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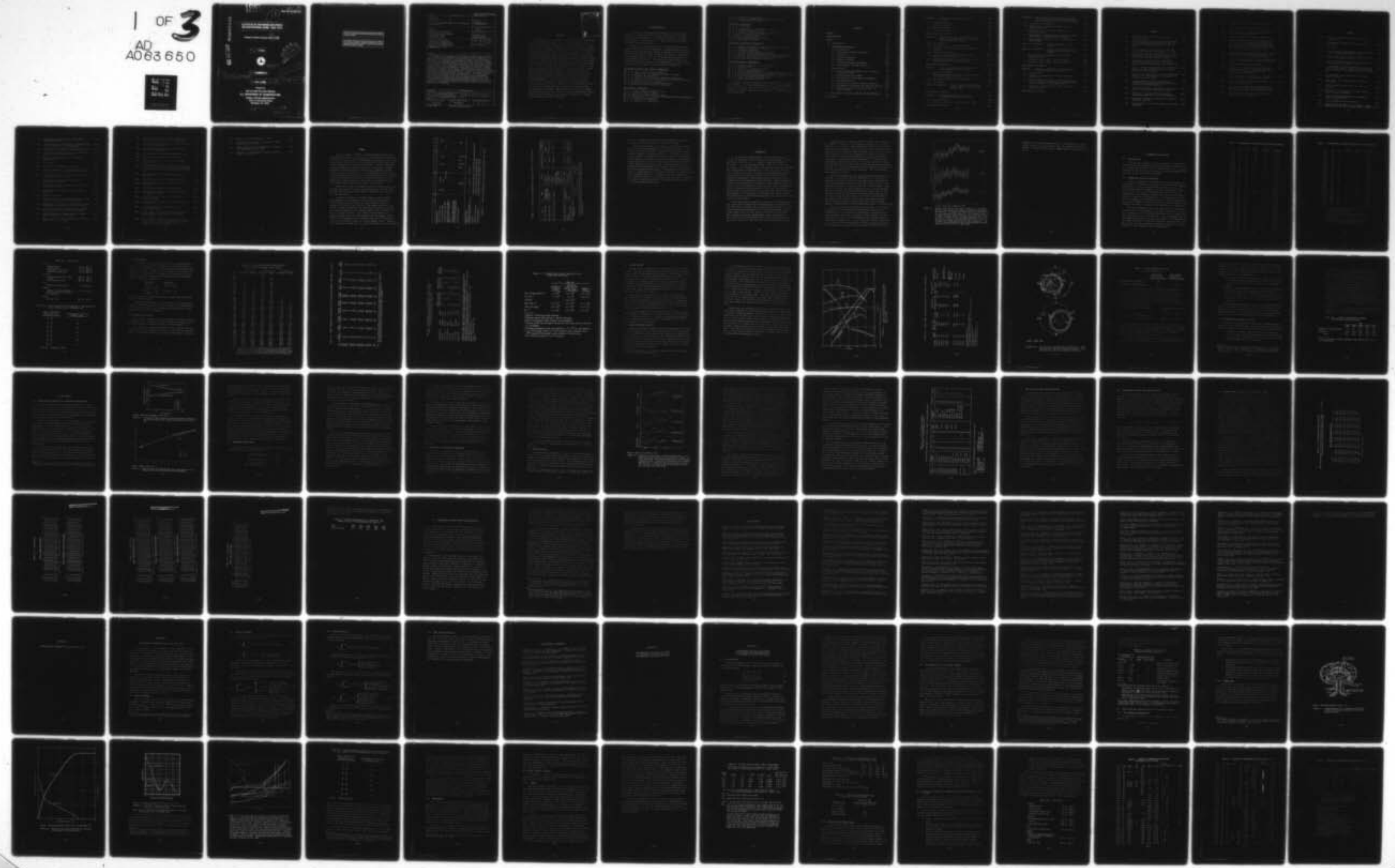

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16. Abstract

Stratospheric ozone depends on the stratospheric concentrations of oxides of nitrogen (NO_x), oxides of hydrogen (HO_x), chlorine and bromine compounds (ClX and BrX), as well as on the flux of solar ultraviolet radiation, the stratospheric temperature, and the parameters of stratospheric dynamics. There exist worldwide data on the total burden of atmospheric ozone since about 1955, and for comparison of these data with calculations using two-dimensional radiative/chemical/dynamics computer codes, a list is needed and is here presented of all major time-varying perturbations that have been suggested over the time frame 1955-1975. Detailed consideration is given to the following: atmospheric nuclear explosions, galactic cosmic rays, solar proton events, relativistic (or energetic) electron precipitation, major volcanic eruptions, halocarbons (fluoro-, chloro-, and bromocarbons), fertilizer manufacture, and other industrial nitrogen fixation. For sources injected directly into the stratosphere, the time-, altitude-, and latitude-dependent source strengths are listed, while for the ground-based sources the time- and latitude-dependent production and atmospheric emission rates are given. Time variations of solar UV (which represent perhaps the most important single perturbation) and of stratospheric temperature, and possible variations in stratospheric dynamics are also discussed.

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ABSTRACT

Stratospheric ozone depends on the stratospheric concentrations of oxides of nitrogen (NO_x), oxides of hydrogen (HO_x), chlorine and bromine compounds (ClX and BrX), as well as on the flux of solar ultraviolet radiation, the stratospheric temperature, and the parameters of stratospheric dynamics. There exist worldwide data on the total burden of atmospheric ozone since about 1955, and for comparison of these data with calculations using two-dimensional radiative/chemical/dynamics computer codes, a list is needed and is here presented of all major time-varying perturbations that have been suggested over the time frame 1955-1975. Detailed consideration is given to the following: atmospheric nuclear explosions, galactic cosmic rays, solar proton events, relativistic (or energetic) electron precipitation, major volcanic eruptions, halocarbons (fluoro-, chloro-, and bromocarbons), fertilizer manufacture, and other industrial nitrogen fixation. For sources injected directly into the stratosphere, the time-, altitude-, and latitude-dependent source strengths are listed, while for the ground-based sources the time- and latitude-dependent production and atmospheric emission rates are given. Time variations of solar UV (which represent perhaps the most important single perturbation) and of stratospheric temperature, and possible variations in stratospheric dynamics are also discussed.

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Because this catalog consists of a collection of diverse items in quite distinct disciplines, I requested assistance of various kinds from separate groups of experts to whom the draft report on the specific topic was sent for critique. Revisions of the separate drafts sent out for review are included here as Appendices B through F. The names and affiliations of the people who provided assistance are listed below; I wish to offer them my heartiest thanks for their help and cooperation.

Atmospheric Nuclear Explosions - Appendix B.

Dr. C. A. Blank, Defense Nuclear Agency
Mr. J. S. Cannon, Div. of Information, Dept. of Energy
Dr. F. R. Gilmore, R&D Associates
Dr. H. S. Johnston, University of California at Berkeley
Drs. F. M. Luther and W. H. Duewer, Lawrence Livermore Laboratory
Dr. A. A. Moghissi, Ga. Tech. and EPA
Mr. K. Telegadas, NOAA-Air Resources Laboratory
Dr. J. Zinn, Los Alamos Scientific Laboratory

Halocarbons: Appendix C.

Dr. F. A. Bower, DuPont de Nemours & Co.
Dr. R. J. Foster, Bureau of Mines
Dr. Wm. Hunt, Great Lakes Chemical Corp.
Dr. A. Jonnard and Mr. T. O'Connell, International Trade Commission
Dr. J. H. Plonka, Dow Chemical Co.
Dr. H. I. Schiff, York University
Mr. R. E. Shamel, A. D. Little, Inc.

Dr. H. B. Singh, SRI International
Mr. J. C. Van Horn, Manufacturing Chemists Association
Dr. S. C. Wofsy, Harvard University

Volcanoes: Appendix D.

Dr. R. D. Cadle, NCAR
Dr. A. W. Castleman, Jr., University of Colorado
Dr. J. P. Friend, Drexel University
Dr. J. M. Mitchell, NOAA Environmental Data Service
Dr. M. Sato, U. S. Geological Survey
Dr. S. Self, Dartmouth College
Dr. Tom Simkin, Smithsonian Institution
Dr. R. S. Stolarski, NASA/GSFC

Cosmic Ray Ionization: Appendix E.

Dr. M. G. Heaps, Atmospheric Science Laboratory, U. S. Army
Dr. D. J. Hofmann, University of Wyoming
Dr. F. B. McDonald, NASA/GSFC
Dr. T. A. Potemra, Applied Physics Laboratory
Dr. J. B. Reagan, Lockheed Missiles & Space Co.
Drs. D. Smart and M. A. Shea, Air Force Geophysics Laboratory
Dr. R. M. Thorne, University California at Los Angeles
Dr. J. Zinn, Los Alamos Scientific Laboratory

Nitrogen Fixation: Appendix F.

Dr. A. P. Altshuller and Mr. C. O. Mann, EPA
Dr. P. J. Crutzen, NCAR
Dr. R. J. Foster, U. S. Bureau of Mines
Dr. C. E. Kolb, Aerodyne Research Inc.
Dr. A. S. Newman, Cooperative State Research Service, U.S.D.A.
Mr. F. Rolf, Economics, Statistics & Cooperative Service, U.S.D.A.
Dr. G. Stanford, Agricultural Research Service, U.S.D.A.
Dr. W. C. White, The Fertilizer Institute
Dr. S. C. Wofsy, Harvard University

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CONTENTS

FIGURES

TABLES

SUMMARY

Here we compile a catalog of time-dependent natural and anthropogenic sources of NO_x, HO_x, and ClX during the time frame 1955-1975 as well as other time-dependent perturbations that would be expected to give rise to time variations of total ozone other than the diurnal and seasonal fluctuations. Factors considered include atmospheric nuclear explosions, halocarbons, volcanic eruptions, solar and galactic cosmic rays, industrially fixed nitrogen, solar ultraviolet (UV), and atmospheric motions. The catalog presents atmospheric or stratospheric inputs as a function of time and latitude, to provide an appropriate input for two-dimensional computer models so that one can establish how well the existing models explain the actual ozone record.

Figure S-1 lists, in schematic form, the major sources considered, and Table S-1 scales the injections due to each source in terms of the ambient stratospheric loading of NO_x, HO_x, and ClX (see Appendix A).

In terms of current (1977-1978) ideas of stratospheric photochemistry, which suggest that the relative importance of ClX as against NO_x injections on ozone is greater than was thought in 1974-1975, the effects of halocarbon emissions, explosive volcanic eruptions, and atmospheric nuclear explosions will be most important, with smaller effects due to cosmic rays and to nitrogen fixation. This refers to the injection of chemical species into the stratosphere, but the biggest single effect on stratospheric ozone may well arise from the variation of solar UV irradiance with the 11-year sunspot cycle. However, the interaction between NO_x, HO_x, and ClX species in the atmosphere,

Year:	1950	2	4	6	8	1960	2	4	6	8	1970	2	4	6
Geophysical Events														
Solar 11-yr Sunspot Cycle		Min		Large Max				Min		Max				Low Min
Galactic Cosmic Rays (GCRs)		Max		Min				Max		Min				Max
Large Solar Proton Events (SPEs)						5-7/59,11/60						8/72		
Quasi-Biennial Oscillation Maximum (Tropical, Angell and Korshover, 1976)	x	x		x	x	x	x	x		x	x		x	
Stratospheric Warmings (only major Northern Hemisphere events listed, R.S. Quiroz, private communication)		x		x	x		x		x	x	x x		x x	
Major Volcanic Eruption				Bezymianny			Agung	Sheveluch	Awu	Fernandina			Fuego	
Anthropogenic Factors														
Atmospheric Nuclear Explosion (yield in Mt, listed only if > 5 Mt/yr)	←	60	→	← 30 →/← 90 →		120	220							
Halocarbons	Fluorocarbon release increased by 12.5 percent per annum compounded, 1955-1975													
Commercial Nitrogen Fixation	Increased by 10 percent per annum compounded, 1955-1975													
Fossil Fuel Combustion	Increased by 5 percent per annum compounded, 1955-1975													

FIGURE S-1. Important Happenings During the 1955-1975 Time Frame

TABLE S-1. POTENTIAL STRATOSPHERIC INJECTION DUE TO A GIVEN SOURCE

Source	Example	Injection	Altitude of Injection	Latitude Range of Injection
Galactic Cosmic Rays (GCRs)	Difference between solar max and solar *min* (bigger at min!)	7×10^{32} HO_x p.a. 5×10^{32} NO_x p.a.	10-30 km	Polar caps ($\Lambda > 60°$, N or S)
Solar Proton Events (SPEs)	5-7 Aug 1972	4.5×10^{33} HO_x 3×10^{33} NO_x	30-35 km	Polar caps: $\Lambda > 65°$
Major Explosive Volcanic Eruption	Mt. Agung, 1963	9×10^{33} ClX H_2O (~ 2% of ambient stratospheric loading) dust: major contributor to ambient 2×10^{34} S atoms as SO_2 of H_2SO_4	16-30/35 km	8.5° S
Atmospheric Nuclear Explosions	U.S.S.R. series, Fall 1962 (180 Mt)	$(0.9 - 1.8) \times 10^{34}$ NO_x	10-35 km	77° N
Halocarbons	1973	7×10^{33} ClX p.a.[a]	Ground level	Mainly 30-55° N
Industrial Fixed Nitrogen	1973	2×10^{35} fixed N atoms p.a.[b]	Ground level	Mainly 30-55° N

Note: Ambient stratospheric loading is: (see Appendix A)

$NO_y = NO_x + HNO_3$ ($NO_x = NO + NO_2$) : $(4\text{-}15) \times 10^{34}$ mols

$HO_x = OH + HO_2$: $(15\text{-}30) \times 10^{32}$ mols

$ClX = Cl + ClO + HCl + ClO\ NO_2$: $\sim 1 \times 10^{34}$ mols

[a] Estimate of ground-level injectants that are sufficiently long-lived to enter the stratosphere.

