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Publication Date
1974-03-01

Submitted to Environmental Conservation

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March 1974

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

Pollution of the Stratosphere

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Abstract

Ozone in the stratosphere is vital to life on earth. Ozone is chemically unstable and is susceptible to catalytic destruction from a long list of chemical substances, including NO_x, HO_x, ClO_x, and metal oxides. In the stratosphere, these catalysts can be very active in ozone destruction, even when present at only one part of catalyst per 10,000 of ozone. Pollutants can reach the stratosphere in two ways: (1) Direct injection as with supersonic transports, military aircraft, rockets, or nuclear bombs. (2) Indirect injection from the troposphere may occur for inert, water insoluble substances, which will eventually work their way up into the stratosphere. The mass of catalysts sufficient to destroy stratospheric ozone at a significant, worldwide rate is less than the mass of the annual waste products from several industrial operations. In particular, the mass of nitrogen oxides from the exhausts of 500 supersonic transports is far above the threshold for significant catalytic destruction of ozone.

INTRODUCTION

That human activity is capable of global pollution has been considered only during the last few years (SCEP, 1970). Some people have felt that the atmosphere is so extensive that man-made pollution will be felt only near urban and industrial sources. However, the stratosphere is especially susceptible to pollution, largely by virtue of the vulnerability of ozone to catalytic destruction (Johnston, 1971 ab; Crutzen, 1972). A large reduction of stratospheric ozone would have deleterious biological effects (McDonald, 1971; Smith, 1972; Environmental Studies Board, 1973; Blum, 1973; Caldwell, 1973; Johnson, 1973; Knipling, 1973; Bartholic _et al_, 1974; Caldwell _et al_, 1974; Calkins, 1974; Urbach, 1974); and it might-or might not-have a long term effect on climate (Stone, 1974). There is a profound temperature inversion in the stratosphere that stabilizes the air against vertical mixing; pollutant residence half-times have been observed as long as four years (Telegadas, 1971). The stratosphere has only 12 per cent of the mass of the atmosphere, ozone averages only 3 parts per million of the stratosphere, and catalysts at only one part per ten thousand of ozone can rapidly decompose ozone. The mass of catalysts sufficient seriously to reduce stratospheric ozone is less than the annual waste products of numerous industrial processes. Thus, human activity is easily capable of reducing stratospheric ozone if artificial products of certain kinds are injected directly or indirectly into the stratosphere.

The most potent ozone-destroying catalysts recognized at present are: the free radicals derived from water (Hunt, 1966); oxides of nitrogen (Johnston, 1968, 1971; Crutzen, 1970, 1971, 1972); oxides of chlorine (Hoshizaki et al, 1973; Stolarski and Cicerone, 1973); and certain metallic oxides (Johnston, 1968). Recent model calculations by 8 different groups (Johnston, 1971; Crutzen, 1972; Hesstvedt, 1972, 1973, 1974; Chang et al, 1973a, 1973b; Stewart & Hoffert, 1973, 1974; McElroy et al, 1974; Whitten et al, 1973, 1974; Shimazaki, 1974) agree very well as to how much stratospheric ozone would be reduced by a given percentage increase in the oxides of nitrogen, such as would occur with supersonic transports. The formation of nitrogen oxides by cosmic rays has been shown to be physically connected to changes of stratospheric ozone (Ruderman & Chamberlain, 1973). Oxides of nitrogen are injected into the stratosphere by nuclear bombs (Foley & Ruderman, 1973); Goldsmith et al (1973) did not find a large effect of this nitric oxide on ozone; Chang et al (1973) and Johnston et al (1973) showed that the distribution of nitrogen oxides from nuclear bombs was such that only a 4 or 5 per cent reduction of ozone should have occurred, and a careful statistical analysis of all total-ozone data indicates effects of this size from the bomb tests (Johnston, 1973, 1974 a,b). A precursor to the oxides of chlorine is injected directly into the stratosphere by the space shuttle. Freons produced and used at the surface of the earth are inert in the troposphere and will probably be photochemically converted ClO_x catalysts in the upper stratosphere (Molina and Rowland, 1974).

These examples show that already there are multiple threats to stratospheric ozone by man-made pollutants.

THE TROPOSPHERE

The atmospheric shell from the surface of the earth to an elevation of about 15 kilometers is called the "troposphere". The temperature decreases with elevation in a manner that is strongly influenced by the evaporation and condensation of water. Air motions can be classified in terms of "winds" with horizontal and vertical components and of "turbulence", which are circular components of motion with a wide range of sizes. A parcel of air is transported by winds and by components of turbulence whose radius is large compared to the size of the parcel; its edges are diffused by turbulent eddies smaller than itself; and the parcel of air is occasionally cut in two by turbulent eddies that are about the same size as the parcel. Air in the troposphere is vigorously mixed, and water-soluble substances are washed out by rain in a few days.

THE STRATOSPHERE

At elevations that vary between about 10 kilometers in polar regions to 16 kilometers in tropical regions the temperature profile goes through a minimum (the "tropopause"), and it then increases with elevation up to about 50 kilometers. This region of temperature inversion is called the "stratosphere". Vertical motion is strongly inhibited in air with a temperature inversion. In the stratosphere winds circle the globe (often in a matter of a few days) in trajectories that more or less parallel latitude zones. Horizontal "eddy diffusion" mixes air from equator to poles typically within a few months. It requires a year or more for vertical "eddy diffusion" to produce a 10 kilometer spread to a sample of air. There is a broad slow upwelling of tropospheric air into the stratosphere in equatorial zones, which tends to restrict horizontal spread of stratospheric air from one hemisphere to another. There are systematic ejections of air from the stratosphere to the troposphere associated with the "jet stream" at temperate latitudes. In the polar winter night the distinction between the troposphere and stratosphere almost fades away; and when sunlight returns to the polar region in the spring, there is a release of stratospheric air into the troposphere, the "spring overturn". At the conclusion of the large scale nuclear bomb tests in December 1962, there was a large cloud of radioactive carbon-14 in the stratosphere. The quantity of carbon-14 in the stratosphere on January 1, 1964 decreased to one-half in 2.4 years; the quantity there on January 1, 1965 decreased by a factor of two in four years (Telegadas, 1971). A detailed study of the history of this cloud of radioactivity indicates a residence half-time for pollutants of about one year in the lower (15 km) polar and temperate stratosphere, but a residence half time of many years in the 20 to 30 kilometer region.

Ozone, O_3, is a natural trace ingredient of the stratosphere (Dütsch, 1969). It is produced and destroyed by photochemical reactions, and it is moved about by air motions. The photochemical reactions of ozone are the primary source of local heating in the stratosphere, which sets up the temperature inversion. Also, the photochemical reactions of ozone determine the distribution of solar radiation that enters the troposphere.

SOLAR RADIATION

Solar X-rays, ionizing radiation, and ultraviolet radiation below 190 nm are removed by air molecules above the stratosphere. In the stratosphere, ultraviolet radiation below 242 nm is completely absorbed by oxygen, O_2, and by ozone, O_3. Ultraviolet radiation between 242 and about 300 nm is almost totally absorbed by ozone, and ozone is the only effective absorber of this radiation. Ozone partly absorbs ultraviolet radiation up to 340 nm, and also very weakly absorbs visible radiation. The ozone absorption cross section $\sigma(\ln I_0/I = \sigma NL$, with N in molecules cm^{-3} and L in cm) is plotted against wavelength in Figure 1, and the fraction of direct sunlight transmitted by ozone is included on the figure. Ultraviolet radiation reaching the biosphere is also affected by molecular and particulate scattering, clouds, reflection from the earth's surface, etc; considering these effects, Green _et al_ (1974) evaluated the quantity of ultraviolet radiation between 290 and 310 nm reaching surface layers of the atmosphere as a function of the overhead ozone column.

BIOLOGICAL ROLE OF STRATOSPHERIC OZONE

Biological systems are sensitive to the ultraviolet radiation that is screened out by ozone (McDonald, 1971; Smith, 1972; Environmental Studies Board, 1973; Blum, 1973; Caldwell, 1973; Johnson, 1973; Knipling, 1973; Bartholic _et al_, 1974; Caldwell _et al_, 1974; Calkins, 1974; Urbach, 1974). DNA has a peak absorption at 265 nm and proteins have a peak absorption at about 285 nm.

Both of these absorption spectra exponentially approach zero above 300 nm. The action spectra for skin damage in humans, for plant damage, and other biological effects parallel the DNA and protein absorption spectra.

There is a small overlap between the solar radiation transmitted by ozone (Figure 1) and a biological sensitivity curve. The product of these two exponentially decreasing functions gives a roughly bell-shaped curve centered just above 300 nm (at a wavelength that depends on solar angle and other factors), and the area under this curve is a measure of potential biological damage (Green & Mo, 1974). The area under this curve increases rapidly with decreasing ozone. A recent estimate (Urbach, 1974) of the increase in skin cancer in the United States as a function of long-term decrease of ozone is given in Table 1. There is a considerable amount of current research (CIAP, 1974) examining the susceptibility of other biological systems (one cell plants and animals, insects, wild plants, domestic plants, etc) to a systematic increase of ultraviolet radiation below 310 nm.

PHOTOCHEMISTRY OF NATURAL OZONE

Ozone (Dutsch, 1969) is formed from oxygen and sunlight at wavelengths shorter than 242 nm.

Table I. Estimated increase in annual number of cases of skin cancer in the United States (based on population of 200 million) as a function of systematic long-term reduction of stratospheric ozone (Urbach, 1974).

Decrease of Ozone %	Increase of Skin Cancer Cases per year
5	42,000
10	88,000
20	200,000
40	536,000

(1) $O_2 + h\nu(\text{below } 242 \text{ nm}) \rightarrow O + O$

(2) $O + O_2 + M \rightarrow O_3 + M$

(2) $O + O_2 + M \rightarrow O_3 + M$

net: $3\ O_2 + h\nu \rightarrow 2\ O_3$

Ozone weakly absorbs visible radiation and strongly absorbs ultraviolet radiation to shield the surface of the earth against wavelengths less than 310 nm, Figure 1. Although this act of absorption dissociates ozone to an oxygen atom and molecule, it does not destroy ozone because the oxygen atom quickly reforms ozone:

(3) $O_3 + h\nu \rightarrow O_2 + O$

(4) $O + O_2 + M \rightarrow O_3 + M$

net: no chemical reaction

If stratospheric ozone should be reduced, additional ultraviolet radiation (290-310 nm) would reach the surface of the earth. This radiation would not form tropospheric ozone from oxygen (it requires 242 nm radiation to do that), but it would have deleterious biological effects.

