Submitted to Journal of Geophysical Research

LBL-5460
Preprint c. 1

EXPECTED SHORT-TERM LOCAL EFFECT OF NUCLEAR BOMBS ON STRATOSPHERIC OZONE

Harold S. Johnston

August 1976

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

DISCLAIMER

LBL-5460

Expected Short-Term Local Effect of Nuclear Bombs on Stratospheric Ozone

Harold S. Johnston
Department of Chemistry
University of California
Berkeley, California 94720

[Abstract]

Nuclear bomb tests in the atmosphere produce both oxides of nitrogen and ozone. For bomb yields of 1 Mt or more, much of the bomb-produced radioactivity, ozone, and NO_x are lifted into the stratosphere. The bomb-produced NO_x is expected catalytically to destroy some stratospheric ozone, and the rate is strongly dependent on elevation. Calculations have been made for the 2 Mt nuclear bomb exploded near 15°S on 4 July 1970. The cloud stabilized between 15 and 20 km, with maximum concentration of radioactivity at 18 km. At 18 km, it requires between 36 and 130 days for the bomb-produced NO_x to destroy the bomb-produced ozone. Christie (1976) deduced the trajectory and size of this nuclear cloud for 10 days, and from this estimate of the cloud volume the time for bomb-produced NO_x to destroy 10% of the ambient ozone would be 16 days for a steady-state distribution equal to that of the one-day old cloud at 18 km and 250 days for that of the ten-day old cloud. Thus the observations by Christie (1976) and by Angell and Korshover (1976) of a small increase of ozone in the path of the newly-formed nuclear bomb cloud are in agreement with current models of nuclear bombs and stratospheric photochemistry. This effect was predicted in 1973.

Christie [1976] deduced the size and trajectory for ten days of the nuclear bomb cloud from a 2 Mt French test of 4 July 1970. He examined the Nimbus 4 satellite record of ozone along the trajectory of the nuclear cloud; he was searching for nitrogen-oxide catalyzed destruction of ozone. Little change in ozone was observed, although there was evidence for a small increase in ozone along the cloud path. A similar small increase in ozone at short times after nuclear explosions was reported by Angell and Korshover [1976]. Christie said: "These results are clearly at odds with current ideas governing ozone photochemistry ... the time constant ... for ozone with the increased NO_x concentrations produced by the bombs is about 1 to 2 hours, suggesting that a fast depletion of ozone should occur." Christie's estimate of the chemical reaction rate is too fast by several orders of magnitude, and he failed to consider the bomb-produced ozone. His observations are not at odds with current ideas of NO_x catalyzed destruction of ozone [CIAP, 1975].

The interaction of NO and NO_2 with ozone can profitably be broken down into two competing cycles [Johnston, 1971]:

A.

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

$$O_3 + h\nu \rightarrow O_2 + O \qquad (2)$$

$$NO_2 + O \rightarrow NO + O_2 \qquad (3)$$

$$\text{net:} \quad 2O_3 + h\nu \rightarrow 3O_2$$

B.

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

$$NO_2 + h\nu \rightarrow NO + O \qquad (4)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (5)$$

net: no reaction

Cycle A destroys ozone and cycle B does not. Reaction (1) is not always followed by reaction (3); usually it is followed by reaction (4). Reaction (2) is not always followed by reaction (3); usually it is followed by reaction (5). Thus reaction (3) is the rate-determining step in the NO_2 catalyzed destruction of ozone. Apparently Christie regarded reaction (1) as the expected rate of destruction of ozone by NO_x. At the elevations of this nuclear-bomb cloud, reaction (1) and cycle B are several thousand times faster than reaction (3) and cycle A.

The chemical composition of the natural atmosphere for 15°S and standard July was taken from Johnston and Whitten [1973]. The quantities of interest are 12 hour average oxygen-atom concentration [O], ozone concentration $[O_3]$, and the daytime ratio of nitrogen dioxide to total NO_x

$$f = [NO_2]/([NO] + [NO_2]) \tag{6}$$

These quantities are entered in Table 1.

