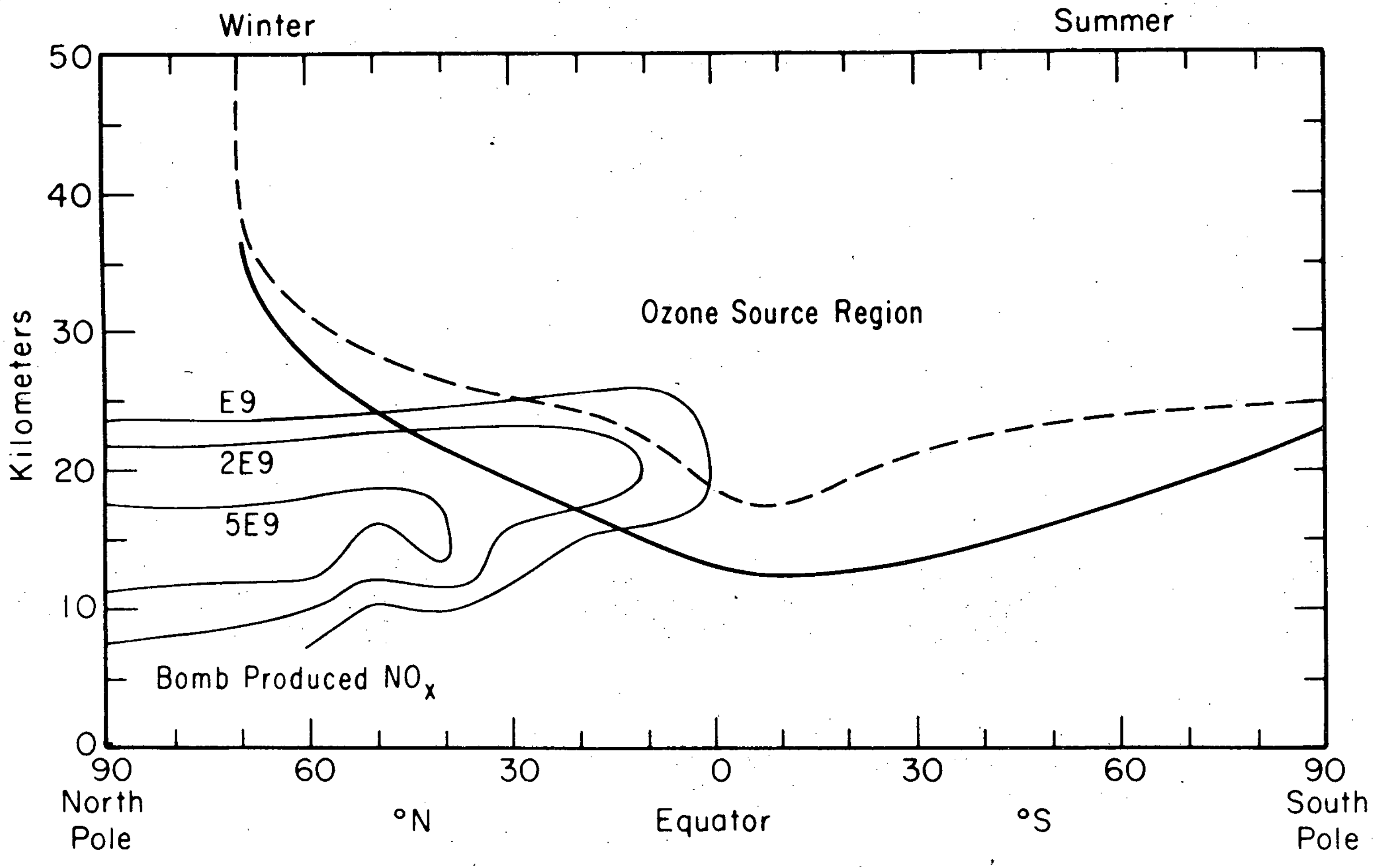
Immediately after the last large bomb tests of December 1962, the nitrogen oxides distribution (Figure 10A) was mostly at low elevations (below 17 kilometers) and far to the north. Of the massive test series of 1961-62, ninety percent was at the USSR station north of the Arctic Circle, and three-quarters of these tests occurred during or just before the polar night. These bomb clouds rose into the dense low-temperature stratosphere, Figure 1; and the vertical height attained was much less than that expected from the US tests at tropical stations[17]. Based on the distribution of NO_x given by Figure 10A, Johnston *et al*[18] found