[b] 6% of total nitrogen fixation representing N_2O which can enter the stratosphere and produce NO by reaction with $O(^1D)$.

as well as radiation and dynamics is recognized as important and thus all effects should be considered together.

For the convenience of the reader, the work is discussed and the results are presented in two levels of detail. The first level, which includes recommendations for inputs due to specific sources, is given in Section 2, followed by a discussion in Section 3 of some other factors that may be important, in particular, of changes in solar UV irradiance with sunspot number (see Section 3.1), but which have not been considered in as much detail as the other items. Detailed reviews of the appropriate stratospheric or atmospheric injections between 1955 and 1975 are given as Appendices B (atmospheric nuclear explosions), C (halocarbons), D (volcanic eruptions), E (cosmic rays), and F (nitrogen fixation). Appendix A provides estimates of stratospheric burdens of the various trace species of interest, to provide a crude indication of the relative significance of the various perturbing sources.

1. INTRODUCTION

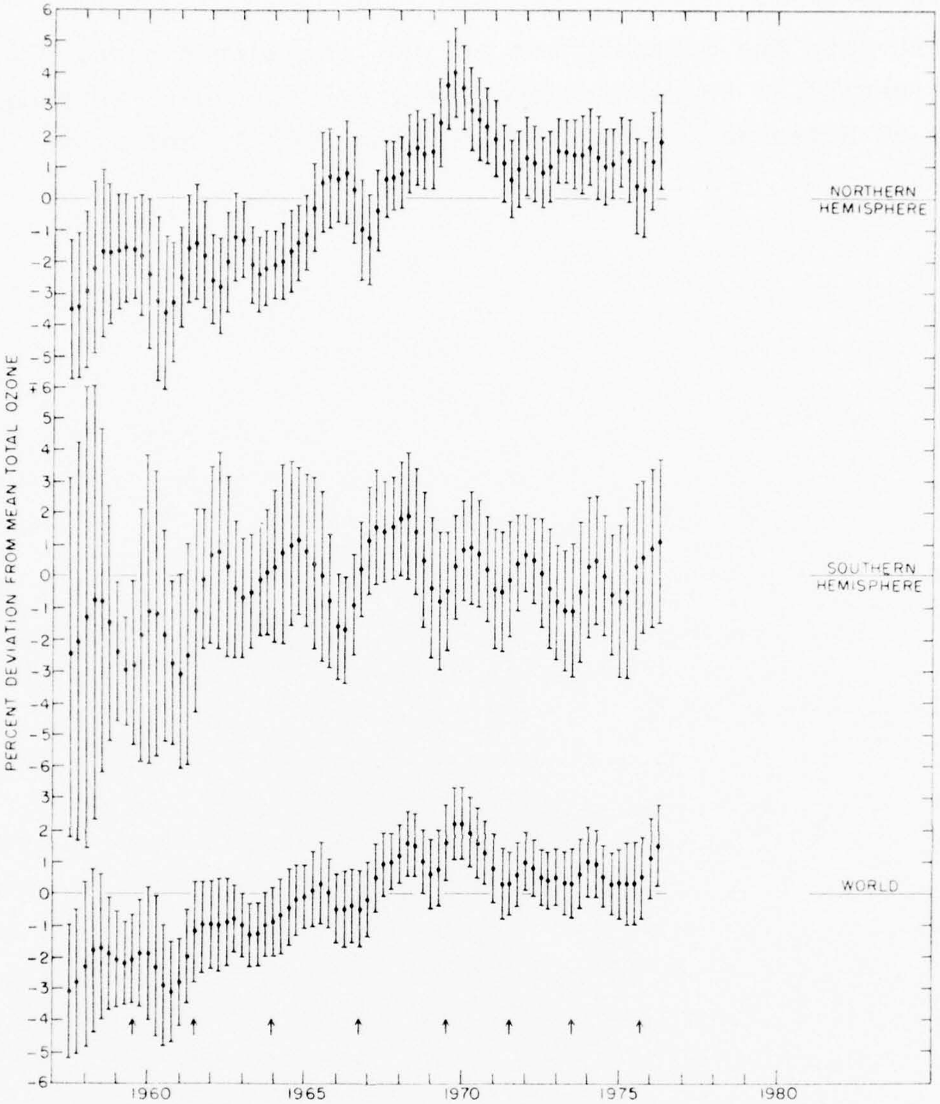
It is known that stratospheric ozone is destroyed by a variety of catalytic reaction cycles involving oxides of nitrogen ("NO_x" = NO + NO_2 + ...), oxides of hydrogen ("HO_x" = OH + HO_2 + ...), and chlorine species ("ClX" = Cl + ClO + HCl + ClO NO_2), also bromine, "BrX," and possibly also other species. The stratospheric concentrations of ozone, NO_x, HO_x, and ClX, are affected by a variety of natural and anthropogenic sources such as solar UV, solar and galactic cosmic rays, volcanic eruptions, atmospheric nuclear explosions, halocarbons, and (industrially and naturally) fixed nitrogen. Other geophysical factors, such as possible variations in stratospheric temperature and in stratospheric motions may also affect stratospheric ozone. Because of the interaction of the NO_x, HO_x, and ClX species with one another, as well as with ozone, with radiation and dynamics it is necessary to incorporate all these factors simultaneously in a photochemical/dynamic computer model to evaluate the total effect.

There exist data on ozone as a function of altitude, latitude, and time with moderately adequate global coverage since the mid-1950's, by which time a global network of some 45 to 90 Dobson spectrophotometers and M-83 filter photometers had been established; since the 1970 launch of Nimbus IV, there have been extensive satellite measurements which will provide a more detailed and fine-grained record once the data are calibrated and reduced so that they fit into the long-term record.

Long-term global trends of total ozone have been evaluated by a number of workers, in particular by Komhyr et al. (1971), Johnston et al. (1973), London and Kelley (1974); see in particular Angell and Korshover (1973, 1976, 1978) and work referenced therein, also the detailed atlas of London et al. (1976). Angell and Korshover (1978) find a significant 5 percent increase in total ozone in the Northern Hemisphere between 1960 and 1970, a marginally significant change thereafter. In the Southern Hemisphere, there appeared to be a 2 percent increase in total ozone between 1960 and 1968, and a 1 percent decrease thereafter; see Fig. 1.1, which demonstrates both the temporal variations and also the error bounds in total ozone data. The other workers find comparable effects.

All these measurements use the strong Hartley-Huggins absorption of ozone below 300 nm. Angione et al. (1976) have analyzed astronomical records in the Smithsonian astrophysical observation program between 1912 and 1950 which cover the weak Chappuis absorption of ozone in the 500- to 700-nm band. There appear to be some long-term variations, but it is not apparent that any inference on global trends can be made prior to 1955. Reference should be made here to the very careful analysis of the ozone record at Arosa from 1926 to 1971 by Birrer (1974), who finds at this single station that trend values decrease with increasing periods of observation and raises warnings against inferring trends from an inadequate period of observations.

The basic reason for compiling this catalog is to provide a check-case for two-dimensional photochemical models of the stratosphere, to see how well a given model can reproduce the time-dependent ozone data. Because of this emphasis on time-variations in ozone (on a scale greater than several months), steady-state sources, such as the continuous natural injections of N_2O, chloro- and bromocarbons from the biosphere, as well as the steady-state production of HO_x arising from natural water



Source: Angell and Korshover, 1978

FIGURE 1.1. Temporal Variation in Total Ozone, Expressed as a Percentage Deviation from the Mean for Northern and Southern Hemispheres and the World. The annual oscillation has been eliminated and the data smoothed by application of a 1-2-1 smoothing twice to successive seasonal values (last data are the northern summer of 1976). The vertical bars represent confidence limits such that there is about a 5 percent chance that the true value of the mean lies outside the vertical extent of these bars. The vertical arrows indicate the time of quasi-biennial west wind maximum at 50 mbar (21 km) in the tropics.

transport into the stratosphere are not considered here. For an overall review of these problems, see, for instance, National Academy of Sciences (1976, 1977), Hudson (1977), and Oliver et al. (1977).

2. RECOMMENDED INJECTIONS

2.1 INTRODUCTION

This section consists of a list of inputs for two-dimensional photochemical/dynamical computer models, extracted from the detailed discussions listed in Appendices B to F. Thus, an explanation for the choice of numerical values recommended here is given in the appropriate appendices.

2.2 ATMOSPHERIC NUCLEAR EXPLOSIONS

Table 2.1 (Table B-12 of Appendix B) lists estimates of stratospheric injections of NO_x due to past atmospheric nuclear explosions. The NO_x injection rate used here is 1.0×10^{32} molecules/Mt yield, as against a best estimate range of (0.4 - 1.5) or (0.6 - 1.1), $\times 10^{32}$ molecules/Mt (see Table B-1 of Appendix B). The latitude of given injections may be found in Table 2.2 (Table B-6 of Appendix B). The distribution of injection heights as a function of yield and latitude comes from Fig. B-5 of Appendix B; within each given altitude range the distribution of Table 2.3 (Table B-2 of Appendix B) is suggested.

Note that submegaton yield explosions are not considered (see Section B.5 of Appendix B), and the injection of H_2O and of O_3 is unlikely to be of critical importance in the present context (see Section B.4 of Appendix B). Also, detrainment is not specifically taken into account (see Section B.3 of Appendix B); its effect would be to reduce the effective injection rate of NO_x per Mt, but the quantitative change is unlikely to be significant in the context of other uncertainties.