Ozone, which is uniquely valuable as an ultraviolet filter, is an extremely unstable substance (Johnston, 1968, 1971, 1972, 1973 a, 1974 a, 1974 b). The overall chemical reaction whereby it reverts to molecular oxygen

$2\ O_3 \rightarrow 3\ O_2$

$\Delta H° = -31{,}100 \text{ cal mole}^{-1}$

$\Delta S° = 33.45 \text{ cal mole}^{-1} \text{ deg}^{-1}$

involves a large release of energy, and it gives a large increase of entropy. Thus, ozone is doubly unstable, both with respect to energy and with respect to entropy. Ozone decomposes exothermally. This great instability of ozone is very familiar in the laboratory: concentrated gaseous or liquid ozone detonates at the slightest provocation; and dilute gaseous ozone mysteriously disappears, since its decomposition is rapidly catalyzed by traces of the oxides of nitrogen, oxides of chlorine, free radicals based on water, and by several metals and metal oxides.

In the natural stratosphere, ozone attains a balance between photochemical production from sunlight and oxygen, transport by air motions, and chemical destruction by several different mechanisms. Some processes that destroy ozone, $2\ O_3 \rightarrow 3\ O_2$, are as follows:

A. Pure air mechanism, O_x system (Chapman, 1930)

$$\begin{array}{l} O_3 + h\nu \rightarrow O_2 + O \\ \underline{O_3 + O \rightarrow O_2 + O_2} \end{array}$$

net: $2\ O_3 + h\nu \rightarrow 3\ O_2$

B. Water reactions, HO_x system (Hunt, 1966)

$$\begin{array}{l} HO + O_3 \rightarrow HOO + O_2 \\ \underline{HOO + O_3 \rightarrow HO + O_2 + O_2} \end{array}$$

net: $2\ O_3 \rightarrow 3\ O_2$

C. NO_2 catalytic cycle, NO_x system (Crutzen, 1970)

$$\begin{array}{l} NO + O_3 \rightarrow NO_2 + O_2 \\ O_3 + h\nu \rightarrow O_2 + O \\ \underline{NO_2 + O \rightarrow NO + O_2} \end{array}$$

net: $2\ O_3 + h\nu \rightarrow 3\ O_2$

D. Chlorine catalytic cycle, ClO_x system (Hoshizaki et al, 1973; Stolarski & Cicerone, 1973)

$$Cl + O_3 \rightarrow ClO + O_2$$
$$O_3 + h\nu \rightarrow O_2 + O$$
$$\underline{ClO + O \rightarrow Cl + O_2}$$
$$\text{net: } 2\,O_3 + h\nu \rightarrow 3\,O_3$$

E. Surface catalysis including destruction at the earth's surface. The materials Ag_2O, MnO_2, MgO, and CuO are known to be especially powerful catalysts for ozone destruction (Johnston, 1968).

The relative importance of these various mechanisms of ozone destruction in the natural stratosphere is given by Table 2. The degree of destruction of ozone by the O_x mechanism, by the HO_x mechanisms, and by transport to the troposphere can be calculated with a fair degree of reliability, and these destruction processes add up to about 30 per cent of the rate of formation of ozone. The oxides of nitrogen could destroy the other 70 per cent, if the concentration of NO averages about 4 x 10^8 molecules cm^{-3} and if the nitrogen oxides are favorably distributed in the stratosphere (concentrated between 28 and 40 km). During the past year, several stratospheric measurements of NO_x have been made (Ackerman et al, 1973; Murcray et al, 1974; Lazrus & Gandrud, 1974; Ridley, Schiff, et al, 1974; Stone et al, 1974; Loewenstein et al , 1974; Girard, 1974; Farmer et al, 1974; Brewer et al, 1974). The observed quantities of NO are low (1 x 10^8 molecules cm^{-3}) in some times and places and much higher (8 to 20 x 10^8 molecules cm^{-3}) in other instances.

Table II. Global ozone balance for formation and destruction of ozone by various mechanisms (Johnston & Whitten, 1973; Johnston, 1974 ab).

Mechanism	Relative ozone rate, %
Formation, O_2 + sun	+ 100
Transport to troposphere	-1
Destruction by O and O_3	-18
Destruction by water reactions	-11
Destruction by NO_x catalysts	- 50 to - 70
Destruction by ClO_x, MO_x, or other	- 20 to 0

It appears that the oxide of nitrogen are present in amounts that are sufficient to destroy 70 per cent of the naturally produced ozone, but it is an open question whether natural chlorine or natural particulates (from meteorites) also play a non-negligible role.

RELATIVE MASS OF ATMOSPHERIC SUBSTANCES AND INDUSTRIAL PRODUCTS

We now return to the question as to whether human activity can significantly perturb the stratosphere. Atmospheric quantities, both in units of number of molecules and in units of millions of tons, MT, are given in Table 3. To get some perspective on these quantities, it may be noted that the worldwide mass of fossil fuel burned per year in 1960 was 3.4×10^3 megatons (SCEP, 1970, p. 150), or about equal to the ozone inventory (When someone suggests manufacturing ozone and releasing it in the stratosphere to repair its loss there, one should note this comparison). The natural NO_x inventory is uncertain to about a factor of three, but it is a small compared to the mass output of a number of industrial operations.

If 500 Boeing-type supersonic transports flew in the stratosphere 8 hours per day for two years, burned 60,000 by fuel per hour per SST, and emitted 18 grams of NO_2 per kilogram of fuel burned, the quantity of NO_x injected into the stratosphere would be 4.2×10^{34} molecules or 3 MT calculated as NO_2, which is equal to or up to three times greater than the natural inventory. The Concorde SST burns fuel at only one third the rate per hour as the proposed Boeing SST, and thus these figures should be reduced by a factor of three in comparisons with 500 Concordes.

Table III. A. Global quantities in the natural atmosphere and stratosphere.

	Molecules	MT[a]
Atmosphere	1.1×10^{44}	5.2×10^{9}
Stratosphere	1.3×10^{43}	6.4×10^{8}
Ozone	4.2×10^{37}	3.3×10^{3}
NO, NO_2, HNO_3	$(1.5 \text{ to } 4.5) \times 10^{34}$	1 to 3
HCl[b]	$< 10^{34}$	< 0.7

a. MT, megatons, 10^{12} grams.

b. Farmer _et al_, 1974.

B. Magnitude of actual and projected industrial processes summed over 2 year period (worldwide).

Use of fossil fuels		7000
NO_x (500 Boeing SST)	4.2×10^{34}	3
NO_x (500 Concorde)	1.4×10^{34}	1
HCl (one space shuttle per week).		0.007

This comparison of natural and artificial NO_x in the stratosphere was based on an assumed two-year mean residence time and the estimated stratospheric inventory of NO_x. There are two other independent comparisons that lead to similar conclusions: one compares the natural rate of formation of NO_x in the stratosphere with the rate of NO_x emission from 500 SST, and the other compares the rate of removal of NO_x (as HNO_3) from the stratosphere with the rate of NO_x emission from 500 SST. Nitrous oxide is formed in the soil by bacteria, is inert in the troposphere, slowly diffuses into the stratosphere, and is destroyed there in three ways - one of which produces nitric oxide

$$N_2O + O(^1D) \rightarrow 2\ NO$$

Since Crutzen, (1971) first carried out this calculation, this rate of production of nitric oxide in the stratosphere has been evaluated by many different investigators (McElroy & McConnell, 1971; Nicolet & Vergison, 1971). Isaksen (1973) evaluated the process for the entire globe and found an average production rate of (4 to 5) x 10^{26} molecules per second. The average emission of nitric oxide from the 500 SST as described above is 6.5 x 10^{26} molecules per second. Lazrus and Gandrud (1974) reported observations of nitric acid vapor as a function of elevation and season from Alaska to the southern tip of South America. In the lowest stratosphere, NO_x is mostly converted to nitric acid by the reaction

$$HO + NO_2 \overset{M}{\rightarrow} HNO_3$$

and as this nitric acid passes into the troposphere it is rapidly washed out by rain. From the distribution of the nitric acid vapor and from a model based on previously observed removal of radioactive debris from the stratosphere, Lazrus and Gandrud calculated the rate of removal of nitric acid vapor to be $(4.2\pm2.1) \times 10^{26}$ molecules per second. This quantity is in excellent agreement with Isaksen's calculation for the global source, and is substantially less than the expected input from 500 Boeing-type SST. The global sources and sinks of natural and artificial oxides of nitrogen in the stratosphere are summarized in Table 4.

These calculations have all been for a uniform world-wide average insertion of artificial NO_x from the SST. There is greatly restricted flow between the two hemispheres, and a zone of heavy traffic (such as North Atlantic, North Pacific latitudes) could develop a long-term local maximum about three times higher than the calculated uniform worldwide average. Relative to the average natural rate of formation of NO in the stratosphere, 500 Concordes emit 50 per cent as a world-wide average or about 150 per cent as a local maximum. The corresponding NO emissions from 500 Boeing SST are 150 per cent on a worldwide basis and 450 per cent for the heavily traveled corridor.

MODEL CALCULATIONS OF REDUCTION OF OZONE BY OXIDES OF NITROGEN

From the previous analysis, it seems that 500 SST would increase stratospheric input of nitrogen oxides between 50% and 450%. How much would such an increase in nitrogen oxides reduce ozone in the stratosphere? This question has been investigated by at least 8 different groups during the past three years. The first

Table IV. Comparison of natural and artificial global sources of stratospheric oxides of nitrogen.

	Global rate 10^{26} molecules sec^{-1}	Reference
Natural source of NO_x from N_2O.	4 to 5	Isaksen (1973)
Natural sink of NO_x as HNO_3.	4±2	Lazrus _et al_ (1974)
500 Boeing SST	6.5	
500 Concorde SST	2.2	

study (Johnston, 1971) used a simple "box" model for atmospheric motions and the distribution of natural and artificial oxides in the stratosphere, several subsequent studies used eddy-diffusion models of one-dimensional motion, and some recent studies have used two-dimensional transport models. The 1971 method will be briefly reviewed, and results from all available models (March 1974) will be presented.