XBL 7310-5514

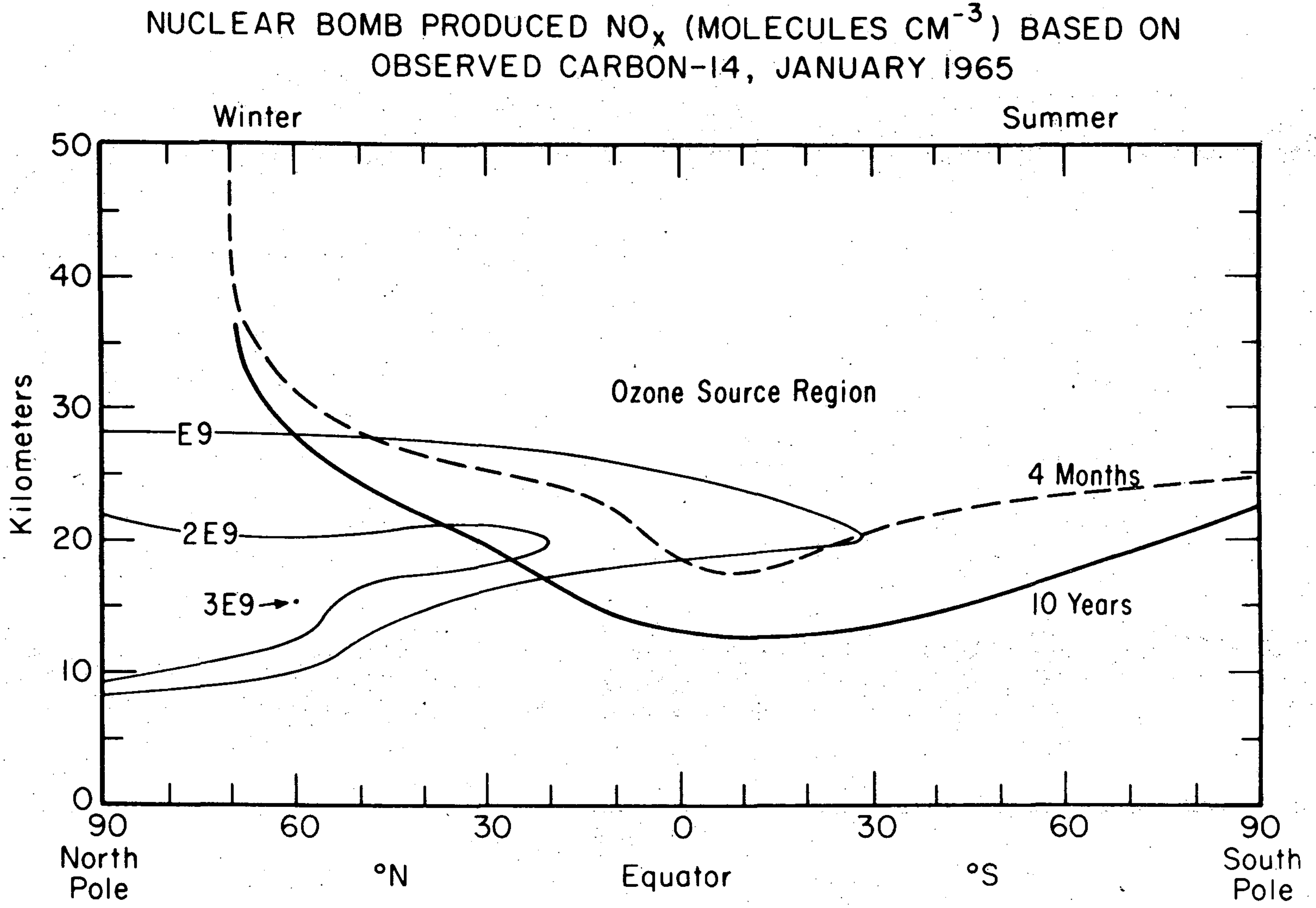
Fig. 10A.

NUCLEAR BOMB PRODUCED NO_x (MOLECULES CM^{-3}) BASED ON OBSERVED CARBON-14, JANUARY 1964



XBL 7310-5513

Fig. 10B.



NUCLEAR BOMB PRODUCED NO_x (MOLECULES CM^{-3}) BASED ON OBSERVED CARBON-14, JANUARY 1965

XBL 7310-5512

Fig. 10C.

steady-state ozone reductions as follows:

60°N	4.4 percent
45°N	5.7
30°N	5.4
15°N	6.3
0°	3.5

In model calculations that included atmospheric motions and the decrease of NO with time (compare Figures 10B and C) Chang et al[21] evaluated the ozone reduction at 45°N by the nuclear bomb tests, Figure 11. The maximum calculated ozone reduction was 4.0 percent.

The raw data for observed ozone at Arosa as presented by Goldsmith et al[19] are given by Figure 12. On the same scale, Chang's calculated change in ozone is shown, and it is very small compared to the scatter of the ozone data. One panel of Figure 12 gives Goldsmith's points at Arosa offset by Chang's calculated change of ozone. Simple inspection of raw data, such as these, is not the way to discover whether the observed ozone records reflect the small changes to be expected from the NO_x distribution of Figure 10A.

The distribution of NO_x a year and two years after the cessation of nuclear tests, Figures 10B and C, gives an interesting example of the scale and nature of atmospheric motions. The contour line, 1×10^9 molecules cm^{-3}, changed very slowly with time. In the temperate and polar zone it rose from 22 km in 1963, to 24 km in 1964, and to 28 km in 1965. The high concentration of NO_x at 15 km in the polar stratosphere decreased from 12×10^9 in 1963, to 5×10^9 in 1964, and to 3×10^9 in 1965. These data show the relatively rapid loss of material from the lowest stratosphere and the extremely slow, but ongoing,