TABLE 2-1. STRATOSPHERIC INJECTION OF NO_x BY NUCLEAR EXPLOSIONS

Date	Country	Location	Effective Yield, Mt	NO_x Injection 10^{32} mols	Altitude Range, km
31 Oct 52	USA	EN	10.4S	5.2	8.3 - 30.7
12 Aug 53	USSR	?M	1	1	7.9 - 16.0
28 Feb 54	USA	BK	15S	7.5	19.1 - 32.8
4 Aug 55	USSR	?M	0.75	0.75	7.3 - 14.9
24 Sep 55	USSR	?M	0.75	0.75	7.3 - 14.9
10 Nov 55	USSR	?M	0.75	0.75	7.3 - 14.9
23 Nov 55	USSR	?M	0.75	0.75	7.3 - 14.9
20 May 56	USA	BK	2	2	13.2 - 21.7
27 May 56	USA	BK	3.5S	1.75	15.3 - 24.7
20 Jul 56	USA	BK	5S	2.5	16.3 - 26.5
30 Aug 56	USSR	?M	1.5	1.5	9.1 - 17.9
2 Sep 56	USSR	?M	1.5	1.5	9.1 - 17.9
10 Sep 56	USSR	?M	1.5	1.5	9.1 - 17.9
17 Nov 56	USSR	?M	1.5	1.5	9.1 - 17.9
10 Apr 57	USSR	?M	3	3	10 - 20.7
16 Apr 57	USSR	?M	3	3	10 - 20.7
15 May 57	UK	XI	1	1	12.5 - 19.5
31 May 57	UK	XI	1	1	12.5 - 19.5
19 Jan 57	UK	XI	1	1	12.5 - 19.5
22 Aug 57	USSR	Sib	2	2	9.3 - 24.3
24 Sep 57	USSR	Arc.	2	2	9.3 - 24.3
6 Oct 57	USSR	?M	2	2	9.3 - 24.3
8 Nov 57	UK	XI	1	1	12.5 - 19.5
23 Feb 58	USSR	Arc.	3	3	10 - 20.7
27 Feb 58	USSR	Arc.	3	3	10 - 20.7
28 Apr 58	UK	XI	1	1	12.5 - 19.5
12 May 58	USA	EN	14S	0.7	13.2 - 20.4
28 Jul 58	USA	EN	8.9S	4.45	17.5 - 28.9
2 Sep 58	UK	XI	1	1	12.5 - 19.5
11 Sep 58	UK	XI	1	1	12.5 - 19.5
10 Oct 58	USSR	Arc.	1	1	7.9 - 16.0
12 Oct 58	USSR	Arc.	3	3	10 - 20.7
15 Oct 58	USSR	Arc.	3	3	10 - 20.7
18 Oct 58	USSR	Arc.	3	3	10 - 20.7
20 Oct 58	USSR	Arc.	3	3	10 - 20.7
22 Oct 58	USSR	Arc.	3	3	10 - 20.7
24 Oct 58	USSR	Arc.	3	3	10 - 20.7
25 Oct 58	USSR	Arc.	1	1	7.9 - 16.0
10 Sep 61	USSR	NZ	3	3	10 - 20.7
12 Sep 61	USSR	NZ	3	3	10 - 20.7
14 Sep 61	USSR	NZ	3	3	10 - 20.7
16 Sep 61	USSR	NZ	1	1	7.9 - 16.0
18 Sep 61	USSR	NZ	1	1	7.9 - 16.0
20 Sep 61	USSR	NZ	1	1	7.9 - 16.0
22 Sep 61	USSR	NZ	1	1	7.9 - 16.0
2 Oct 61	USSR	NZ	1	1	7.9 - 16.0
4 Oct 61	USSR	NZ	3	3	10 - 20.7
6 Oct 61	USSR	NZ	3	3	10 - 20.7
20 Oct 61	USSR	NZ	3	3	10 - 20.7
23 Oct 61	USSR	NZ	25	25	13.0 - 26.9
30 Oct 61	USSR	NZ	58	58	15.7 - 29.7
31 Oct 61	USSR	NZ	3	3	10 - 20.7

TABLE 2-1. STRATOSPHERIC INJECTION OF NO_x BY NUCLEAR EXPLOSIONS (cont)

Date	Country	Location	Effective Yield, Mt	NO_x Injection 10^{32} mols	Altitude Range, km
4 Nov 61	USSR	NZ	3	3	10 - 20.7
2 May 62	USA	XI	3	3	14.7 - 23.5
10 Jun 62	USA	XI	3	3	14.7 - 23.5
27 Jun 62	USA	XI	11	11	18.1 - 30.9
30 Jun 62	USA	XI	3	3	14.7 - 23.5
11 Jul 62	USA	XI	3	3	14.7 - 23.5
5 Aug 62	USSR	NZ	30	30	14.4 - 29.6
20 Aug 62	USSR	NZ	7	7	11.3 - 23.7
22 Aug 62	USSR	NZ	3	3	10 - 20.7
25 Aug 62	USSR	NZ	7	7	11.3 - 23.7
27 Aug 62	USSR	NZ	7	7	11.3 - 23.7
8 Sep 62	USSR	NZ	1	1	7.9 - 16.0
15 Sep 62	USSR	NZ	7	7	11.3 - 23.7
16 Sep 62	USSR	NZ	7	7	11.3 - 23.7
18 Sep 62	USSR	NZ	3	3	10 - 20.7
19 Sep 62	USSR	NZ	24	24	13.9 - 29.1
21 Sep 62	USSR	NZ	3	3	10 - 20.7
25 Sep 62	USSR	NZ	27	27	14.1 - 29.2
27 Sep 62	USSR	NZ	24	24	13.9 - 29.1
18 Oct 62	USA	J1	3	3	14.7 - 23.5
22 Oct 62	USSR	NZ	7	7	11.3 - 23.7
30 Oct 62	USA	J1	10	10	17.9 - 30.0
23 Dec 62	USSR	NZ	20	20	13.6 - 28.0
25 Dec 62	USSR	NZ	3	3	10 - 20.7
17 Jun 67	CHINA	LN	3	3	13.1 - 22.7
24 Aug 68	FRANCE	CEP	2.5	2.5	14.4 - 22.9
8 Sep 68	FRANCE	CEP	1	1	12.5 - 19.5
27 Dec 68	CHINA	LN	3	3	13.1 - 22.7
29 Sep 69	CHINA	LN	3	3	13.1 - 22.7
30 May 70	FRANCE	CEP	1	1	12.5 - 19.5
30 Jun 70	FRANCE	CEP	1	1	12.5 - 19.5
14 Oct 70	CHINA	LN	3	3	13.1 - 22.7
14 Aug 71	FRANCE	CEP	1	1	12.5 - 19.5
26 Jul 73	CHINA	LN	2.5	2.5	12.5 - 21.6
17 Nov 76	CHINA	LN	4	4	13A - 24.7

NOTES: For locations see Table 2.2 where identified, otherwise:

?M (USSR, 1953-1957) take 50-52^{0}N, 78-80^{0}E

Arc (USSR, 1958) take NZ: 75^{0}N, 55^{0}E

For effective yields, S denotes surface burst: height corresponds to actual yield, NO_x injection is half that of equivalent air burst.

For NO_x injection, see Table B-1. I suggest 1×10^{32} NO_x mols/Mt as a plausible choice.

For altitude range, see Fig. B-5. For equatorial bursts I suggest Peterson's (1970) curves, for polar bursts, Seitz (1968) curves as shown there. Table B-2 [from Peterson (1970)] is the recommended NO_x injection within the altitude range quoted here.

TABLE 2-2. TEST SITES

U.S.A.	
Eniwetok (EN)	11° N, 162° E
Bikini (BK)	11° N, 165° E
Christmas Island (XI)	2° N, 157° W
Johnston Island (JI)	17° N, 169° W
U.S.S.R.	
Novaya Zemlya/Arctic (NZ)	75° N, 55° E
Siberia	52° N, 78° E
Semipalatinsk (SP)	50° N, 80° E
U.K.	
Christmas Island (XI)	2° N, 157° W
FRANCE	
Centre d'Experimentation du Pacifique (CEP), Tuamotu Archipelago	21° S, 137° W
CHINA	
Lop Nor (LN)	40° N, 90° E

TABLE 2-3. INITIAL VERTICAL DISTRIBUTION OF RADIOACTIVITY OR NO_x ASSUMED WITHIN "MUSHROOM CAP"

Layer, Fraction of "Mushroom Cap" (from base to top)	Percentage of Activity Within Layer
$0 - \frac{1}{7}$	1
$\frac{1}{7} - \frac{2}{7}$	14
$\frac{2}{7} - \frac{3}{7}$	25
$\frac{3}{7} - \frac{4}{7}$	25
$\frac{4}{7} - \frac{5}{7}$	15
$\frac{5}{7} - \frac{6}{7}$	15
$\frac{6}{7} - \frac{7}{7}$	5

Source: Peterson, 1970

2.3 HALOCARBONS

Atmospheric injection rates per year for fluorocarbons 11 ($CFCl_3$), 12 (CF_2Cl_2), and 22 (CHF_2Cl) are listed in Table 2.4 (Table C-2 of Appendix C), and release rates of various chlorocarbons are given in Table 2.5 (from Tables 2-3, 2-4, and 2-5 of Appendix C). These are all ground-level injections; for the latitude range of injection, we suggest Option I, with Option II as a secondary alternative:

Option I		Option II	
50-60° N	5%	30-55° N	96%
30-50° N	90%		
30° N-30° S	2%	30-40° S	4%
30-40° S	3%		

where the emission should be distributed uniformly within each relevant latitude band.

During the time period of interest here, the anthropogenic release of bromocarbons is so small relative to the natural production that it should not be considered (see Section C.4 and especially Table C-9 of Appendix C).

2.4 VOLCANIC ERUPTIONS

The volcanic eruptions to be considered are listed in Table 2-6 (Table D-3 of Appendix D), and the suggested source function of Agung is given in Table 2-7 (Table D-2 of Appendix D).

Note there is a large uncertainty in both relative and absolute amounts of injectants, and also in the effective injection height. This simply reflects our lack of knowledge in the area.

TABLE 2-4. GLOBAL PRODUCTION AND RELEASE RATES FOR FC-11, -12, AND -22 THROUGH 1976 (in 10^6 kg)

	FC-11		FC-12		FC-22	
Year	Production	Release	Production	Release	Production	Release
1931			0.5			
1932			0.1			
1933			0.3	0.1		
1934			0.7	0.2		
1935			1.0	0.2		
1936	0.1		1.7	0.4		
1937	0.1		3.1	0.6		
1938	0.1		2.8	0.9		
1939	0.1	0.1	3.9	1.8		
1940	0.2	0.1	4.5	1.7		
1941	0.3	0.1	6.3	2.3		
1942	0.3	0.1	5.9	2.9		
1943	0.4	0.2	8.2	3.5		
1944	0.4	0.2	16.7	4.7		
1945	0.4	0.3	20.1	6.1	0.1	
1946	0.7	0.6	16.6	11.9		
1947	1.3	1.2	20.1	19.0	0.1	
1948	3.0	2.3	24.8	22.2	0.2	
1949	4.5	3.7	26.1	24.2	0.3	0.1
1950	6.6	5.4	34.9	27.4	0.8	0.1
1951	9.1	7.5	37.0	30.8	1.0	0.2
1952	13.7	10.9	38.5	32.6	1.6	0.3
1953	17.6	14.9	48.2	37.0	2.2	0.4
1954	21.4	18.7	51.3	42.2	2.9	0.6
1955	27.0	23.2	60.3	47.5	3.5	0.8
1956	33.5	29.1	71.9	55.4	6.1	1.2
1957	35.3	32.8	77.9	63.1	6.4	1.1
1958	31.3	31.2	77.8	66.4	7.7	1.4
1959	37.9	32.3	92.5	73.9	11.4	2.7
1960	52.5	42.2	105.0	88.1	12.3	3.3
1961	63.9	54.1	114.7	98.6	12.3	3.6
1962	82.1	67.6	135.0	113.1	15.6	4.7
1963	98.0	82.6	154.0	132.5	17.8	5.7
1964	116.6	97.9	178.4	153.8	22.6	6.9
1965	129.1	111.7	199.2	173.6	25.4	8.2
1966	148.1	125.1	226.1	192.9	31.9	9.9
1967	167.8	141.9	253.5	217.6	37.8	12.5
1968	192.1	161.6	279.3	248.9	46.1	16.5
1969	227.3	187.0	310.0	271.1	56.6	20.6
1970	249.2	212.3	334.8	296.1	59.3	23.5
1971	275.5	233.2	356.3	317.7	65.2	26.5
1972	315.8	260.3	391.1	343.5	70.8	31.3
1973	359.5	295.6	434.7	378.0	77.4	36.1
1974	379.7	324.1	455.0	408.4	88.7	42.3
1975	326.5	314.9	396.1	396.3	74.4	47.6
1976	355.2	308.2	427.9	380.1	94.1	60.2

Note: For FC-11 and -12 the data from Table 5 of DuPont (1977). For FC-22, the production figures are from Grant (1977) corrected for global production as indicated in the text (Section 2). The FC-22 release figures are obtained from the production figures by multiplying by the release/production ratio from Table 7 of McCarthy et al. (1977) on a year-by-year basis; but for 1976 the 1975 ratio, 47.1/73.6 = 0.640, was used.

TABLE 2-5. GLOBAL ATMOSPHERIC RELEASE RATES OF SELECTED CHLOROCARBONS, 1955-1974 (in 10^6 kg)

Year	Carbon Tetrachloride	Methyl Chloroform	Ethylene Dichloride	Methylene Chloride	Perchlor-ethylene	Trichlor-ethylene	Vinyl Chloride	Methyl Chloride	Chloroform	Ethyl Chloride
1955	52	8	31	49	154	453	35	.5	2	-
1956	51	12	37	63	160	496	39	.6	3	14
1957	48	20	49	63	170	485	41	.7	3	13
1958	47	21	47	59	161	423	45	.6	2	12
1959	50	30	70	75	175	516	64	1.0	4	12
1960	46	36	77	75	180	506	68	1.2	4	12
1961	41	38	83	77	194	443	69	1.5	4	11
1962	47	56	108	96	276	511	86	1.6	5	12
1963	48	51	109	99	280	528	94	1.7	5	13
1964	48	57	134	119	316	531	106	1.9	6	15
1965	48	73	149	141	370	624	132	2.7	8	15
1966	54	133	220	178	400	689	164	3.4	9	15
1967	62	131	241	175	460	703	159	4.0	9	14
1968	65	161	292	202	549	744	195	4.4	9	13
1969	75	170	367	244	548	856	245	5.9	11	15
1970	80	186	454	268	610	877	266	6.1	12	15
1971	73	214	460	267	608	738	285	6.3	11	14
1972	71	246	477	314	633	613	334	6.6	12	13
1973	61	387	565	346	609	648	352	7.9	12.4	14.6
1974	67	356	470	394	630	622	375	6.7	15	15
1975	54	319	485	331	586	420	276	5.3	13	13
1976	51	401	489	356	577	453	373	5.5	14	15

Note: Data for carbon tetrachloride come from Table C-4, and for methyl chloroform from Table C-6. In each case, we list here the arithmetic mean of all the release figures quoted in the approximate table. All the other figures come from Little (1975) using the analysis of Annex A to Appendix C.