The properties of the bomb-perturbed atmosphere were obtained from several sources. The number of molecules of NO_x produced by the nuclear bomb is [Bauer and Gilmore, 1975]

$$\begin{aligned} NO_x &= (0.4\text{-}1.5) \times 10^{32}\ Y_{Mt} \\ &= (0.8\text{-}\ 3\ ) \times 10^{32} \text{ molecules} \end{aligned} \tag{7}$$

where Y_{Mt} is the bomb yield in megaton equivalents. This estimate considers the NO_x formed both from the shockwave and from the late fireball. The number of molecules of ozone produced by ultraviolet radiation from the fireball is [Johnston et al., 1973]

$$O_3 = 3 \times 10^{31}\ Y_{Mt} = 6 \times 10^{31} \text{ molecules} \tag{8}$$

and the number produced by ionization of air by nuclear radiation [G. W. Griffing, 1975] is

$$O_3 = 2 \times 10^{32}\ Y_{Mt} = 4 \times 10^{32} \text{ molecules} \tag{9}$$

In November 1970, the observed vertical spread of the 4 July 1970 event at 15°S was 15 to 20 km with the peak concentration at 18 km [Fabian and Libby, 1974]. Christie [1976] estimated the trajectory of the bomb cloud and inscribed on his Figure 1 ellipses that represent the base and top of the bomb cloud. From the semiaxes (a_1, b_1; a_2, b_2) of these ellipses I deduced the volume of the cloud for each day, July 4-13, 1970.

$$V = Z\pi(a_1b_1 + a_2b_2)/2 \tag{10}$$

The height Z was taken to be 5 km in all cases [Fabian and Libby, 1974]. For even day numbers where July 4 is day zero, these cloud volumes are entered in Table 2. The concentration of bomb-produced NO_x was assumed to be uniform throughout the cloud. The concentration of bomb-produced nitrogen dioxide at any elevation is

$$[NO_2]_B = f(0.8\text{-}3) \times 10^{32}/V \tag{11}$$

The concentration of bomb-produced ozone is

$$[O_3]_B = 4.6 \times 10^{32}/V \tag{12}$$

The average concentration of bomb-produced ozone in the cloud is estimated to be 8×10^{11} molecules cm^{-3} on the day of the test, which is a substantial fraction of the natural ozone concentration at 18 km, Table 1.

The rate of NO_x catalyzed destruction of ozone is 2 $k_3[O][NO_2]$. The time for bomb-produced NO_x to destroy bomb-produced ozone is

$$\tau = \frac{4.6 \times 10^{32}/V}{2 \times 9.1 \times 10^{-12}\ [O] f (0.8\text{-}3) NO^{32}/V} \tag{13}$$

where 9.1×10^{-12} cm^3 sec^{-1} is the value of k_3 [CIAP, 1975]. The poorly known volume V of the bomb cloud cancels in this expression, and the time for bomb-produced NO_x to destroy bomb-produced ozone depends only on the concentration of oxygen atoms and the fraction f. For Bauer and Gilmore's upper and lower limit of the amount of NO_x produced by the nuclear bomb, the numbers of days for the bomb-produced ozone to be destroyed at 16 to 20 km are entered in Table 1. It can be seen that it takes much longer than the 10 days of Christie's study for bomb-produced NO_x to destroy bomb-produced ozone. Thus the excess ozone that Christie detected along the bomb trajectory probably was formed by the nuclear bomb itself. Johnston et al. [pp. 6111-6113, 1973] predicted this effect.

Nitrogen dioxide, as well as nitric oxide, is produced in nuclear bomb clouds [Johnston et al., p. 6110, 1973]. It is produced by reaction of bomb-produced nitric oxide with ozone and also with molecular oxygen at the high partial pressures of NO in the early bomb cloud. The fraction of bomb-produced NO_2 relative to NO_x is f_B and the natural stratospheric value of this ratio at the elevation of the stabilized bomb cloud is f_N, compare (6). If f_B differs from f_N, cycle B will rapidly (minutes) adjust the bomb-produced NO_2 to satisfy the ambient ratio f_N. If f_B is less than f_N, this process will rapidly consume ozone. If f_B is greater than f_N, this process will produce additional ozone in the stratospheric bomb cloud. The ratio of ozone destroyed or produced by this process to ozone produced by the other bomb mechanisms is (7, 8, 9),

$$\frac{\Delta[O_3]_B}{[O_3]_B} = \frac{(f_B - f_N)(0.8-3) \times 10^{32}}{4.6 \times 10^{32}} \tag{14}$$

Under the extreme condition of $f_B = 0$, $f_N = 0.4$, (Table 1), this ratio is $-1.2/4.6$, that is, the net effect of the nuclear bomb at early times is to produce ozone, not to destroy it.