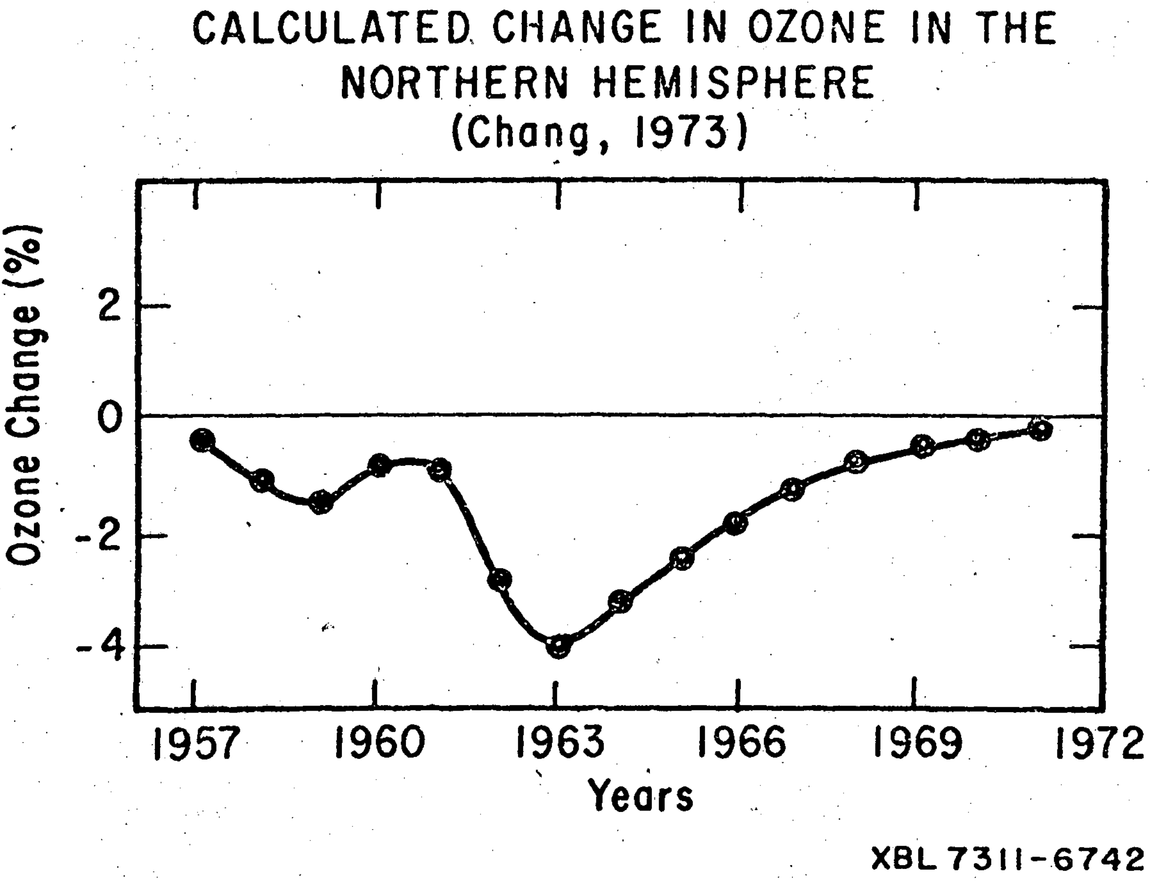
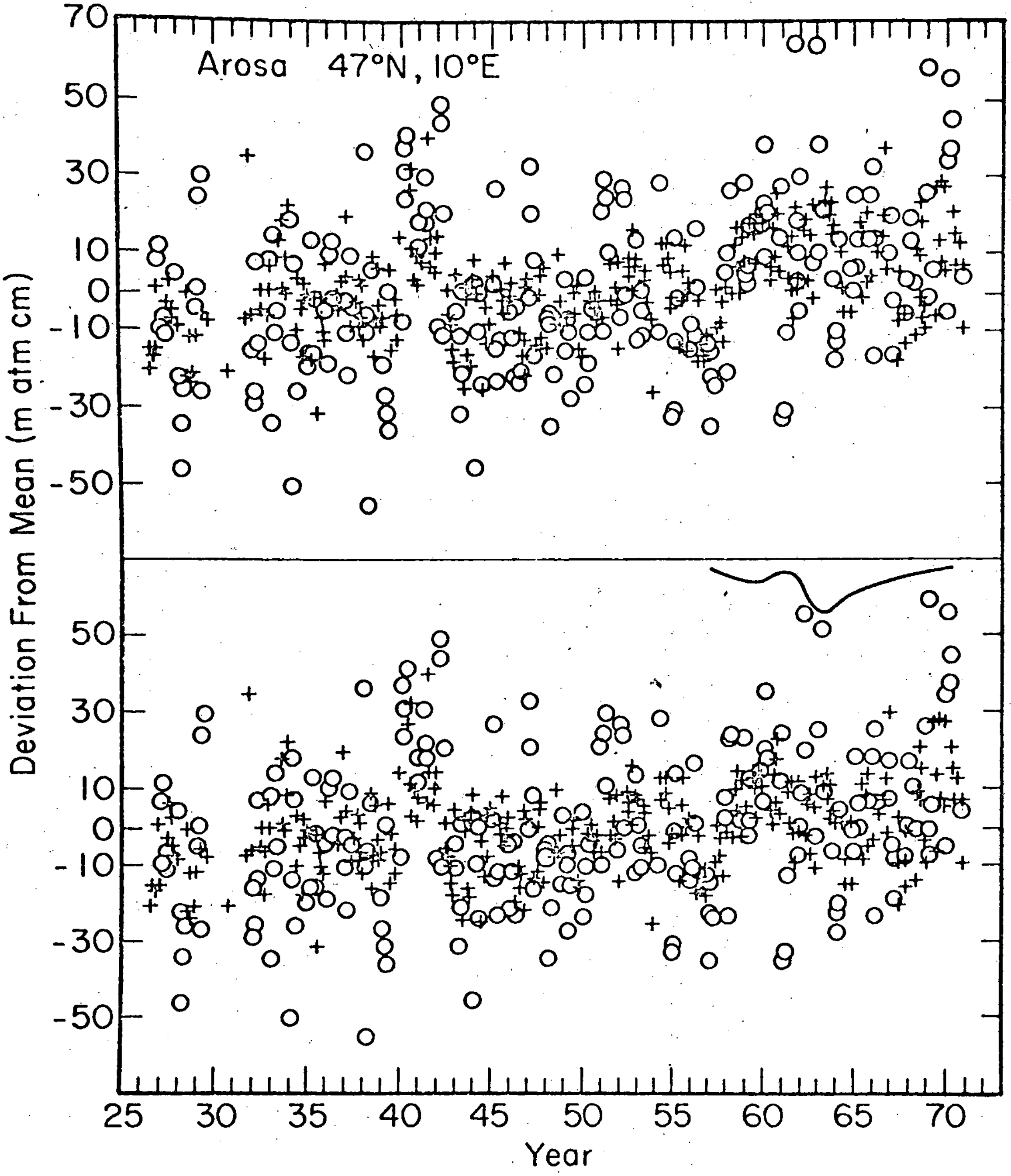

CALCULATED CHANGE IN OZONE IN THE NORTHERN HEMISPHERE
(Chang, 1973)
Ozone Change (%)
2
0
-2
-4
1957
1960
1963
1966
1969
1972
Years
XBL 7311-6742

Fig. 11.



XBL 7311-6739

Fig. 12.

vertical transport between 20 and 30 km.

One noticeable feature of Figures 10A, B, C is that only a small fraction of the NO_x from the nuclear bombs entered the "ozone source region", even when one considers the summer season in the northern hemisphere. Most of the bomb-produced NO_x lay low in elevation and far to the north in the "detached ozone region". This distribution was not conducive to a large reduction of ozone.

In 1971, Komhyr *et al* made a proper statistical study of the ozone data at several stations over the globe. They found a statistically significant increase of ozone during the period 1961-70. Johnston *et al*[18] applied Komhyr's method to all ozone-observing stations of the world, and these stations were averaged together with appropriate weighting factors. The results are given in Table 4. There were no statistically signficant changes in the southern hemisphere. In the northern hemisphere there was a marginally significant decrease of ozone of -2.3±2.1 percent during the three-year period 1960-62, and there was a statistically significant increase of ozone of +4.5±1.2 percent from 1963-70.

These statistical studies, especially that for the period 1960-62, are complicated by the "quasi-biennial" oscillations of ozone. From the analysis of these cycles by Angell and Korshover[23], it can be seen that 1962 corresponds to a maximum in the quasi-biennial ozone cycle; and thus the trends shown in Table 4 would have been larger if there had not been the biennial cycles. The record of global ozone before 1960 is lost for lack of enough data; there were too few stations before 1958 for any estimate to be made of global ozone.