TABLE 2-6. A RECOMMENDED LIST OF STRATOSPHERIC INJECTIONS DUE TO MAJOR VOLCANIC ERUPTIONS FROM 1955-1975, SCALED IN TERMS OF THE AGUNG INJECTION OF TABLE 2-7[a]

Date of Eruption	Volcano	Latitude	Magnitude of Injection Relative to Agung			Maximum Height of Injection, kg			Local Tropopause Height, km[e]
			b	c	d	b	c	d	
30 Mar 1956	Bezymianny	56° N	(1)	2	1.4	45	47	47	9.5
21-24 May 1960	Puyehue	40° S	-	0.5	0.2	-	18	18	11.5
17 Mar, 5 May 1963	Agung	8.5° S	1.0	1.0	1.0	52	23	23	16.3
12 Nov 1964	Sheveluch	56° N	(1)	-	(0.3)	(25)	-	(25)	9.8
12 Aug 1966	Awu	3.5° N	0.3	-	0.1	(20)	-	(20)	16.5
11-12 Jun 1968	Fernandina	0.5° S	0.3	-	0.1	(20)	22[f]	22	16.3
10-23 Oct 1974	Fuego	14.5° N	0.2	0.5	0.3	20	19	19	16

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[a] Preliminary estimate. Material injected should be distributed uniformly between the local tropopause height and the maximum height of injection. Numbers in parentheses are especially uncertain.

[b] Estimate extracted by E. Bauer from diverse published and unpublished sources, in particular, Lamb (1970), Friend (1972), and private communication, and Cadle et al. (1976, 1977).

[c] Private communication from S. Self, April 1978 - computed from Wilson et al. (1978).

[d] Revised estimate using b and c.

[e] Source: Crutcher and Davies, 1969.

[f] Observed.

TABLE 2-7 STRATOSPHERIC SOURCE FUNCTION OF THE AGUNG ERUPTION CLOUD

	Mass, kg		
	Estimate of Cadle et al. (1977)	Estimate of S. Self (private communication, May 1978)[a]	Suggested Value[b]
Total erupted material[c]	5×10^{12}	1.4×10^{12}	2.6×10^{12}
Fine ash[d]	1×10^{10}	9×10^{9}	9.5×10^{9}
Total gas	-	2.9×10^{10}	-
Water vapor[e]	1.2×10^{11}	2.2×10^{10}	5.1×10^{10}
Total S as H_2SO_4[f]	1.8×10^{10}	2.1×10^{9}	6.1×10^{9}
HCl[g]	1.2×10^{9}	7.3×10^{8}	9.4×10^{8}

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[a] Based on 17 March and 16 May eruptions.

[b] Geometric mean of the Cadle et al. and Self estimates.

[c] Most of this material does not enter the stratosphere.

[d] Cadle et al(1977) do not specify the particle size; Self refers to particles < 2 μm diameter.

[e] The mean stratospheric water vapor loading is $\sim 2 \times 10^{12}$ kg, see Appendix A.

[f] 5.1×10^{9} kg H_2SO_4 contain 3.3×10^{34} S atoms so that presumably $(3\text{-}6) \times 10^{34}$ OH radicals are consumed in the formation of sulfuric acid.

[g] 9.4×10^{8} kg HCl contain 9×10^{33} molecules.

2.5 CARBONYL SULFIDE*

Crutzen (1976) suggested that the gaseous species carbonyl sulfide (COS) may be a significant source for the stratospheric aerosol layer in volcanically quiet times. This species, which is produced in a variety of ways--biologically, in volcanic eruptions, and in coal combustion--is relatively inert in the troposphere in comparison with the common atmospheric sulfur-containing gases, H_2S and SO_2, but will presumably be oxidized to sulfuric acid in the stratosphere, and thus will contribute to the Junge layer, and conceivably may affect stratospheric ozone, cf. Cadle et al. (1975).

Observations of Maroulis et al. (1977) and of Sandalls and Penkett (1977) indicate that the species is fairly widely and uniformly distributed, which supports Crutzen's suggestion and implies either a long atmospheric life time (compared with H_2S and SO_2) or uniform terrestrial sources (i.e. not concentrated in urban or other limited areas), or both.

At present there exist insufficient data to make a reasonable estimate of atmospheric COS input rates, but its production in coal combustion makes it at least a potential future source for the stratospheric aerosol layer (see Turco et al. (1978) for a discussion of this topic).

2.6 COSMIC-RAY-INDUCED IONIZATION

Cosmic rays produce ionization in the atmosphere; explicitly in the stratosphere one ion pair gives rise to 1.3 NO molecules and 2.0 OH radicals on the average (see Section E.3, Appendix E). The OH radicals are short-lived, so that vertical transport for distances greater than about 1 km is never important; below about 45 km, NO molecules are sufficiently long-lived so that vertical transport into regions where they can affect the bulk of stratospheric ozone may be significant.

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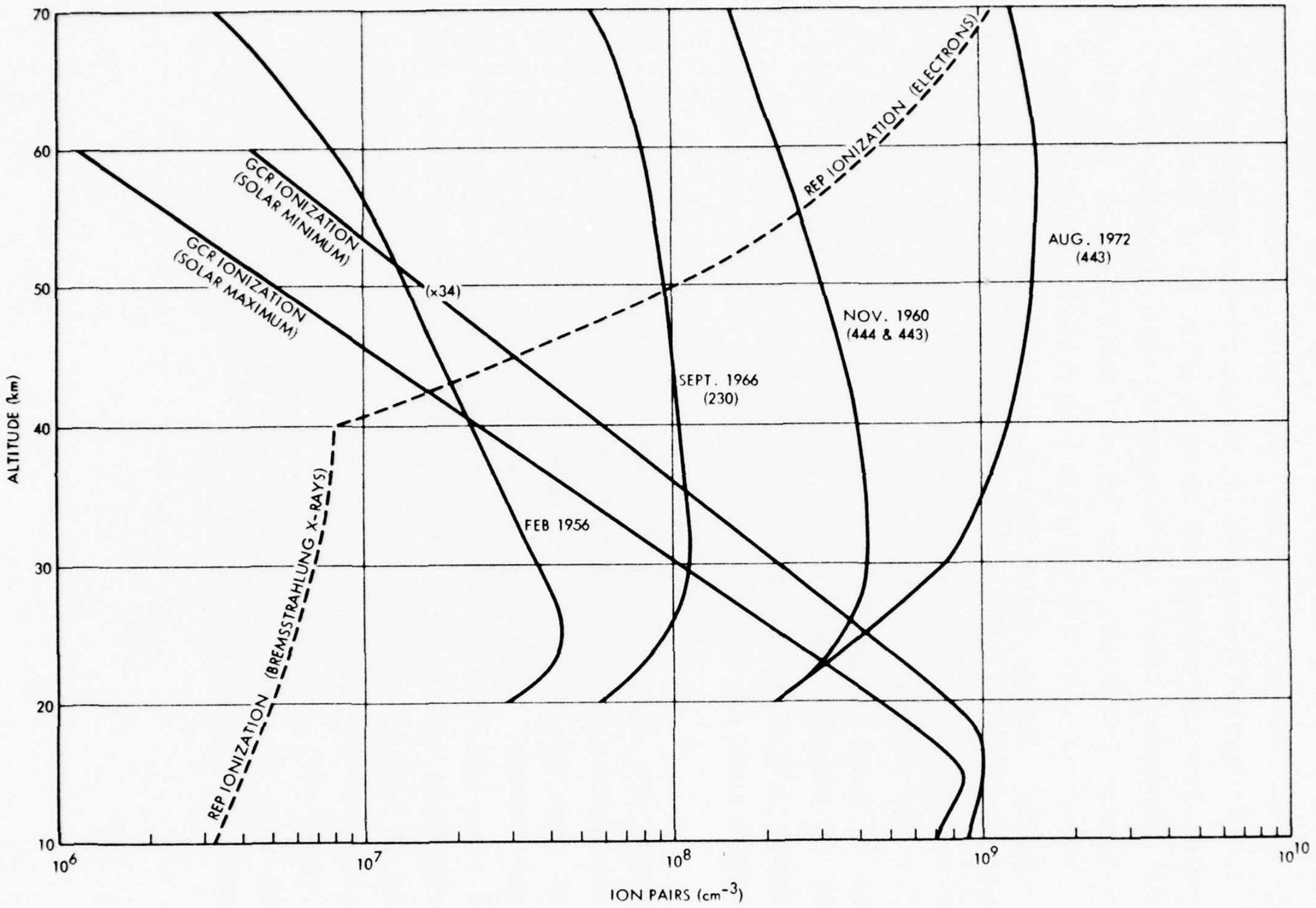
*Drs. A. C. Aikin and J. P. Friend suggested that this species should be discussed separately.

For ionization in the stratosphere, cosmic ray energies in the range 30 to 500 MeV are required, and thus we are interested in galactic cosmic rays (GCRs) and in solar proton events (SPEs). Galactic cosmic rays are modulated by the solar wind and peak during sunspot minimum; these are comparatively energetic particles whose ionization peaks near 15 km [see Fig. 2.1 (Fig. E-6)]. By contrast, solar protons are produced by active solar regions which give rise to intense solar flares near solar maximum; the kind of large event which affects the stratosphere occurs perhaps 1 to 5 times per 11-yr solar sunspot cycle and has a duration of 1 to 3 days on the average. Figure 2.1 also shows the ionization profiles of some large SPEs. Note that the mean energy of solar protons is significantly lower than that of galactic cosmic rays. Table 2.8 lists those large SPEs during the 1955-1975 time period that should be considered in the present context.

Cosmic rays are affected by the earth's magnetic field, and thus their ionization is particularly important in the polar caps or regions of high geomagnetic latitude Λ. Figure 2.2 (Fig. E-2) shows both the "outer" polar caps C_o which correspond roughly to $\Lambda \gtrsim 60^\circ$, and also the "inner" polar caps C_i corresponding $\Lambda \gtrsim 65^\circ$. The relatively high energy GCRs are significant in the outer polar caps and also at low latitudes (see Table 2-9), while the less energetic solar protons are only important within the inner polar caps. (See Table E-1 and Fig. E-3 for a representation of both sets of polar caps in terms of geographic latitude θ for use in two-dimensional photochemical models.)



Sources: Crutzen, Isaksen and Reid (1975), Thorne (1978), and Reid private communication.

4-30-78-41

FIGURE 2-1. Total Ionization Profiles Due to Some SPEs and the Total Annual Ionization Due to GCRs.