A characteristic reaction "half time" can be defined as one-half the local concentration of ozone divided by the instanteous rate of catalytic cycle A:

$$\tau_{1/2} = \frac{[O_3]/2}{2\ k_3[O][NO_2]} \tag{15}$$

The natural ozone concentrations and the oxygen atom concentrations are given in Table 1, and the nitrogen dioxide concentrations can be calculated from (11) and (10). The resulting half-times are given in Table 2 as a function of day-number after the bomb test, elevation between 16 and 20 km, and for both upper limit and lower limit of the NO_x yield from nuclear bombs. These half-times are the order of magnitude of tens to hundreds of days, not the one to two hours expected by Christie [1976]. One expects very little destruction of ozone from the nuclear bomb studied by Christie during the 10 days that he studied it. It did not rise high enough into the stratosphere to cause a fast destruction of ozone.

Acknowledgment. This work was supported in part by the National Science Foundation, Grant No. MPS75-17833, and by the Materials and Molecular Research Division of the Lawrence Berkeley Laboratory.

References

Angell, J. K. and J. Korshover, Gobal analysis of recent total ozone fluctuations, *Mon. Weather Rev.*, *104*, 63-75, 1976.

Bauer, E. and F. R. Gilmore, Effect of atmospheric nuclear explosions on total ozone, *Rev. Geoph. Space Phys.*, *13*, 451-458, 1975.

Christie, A. D., Atmospheric ozone depletion by nuclear weapons testing, *J. Geophys. Res.*, *81*, 2581-2594, 1976.

CIAP, Monograph 1, The natural stratosphere of 1974, Rep. DOT-TST-75-51, National Technical Information Service, Springfield, VA 22151, 1350 pp., 1975.

Fabian, P. and W. F. Libby, The stratospheric residence time of odd nitrogen and the effect of the SST, studied in a two-dimensional model derived from high-altitude sampling of radioactive debris, Third Conference of the Climatic Impact Assessment Program, February 26-March 1, 1974, Rep. DOT-TSC-OST-74-15, National Technical Information Service, Springfield, VA 22151, 103-116, 1974.

Griffing, G. W., private communication, 1975.

Johnston, H. S., Catalytic reduction of stratospheric ozone by nitrogen oxides, Rep. UCRL-20568, TID-4500 (57th Ed.), pp. 14-15, 1971.

Johnston, H., G. Whitten, and J. Birks, The effect of nuclear explosions on stratospheric nitric oxide and ozone, *J. Geophys. Res.*, *78*, 6107-6135, 1973.

Johnston, H. and G. Whitten, Instantaneous photochemical rates in the global stratosphere, *Pure Appl. Geophys.*, *106-108*, 1468-1489, 1973.

Table 1. Standard atmosphere properties 16 to 21 kilometers, 15°S, July.

Elevation, km	16	17	18	19	20	Ref.
$[O]/10^5$, 12 hr av.	.55	1.1	2.2	4.4	8.5	a
$[O_3]/10^{12}$	.99	1.2	1.5	1.8	2.1	a
$f = [NO_2]/[NO_x]$	.14	.18	.25	.32	.40	a
τ (Eq. 11), days	253	98	36[d]	14	6	b
	949	369	133[d]	52	22	c

---

[a] Johnston and Whitten [1973].

[b] Time for bomb-produced NO_x catalytically to destroy bomb-produced ozone, upper limit of NO_x production from nuclear bomb.

[c] Same as b, lower limit of NO_x from nuclear bomb.

[d] These numbers would be 5 days and 17 days if one considers only the ozone produced by ultraviolet radiation from the bomb.

Table 2. Cloud volumes, bomb-produced NO_x concentrations, and times for bomb-produced NO_2 to destroy half of the local ozone as a function of days after the bomb test and elevation (Eq. 15).

	Day no.	0	2	4	6	8	Ref.
	$V/10^{21}$ cm^3	.58	1.6	4.3	8.1	10	
	$NO_x/10^{10}$ cm^{-3}	51	18	6.9	3.8	2.9	a
	$NO_x/10^{10}$ cm^{-3}	14	4.8	1.8	1.0	.7	b
km 16	$\tau_{1/2}$ days	157	440	1173	2200	2800	a
	$\tau_{1/2}$ days	589	1650	4400	8250	10500	b
18	$\tau_{1/2}$ days	33	93	247	460	587	a
	$\tau_{1/2}$ days	124	349	925	1725	2200	b
20	$\tau_{1/2}$ days	7	20	57	107	133	a
	$\tau_{1/2}$ days	25	75	213	400	500	b

---

[a] Maximum bomb-produced NO_x [Bauer and Gilmore, 1975].

[b] Minimum bomb-produced NO_x.

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