Table 4. Average percentage ozone changes for all stations for 1960-62 (inclusive) and for 1963-70 (plus or minus two standard deviations).

Latitude	1960-62	1963-70
50-90°N	-3.8±3.2	+6.1±2.6
0-90°N	-2.3±2.1	+4.5±1.2
0-90°S	-1.0±6.0	-1.0±2.5

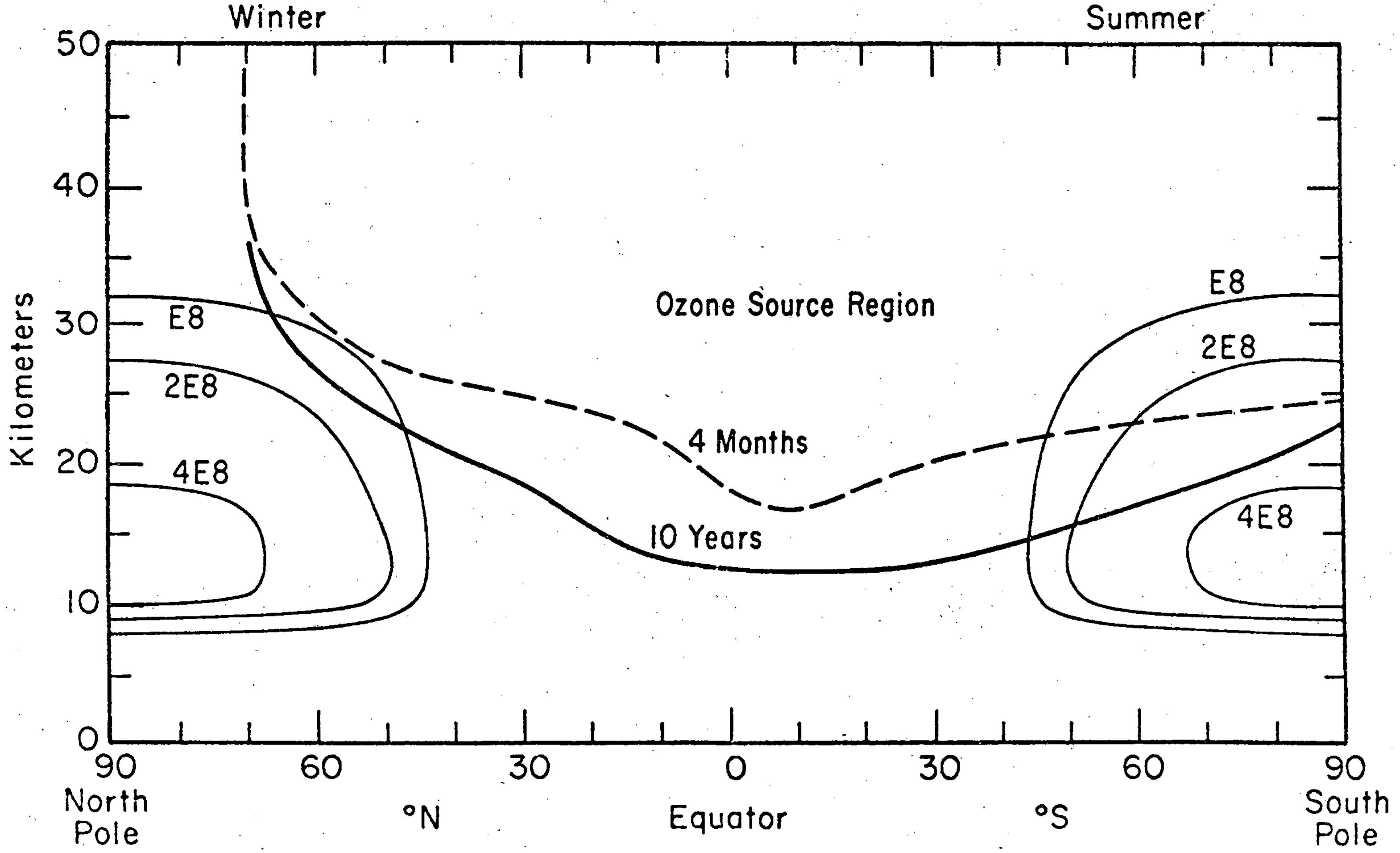
Cosmic rays.

Ruderman and Chamberlain[24] pointed out that a natural cycle with respect to cosmic rays may be interpreted in terms of the effect of nitrogen oxides on ozone. Cosmic rays are guided into the polar regions and deflected from equatorial regions by the Earth's magnetic field. This magnetic field changes markedly with the eleven year sunspot cycle. The cosmic rays produce atoms and ions in the stratosphere. This ion production has been measured as a function of latitude and elevation for several decades[25]. It is straightforward to calculate how much nitric oxide is produced from stopping the cosmic rays in the stratosphere. The production of nitric oxide is modulated in polar regions by the eleven-year sunspot cycle, and this modulated effect should spread with an increasing phase shift and decreasing amplitude from the poles to the equator.

The source strength of modulated nitric oxide in polar regions is given by Figure 13. The geographical distribution and the variation with elevation is based directly on observed rate of formation of ion pairs by cosmic rays. The magnitude of the nitric oxide production in Figure 13 is the difference between nitric oxide production at the maximum minus the production at the minimum with respect to the 11 year solar cycle. This modulation is about 50 percent of the maximum value of the signal itself. Although the maximum amplitude of the modulated signal occurs at about 14 kilometers, where NO_x photochemistry is very slow, a large amount of the NO_x production occurred above 25 kilometers, where NO_x destruction of ozone is fairly fast.

Angell and Korshover[23] have examined ozone data for evidence of correlation with the sunspot cycle. Only Tromso and Arosa have total

MODULATION AMPLITUDE OF NITRIC OXIDE FORMATION FROM COSMIC RAYS PER YEAR



XBL 7310-5539

Fig. 13.

ozone data that go back continually to the 1940's. Angell and Korshover analyzed these data, smoothed the data with a 30 month running mean to take out the biennial cycles, and found a pronounced correlation of total ozone with the sunspot cycle, Figure 14. There was a phase shift of 32 months at Tromso (70°N) and 38 months at Arosa (48°N) in close agreement with Ruderman and Chamberlain's calculations. The amplitude of the ozone change is greater at Tromso (closer to the source) than at Arosa in agreement with the calculations. The coherence between the sunspot cycle and the ozone response is largely destroyed in the late 1950's and early 1960's, presumably as an effect of nitric oxide from nuclear bombs.