TABLE 2-8. SOME LARGE SOLAR PROTON EVENTS AND THEIR IONIZATION

Event Date	Shea-Smart Index	Peak Flux >30 Mev (part/cm^2 sec ster)[a]	GLE (%)[b]	Rigidity Spectrum[c] J_o (part/cm^2 sec ster)	P_o (Mv)	Total No. of Ion Pairs (x10^{32}) Reid[d]	This work[e,f]	Suggested Ionization used for this event
23 Feb 56	X34	6,200	4550-9000	140	300	0.74[g]	1.99	Event shown
10 May 59	X40	7,000	0	30,000	65	-	4.80	1.34 * profile for November 1960 (see text)
10 July 59	X40	4,000	0	7,800	90	-	1.71	
14 July 59	X40	11,000	0	35,000	68	-	5.72	
16 July 59	X42	17,000	0	3,200	125	-	6.14	
4 May 60	(1)24	200	175-290	6.7	280	-	0.25	Negligibly small: $\frac{0.25}{1.99} = 0.126$ x Feb 56 event
12 Nov 60	444	120,000	100-135	1,100 3,400	280 185	17	8.2	Event shown
15 Nov 60	443	6,000	88-150	250 3,300	375 120		5.5	
2 Sep 66	230	150	0	-	-	2.5	-	Event shown
2 Nov 69	330	737	0	-	-	-	-	---
4 Aug 72	443	21,000	15	-	-	25	-	Event shown

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[a] From Sauer and Stonehocker (1977)

[b] From Svestka and Simon (1975); Pomerantz and Duggal (1974)

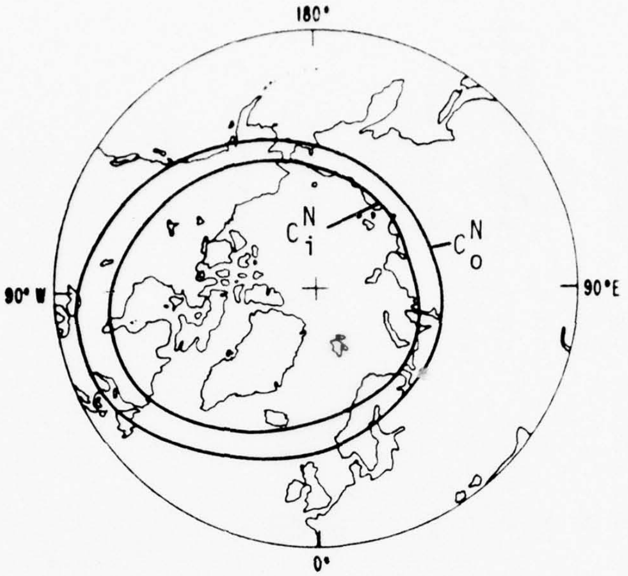
[c] From Freier and Webber (1963)--see Table D.3 and Eq. (D.3), where J_o and P_o are defined

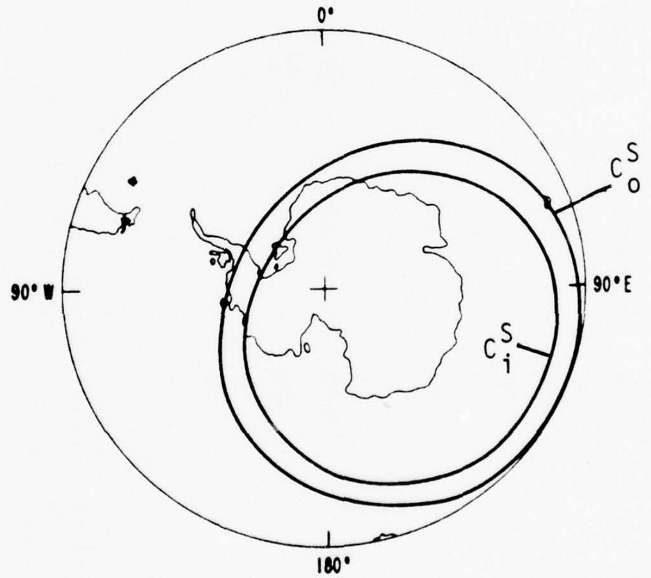
[d] In Crutzen, Isaksen and Reid (1975)

[e] See Appendix D, item 3

[f] Three figures are not significant

[g] G.C. Reid, private communication, Dec. 1977





Source: Reid, 1974

FIGURE 2-2. The Northern and Southern "Polar Caps." SPE effects are important inside curves C_i, while GCR effects are most important inside C_o.

TABLE 2-9. TOTAL IONIZATION DUE TO GCRs
(in 10^{32} ion pairs/yr)

	Solar Sunspot Minimum (i.e., maximum ionization)	Solar Sunspot Maximum (i.e., minimum ionization)
High Latitudes--in curves C_o	13	7
Low Latitudes--outside curves C_o	26	20

The ionization profile due to GCRs may be expressed as a function of both time (relative to the year of GCR maximum, i.e., solar sunspot minimum) and of latitude (where we distinguish between the polar cap region, defined in terms of the curves C_o of Fig. 2.2 (or $\Lambda > 60^o$) and the rest of the earth, i.e., curve "$1-C_o$" (or $\Lambda < 60^o$) as follows in terms of equations of Section E.4 in Appendix E.

High geomagnetic latitude, C_o	Low geomagnetic latitude $(1-C_o)$
$z > 20$ km Eq (E4.1)	$z > 31$ km Eq (E4.4)
15 km $< z <$ 20 km Eq (E4.2)	
10 km $< z <$ 15 km Eq (E4.3)	18 km $< x <$ 31 km Eq (E4.5)

The ionization profile due to SPEs may be taken as uniform with latitude over the polar caps defined in terms of the inner curves C_i of Fig. 2.2, or equivalently, for geomagnetic latitudes $\Lambda \gtrsim 65^o$. The altitude profile of ionization due to SPEs is shown in Fig. 2.1 (Fig. E-6, Section E.5).

A crude appreciation of the overall significance of cosmic ray ionization on stratospheric ozone can be seen from Tables 2.8

and 2.9, which show a source of order 20 x 10^{32} ion pairs per event* or per year. Since one ion pair gives rise to 1.3 NO molecules and 2.0 OH radicals on the average, we have a source of about 25 x 10^{32} NO molecules and 40 x 10^{32} OH radicals per event or per year. By comparison:

- The Soviet atmospheric nuclear test series of Fall 1961 (the largest ever, corresponding to 180 Mt total yield) injected (70-270) x 10^{32} NO molecules into the stratosphere.
- The global stratospheric loading of $NO_y = NO + NO_2 + HNO_3$ is of order (4-15) x 10^{34} molecules (see Appendix A).
- The global stratospheric loading of HO_x radicals (= OH + HO_2) is of order (7-16) x 10^{32} molecules, but with large uncertainties and with a very rapid turnover rate (see Appendix A).

Thus we conclude that while cosmic ray ionization effects are not negligible, they are not of primary importance in the present context, as compared either with nuclear test series which put more NO_x into the stratosphere or in particular with sources of ClX such as halocarbons and volcanic eruptions.

2.7 ANTHROPOGENIC NITROGEN FIXATION

Recommended time-varying anthropogenic nitrogen fixation rates are listed in Table 2-10. The numbers come from the discussion in Appendix F, and the following points should be noted:

a. Commercial nitrogen fixation, which is principally ($\gtrsim$ 75 percent) fertilizer production, has been increasing at a rate of 10 percent per annum, much faster than the combustion source (5 percent).

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*During the 1955-1975 time frame, there have been just three major series of SPEs that should be considered in the present context, namely, those of May-July 1959, November 1960, and August 1972.

b. The numbers listed are production rates of fixed nitrogen. There is a significant delay before the fixed nitrogen is denitrified, a process in which approximately 6 percent of total nitrogen goes into N_2O (see CAST, 1976), while the remainder reverts to N_2. Then there are further delays before this N_2O is mixed throughout the troposphere, and before the N_2O is decomposed in the stratosphere to produce NO, which, in turn, reacts with ozone. The total time delay involved here is probably in excess of 10 years, and thus because of the rapid increase in anthropogenic nitrogen fixation it appears unlikely that a significant effect on ozone would be apparent as early as 1970-1975. This point is discussed in Section F-1 of Appendix F.

c. Because of this long delay, the latitude variation of production or injection should not be critical, but see Table F-3 for the latitude variation.

TABLE 2-10. ESTIMATE OF ANTHROPOGENIC NITROGEN FIXATION RANGE, 1955-1957, MT(N)/yr

	Year				
	1955	1960	1965	1970	1975
Commercial nitrogen fixation	7.4	11.9	19.1	30.7	49.5
Combustion	10.9	14.0	17.8	22.7	29.0
Total*	18.3	25.9	36.9	53.4	78.5

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*Effect of soybeans and other leguminous crops (see Section F.2.3) is not included here.

3. OTHER FACTORS[*]

3.1 SOLAR ULTRAVIOLET RADIATION AS A FUNCTION OF SOLAR ACTIVITY

The solar ultraviolet irradiance determines the overall level of stratospheric ozone, principally by the photodissociation processes which lead to the formation of ozone in the first place, and also by the local heating resulting from the absorption of solar UV and the changes in temperature, photochemistry, and dynamics resulting from this heating.

Different measurements of solar UV radiation in the 120 to 300/400 nm wavelength range have been reviewed by Heath and Thekaekara (1977), by Delaboudiniere et al. (1977), and by Simon (1978), all of whom infer a significant variation of the solar 200 to 300 nm irradiance (20 to 50 percent variation) with the 11-year solar sunspot cycle, with more radiation at solar maximum than at solar minimum. This is not inconsistent with comparable or larger effects--factor two at 170 to 200 nm and at Lyman- α [see also Vidal-Madjar (1977)] at shorter wavelengths.

The results of Heath and Thekaekara (1977) are shown in Fig. 3.1, were redrawn by the 1977 NASA Committee [see Hudson (1977)] as shown in Fig. 3.2, and have been incorporated in several model calculations of stratospheric ozone, see Brasseur and Simon (1977); Nealy, Callis, and Natarajan (1977); and in

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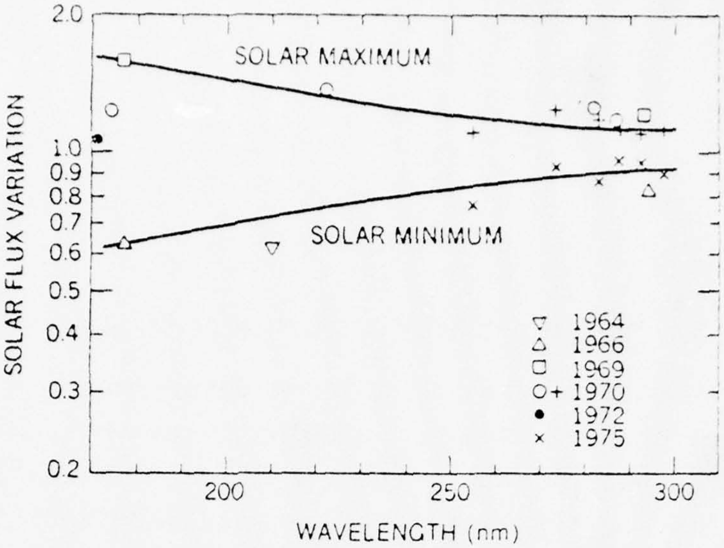
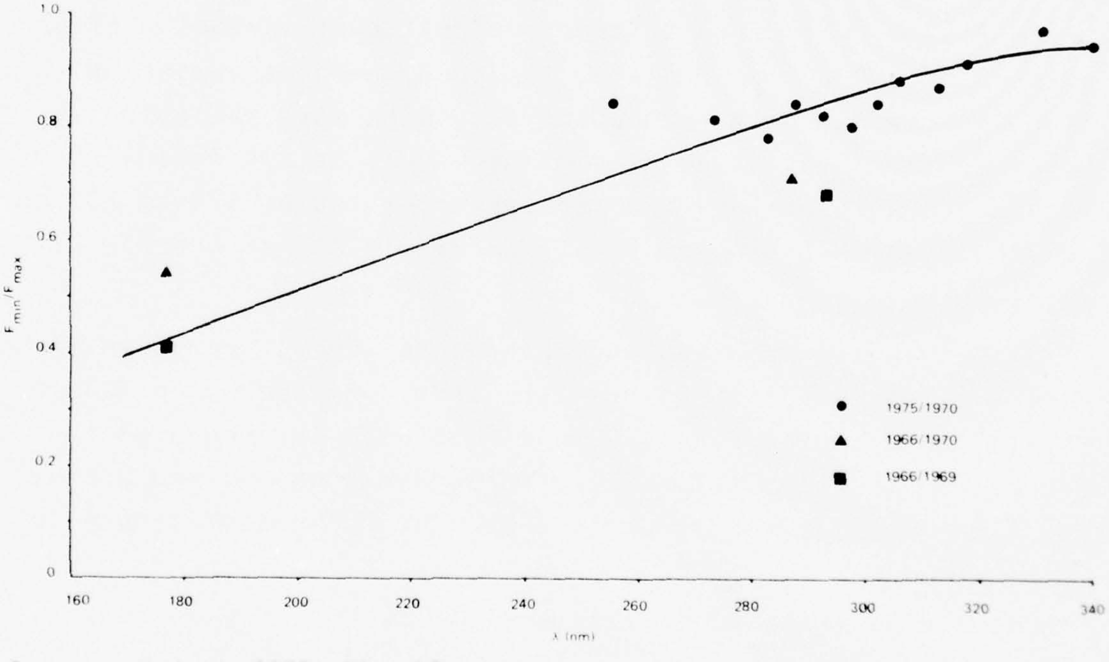
[*] These are not treated at the level of detail of the items in Chapter 2, but they are potentially of considerable importance.



Source: Heath and Thekaekara, 1977, Fig. 8

FIGURE 3-1. Variations in Solar Spectral Irradiance Apparently Related to the 11-year Sunspot Cycle, Based on Observations from 1964 to 1975.