OZONE REDUCTIONS AS CALCULATED IN 1971

In 1971 there were no direct experimental observations of NO or NO_2 in the stratosphere, although there were a few measurements of NO above and below the stratosphere and there were a few measurements of nitric acid vapor in the stratosphere. From these considerations, a non-uniform distribution of $NO_x(NO + NO_2)$ was proposed, Figure 2. This estimated distribution of NO_x is compared with a distribution asserted by Goldberg (1972) and with an observed distribution reported by Ackerman & Muller (1972). The distribution of exhaust gases from the supersonic transports was also not known in 1971, and thus a wide range of possibilities was considered. One extreme model was that there was virtually no vertical diffusion, that the exhaust gases filled a uniform world-wide shell one kilometer thick, and that this material left the stratosphere in flat unmixed sheets at the polar "spring overturn". This model is illustrated by the narrow block in Figure 3. The quantity of NO_x in this shell between 20 and 21 kilometers was the two year accumulation from 500 Boeing SST (This quantity was estimated to be 4.8×10^{34} molecules in 1971; the current estimate is 4.2×10^{34} molecules). Alternatively to this very narrow spread, the two year burden of exhaust gases might be spread over a band averaging x kilometers in thickness, variously indicated in Figure 3.

The model of atmospheric motions used in these calculations was full steady state: steady state unperturbed ozone for reference, steady number of SST in the perturbed model, balanced injection and removal of artificial NO_x (via polar spring overturn), uniform world-wide horizontal spread, steady-state chemistry and photochemistry, but with interactive distribution of radiation and computed ozone. This model does not derive the NO_x distribution of the perturbed and unperturbed atmosphere, and thus it is very incomplete, especially to meteorologists. To solve the total problem, it is, of course, necessary to derive realistic distributions for natural and perturbed NO_x and ozone. However, to assess the magnitude of the power of nitrogen oxides to reduce stratospheric ozone, the full steady state model is reliable.

With this self-consistent, full steady-state model and with the natural background shown in Figure 2, the percentage reduction of the vertical ozone column was calculated for the various spreads of artificial NO_x as indicated by Figure 3. For the thin one-kilometer thick shell, ozone was reduced to a very low value, but little of the ozone column was contacted, and the overall reduction was only 3 per cent. For wider vertical spreads of the fixed quantity of NO_x, there was a greater reduction of the ozone column than for the narrow vertical spread: 3% for 1 km, 12% for 4 km, 23% for 10 km, and 20% for 16 km vertical spread. An intermediate spread of about 10 kilometers causes greater ozone reduction than a much narrower or much wider vertical spread. In case there was a 10-fold local maximum over the heavily traveled north temperate zone (a value regarded as reasonable in 1971, and also it has some aspects of a safety factor), similar calculations gave ozone column reductions between 3 per cent and 50 per cent, depending on the vertical spread of exhaust.

A notable aspect of these model calculations is that it shows the great importance of the distribution of stratospheric pollutants. For a given NO_x background (Figure 2) and for a fixed number of molecules of artificial NO_x (4.8×10^{34}) the steady-state reduction of stratospheric ozone varies between 3 per cent and 50 per cent depending on vertical and horizontal distribution. It requires a realistic consideration of air motions in the stratosphere to determine the distribution of exhaust gases; meteorology and chemistry are equally important in this problem.

Late in 1971, calculations were made for a continuous range of increases in the NO_x in the stratosphere and for a wide range of uniform NO_x backgrounds. These calculations were not tied to any number of SST. These calculations were for the various vertical spreads indicated in Figure 3. The maximum ozone reduction in each case is plotted in Figure 4, which gives percentage residual ozone for a wide range of increases of NO_x ($\Delta NO_x/NO_x$) for four values of the assumed NO_x background. These 1971 calculations are compared below with similar calculations made in 1973 and 1974, including various degrees of atmospheric motion.

RECENT RESULTS OF CALCULATED OZONE REDUCTIONS

A portion of results of model calculations by 8 different investigators is given in Table 5. These results were abstracted by Chang and Johnston (1974) from the original articles and reports, and the shortened list given here is selected to illustrate the range of current modelers. All results by these eight investigators that give percentage ozone reduction as a function of percentage increase in NO_x are given in Figure 5 for injection at 17 km (Concorde) and in Figure 6 for injection at 20 km (Boeing SST). The recent results at 20 km are compared with the 1971 calculations in Figure 6. It can be seen that the 1971 and 1974 calculations give very nearly the same sensitivity of stratospheric ozone to fractional increase of nitrogen oxides.

In an earlier section it was pointed out that simple comparison of the emission rate of the SST's with the natural rate of formation of NO or rate of removal of HNO_3 indicates that 500 SST would increase the rate of input of stratospheric NO_x between 50% (Concordes, world-wide average) to 450% (Boeings, 3 fold local maximum). From Figure 5, it can be seen that the concensus of atmospheric modelers is that a 50% increase in NO_x would decrease ozone by 7 to 12%, and from Figure 6 a 450% increase in NO_x would decrease ozone by 40±5% (It should be pointed out that the modelers do not agree as to stratospheric residence time, and thus they differ as to the relation between increased rate of NO_x insertion and the resultant fractional increase in stratospheric NO_x). In 1974, as in 1971, it appears that 500 Boeing-type SST would cause a major reduction in stratospheric ozone.

Table V. Representative results of model calculations.

Supersonic Transports		NO_x Emissions			Ozone Column	
No.	Type	Elev. km	10^{34} molecules yr^{-1}	% Increase of NO_x Column	% Decrease	Reference
500	B	20	2.4	47	23	①
500	B	20	24	470[(a)]	50	
500	B	20	2.4		15-25	②
200	C	18	0.3		1	2⃞
				10	3	③
				100	18	
				400	40	
200	C	18	0.3	0.6	0.1 (winter)	3⃤
200	C	18	0.3	3.0	0.5 (summer)	
200	C	23	0.3	2.6	0.8 (winter)	
200	C	23	0.3	5.0	1.8 (summer)	
		17	1.0		1.7	3⃞
		17	2.4		3.7	
		17	6.5		9	
		20	1.0		5.8	
		20	2.4		12	
		20	6.5		27	
300	C	20	0.5		8	④
600	C	20	1.0		16	
500	B	20	2.4		28	
500	B	20	5.6[(b)]		47	
		20	0.8	13	3	4⃤
		20	1.6	27	6	

Table V. Representative results of model calculations. (Continued)

Supersonic Transports		NOx Emissions			Ozone Column	
No.	Type	Elev. km	10^{34} molecules yr^{-1}	% Increase of NO_x Column	% Decrease	Reference
		20	3.3	54	10	
		17	0.8	8	1.3	
		17	1.6	16	2.5	
		17	3.3	31	5.0	
1000	B	27	11		23	⑤
1000	B	27	420$^{(c)}$		70	
			33		8	5⃞
			66		12	
			130		19	
	B	20	0.7	16	3	6⃤
	B	20	3.7	86	17	
	B	20	6.8	155	26	
	C	17	1.0	11	2.4	
	C	17	9.7	71	21	
		16	20	30	2	7⃤
		20	20	128	15	7⃤
		16	6.4	170	27	8⃞
		16	6.4	320	37	

Footnotes and references

(a) 10-fold local maximum
(b) 3-fold local maximum
(c) High local maximum
① Johnston, 1971
② Crutzen, 1972; 2⃞, 1973
③ Hesstvedt, 1972; 3, 1973; 3 , 1974
④ Chang, 1973a, 4 Chang et al, 1973b

⑤ Stewart & Hoffert, 1973; 5, 1974
6⃤ McElroy et al, 1974
7⃤ Whitten & Turco, 1973; 7⃞, Whitten, 1974
8⃞ Shimazaki, 1974

COSMIC RAYS

Willett (1962) found that total ozone seemed to be strongly correlated with the eleven-year sunspot cycle. Using total-ozone data for another 10 years, Christie (1973) confirmed Willett's analysis. Angell and Korshover (1973), using a different method of treating the data, also found a very strong correlation of total ozone with the sunspot cycle. These studies were statistical in nature; there was no apparent physical explanation.

Warneck (1972) pointed out that cosmic rays penetrate the stratosphere and form some nitric oxide there. Brasseur and Nicolet (1973) discussed the question and showed that the global rate of production of NO_x from this mechanism is small compared to that from nitrous oxide. Ruderman and Chamberlain (1973) gave the physical interpretation for the correlation of ozone with sunspots in terms of cosmic ray formation of nitric oxide. The following analysis paraphrases the work of Ruderman and Chamberlain.

Cosmic rays are steered by the earth's magnetic field, being deflected from the equator and focused into polar regions. The cosmic rays are largely stopped in the stratosphere and uppermost troposphere; ion pairs, electrons, and atoms are produced. The formation of ion pairs from cosmic rays has been measured as a function of latitude and elevation for several decades (Neher, 1971). The earth's interplanetary magnetic field is affected by the stream of charged particles from the sun, and it is strongly modulated by the eleven year sunspot cycle. Ruderman and Chamberlain pointed out the cause-and-effect sequence: the solar cycle affects the earth's magnetic field; the earth's magnetic field controls the flux of cosmic rays into the earth's atmosphere; the cosmic rays produce ions and nitric oxide in the polar stratosphere; the nitric oxide strongly and promptly affects ozone in the upper polar stratosphere and it weakly and somewhat later affects ozone in temperate and tropical zones. They were very successful in explaining the phase shift between the sunspot cycle and total ozone, and they explained the decreasing amplitude of the effect as one moves from polar to equatorial zones.

The correlation of sunspot number with global ozone, as deduced from the data by Christie, for the period 1930-70 is given by the first two panels of Figure 7. The second panel of Figure 9 shows the annual variation of ozone and an eleven year running average. There was a clear peak in total ozone in 1941 and in 1952. However, the expected peak in 1963 is absent (the reason for this missing 1963 peak is given in the section on nuclear bombs).

The amplitude of the variation of ozone with sunspot cycle is rather large: the 1941 and 1952 peaks are 10 per cent higher than the 1946 minimum and 7 per cent higher than the 1956 minimum. The rate of production of nitric oxide from cosmic rays is uncertain by perhaps a factor of two. On the basis of current estimates of this number, the rate of production of nitric oxide at the peak rate exceeds that at the eleven-year minimum by about 8×10^{32} molecules per year. This difference would be produced by 17 Boeing SST or by 50 Concordes. The deduction is that if 17 Boeing SST emitted its exhaust with the same vertical and latitudinal distribution as nitric oxide from the cosmic rays, then ozone would be reduced by 7 to 10 per cent. This reduction of ozone by SST's is considerably greater than that indicated by model calculations

NUCLEAR BOMBS

Nuclear bombs heat air to very high temperatures and produce large amounts of nitric oxide (Foley and Ruderman, 1973). The hot-air clouds rise into the stratosphere if the energy of the bomb exceeds one megaton TNT. There was a period, 1961-62, of very heavy testing of nuclear bombs. During this period 90 per cent of the bombs were fired at the USSR station at 75°N, and most of these tests were conducted during or just before the polar night. These bomb clouds rose into the dense cold polar stratosphere and did not attain as great a vertical height as that expected from US tests at tropical stations.