There is a ±5 percent change of ozone at Tromso correlated with the 11 year sunspot cycle before the 1950's, Figure 14. The corresponding change of nitric oxide at Tromso is 0.2×10^{8} molecules cm^{-2} sec^{-1}. The total change of nitric oxides at the two poles is 7.4×10^{32} molecules per year. This quantity of NO_x would be produced in one year by about 50 Concordes or by about 17 Boeing-type SST. Thus it can be seen that the correlation of ozone with the sunspot cycle implies a substantially greater sensitivity of ozone to changes in nitrogen oxides than is given by the model calculations, Table 3.

There are two lines of evidence that the nuclear bomb tests of 1961-62 did reduce ozone by virtue of the nitric oxide formed by the bombs, Table 4 and Figure 14. Table 4 demonstrates ozone changes in the northern hemisphere that were not observed in the southern hemisphere. Figure 14 shows the breakdown of the cosmic-ray modulated changes of ozone when the nuclear bomb tests occurred. Ninety percent of the 1961-62 tests were conducted north of the Arctic Circle, and the bomb

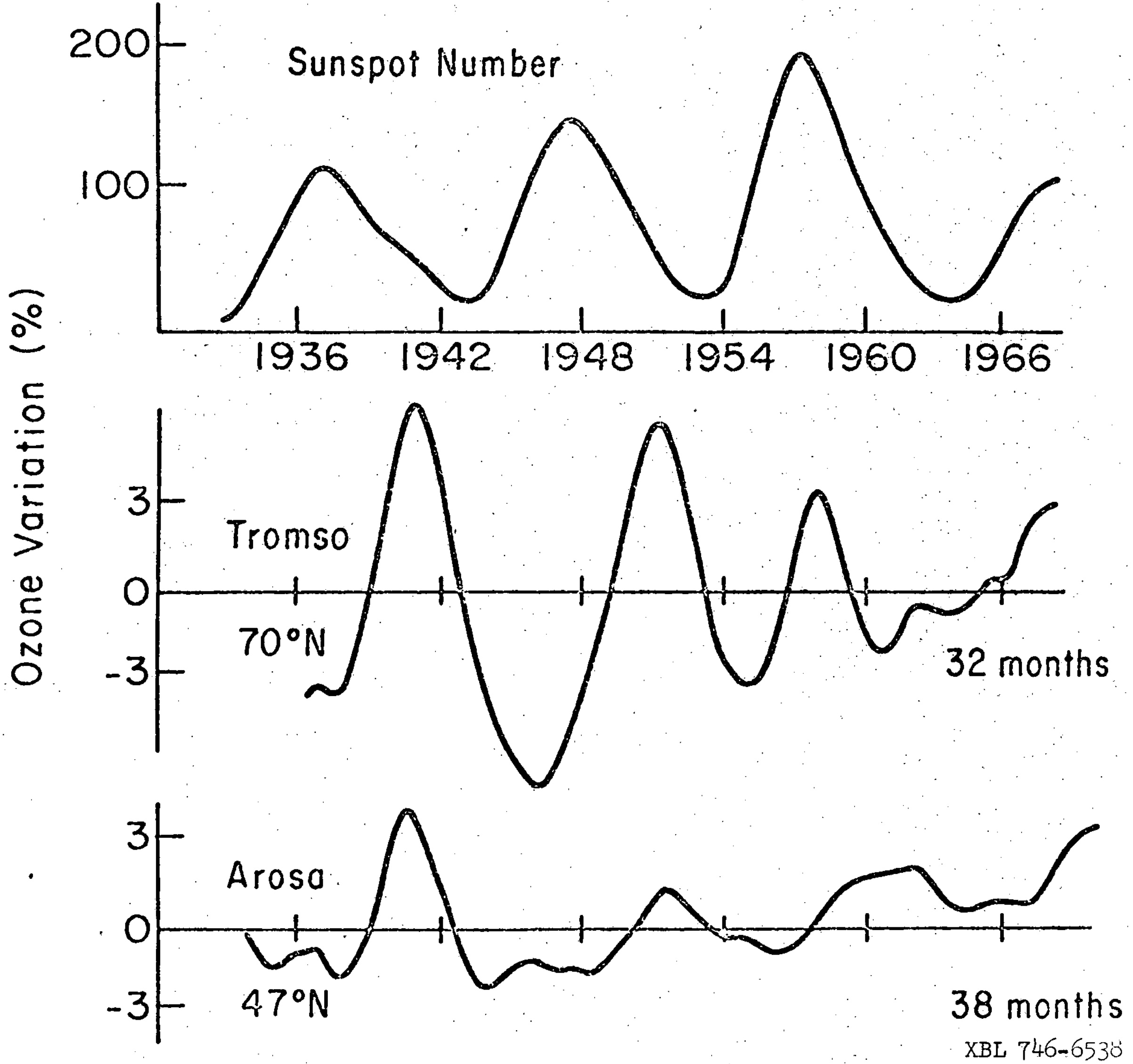

Sunspot Number
200
100
1936
1942
1948
1954
1960
1966
Ozone Variation (%)
3
Tromso
0
70°N
-3
32 months
3
Arosa
0
-3
47°N
38 months
XBL 746-6538

Fig. 14.