Source: Hudson, 1977, Fig. 17

FIGURE 3-2. Ratio of Solar Flux Measured Near Solar-Cycle Minimum to that Measured Near Solar-Cycle Maximum Versus Wavelength.

particular Callis and Nealy (1978). These modelers typically find an increase in total ozone of 8 percent as one goes from solar minimum to solar maximum. This is a very large effect, which could overwhelm all others during the 1955 to 1975 time period.

The conclusions of Heath and Thekaekara (1977) have been criticized by a number of workers, see White (1977), pp. 212 and 325; also Delaboudiniere et al. (1977); while Simon (1978) estimates a somewhat smaller effect; indeed Heath (private communication, February 1978) considers that while the effect is real, its magnitude is not yet established.

I suggest that the correlation of Heath and Thekaekara (1977) should be used but with the caveat that the existing length of record (from 1964 on) is inadequate to establish such a variation: two cycles (22 years) would be needed as a minimum. The Heath-Thekaekara estimate of Fig. 3.1 is the largest variation currently proposed; if it withstands criticism, UV variability may well be the single most important contributor to changes in stratospheric ozone during the 1955 to 1975 time period, but at present (June 1978) there is not sufficient evidence to provide a quantitative estimate of the effect.

3.2 STRATOSPHERIC WATER VAPOR

The stratospheric odd-oxygen concentration is reduced to a significant extent by the HO_x cycle:

$$\begin{array}{lr} O_3 + OH \rightarrow HO_2 + O_2 & \text{(a)} \\ HO_2 + O \rightarrow OH + O_2 & \text{(b)} \\ \hline \text{Net: } O + O_3 \rightarrow 2\ O_2 & \text{(c)} \end{array} \qquad (3.1)$$

Also, the HO_x species react with NO_x and ClX species in a variety of ways. The HO_x comes from stratospheric water, and $O(^1D)$; the $O(^1D)$ is produced by photodissociation of O_3 (and of O_2) while the water comes mainly by transport from the troposphere, but partly by oxidation in the stratosphere of methane (CH_4) transported from the ground.

Our knowledge of the burden of stratospheric water vapor is very poor--see Kuhn et al. (1975) and Harries (1976). There are data in England and in Washington, D. C., extending over almost 20 years, which give some indication that the overall level of stratospheric water vapor may have been increasing over the 1950 to 1970 time period--see, e.g., Figs. 5 and 6 of Harries (1976). However, the stratosphere is so very dry compared with the troposphere that measurements are very difficult, and there is a considerable spread of data given by different methods. Indeed, Harries does not think that an increasing trend has been established.

There are other analyses which support the suggestion of an increase in stratospheric water vapor during this time period. Thus, Angell and Korshover (1974) find some evidence for an increase in the tropopause pressure and temperature in the 1960 to 1970 decade, particularly in tropical latitudes, which may perhaps be related to an increase in stratospheric water vapor in terms of the still-current model, due originally to Brewer (1949), that the concentration of water vapor in the stratosphere is limited by the "cold trap" in the tropical torpopuase. Also, systematic reports of noctilucent clouds (see Newell et al., 1974, p. 265) indicate a relative maximum in cloud sightings in 1967 to 1968, which may imply a corresponding maximum in stratospheric water vapor (or a minimum in stratopause/mesophere temperature!).

Overall, the current status of stratospheric water vapor data bears some resemblance to the ozone data of the early 1950s, when there had been some decades of observations at a few closely spaced locations in Western Europe (mainly Oxford, Arosa, and Tromsö), but simply not enough global coverage to permit any inference of long-term worldwide trends.

Further, we do not yet understand the budget, sources, and sinks of stratospheric water vapor very well, particularly as it relates to general stratospheric transport. The current interpretation is based on transport both into and out of the stratosphere by the Hadley circulation, with considerable disagreement about what happens at higher latitudes (the Hadley circulation is restricted to latitudes less than 30 to 35°, north or south). Thus, Kuhn et al. (1975) and Ellsaesser (1974) present quite different models.

Long-term global measurements of stratospheric water vapor and relative humidity in the lower stratosphere and upper troposphere are urgently needed. The best platform would presumably be a satellite, calibrated against balloon-borne (or other ground-based) data, in a limb scan mode. For budget purposes, the concentration data clearly have to be supplemental with velocities of upwelling and subsidence as a function of place and time.

3.3 VARIATIONS IN STRATOSPHERIC TEMPERATURE

There is an interaction between solar irradiance, ozone concentration, temperature, and dynamics which is now being characterized by two-dimensional models [see, e.g., Louis, London, and Danielsen (1974)]. Further, the rate constants for most of the chemical and photochemical processes that determine stratospheric ozone depend on temperature, and thus changes in stratospheric temperature--by affecting the rates of different reactions differently--may be expected to change the total ozone concentration [see, e.g., Boughner (1978) and Luther and Duewer (1978)].

In addition to diurnal variations, the stratospheric temperature shows also semi-annual, annual, biennial, and longer term variations--see Newell et al. (1974). A number of workers have looked at longer term variations, in particular in its relation to the (tropical) quasi-biennial oscillation (QBO)[*] and the solar cycle. Thus, diurnal and seasonal variations are well established, as is the QBO at low latitudes ($\lesssim 30^\circ$) (cf. e.g., Angell and Korshover (1973, 1976, 1978). Figure 3-3 shows some of the correlations between total ozone, tropical tropopause temperature, and stratospheric water vapor measured at Washington, D. C. Correlations between total ozone and temperature at different temperatures in the stratosphere are found at a number of mid-latitude stations on a scale of 1 to 3 years [cf. Sekihara et al. (1977)]. This may just be a representation of the QBO. There are also longer term effects, such as an apparent breakdown of the QBO associated with the volcanic eruption of Mt. Agung in 1963, which is discussed further in Section 3.5, and a significant long-term cooling in the Northern Hemisphere at 21 to 24 km altitudes of almost 1° K between 1957 and 1972 (cf. Zerefos and Mantis, 1977).

It is not apparent that these effects can yet be incorporated in models of stratospheric photochemistry in a significant way.

3.4 DYNAMICAL EFFECTS

Two-dimensional photochemical models incorporate atmospheric transport in a semi-phenomenological way, typically separating large-scale mean motions from smaller scale (sub-grid) eddy transport, see Danielsen and Louis (1977). The parameterization gives seasonal averages and provides a reasonably satisfactory representation of ozone, which is created and mostly destroyed in the

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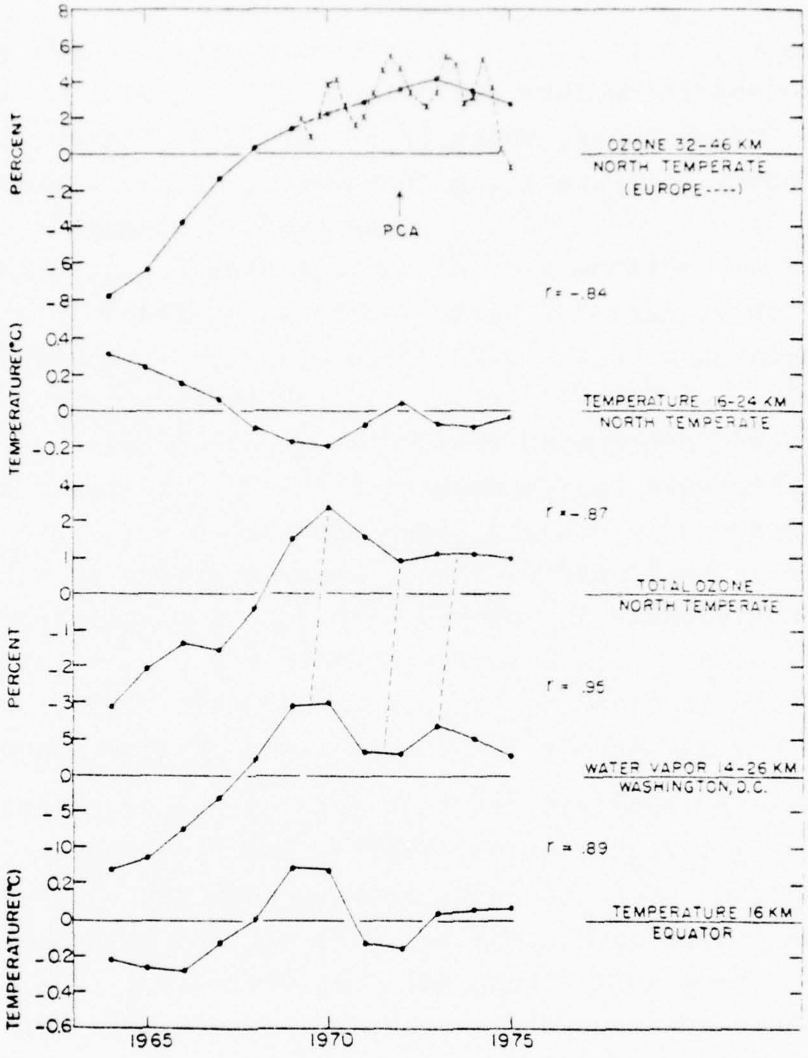
[*] The QBO is apparently due to a tidal forcing by the planet Mars with a period of 25.6 months (see, e.g., Fairbridge, 1978).



Source: Angell and Korshover, 1978

FIGURE 3-3. Comparison of Time Trends in Given Parameters Where a 1-2-1 Smoothing Has Been Applied to Successive Annual Values. The 16-km temperature at the equator approximates the tropopause temperature there. The data are expressed as either percentage deviations or temperature deviations (degrees Celsius) from the mean. The arrow at the top indicates an intense polar cap absorption (PCA) event.

stratosphere, as well as of some radioactive tracers associated with atmospheric nuclear explosions. It can also be used to represent water vapor, which is brought into the stratosphere by the Hadley cell upwelling through the tropical tropopause, i.e., by large-scale motions, supplemented to some extent by smaller-scale motions such as cumulus convection. The principal return flow is near 30° North and South at the tropopause folding associated with the subtropical jets and the downdraft in both Hadley and Ferrell cells. In the stratosphere there is a significant horizontal transport, supplemented to some extent by upwelling near the subpolar jet stream associated with the updraft near 60° North and South associated with both Ferrell and polar cells of circulation. This is strong in winter, but often nondetectable in summer, with some downward transport near the poles. A good review of both the physics and parameterization is given by Danielsen and Louis (1977), who, however, do not say much about the problems of water vapor transport.

There is some evidence that this circulation applies to all tracers, e.g., Vedder et al. (1978), who find higher stratospheric concentrations of halocarbons and N_2O near the equator than at higher latitudes consistent with the picture of Hadley cell upwelling. There is a strong seasonal variation: thus, mid-latitude stratosphere-to-troposphere transfer is much more vigorous in winter than in summer [see, e.g., Reiter (1975), and work quoted therein].

This picture describes an average of motions on a variety of time (and space) scales from very short to rather long, whose relative contribution is not yet understood. Thus, for instance, stratospheric sudden warmings (SSWs) [see Quiroz et al. (1975), McInturff (1978), and R. S. Quiroz, private communication] are very dramatic phenomena, occurring in variable strength during many winters, and of different strengths in the Northern and Southern Hemispheres, leading to dramatic enhancements in troposphere/stratosphere mixing. In particular, there is some evidence that in the years of major stratospheric warmings (which are characterized by reversals in zonal circulation of the polar vortex at 10 mbar) the normal springtime maximum in stratospheric ozone occurs significantly earlier than usual -- cf. Züllig (1973), p. 133 in McInturff (1978), Ellsaesser (1976). Table 3.1 gives a representative listing of Northern Hemisphere SSWs; there is much less evidence on Southern Hemisphere SSWs, but one (or more) minor SSWs appear to occur during each Northern and Southern Hemisphere winter (i.e., January/February and July/August, respectively). However, to date, no major warmings have been reported in the Southern Hemisphere. In any case, to date, SSWs have not been incorporated in models of stratospheric ozone.

It must also be stressed that the parameterization of motions as used in the two-dimensional models, with a mean wind u_y (horizontal, N-S), and u_z (vertical) supplemented by subscale eddy transport coefficients K_{yy}, K_{yz}, K_{zz} is not necessarily adequate; certainly, smaller scale transport is not always downgradient, so that the parameterization in terms of eddy transports is open to serious question.

In conclusion, while the standard parameterization can describe the long-term averaged overall motion of ozone and water in the stratosphere, not all sets of values used for the numerical coefficients K_{yy}, etc., are equally satisfactory. Further, we know that there have been changes in stratospheric motions in different years, associated with such events as major volcanic eruptions (e.g., Agung in 1963), the quasi-biennial oscillations and SSWs [cf. Fig. 2-1 and also Newell et al. (1974), Chapter 10]. The effects of these phenomena on stratospheric transport and hence on the action of the various time-dependent injectants on stratospheric ozone cannot yet be modeled adequately.