There is a linear relationship between nuclear bomb yield, radioactive carbon 14 produced, and nitric oxide produced (Johnston, 1974b). There were extensive measurements of atmospheric carbon 14 during and after the 1961-62 bomb tests. The distributions of nitric oxide every three months from January 1963 to January 1964 are given by Figure 8. The great stability of the stratosphere can be seen from the very slow change of the nitric oxide (or carbon 14) cloud shown here. There is a noticeable loss of nitric oxide at and below 15 kilometers, but changes between 18 and 30 kilometers were exceedingly small.

From the distribution of NO_x given by these figures, one can readily calculate the ozone reduction by the models discussed above. Johnston _et al_ (1973) calculated the latitude dependent reduction of ozone to be between 3 and 6 per cent in the northern hemisphere.

Chang et al (1973 b) calculated the time dependent ozone reduction between 1957 and 1971; they found a maximum ozone reduction of 4 percent with 2-1/2 years for half recovery time. Chang's calculated amount of ozone reduction is inverted and added to Christie's average ozone in the third panel of Figure 7. This correction of the total ozone record with the calculated effect from nuclear bomb tests restores the missing 1963 peak to Christie's correlation of ozone with the eleven year sunspot cycle.

There has been considerable discussion about the increase of total ozone during the 1960's (Komyhr et al, 1971). In his analysis of this trend, Christie (1973) makes two points: "1. There has been an increase in ozone in a vertical column amounting to about 32 m. atm. cm, but this represents an increase from a value about 9 m. atm. cm below the zero deviation level . 2. The maximum level reached to date does not represent a value substantially higher than has been reached on earlier occasions of high positive ozone deviation". Johnston et al (1973) found a percentage increase of ozone of 4.5±1.2(2σ) for 74 stations in the northern hemisphere involving 129,000 observation-days for the period 1963-70, inclusive; but there was no significant trend in the southern hemisphere. For this article we obtained total ozone data back to 1957 and find a percentage decrease of ozone (1957-1962, inclusive) of 2.7±2.0(2σ). These are small effects, they require careful data analysis to be seen, and they require rigorous statistical criteria as to weighting factors. These small trends before and after 1963 are operating against the expected ozone maximum from cosmic rays. It appears that the nuclear bomb reduction of ozone was slightly greater in magnitude and opposite in sign to the eleven-year sunspot cycle.

The increase of ozone during the 1960's is a complex superposition of recovery from the effect of nuclear bombs and the restoration of the normal eleven year cycle.

Goldsmith et al (1973) rederived the expression for the rate of production of nitric oxide from nuclear bombs. Their derivation treated air as a monatomic ideal gas so far as its gas dynamics was concerned. They calculated temperature as a function of space and time with this model. Next they took this temperature history and let the molecules of air dissociate to atoms and to form nitric oxide. If one takes their calculated distribution of atoms at certain stages of the shock waves, the energy required to produce the atoms is much greater than the energy of the original bomb. Their failure to couple the endothermic chemistry with the gas dynamics leads to this conflict with the Law of Conservation of Energy. Goldsmith et al (1973) made a superficial examination of the total ozone data for Arosa and for Oxford, and they found neither the correlation with sunspot cycle nor the nuclear bomb effect. They plotted all the monthly deviations for 45 years of observations on one tight figure, and simply inspected the scatter pattern that resulted. This approach would not be expected to pick up the small effects calculated from the nitric oxide distributions of Figure 8.

Whereas the atmospheric nuclear bomb tests of 1961-62 gave only a moderate (about 5%) transient (about 5 year) reduction of ozone, the much more numerous nuclear bombs of an all-out war would have a global side effect of drastically reducing stratospheric ozone via bomb-produced nitric oxide.

THE SPACE SHUTTLE

The U.S. space shuttle uses ammonium perchlorate as an oxidizing agent and metallic aluminum as a reducing agent in its solid, booster rockets. This rocket burns in the stratosphere between 12 and 42 kilometers. Each flight releases 69 tons of hydrochloric acid and 97 tons of aluminum oxide in the stratosphere. The hydrochloric acid is converted to chlorine atoms by hydroxyl radicals

$$\dot{H}O + HCl \rightarrow H_2O + Cl$$

and the chlorine atom is reconverted to hydrochloric acid by methane

$$Cl + CH_4 \rightarrow HCl + \dot{C}H_3$$

Also the chlorine atoms may enter a catalytic cycle to destroy ozone, Equation D. Supersonic transports deposit ozone-destroying catalysts at one elevation (17 to 21 km), and to destroy much ozone the nitric oxide catalysts must work their way up to the most important ozone-forming region, that between 25 and 35 kilometers. The space shuttle deposits its exhaust at all elevations of the stratosphere, and thus it makes prompt contact with the most sensitive region. On the other hand, the mass of chlorine from one space shuttle per week is much less than the mass of nitrogen oxides from 500 SST (Table III-B). Molecule for molecule, ClO is 6 times as effective in destroying ozone as is NO_2; but it now appears that more chlorine is tied up as the photochemically inactive HCl than NO_x is tied up as nitric acid.

The problem of chlorine in the stratosphere has only recently been recognized, and much further study is needed accurately to assess the problem. It now appears that 500 SST operating 8 hours per day are very much worse than one space shuttle per week, but it is not yet clear whether the space shuttle would or would not have a deleterious effect on ozone.

CHLORINATED HYDROCARBONS

Another mode of stratospheric pollution has recently been pointed out by Molina and Rowland (1974). Freons ($C\,Cl_xF_{4-x}$) have been measured in the troposphere, and the quantity in the atmosphere is comparable to the total amount ever manufactured. Freons are inert to water and sunlight in the troposphere, and are probably inert to the hydroxyl radicals in the lower stratosphere. However, freons would be photolyzed by short wavelength solar radiation (below 200 nm) in the upper part of the stratosphere and probably would react with singlet oxygen atoms. The time for freons to percolate from the surface of the earth to the upper stratosphere is a matter of decades. Further escalation in the use of freons and other chlorinated hydrocarbons may make them a serious case of stratospheric pollution.

CONCLUSIONS

There are many possible modes of man-made pollution of the stratosphere to cause a serious reduction of ozone there and an increase of destructive ultraviolet radiation at the earth's surface.

ACKNOWLEDGEMENT

This work was supported by the Climatic Impact Assessment Program by means of an interagency agreement between the Department of Transportation and the U. S. Atomic Energy Commission.

References

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

Ackerman, M. & Muller, C., (1973). Stratospheric Methane and Nitrogen Dioxide from Infrared Spectra, Pure and Applied Geophysics, Vol. 106-108, pp. 1325-35.

Ackerman, M. & Muller, C., (1972). Stratospheric Nitrogen Dioxide from Infrared Absorption Spectra, Nature 240, pp. 300-1.

Angell, J. K. & Korshover, J., (1973). Quasi-biennial and Long-Term Fluctuations in Total Ozone, Monthly Weather Review, 101, pp. 426-43.

Bartholic, J. F., Halsey, L. H., Briggs, R. H., & Garrard, L. A., (1974). Effect of UV Radiation on Agricultural Products, Third Conference on the Climatic Impact Assessment Program, Cambridge, Massachusetts, USA.

Blum, H. F., (1973). Ultraviolet Radiation and Skin Cancer, Proceedings of Second CIAP Conference, DOT-TSC-OST-73-4, pp. 373-6..

Brasseur, G. & Nicolet, M., (1973). Chemospheric Processes on Nitric Oxide in the Mesosphere and Stratosphere, Planetary and Space Sciences 21, pp. 939-61.

Brewer, A. W., McElroy, C. T., & Kerr, J. B., (1974). Measurements of Nitrogen Dioxide from Concorde 002", Third Conference on the Climatic Impact Assessment Program, Cambridge, Massachusetts, USA.

Caldwell, M. M., (1973). Ecologic Considerations of Solar Radiation Change, Proceedings of Second CIAP Conference, DOT-TSC-OST-73-4, pp. 386-93.

Caldwell, M. M., Campbell, W. F., & Sisson, W. B., (1974). Plant Response to Elevated UV Intensities", Third Conference on the Climatic Impact Assessment Program, Cambridge, Massachusetts.

Calkins, John (1974). A Preliminary Assessment of the Effects of UV Irradiation of Aquatic Microorganisms and Their Ecosystems", Third Conference on the Climatic Impact Assessment Program, Cambridge, Massachusetts.

Chang, J. S., (1973a). Global Transport and Kinetics Model, UCRL-51336, Lawrence Livermore Laboratory Report.

Chang, J. S., Hindmarsh, A. C., & Madsen, N. K., (1973b). Simulation of Chemical Kinetics Transport in the Stratosphere, UCRL-74823, Lawrence Livermore Laboratory Report.

Chang, J. S., & Johnston, H. S., (1974). The Effect of NO_x Effluents on Ozone, Third Conference on the Climatic Impact Assessment Program, Cambridge, Massachusetts.

Chapman, S., (1930). A Theory of Upper-Atmosphere Ozone, Mem. Roy. Meteorol. Soc. 3, pp. 103-25.

Christie, A. D., (1973). Secular or Cuclic Change in Ozone", Pure and Applied Geophysics, vol. 106-108, pp. 1000-9.

CIAP (1974). Third Conference on the Climatic Impact Assessment Program, Cambridge, Massachusetts, USA, March. Proceedings of the Conference will be published, Fall 1974.

Crutzen, P. J., (1972). SST's - A Threat to the Earth's Ozone Shield, Ambio 1, pp. 41-51.

Crutzen, P., (1974). A Review of Upper Atmospheric Photochemistry, Canadian Journal of Chemistry, 52, pp. 1569-81.

Crutzen, P. J., (1970). The Influence of Nitrogen Oxides on the Atmosphere Ozone Content, Quarterly J. Roy. Meteorol. Soc. 96, pp. 320-25.

Crutzen, P. J., (1971). Ozone Production Rates in an Oxygen-Hydrogen-Nitrogen Atmosphere, J. Geophys. Res. 76, pp. 7311-37.

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

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

Farmer, C. B., Toth, R. A., Raper, O. F., & Schindler, R. A., (1974). Recent Results of Aircraft Infrared Observations of the Stratosphere, Third Conference on the Climatic Impact Assessment Program, Cambridge, Massachusetts.