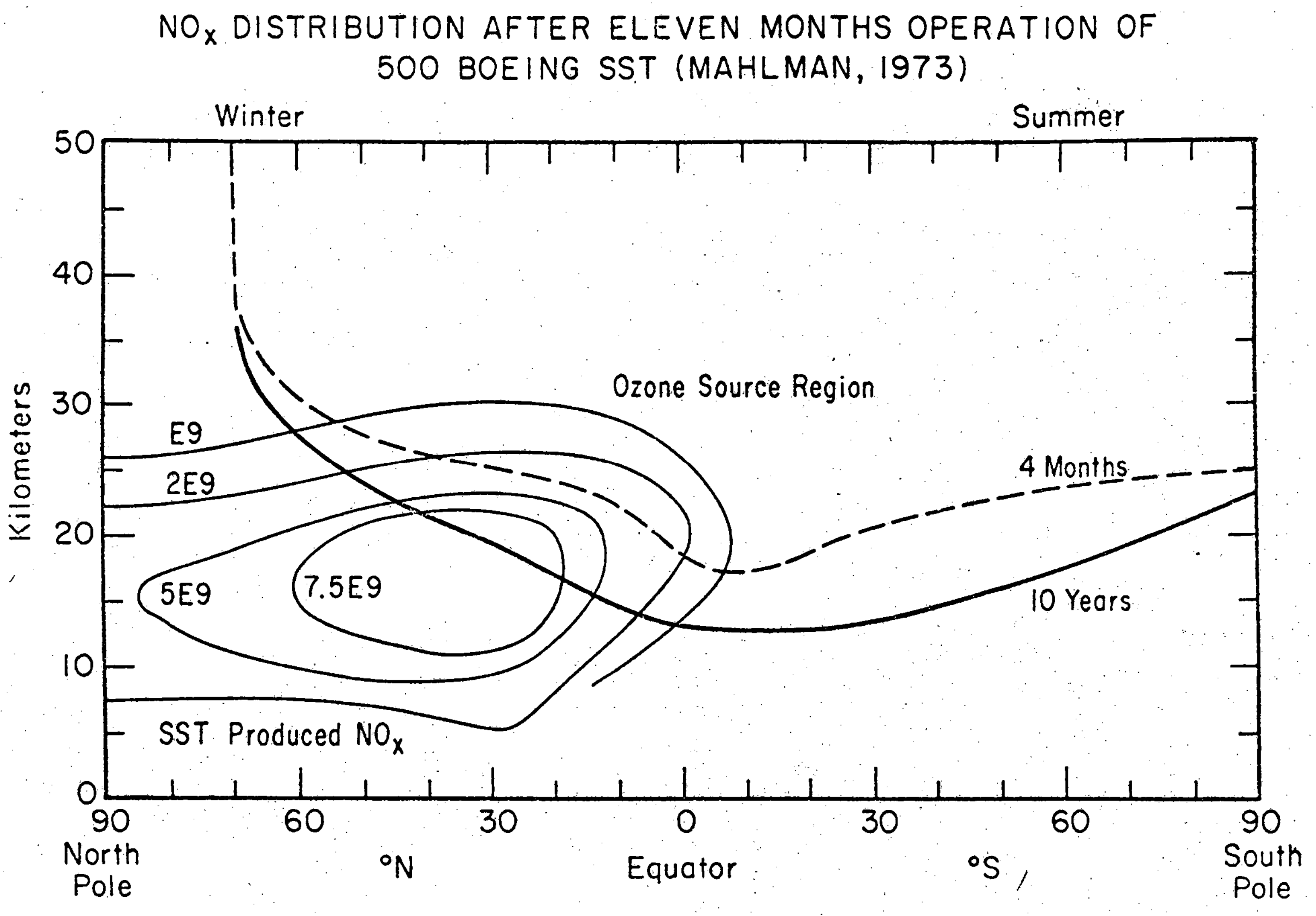
clouds did not rise nearly so high in the cold polar stratosphere as they would have in tropical regions[17]. As can be seen from Figures 10ABC, the bomb-produced nitric oxide mostly lay low in elevation and far to the north. If the 330 megatons of bombs 1961-62 had all been detonated in tropical regions, the nitric oxide cloud would almost certainly have spread between 20 and 30 kilometers, where there would have been a major overlap of artificial NO_x and the ozone formation region. In this case there probably would not have been any debate in 1971-74 as to whether artificial NO_x would reduce stratospheric ozone. There would probably have been a conspicuous decrease of ozone in the tropical zone, which would have been seen ten years ago.

SST exhaust

The distribution of NO_x from the SST exhaust has been calculated by Mahlman[26]. The exhaust gases were regarded as an inert tracer. Using a three-dimensional, global-circulation model, Mahlman followed the spread of an inert tracer injected at 20 kilometer elevation and 30°N latitude for a simulated period of 11 months. The resulting distribution of NO_x from 500 Boeing SST is given by Figure 15. This distribution is to be compared with those of the nuclear bombs (Figure 10) and from cosmic-ray modulation (Figure 13). The vertical distribution more nearly parallels that from the cosmic-ray modulation than that from the nuclear bombs, that is, the distribution is one that would have a strong effect on ozone.

Perturbed biosphere

Natural ozone in the stratosphere is the only effective shield of the biosphere against solar radiation between 300 and 250 nm[27]. DNA



NO$_x$ DISTRIBUTION AFTER ELEVEN MONTHS OPERATION OF 500 BOEING SST (MAHLMAN, 1973)

XBL 7310-5538

Fig. 15.

has a maximum absorption coefficient at 265 nm, and the long wavelength, extreme of this absorption band extends to just above 300 nm. Proteins have absorption maxima, typically around 275 to 285 nm, and these absorption bands also extend only slightly above 300 nm. In the natural atmosphere there is only a very small overlap of these absorption spectra with the ultraviolet radiation transmitted by ozone. Even so, there are now a number of damaging effects of ultraviolet radiation. Human skin is sunburned, made leather-like, aged; and skin cancers are primarily caused by ultraviolet solar radiation[27]. A relatively small increase in the normal exposure of human or animal eyes to ultraviolet radiation, as with reflection from snow or rocks, leads to temporary "snow-blindness"[28]. Plants are sensitive to ultraviolet radiation below 310 nm; they are subject to inhibition of photosynthesis, to stunted growth, and to death[27,29]. All higher forms of plants and animals have repair mechanisms against ultraviolet radiation damage, and their life seems to depend on the ability of the repair mechanisms to keep up with naturally occuring radiation damage[27C]. The action spectra for skin, eye, and plant damage are essentially the same, and they rather closely parallel the DNA absorption curve.

The sharp cut-off of solar radiation near 300 nm (Figure 3) is brought about by ozone. A reduction of ozone permits the transmission of radiation farther to the ultraviolet. The percentage increase of the biologically damaging radiation between 290 and 310 nm is greater than the percentage decrease of ozone. A four percent decrease in ozone would cause a 10 percent increase in this radiation. A large decrease of ozone would admit so much ultraviolet radiation between

290 and 310 nm that it would overwhelm the defenses of plants and some animals; the threshold for such effects has not yet been established.