TABLE 3-1. A LIST OF NORTHERN HEMISPHERE STRATOSPHERIC SUDDEN WARMINGS (SSWs)

(Table kindly provided by R. S. Quiroz, NOAA, private communication)

Winter Years	Approximate Dates	Major?	Source
1955-56	9-20 Jan	No	1
1956-57	19 Jan - 6 Feb	Yes	1
1957-58	22-30 Jan	Yes	1
1958-59	23-28 Jan	No	1
1959-60	21-24 Feb	No	1
1960-61	25-28 Jan	No	1
1961-62	15-17 Feb	No	1
1962-63	18-27 Jan	Yes	1
1963-64	27-30 Jan	No	1
1964-65	30 Dec - 6 Jan	No	1
1965-66	19-31 Jan	Yes	1
1966-67	29 Dec - 23 Jan	No	1
	1-18 Mar	No	2
1967-68	17 Dec - 15 Jan	Yes	1, 3, 4
	9-20 Mar	No	2
1968-69	29 Nov - 22 Dec	No	1
	25 Jan - 4 Feb	No	2
	5-25 Mar	No	2
1969-70	8 Dec - 28 Jan	Yes	5, 6, 7
1970-71	12 Dec - 18 Jan	Yes	7, 8
	5-25 Mar	Yes?	9
1971-72	8 Feb - 2 Mar	No	1
	15-30 Mar	No?	9
1972-73	30 Dec - 8 Feb	Yes	1, 7
1973-74	25 Dec - 5 Jan	No	7
	20 Feb - 20 Mar	Yes	7
1974-75	25 Dec - 15 Jan	No	10
	22 Feb - 15 Mar	Yes	10
1975-76	Late Nov	No	11
	Late Dec - Early Jan	No	11
	Late Jan - Early Feb	No	11
	Late Mar - Early Apr	Yes	11

Note: For Southern Hemisphere Warmings, see Quiroz (1974), Barnett (1975).

Sources:

1 Finger et al., 1974
2 Berlin 10-mbar maps
3 Johnson, 1969
4 Iwashima, 1973
5 Quiroz, 1971
6 Miller et al., 1972
7 Quiroz, 1975
8 Labitzke and Barnett, 1973
9 Berlin 30-mbar maps
10 Quiroz, Miller and Nagatani, 1975
11 Quiroz and Nagatani, 1976

3.5 SOME EFFECTS OF MAJOR VOLCANIC ERUPTIONS

The large eruption of Mt. Agung in March 1963 occurred at a time when there was available a significant global network capable of providing estimates of upper-atmosphere as well as of ground-level effects. Thus, we have very much more information on the Agung eruption than on the significantly larger ones of Krakatoa (1883) and of Tambora (1816) for which, in addition to information on physical destruction and on enhanced "dust veils" (Lamb, 1970), we only have data on decreases in surface temperature [e.g., Newell et al. (1974), p. 246].

Thus, we know that the volcanic eruption of Agung not only injected large amounts of material into the stratosphere (see Section 2.4 and Appendix D), but also led to an increase in temperature in the tropical and subtropical lower stratosphere (presumably due to absorption of solar radiation by aerosols of volcanic origin) and a probably related decrease in tropospheric and ground-level temperatures [see Newell et al. (1974), pp. 264-267].

Since water is thought to enter the stratosphere principally through the "cold trap" at the tropical tropopause, such an increase in tropical tropopause temperature would be expected to lead to an increase in stratospheric water vapor content, and Newell (op. cit.) suggests that the maximum in noctilucent cloud observations in 1967 and 1968 may thus be due to the Agung eruption, which raised the temperature of the tropical tropopause and thus permitted more water to enter the stratosphere. Presumably, the 4-year delay between the eruption and the effect on noctilucent clouds is related to the time required for water to be transported from the tropical tropopause to the polar stratopause.

3.6 TROPOSPHERIC POLLUTANTS AND CHEMISTRY EFFECTS

As our understanding of the complex photochemical interactions of trace species in the atmosphere has progressed, additional processes by which stratospheric ozone may be affected have been noted. Thus, it has been suggested by various workers in this field that any tropospheric pollutant which affects the OH concentration can result in changes to stratospheric ozone because reaction with OH is the principal tropospheric destruction mechanism for species such as CH_4 and CH_3Cl. If OH is reduced (e.g., by reaction with CO), or enhanced e.g., by the reaction

$$HO_2 + NO \rightarrow NO_2 + OH, \qquad (3.2)$$

the tropospheric lifetimes of these compounds are altered and their fluxes into the stratosphere change. Increases in CH_4 lead to increased H_2O at altitudes where HO_x-mediated ozone depletion is important, while increases in CH_3Cl increase the ClX effects.

These preliminary suggestions ought to be considered in detailed modeling studies. In particular, if ground-level sources of halocarbons, hydrocarbons, and fixed nitrogen are taken into account, it is important that tropospheric as well as stratospheric photochemistry should be included in the models.

Note that the atmospheric carbon dioxide level has been increasing during the past 100 years or so, principally as a result of fossil fuel combustion resulting from the industrial revolution. Presumably, this has led to a small increase in stratospheric ozone through changes in stratospheric temperature, see Boughner (1978) and Groves et al. (1978).

3.7 AIRCRAFT SOURCES (OF NO_X, H_2O, ETC) AND ROCKET SOURCES

A listing of aircraft sources for 1975 is given in Table 3.2 as a function of altitude and latitude. The data come from A. D. Little (1976), corrected as indicated by Oliver et al. (1977), p. 2-30 ff for the fact that NO_x emissions of CF-6 engines are roughly equal to those of JT9D engines; this correction amounts to approximately 14 percent. Overall aircraft operations have been increasing very rapidly since jet transport aircraft came into widespread use in the 1960s. Thus, ICAO figures on passenger travel per year (Source: Interavia, October 1974, p. 977; ibid. October 1976, p. 927; ibid. October 1977, p. 957) show a mean annual increase of 9.4 percent per annum compounded. While passenger travel on scheduled airlines and total NO_x emissions are not strictly proportional, and indeed the flight altitude has been increasing somewhat since the mid-1960s, reasonable scaling factors for reducing the 1975 injection rates of Table 3.2 to those for earlier years are given in Table 3.3.

Regarding the effect of a steady-state airplane injection, note that scaling from the calculations of Hidalgo and Crutzen (1977) and of Widhopf, Glatt, and Kramer (1977) to take into account changes in fuel flow rates assumed, and also a revision in the rate constant for the reaction (3.2) by a factor 40 [Howard and Evenson (1977) and other workers] one would expect some ozone redistribution and, in particular, a net ozone increase of order 0.3 percent to result from a steady-state airplane injection at the 1975 rate. Evidently, the effect of actual aircraft operations during the 1955 to 1975 time period is much smaller than this because of the very rapid increase in injections shown in Table 3.3.

Rocket sources were very small during the 1955 to 1975 time period: current estimates indicate that 60 space shuttle launches per year--which would represent a far greater activity than any

TABLE 3-2. 1975 WORLDWIDE AIRCRAFT EMISSIONS

Total Emissions for all Aircraft by Pollutants (kg/Year) (Source: A. D. Little, 1976) except NO_x, modified as indicated in text)

TOTAL NO_x EMISSIONS (AS NO_2)

ALT (KM)	6-8	8-9	9-10	10-11	11-12	12-13	13-14
N POLE	5.23E 05	4.90E 05	4.15E 06	3.55E 06	3.56E 06	1.65E 04	2.94E 03
50 TO 60	2.52E 06	3.42E 06	2.26E 07	2.05E 07	1.86E 07	2.29E 05	1.75E 04
40 TO 50	9.99E 06	1.54E 07	4.03E 07	4.60E 07	2.63E 07	1.78E 06	2.06E 05
30 TO 40	1.12E 07	1.86E 07	4.05E 07	5.55E 07	2.62E 07	2.77E 06	2.14E 05
20 TO 30	3.89E 06	4.63E 06	1.46E 07	1.83E 07	1.26E 07	9.24E 05	5.64E 04
10 TO 20	1.48E 06	1.67E 06	4.13E 06	5.98E 06	4.11E 06	5.03E 05	3.33E 04
0 TO 10	5.48E 05	6.59E 05	2.46E 06	2.61E 06	2.03E 06	1.16E 05	9.66E 03
-10 TO 0	4.82E 05	6.82E 05	2.39E 06	2.43E 06	1.78E 06	6.97E 04	2.76E 03
-20 TO -10	3.47E 05	5.84E 05	2.24E 06	2.79E 06	1.84E 06	1.10E 05	1.28E 04
-30 TO -20	6.01E 05	7.87E 05	1.82E 06	2.39E 06	1.30E 06	1.13E 05	1.37E 04
-40 TO -30	6.29E 05	9.01E 05	1.39E 06	2.13E 06	8.42E 05	1.37E 05	6.15E 03
-50 TO -40	3.30E 04	6.01E 04	7.79E 04	1.25E 05	3.49E 04	6.20E 03	3.89E 00
-60 TO -50	6.08E 03	5.20E 03	3.95E 03	2.50E 03	2.82E 02	1.06E 00	0.0
S POLE	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TOTAL OF ALL NO_x = 4.855E 08 (kg/yr)

TABLE 3-2. (Continued)

TOTAL WATER EMISSIONS

ALT (KM)	6-8	8-9	9-10	10-11	11-12	12-13	13-14	14-15
N POLE	5.13E 07	1.25E 08	3.81E 08	4.02E 08	4.14E 08	6.13E 06	1.08E 06	0.0
50 TO 60	2.62E 08	7.16E 08	2.22E 09	2.51E 09	2.23E 09	7.34E 07	7.25E 06	0.0
40 TO 50	1.02E 09	2.65E 09	4.20E 09	5.43E 09	3.41E 09	4.36E 08	7.73E 07	0.0
30 TO 40	1.11E 09	2.96E 09	4.26E 09	6.50E 09	3.41E 09	6.04E 08	8.17E 07	0.0
20 TO 30	3.50E 08	1.00E 09	1.46E 09	2.15E 09	1.57E 09	2.06E 08	2.21E 07	0.0
10 TO 20	1.47E 08	4.67E 08	5.03E 08	8.26E 08	6.28E 08	1.11E 08	1.22E 07	0.0
0 TO 10	6.55E 07	1.44E 08	3.03E 08	3.90E 08	3.19E 08	3.37E 07	3.57E 06	0.0
-10 TO 0	5.99E 07	1.26E 08	2.82E 08	3.42E 08	2.58E 08	2.02E 07	1.09E 06	0.0
-20 TO -10	4.73E 07	1.09E 08	2.56E 08	3.65E 08	2.71E 08	2.96E 07	4.70E 06	0.0
-30 TO -20	6.01E 07	1.49E 08	2.20E 08	3.19E 08	2.05E 08	3.06E 07	5.00E 06	0.0
-40 TO -30	6.40E 07	1.75E 08	1.30E 08	2.33E 08	1.33E 08	3.01E 07	2.27E 06	0.0
-50 TO -40	4.17E 06	7.69E 06	1.10E 07	1.37E 07	6.24E 06	1.70E 06	5.66E 03	0.0
-60 TO -50	5.61E 05	5.24E 05	4.41E 05	3.21E 05	3.10E 04	1.46E 03	0.0	0.0
S POLE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TOTAL OF ALL H2O = 6.03312E 10 (KILOGRAMS/YEAR)