Foley, H. M., & Ruderman, M. A., (1973). Stratospheric Nitric Oxide Production from Past Nuclear Explosions and Its Relevance to Projected SST Pollution, Journal of Geophysical Research 78, pp. 4441-50.

Girard, Andre' (1974). Study of Minor Constituents in the Stratosphere by Absorption Spectrometry, Third Conference on the Climatic Impact Assessment Program, Cambridge, Massachusetts.

Goldburg, A., (1972). Climatic Impact Assessment for High-Flying Aircraft Fleets, Astronautics and Aeronautics, 10, pp. 56-64.

Goldsmith, P., Tuck, A. F., Foot, J. S., Simmons, E. L., & Nelson, R. L., (1973). Nitrogen Oxides, Nuclear Weapons Testing, Concorde, and Stratospheric Ozone, Nature, 244, pp. 545-51.

Green, A.E.S. & Mo, T., (1974). An Epidemiological Index for Skin Cancer Incidence, Interdisciplinary Center for Aeronomy and Atmospheric Sciences, University of Florida, Gainesville, Florida, USA. Mimeographed laboratory report.

Green, A.E.S., Sawada, T. & Shettle, E. P., (1974). The Middle Ultraviolet Reaching the Ground, Photochem. Photobiol., in press.

Hesstvedt, E., (1973). Effect of Supersonic Transport Upon the Ozone Layer Studied in a Two-Dimensional Photochemical Model with Transport, AGARD Conference Proceedings No. 125, Item 6, London, England.

Hesstvedt, E., (1974). Reduction of Stratosphere Ozone from High Flying Aircraft Studied in a Two-Dimensional Photochemical Model with Transport, Canadian Journal of Chemistry, 52, pp. 1592-98.

Hesstvedt, E., (1974). Private communication.

Hoshizaki, H., Myer, J. W., & Redler, K. O. (1973). Potential Destruction of Ozone by HCl in Rocket Exhausts, Chapter 4 in Advances in Aircrafts and Fuels. Also Report LMC-D-354204, Lockheed, Palo Alto, California.

Hunt, B., (1966). The Need for a Modified Photochemical Theory of the Ozonosphere, J. Atmos. Sci. 23, pp. 88-95.

Isaksen, I. A., (1973). The Production and Distribution of Nitrogen Oxides in the Lower Stratosphere, Pure and Applied Geophysics, vol. 106-108, pp. 1438-45.

Johnson, F. S., (1973). SST's, Ozone, and Skin Cancer, Astronautics and Aeronautics 11, pp. 16-21.

Johnston, H. S. (1968). Gas Phase Kinetics of Neutral Oxygen Species, National Standard Reference Data Series - National Bureau of Standards, Number 20.

Johnston, H. S., (1971). (a) Reduction of Stratospheric Ozone by Nitrogen Oxide Catalysts from Supersonic Transport Exhaust, Science 173, pp. 517-22. (b) Johnston, H. S., (1971). Catalytic Reduction of Stratospheric Ozone by Nitrogen Oxides, UCRL Report No. 20568, pp. 1-106.

Johnston, H. S., (1972). Ozone and the SST, Environmental Affairs, I, pp. 735-81.

Johnston, H. S., Whitten, G., & Birks, J., (1973). The Effect of Nuclear Explosions on Stratospheric Nitric Oxide and Ozone, Journal of Geophysical Research 78, pp. 6107-35.

Johnston, H. S., (1974a). Photochemistry in the Stratosphere, Acta. Astronautica 1, pp. 135-56.

Johnston, H. S., (1974b). Supersonic Aircraft and the Ozone Layer, Environment and Change, 2, pp. 339-50.

Knipling E. B., (1973). Ultraviolet Radiation and Photosynthesis, Proceedings of Second CIAP Conference, DOT-TSC-OST-73-4, pp. 379-85.

Komhyr, W. D., Barrett, E. W., Slocum, G., & Weickman, H. K., (1971). Atmospheric Ozone Increase During the 1960's", Nature 232, pp. 390-91.

Lazrus, A. L., & Gandrud, B. W., (1974). Summary of Nitric Acid Vapor Distribution, Third Conference on the Climatic Impact Assessment Program, Cambridge, Massachusetts.

Loewenstein, M., Paddock, J. P., Poppoff, I. G., & Savage, H. F., (1974). Stratospheric Nitric Oxide Measurements, Third Conference on the Climatic Impact Assessment Program, Cambridge, Massachusetts.

McDonald, J. E., (1971). The SST: Could It Increase the Incidence of Skin Cancer, U.S. Congressional Record, March 19, S3483.

McElroy, M. B. & McConnell, J. C., (1971). Nitrous Oxide: A Natural Source of Stratospheric NO, J. Atmosph. Sci. 28, pp. 1095-98.

McElroy, M., Wofsy, S., Penner, J., McConnell, J., (1974). Atmospheric Ozone: Possible Impact of Stratospheric Aviation, Journal of Atmospheric Sciences, 31, pp. 287-300.

Molina & Rowland, (1974). Stratospheric Sink for Chlorofluoromethanes - Chlorine Atom Catalyzed Destruction of Ozone, Nature, 249, pp. 810-12.

Murcray, D. G., Golman, A., Williams, W. J., Murcray, F. H., Brooks, J. N., Van Allen, J., Stocker, R. N., Kosters, J. J. & Barker, D. B., (1974). Recent Results on Stratospheric Trace-Gas Measurements from Balloon-Borne Spectrometers, Third Conference on the Climatic Impact Assessment Program, Cambridge, Massachusetts.

Neher, H. V., (1971). Cosmic Rays at High Latitudes and Altitudes Covering Four Solar Maxima, Journal of Geophysical Research 76, pp. 1637-51.

Nicolet, M. & Vergison, E., (1971). L'Oxyde Azoteux dans la Stratosphere, Aeronomica Acta 90, pp. 1-16.

Ruderman, M. A. & Chamberlain, J. W., (1973). Origin of the Sunspot Modulation of Ozone: Its Implications for Stratospheric NO Injection, Institute for Defense Analysis JSS-73-18-3.

Schiff, H. I., Measurements of NO, NO_2 and HNO_3 in the Stratosphere, Canadian Journal of Chemistry 52, pp. 1536-43.

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

Shimazaki, T., & Ogawa, T., (1974). Theoretical Models of Minor Constituents' Distributions in the Stratosphere and the Impacts of the SST Exhaust Gases, paper presented at the IAMAP/IAPSO First Special Assemblies, Melbourne, Australia.

Smith, K. C., (1972). The Biological Effects of Ultraviolet Radiation on Man, Animals, and Plants, Proceedings of the First CIAP Survey Conference, DOT-TSC-OST-72-13, pp. 243-49.

Stewart, R. W., & Hoffert, M. I., (1973a). Stratospheric Contamination Experiments with a One-dimensional Atmospheric Model, AIAA Paper 73-531, Paper presented at the AIAA/AMS International Conference on the Environmental Impact of Aerospace Operations in the High Atmosphere, Denver, Colorado, June.

Stewart, R. W., (1973b). Response of Stratospheric Ozone to the Simulated Injection of Nitric Oxide, paper presented at the Fall American Geophysical Union Meeting, San Francisco, California.

Stolarski, R. S., & Cicerone, R. J., (1973). Stratospheric Chlorine: Possible Sink for Ozone, Canadian Journal of Chemistry, 52, pp. 1610-15.

Stone, N.W.B., Harries, J. E., Birch, J. R., Bangham, M. J., Swann, N.R.W., & Neill, G. F., (1974). Studies of Stratospheric H_2O, O_3, HNO_3, N_2O, and NO_2 from Aircraft and Balloons, Third Conference on the Climatic Impact Assessment Program, Cambridge, Massachusetts.

Stone, Peter H. (1974). Limitations of Climate Modeling, Third Conference on the Climatic Impact Assessment Program, Cambridge, Massachusetts.

Telegadas, K., (1971). 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, 3-86.

Urbach, F., (1974). Field Measurements of Biologically Effective Ultraviolet RAdiation and Its Relation to Skin Cancer in Man, Third Conference on the Climatic Impact Assessment Program.

Warneck, P., (1972). Cosmic Rays as a Source of Odd Nitrogen in the Stratosphere, Journal of Geophysical Research, 77, pp. 6589-91.

Whitten, R., & Turco, R. P., (1973). A Model of Studying the Effects of Injecting Contaminants into the Stratosphere and Mesosphere, AIAA Paper 73-539, Paper presented at the AIAA/AMS International Conference on the Environmental Impact of Aerospace Operations in the High Atmosphere, Denver, Colorado.

Whitten, R. C., & Turco, R. P., (1974). The Effect of SST Emission on the Earth's Ozone Layer, paper presented at the IAMAP/IAPSO First Special Assemblies, Melbourne, Australia.

Willett, H. C., (1962). The Relationship of Total Atmospheric Ozone to the Sunspot Cycle, Journal of Geophysical Research 67, pp. 661-70.

TITLES TO FIGURES

Figure 1 - Optical absorption cross section of ozone as a function of wavelength of radiation, and the fraction of sunlight transmitted to the earth's surface by a column of ozone equivalent to 0.37 cm STP. (This figure adapted from Johnston 1974-b).

Figure 2 - The distribution of natural NO_x in the stratosphere used by Johnston (1971-a) compared to the distribution of NO_x asserted by Goldburg (1972) and observed by Ackerman & Muller (1972).

Figure 3 - Distributions of world-wide artificial NO_x used by Johnston (1971-ab) as box models to embrace probable spread exhaust gases from supersonic transports. Calculated per cent reduction of vertical ozone column indicated for each distribution.

Figure 4 - Calculated reductions of stratospheric ozone with the NO_x insertion model indicated by Figure 3 for four assumed uniform natural distributions of NO_x.

Figure 5 - Calculated reduction of vertical ozone column in terms of relative perturbation of NO_x vertical column for models where NO_x is injected at 17±1 km, simulating the Concorde. References are identified in Table 4.

Figure 6 - Same as Figure 5, but for NO_x injection at 20 km, simulating the Boeing SST. The lines are based on Figure 4, which gives a comparison of 1971 and 1973 results.

Figure 7 - The correlation of sunspot number (Panel 1) with total observed ozone as interpreted by Christie (Panel 2); (Note the peaks in 1941 and 1952 with the absence of a peak in 1963. The calculated reduction of ozone (Chang <u>et al</u>, 1973) by nuclear bombs was inverted and added Christie's average observed ozone (Panel 3); note the restoration of 1963 ozone peak as expected from the solar cycle.