It is sometimes argued that natural variations of ultraviolet radiation are large compared to that to be cause by SST reduction of ozone. Of course, this statement is true; every night and every day the ultraviolet radiation goes from zero to some finite value. The effect of DNA damaging ultraviolet radiation is cumulative, and it is the integrated dose over many years that produces skin cancer in individual human cases or causes mutations in plant species. The problem of ultraviolet damage is a long-term one, and short term cost-benefit calculations must be critically inspected. The problem is a global one. However, the half of the world between 30°N and 30°S is much more vulnerable than the rest of the world. Here the sun is often very nearly overhead, and the natural ozone shield is the thinnest in the world.

The problems related to ozone reduction by supersonic transports are not all solved yet. However, it is now reasonably well established that stratospheric ozone is vulnerable to artificial nitric oxide from supersonic transports. The unsolved problems largely concern the magnitude of the effect, not whether it exists.

Acknowledgement

This work was supported in part by the U. S. Atomic Energy Commission through the Inorganic Materials Research Division of Lawrence Berkeley Laboratory.

REFERENCES

1. a. Dütsch, H. U., Atmospheric Ozone and Ultraviolet Radiation, World Survey of Climatology, vol. 4, pp. 383-432, edited by D. F. Rex, Elsevier Publishing Company, Amsterdam, London, New York, (1969).

   b. Brewer, A. W. and Wilson, A. W., "The regions of formation of atmospheric ozone", Roy. Meterorol. Soc. Quart. J. 94, 249-265, (1968).

2. Canadian Department of Transport, Meteorological Branc, Ozone Data for the World, vols. 1-11, Toronto, Canada (1960-1970).

3. Krueger, A. J., "The mean ozone distribution from several series of rocket soundings to 52 km at latitudes from 58°S to 64°N, Goddard Space Flight Center, Greenbelt, Maryland. Preprint X-651-73-67 (February 1973).

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

5. Telegadas, K., "The seasonal stratospheric distribution and inventories of excess carbon-14 from March 1955 to July 1969, Health and Safety Laboratory Report 243. U.S. Atomic Energy Commission (1971), 3-86.

6. Johnston, H. S. and Whitten, G., "Reaction of ozone with nitrogen oxides at high altitudes, AGARD Conference on Atmospheric Pollution by Aircraft Engines (April 1973).

7. Crutzen, P. J., (a) "The influence of nitrogen oxides on the atmosphere ozone content", Quarterly J. Roy. Meteorol. Soc. 96 320-325 (1970). (b) "Ozone production rates in an oxygen-hydrogen-nitrogen atmosphere", J. Geophys. Res. 76, 7311-7237 (1971).

8. Johnston, H. S., (a) "Reduction of stratospheric ozone by nitrogen oxide catalysts from supersonic transport exhaust", Science 173, 517-522 (1971). (b) The same material in much fuller form, Lawrence Radiation Laboratory Report UCRL-20568 TID-4500.

9. Ackerman, M., Fontanella, J. C., Frimout, D., Girard, A., Gramont, L., Louisnard, N., Muller, C., and Nevejans, D., "Recent spectra of NO and NO_2" Aeronomica Acta 120, 1-13 (1973).

10. Crutzen, P. J., "SSTs - a threat to the earth's ozone shield", Ambio 1, 41-51 (1972).

11. a. First Annual Report, DOT-CIAP Program, Lawrence Livermore Laboratory, UCRL-51336 (February 1973).
b. Chang, J. S., Hindmarsh, A. C., and Matsen, N. K., "Simulation of chemical kinetics transport in the stratosphere", Lawrence Livermore Report UCRL-74823 (October 1973).

12. Hesstvedt, E., (a) "Effect of water vapor and nitrogen oxides upon the ozone layer" Symposium on Atmospheric Ozone, Arosa, Switzerland (August 1972); (b) "Effect of supersonic transport upon the ozone layer, studied in a two-dimensional photochemical model with transport", AGARD Symposium, London (April 1973); (c) Preprint of a report using Fred Luther's values of eddy diffusion coefficients.

13. Stewart, R. W. and Hoffert, M. I., "Stratospheric contamination experiments with a one-dimensional atmospheric model", AIAA/AMS International Conference on the Environmental Impact of Aerospace Operations in the High Atmosphere (June 11-13, 1973).

14. McElroy, M. B., Wofsy, S. C., Penner, J. E., and McConnell, J. C., "Atmospheric ozone: possible impact of stratospheric aviation", to be published, Journal of the Atmospheric Sciences, 1974.

15. Shimazaki, T., private communication.

16. Man's Impact on the Global Environment, Study of Critical Environmental Problems (SCEP), The MIT Press, Cambridge, Mass. (1970).

17. Foley, H. M. and Ruderman, M. A., "Stratospheric nitric oxide production from past nuclear explosions and its relevance to projected SST pollution", Journal of Geophysical Research 78, 4441 (1973).

18. Johnston, H. S., Whitten, G., and Birks, J., "The effect of nuclear explosions on stratospheric nitric oxide and ozone", Journal of Geophysical Research 78, 6107 (1973).

19. Goldsmith, P., Tuck, A. F., Foot, J. S., Simmons, E. L., and Nelson, R. L., "Nitrogen oxides, nuclear weapons testing, concorde, and stratospheric ozone", Nature, 244, 545 (1973).

20. Gilmore, F. R., "The production of nitrogen oxides by low altitude nuclear explosions", Preprint, Institute for Defense Analysis, July 1973.

21. Chang, J. S. and Duewer, W., "On the possible effect of NO_x injection in the stratosphere due to past atmospheric nuclear weapons tests", AIAA/AMS International Conference on the Environmental Impact of Aerospace Operations in the High Atmosphere (June 11-13, 1973).

22. Komhyr, W. D., Barrett, E. W., Slocum, G., and Weickman, H. K., "Atmospheric ozone increase during the 1960's", Nature 232, 390-391 (1971).

23. Angell, J. K. and Korshover, J., "Quasi-biennial and long-term fluctuations in total ozone", submitted to Monthly Weather Review (1973).

24. Ruderman, M. A. and Chamberlain, J. W., "Origin of the sunspot modulation of ozone: its implications for stratospheric NO injection", Institute for Defense Analysis JSS-73-18-3 (July 1973).