Figure 8 - 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. Large scale nuclear bomb tests in the atmosphere ended December 1962. Distribution of bomb-produced NO_x: January 1963, April 1963, July 1963, October 1963, and January 1964 (additional figures of this type are given by Johnston, 1974-b).

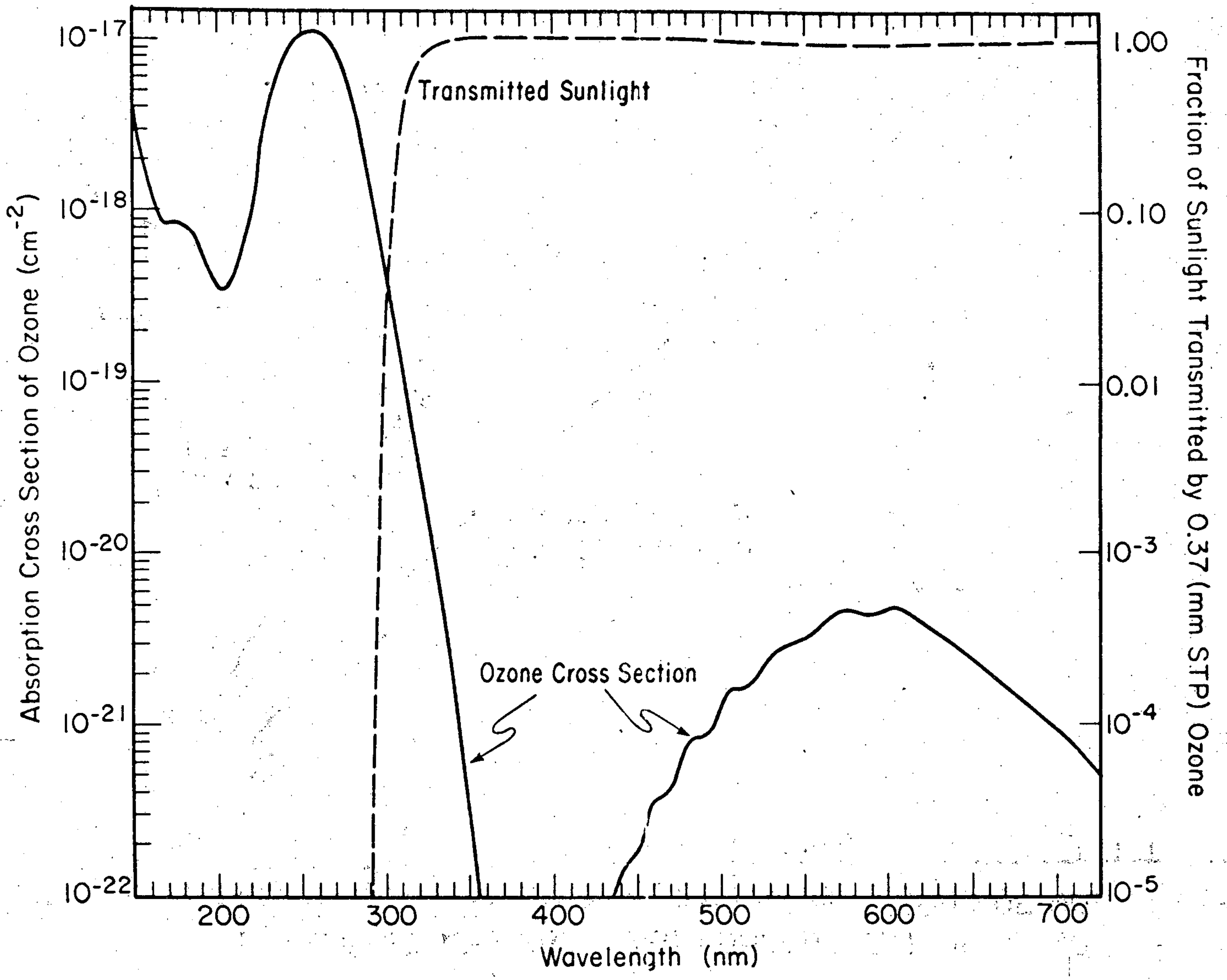

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Fig. 1

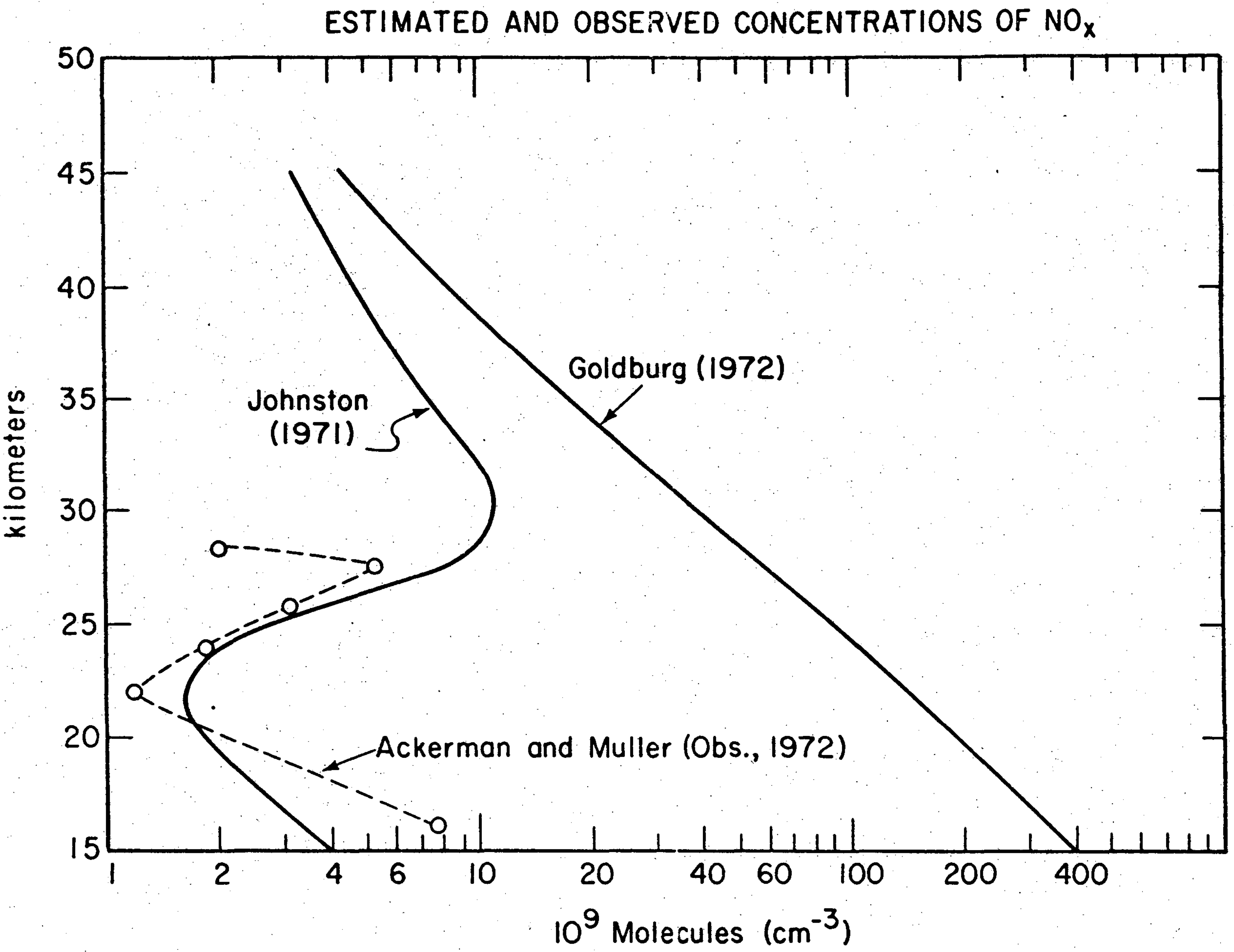

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Fig. 2

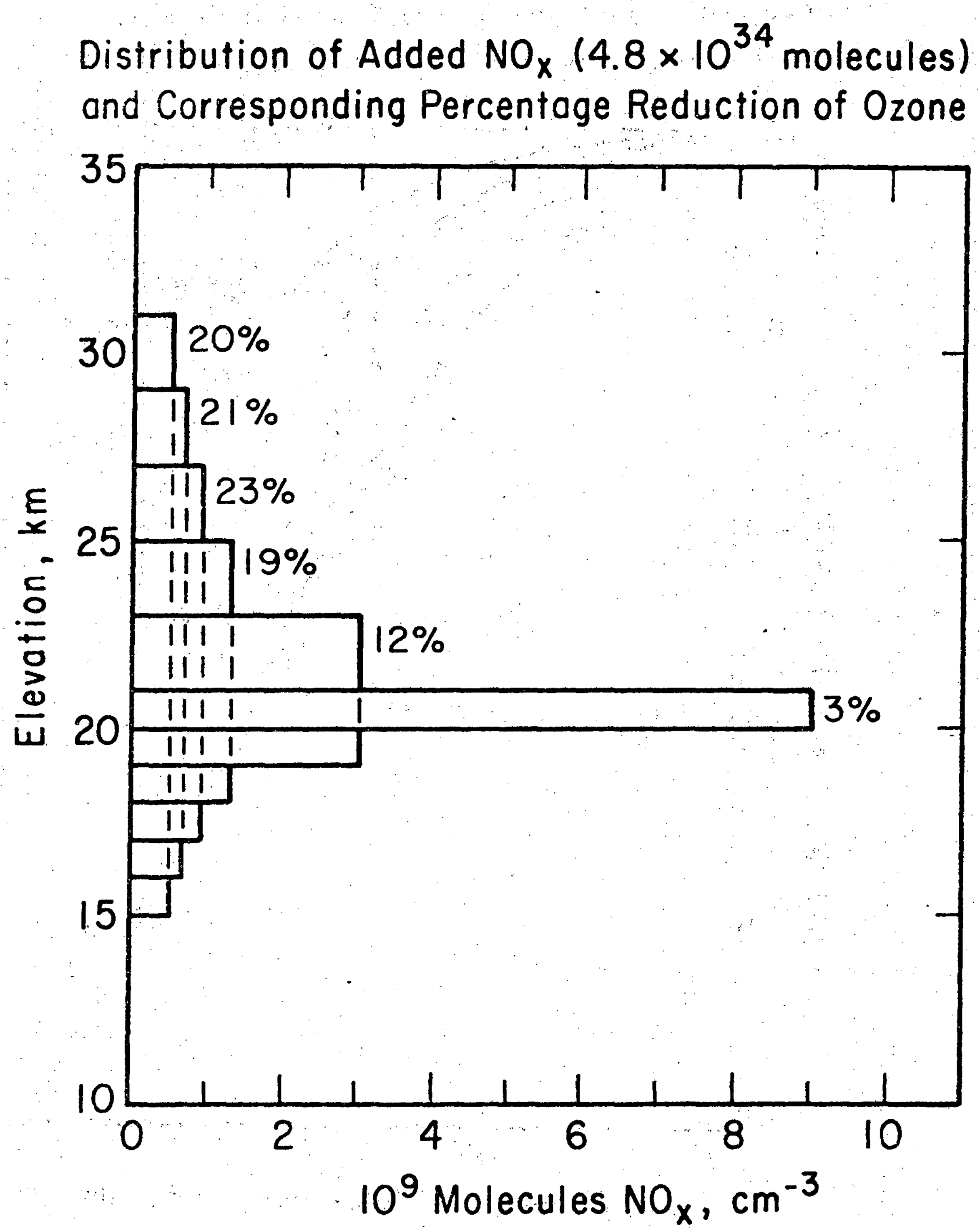

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Fig. 3

Reduction of Ozone Vertical Column by Addition of Nitrogen Oxides for Various NO_x Natural Backgrounds