25. Neher, H. V., "Cosmic rays at high latitudes and altitudes covering four solar maxima", Journal of Geophysical Research 76, 1637-1651 (1971).

26. Mahlman, J. D., "A three dimensional stratospheric point-source tracer experiment and its implications for dispersion of effluent from a fleet of supersonic transport", AIAA/AMS International Conference on the Environmental Impact of Aerospace Operations in the High Atmosphere, Denver, Colorado (June 11-13, 1973).

27. a. Johnson, F. S., "SSTs, ozone, and skin cancer", Astronautics and Aeronautics 11, 16-21 (1973).

b. Blum, H. F., "Ultraviolet radiation of sunlight and skin cancer", Second Conference on CIAP (November 1972) 373-378.

c. Environmental Studies Board, Biological Impacts of Increased Intensities of Solar Ultraviolet Radiation, National Academy of Sciences, National Research Council (1973).

28. Pitts, D. G., "The effect of ultraviolet radiation on the eye" Report SAM-TR-69-10, USAF School of Aerospace Medium, Aerospace Medical Division (AFSC), Brooks Air Force Base, Texas (1969).

29. Knipling, E. B., "Ultraviolet radiation and photosynthesis", Second Conference on CIAP (November 1972) 386-393.

TITLES TO FIGURES

Figure 1. - Standard temperature for the globe, presented as "zonal average", January 15.

Figure 2. - Standard ozone concentration for the globe, presented as "zonal average", January 15. These data are based on 10 years of ground based data from 30 to 100 stations, supplemental by vertical rocket soundings. Recent satellite observations of global ozone have confirmed these ground-based data with a standard deviation of ±6 percent. 7E12 means $7x10^{12}$.

Figure 3. - Absorption spectrum for ozone. Light-absorption cross section σ as a function of wave length. $Ln\ I_o/I = \sigma\ NL$, where N is expressed in molecules cm^{-3}, L is the optical path in cm, and I is radiation intensity. The role of ozone in reducing solar radiation is indicated by the dashed curve; the vertical column of ozone is 0.37 cm (STP).

Figure 4. - Global rate of photolysis of molecular oxygen, calculated from observed intensity of sunlight above the atmosphere, the concentration of ozone shown in Figure 2, the observed light-absorption cross sections for oxygen and for ozone (ozone and oxygen compete for ultraviolet radiation below 250 nm). Note the almost uniform high rate of formation of oxygen atoms above 30 kilometers in the tropics and in the summer hemisphere.

Figure 5. - Ozone replacement time by photochemical processes. The local concentration of ozone (Figure 2) is divided (point-by-point) by the local rate of formation of ozone (twice

the rates of Figure 4). The ozone replacement time is to be interpreted as a measure of an instantaneous rate (compare the use of 4.5 billion year half time to characterize the rate of radioactive decay of uranium).

Figure 6. - The contrast between the location of ozone and the rate of photochemical formation of ozone, which shows the great importance of atmospheric motions in the global distribution of ozone. Note the large quantity of ozone, especially in the winter polar region, that is completely detached from the ozone formation region. Above the dashed line the ozone replacement time is 4 months or less; below the heavy solid line the ozone replacement time is greater than 10 years.

Figure 7. - Persistent time of an inert tracer, radioactive carbon-14 as carbon dioxide, in the global stratosphere. Between 1952 and the end of 1962, there were four periods of testing large nuclear bombs in the atmosphere. The duration of the periods of testing and the total bomb yields in units of megatons (MT) of TNT are indicated on the figure. After the conclusion of the large scale tests in December 1962, the half-times for removal of ^{14}C from the stratosphere were: 1963, 1.6 years; 1964, 2.4 years; 1965, 4 years; 1966, 4 years.

Figure 8. - Ratio of rate of destruction of ozone by the NO_2 catalytic cycle to rate of destruction of ozone by the pure air O_x reactions. The ratios are given at one temperature (220°K)

and for the full stratospheric range of the independent variables, nitric oxide and oxygen atoms. The average concentration of oxygen atoms in the stratosphere increases monotonically with elevation, and this relation gives approximately the elevations on the right-hand-side of the figure. Note that this ratio of rates depends only on nitric oxide concentration below 35 kilometers and only weakly on oxygen atom concentrations in the uppermost stratosphere.

Figure 9. - Concentrations of nitric oxide in the stratosphere as observed by Ackerman _et al_ (1973) by means of infrared absorption from a balloon. The horizontal bars represents the authors estimate of the uncertainty of the experimental determination.

Figure 10. - Nuclear-bomb produced NO_x based directly on the observed distribution of carbon-14. The yield of NO is taken to be 1.0×10^{32} molecules per megaton bomb yield.

A. Distribution of bomb-produced NO_x, January 1963 (Large scale nuclear bomb tests in the atmosphere ended December 1962).

B. Distribution of bomb-produced NO_x, January 1964.

C. Distribution of bomb-produced NO_x, January 1965.

Figure 11. - Calculated change of ozone in the northern hemisphere as a result of the increase in NO_x from atmospheric nuclear-bomb tests according to Chang (1973).

Figure 12. - Ozone data for Arosa for the period 1925-1970, expressed as deviation of the monthly mean from the long-term monthly average.

Lower. Data for Arosa as presented by Goldsmith et al (1973).

Upper. Data for Arosa with the calculated reduction of ozone by nuclear bombs (Figure 10) removed from the observed points. The magnitude of the calculated ozone reduction is shown at the base of the upper figure.

Figure 13. - Cosmic-ray produced nitric oxide, expressed as difference between maximum and minimum annual rate over the 11 year solar cycle. The distribution in terms of latitude and elevation is based on directly observed rate of ion-pair formation from cosmic rays. The translation from rate of ion-pair formation to nitric oxide formation is the only aspect of chemical modeling in this figure.

Figure 14. - Correlation of total ozone (expressed as deviation from average as in Figure 12) with the 11 year solar cycle. Upper curve, sunspot number; center curve, percent ozone variation of ozone at Tromso with 30 month running mean smoothing function; lower curve, percent ozone reduction at Arosa. Based on an analysis by Angell and Korshover (1973).

Figure 15. - The distribution of NO_x after 11 months of operation of 500 Boeing supersonic transports at 20 kilometers elevation and at 30° north latitude, according to a three-dimensional global circulation model (Mahlman, 1973).

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720