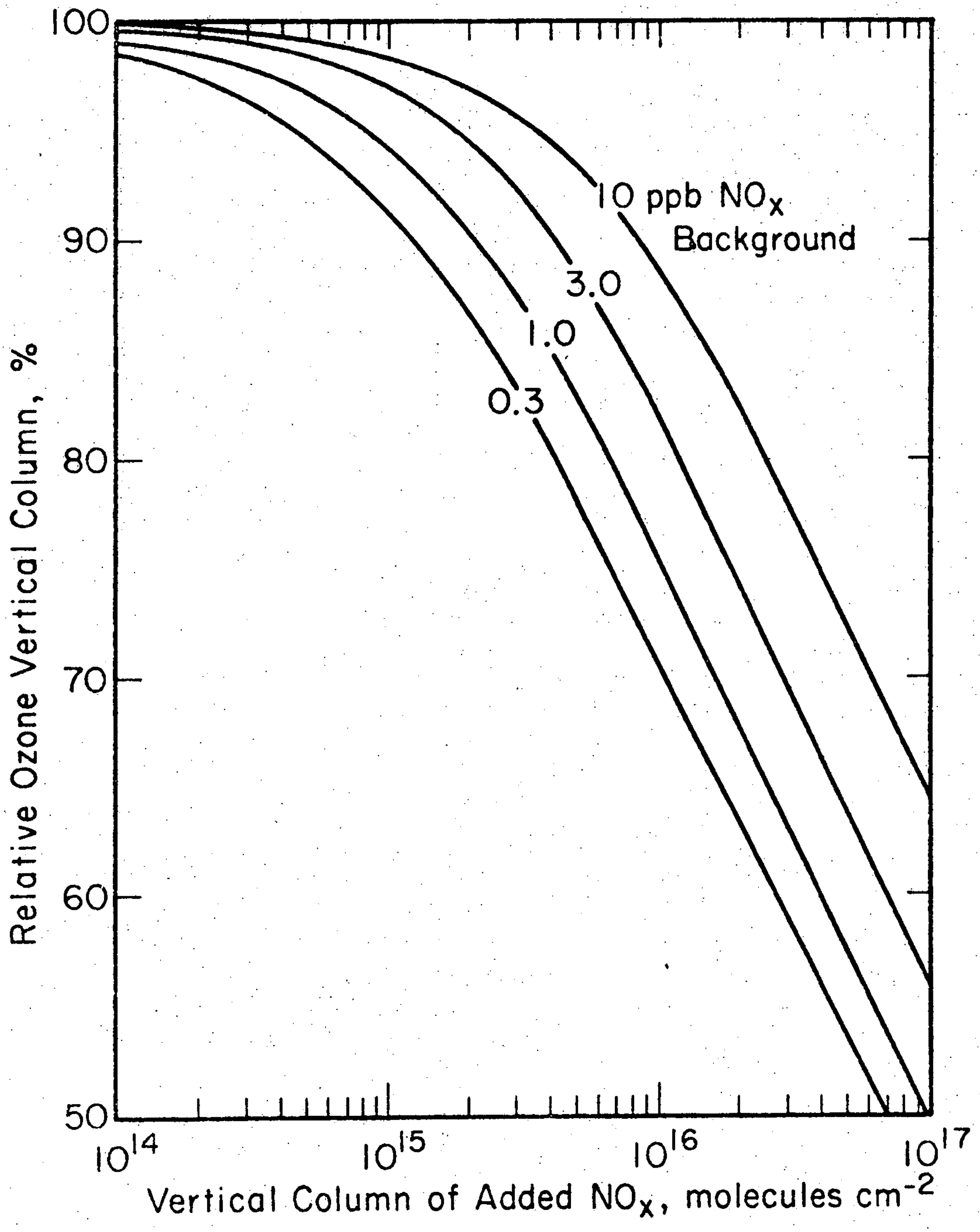

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Fig. 4

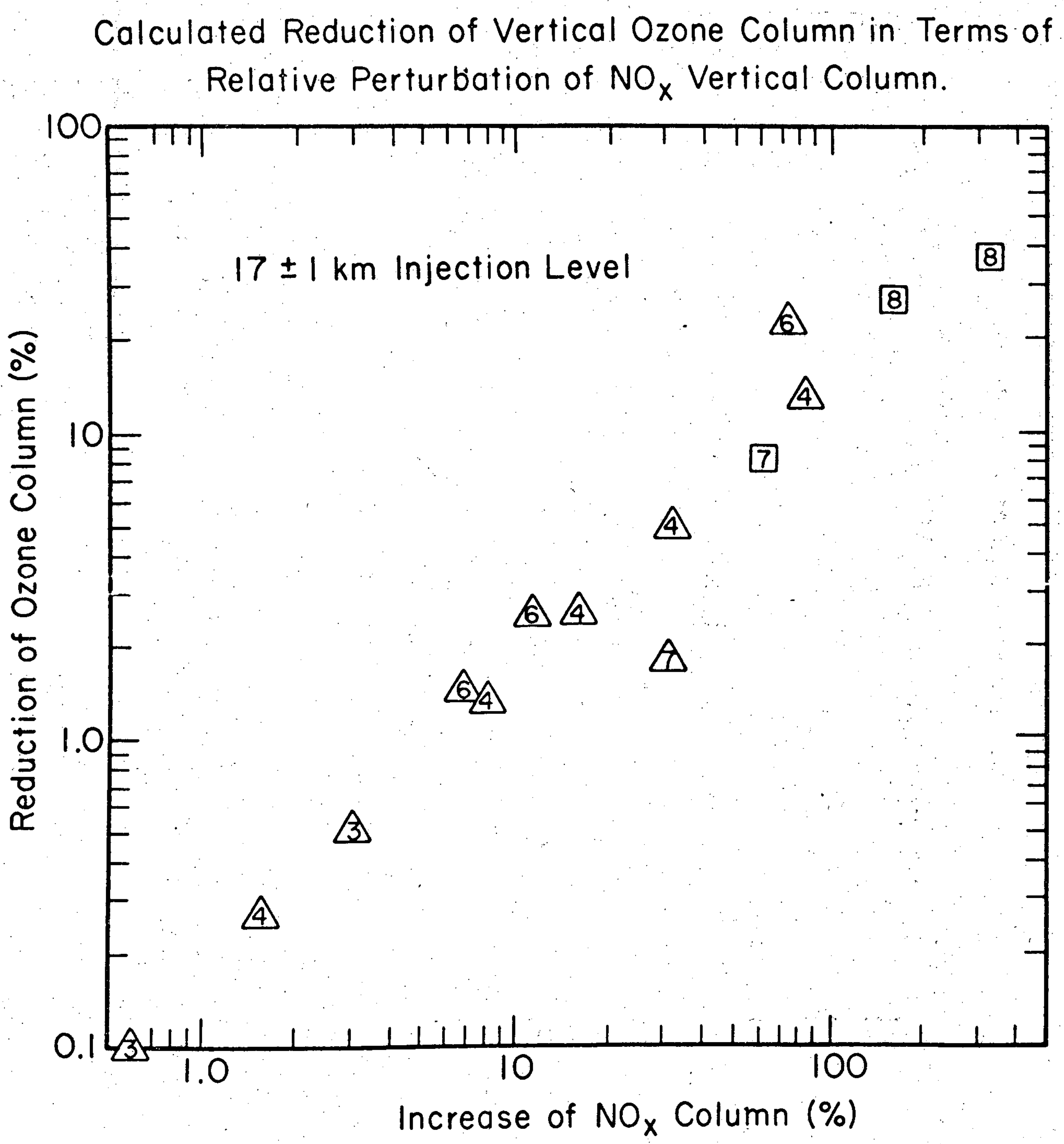

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Fig. 5

Comparison of 1971 and 1973 Results of Calculated Reduction of Stratospheric Ozone By Artificial Increases of NO_x.

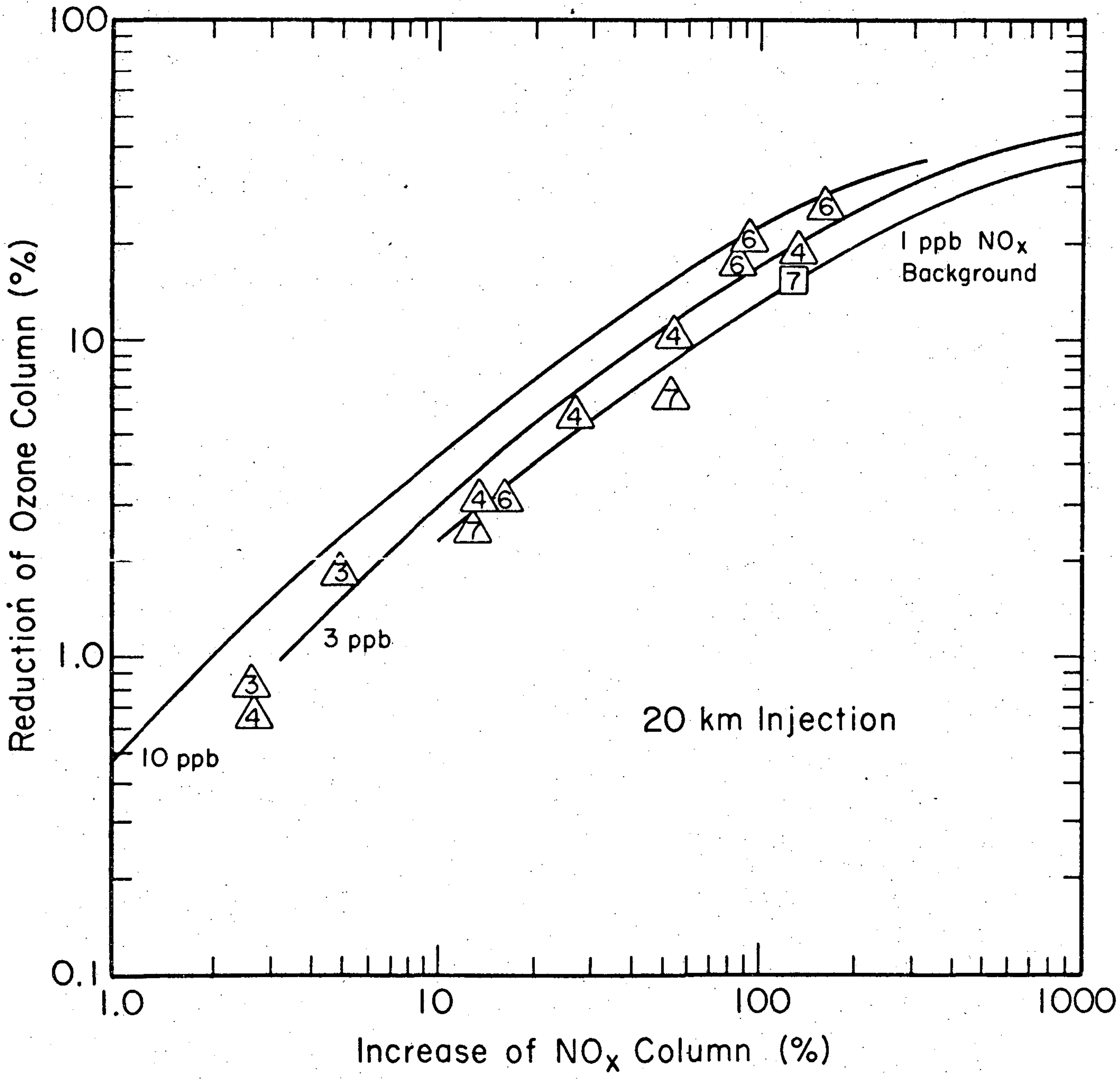

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Fig. 6

Global Ozone and Sunspot Number (Christie, 1973)

Compared to Nuclear Bomb Effect (Chang, 1973)

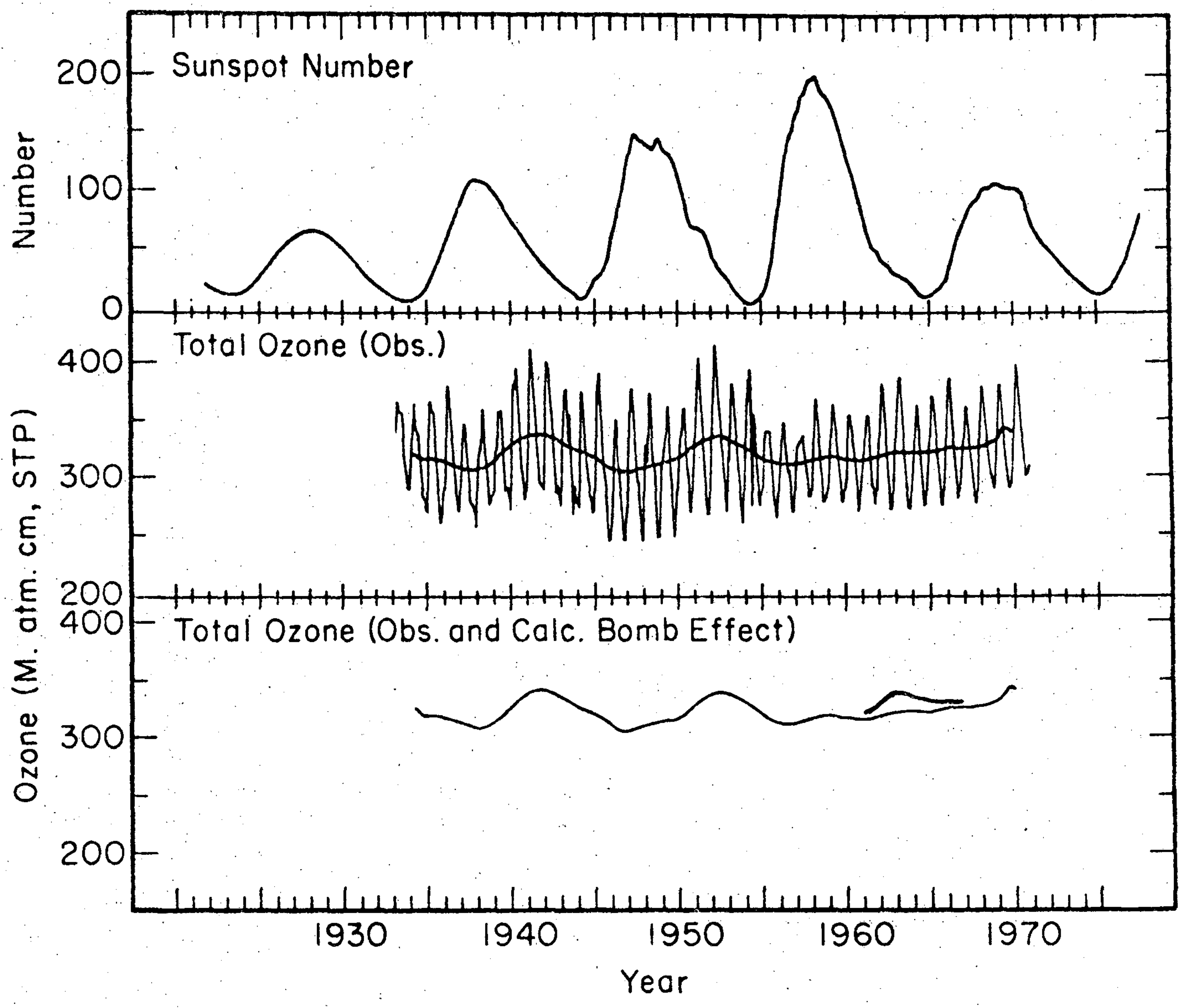

Fig. 7

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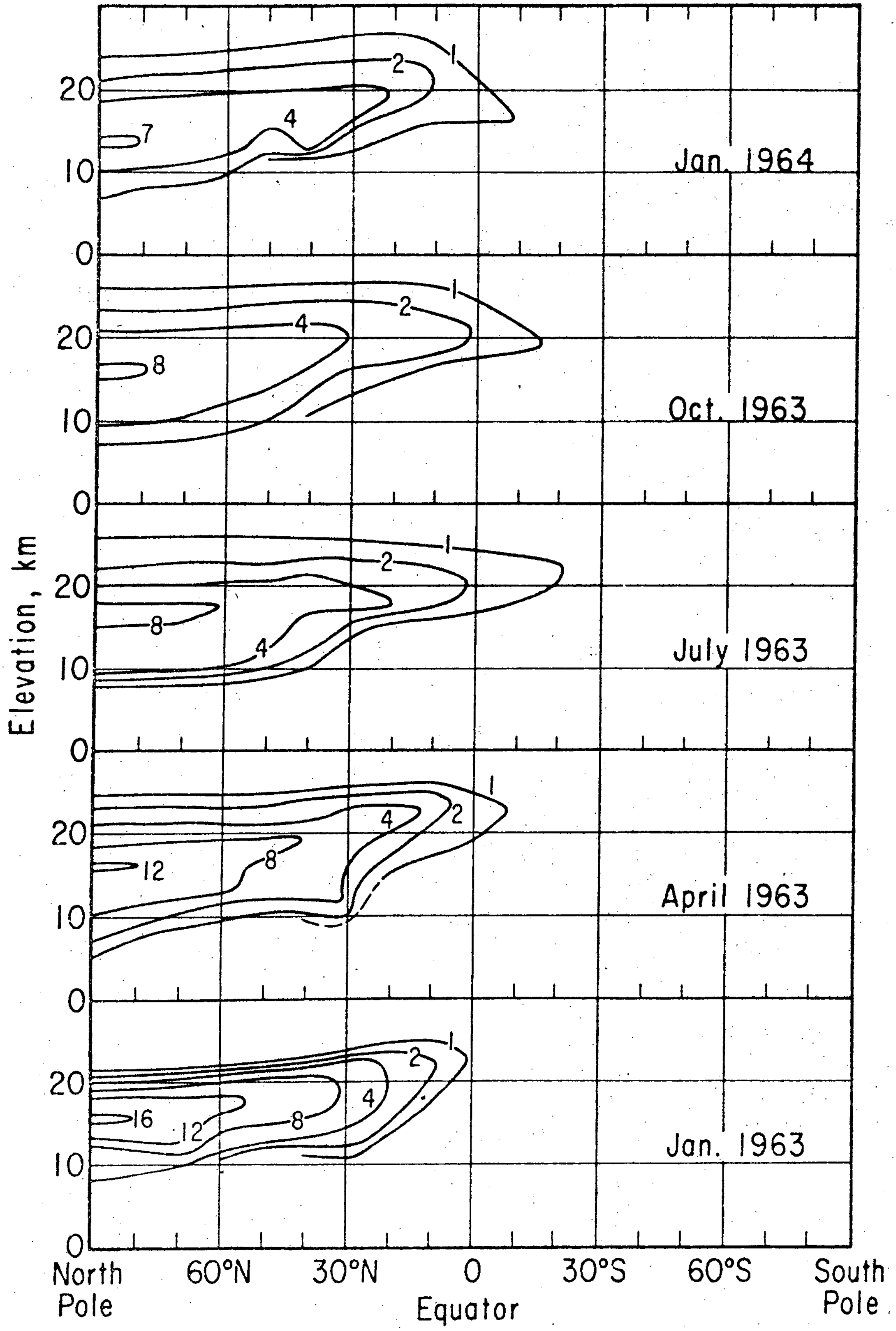

Nitrogen Oxides From Nuclear Bombs (units of 10^9 molecules cm^{-3}) Based on Observed Carbon-14

XBL 741-5462

Fig. 8

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