TOTAL CARBON DIOXIDE EMISSIONS

ALT (KM)	6-8	8-9	9-10	10-11	11-12	12-13	13-14	14-15
N POLE	1.29E 08	3.16E 08	9.61E 08	1.02E 09	1.05E 09	1.55E 07	2.73E 06	0.0
50 TO 60	6.63E 08	1.81E 09	5.60E 09	6.35E 09	5.53E 09	1.85E 08	1.83E 07	0.0
40 TO 50	2.57E 09	6.69E 09	1.06E 10	1.37E 10	8.51E 09	1.10E 09	1.94E 08	0.0
30 TO 40	2.80E 09	7.47E 09	1.07E 10	1.65E 10	9.51E 09	1.52E 09	2.05E 08	0.0
20 TO 30	8.85E 08	2.53E 09	3.67E 09	5.43E 09	3.96E 09	5.19E 08	5.57E 07	0.0
10 TO 20	3.71E 08	1.18E 09	1.27E 09	2.09E 09	1.56E 09	2.80E 08	3.07E 07	0.0
0 TO 10	1.66E 08	3.65E 08	7.64E 08	9.88E 08	8.05E 08	8.50E 07	8.98E 06	0.0
-10 TO 0	1.51E 08	3.19E 08	7.12E 08	8.56E 08	6.51E 08	5.09E 07	2.73E 06	0.0
-20 TO -10	1.09E 08	2.75E 08	6.47E 08	9.23E 08	6.85E 08	7.48E 07	1.18E 07	0.0
-30 TO -20	1.52E 08	3.74E 08	5.55E 08	8.06E 08	5.24E 08	7.73E 07	1.26E 07	0.0
-40 TO -30	1.62E 08	4.43E 08	4.54E 08	7.17E 08	3.34E 08	7.60E 07	5.69E 06	0.0
-50 TO -40	1.05E 07	1.94E 07	2.78E 07	4.73E 07	1.57E 07	4.29E 06	1.43E 04	0.0
-60 TO -50	1.42E 06	1.33E 06	1.11E 06	8.12E 05	7.81E 04	3.69E 03	0.0	0.0
S POLE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TOTAL OF ALL CO2 = 1.52379E 11 (KILOGRAMS/YEAR)

TABLE 3-2. (Continued)

TOTAL SULFUR EMISSIONS (AS SO_2)

ALT (KM)	6-8	8-9	9-10	10-11	11-12	12-13	13-14	14-15
N POLE	4.10E 04	4.35E 04	3.04E 05	3.22E 05	3.31E 05	4.90E 03	8.67E 02	0.0
50 TO 60	2.10E 05	3.38E 05	1.77E 06	2.01E 06	1.78E 06	5.87E 04	5.79E 03	0.0
40 TO 50	8.12E 05	1.33E 06	3.36E 06	4.35E 06	2.73E 06	3.49E 05	6.15E 04	0.0
30 TO 40	8.87E 05	1.55E 06	3.40E 06	5.20E 06	2.73E 06	4.82E 05	6.53E 04	0.0
20 TO 30	2.80E 05	3.99E 05	1.15E 06	1.72E 06	1.25E 06	1.64E 05	1.77E 04	0.0
10 TO 20	1.17E 05	1.62E 05	4.02E 05	6.61E 05	5.02E 05	8.86E 04	9.77E 03	0.0
0 TO 10	5.24E 04	7.52E 04	2.42E 05	3.12E 05	2.55E 05	2.69E 04	2.86E 03	0.0
-10 TO 0	4.79E 04	7.61E 04	2.26E 05	2.74E 05	2.06E 05	1.61E 04	8.68E 02	0.0
-20 TO -10	3.46E 04	6.08E 04	2.05E 05	2.92E 05	2.17E 05	2.37E 04	3.76E 03	0.0
-30 TO -20	4.81E 04	7.60E 04	1.76E 05	2.55E 05	1.66E 05	2.45E 04	3.99E 03	0.0
-40 TO -30	5.12E 04	8.44E 04	1.44E 05	2.27E 05	1.06E 05	2.41E 04	1.81E 03	0.0
-50 TO -40	3.33E 03	6.15E 03	8.80E 03	1.49E 04	4.99E 03	1.36E 03	4.53E 00	0.0
-60 TO -50	4.49E 02	4.19E 02	3.53E 02	2.56E 02	2.48E 01	1.17E 00	0.0	0.0
S POLE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TOTAL OF ALL SOX = 4.55398E 07 (KILOGRAMS/YEAR)

TOTAL PARTICULATE EMISSIONS

ALT (KM)	6-8	8-9	9-10	10-11	11-12	12-13	13-14	14-15
N POLE	4.09E 03	4.35E 03	3.04E 04	3.22E 04	3.31E 04	4.90E 02	8.67E 01	0.0
50 TO 60	2.10E 04	3.38E 04	1.77E 05	2.01E 05	1.73E 05	5.87E 03	5.79E 02	0.0
40 TO 50	8.11E 04	1.33E 05	3.36E 05	4.35E 05	2.73E 05	3.49E 04	6.15E 03	0.0
30 TO 40	8.86E 04	1.55E 05	3.40E 05	5.20E 05	2.73E 05	4.82E 04	6.53E 03	0.0
20 TO 30	2.79E 04	3.99E 04	1.16E 05	1.72E 05	1.25E 05	1.64E 04	1.77E 03	0.0
10 TO 20	1.17E 04	1.62E 04	4.02E 04	6.61E 04	5.02E 04	8.86E 03	9.77E 02	0.0
0 TO 10	5.23E 03	7.52E 03	2.42E 04	3.12E 04	2.55E 04	2.69E 03	2.86E 02	0.0
-10 TO 0	4.79E 03	7.61E 03	2.26E 04	2.74E 04	2.06E 04	1.61E 03	8.68E 01	0.0
-20 TO -10	3.46E 03	6.08E 03	2.05E 04	2.92E 04	2.17E 04	2.37E 03	3.76E 02	0.0
-30 TO -20	4.81E 03	7.60E 03	1.76E 04	2.55E 04	1.66E 04	2.45E 03	3.99E 02	0.0
-40 TO -30	5.12E 03	8.44E 03	1.44E 04	2.27E 04	1.06E 04	2.41E 03	1.81E 02	0.0
-50 TO -40	3.33E 02	6.15E 02	8.80E 02	1.49E 03	4.99E 02	1.36E 02	4.53E-01	0.0
-60 TO -50	4.49E 01	4.19E 01	3.53E 01	2.56E 01	2.48E 00	1.17E-01	0.0	0.0
S POLE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TOTAL OF ALL PAR = 4.55371E 06 (KILOGRAMS/YEAR)

TOTAL HYDROCARBON EMISSIONS

ALT (KM)	6-8	8-9	9-10	10-11	11-12	12-13	13-14	14-15
N POLE	3.37E 04	3.22E 04	9.48E 04	1.04E 05	9.44E 04	4.03E 03	3.59E 02	0.0
50 TO 60	1.01E 05	1.59E 05	5.69E 05	7.17E 05	5.72E 05	5.77E 04	4.42E 03	0.0
40 TO 50	2.08E 05	3.55E 05	8.74E 05	1.17E 06	8.14E 05	1.52E 05	2.68E 04	0.0
30 TO 40	2.04E 05	3.49E 05	7.40E 05	1.20E 06	7.72E 05	1.97E 05	2.67E 04	0.0
20 TO 30	8.41E 04	1.33E 05	3.40E 05	5.36E 05	3.94E 05	8.07E 04	9.15E 03	0.0
10 TO 20	5.60E 04	9.07E 04	1.85E 05	2.94E 05	2.07E 05	5.05E 04	4.12E 03	0.0
0 TO 10	3.06E 04	4.38E 04	1.05E 05	1.42E 05	1.08E 05	1.73E 04	1.29E 03	0.0
-10 TO 0	4.63E 04	6.91E 04	1.21E 05	1.43E 05	8.98E 04	1.79E 04	5.35E 02	0.0
-20 TO -10	2.43E 04	4.48E 04	9.18E 04	1.32E 05	9.15E 04	2.06E 04	1.68E 03	0.0
-30 TO -20	3.02E 04	5.09E 04	8.89E 04	1.17E 05	7.39E 04	1.81E 04	1.71E 03	0.0
-40 TO -30	2.20E 04	3.87E 04	6.32E 04	9.15E 04	5.19E 04	1.62E 04	7.48E 02	0.0
-50 TO -40	2.38E 03	4.01E 03	5.38E 03	7.01E 03	2.97E 03	1.18E 03	3.62E 00	0.0
-60 TO -50	9.93E 01	1.09E 02	9.48E 01	8.20E 01	2.23E 00	9.34E-01	0.0	0.0
S POLE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TOTAL OF ALL HC = 1.41437E 07 (KILOGRAMS/YEAR)

TABLE 3-2. (Continued)

TOTAL FUEL EMISSIONS

ALT (KM)	6-8	8-9	9-10	10-11	11-12	12-13	13-14	14-15
N POLE	4.10E 07	4.35E 07	3.04E 08	3.22E 08	3.31E 08	4.90E 06	8.67E 05	0.0
50 TO 60	2.10E 08	3.38E 08	1.77E 09	2.01E 09	1.78E 09	5.87E 07	5.79E 06	0.0
40 TO 50	8.12E 08	1.33E 09	3.36E 09	4.35E 09	2.73E 09	3.49E 08	6.15E 07	0.0
30 TO 40	8.87E 08	1.55E 09	3.40E 09	5.20E 09	2.73E 09	4.82E 08	6.53E 07	0.0
20 TO 30	2.80E 08	3.99E 08	1.16E 09	.72E 09	1.25E 09	1.64E 08	1.77E 07	0.0
10 TO 20	1.17E 08	1.62E 08	4.02E 08	5.61E 08	5.02E 08	8.86E 07	9.77E 06	0.0
0 TO 10	5.24E 07	7.52E 07	2.42E 08	3.12E 08	2.55E 08	2.69E 07	2.86E 06	0.0
-10 TO 0	4.79E 07	7.61E 07	2.26E 08	2.74E 08	2.06E 08	1.61E 07	8.68E 05	0.0
-20 TO -10	3.46E 07	6.08E 07	2.05E 08	2.92E 08	2.17E 08	2.37E 07	3.76E 06	0.0
-30 TO -20	4.81E 07	7.60E 07	1.76E 08	2.55E 08	1.66E 08	2.45E 07	3.99E 06	0.0
-40 TO -30	5.12E 07	8.44E 07	1.44E 08	2.27E 08	1.06E 08	2.41E 07	1.81E 06	0.0
-50 TO -40	3.33E 06	6.15E 06	8.80E 06	1.49E 07	4.99E 06	1.36E 06	4.53E 03	0.0
-60 TO -50	4.47E 05	4.19E 05	3.53E 05	2.56E 05	2.48E 04	1.17E 03	0.0	0.0
S POLE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TOTAL OF ALL FUEL = 4.55403E 10 (KILOGRAMS/YEAR)

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during the 1955 to 1975 time frame--would produce a steady-state ozone depletion of order 0.2 percent [see NASA (1977) addendum, also Wuebbles (1977)].

TABLE 3-3. AIRCRAFT EMISSION RATES AS A FUNCTION OF TIME, NORMALIZED TO THE 1975 EMISSION RATES OF TABLE 3.2.

Year	1955	1960	1965	1970	1975
Emission Factor	0.17	0.27	0.41	0.64	1.00

4. DISCUSSION OF RELATIVE EFFECTS AND UNCERTAINTIES

Our understanding of the relative importance of NO_x, HO_x, and ClX injections to ozone has been changing rapidly since 1974. Thus, it is now thought that ClX injections are twice as effective in reducing ozone (relative to NO_x injections) as was the feeling in 1976--see, e.g. National Academy of Sciences (1977). These changes have resulted from revised estimates of reaction rates, the most important of which is for HO_2 + NO going to OH and NO_2. The first direct measurement of this reaction rate was made by Howard and Evenson (1977). See Hampson and Garvin (1978), p. 38, for a listing of other measurements.

Predictions of ozone reduction due to the nuclear test series of 1961 and 1962 have been changing; thus Chang et al. (1977), using a one-dimensional model, predicted an 8 percent ozone reduction using 1974 chemistry as against a 4 percent reduction using 1977 chemistry. Their estimates of injection height are higher than those adopted here; our estimate of injection heights should reduce the expected ozone depletion still further. Explicitly, in 1974 it was thought that NO_x injections reduce total ozone above 13 km, but increase it (by "smog" reactions) below 13 km (cf. Johnston, 1975). By late 1977, this cross-over height had gone up to 17 km (cf. H. S. Johnston, private communication) which, together with couplings between the HO_x, NO_x, and ClX cycles, contribute to the Chang et al. (1977) result.

Overall, it now appears that the predicted ozone reduction arising from a given ClX injection is roughly twice as large as was expected in 1976--see, e.g., NASA, 1977 Addendum.* Thus, the effects of halocarbons and of volcanic eruptions [especially if the latter inject as much HCl into the stratosphere as is suggested by Cadle et al. (1977)] may well be as important as were the 1961 to 1962 atmospheric nuclear explosions.

It is probably impossible to make a reliable quantitative estimate of the various uncertainties in the catalog, but some indications can be provided. As far as nuclear explosions go, there are uncertainties in NO_x production/Mt, from (0.4 to 1.5) x 10^{32} molecules/Mt, in injection height (see Fig. B-5 of Appendix B), and in detrainment (see Section B.3.3 of Appendix B). Regarding halocarbons, production and injection rates are presumably quite accurate (± 10 percent for production, somewhat worse for atmospheric injections), although different estimates for current carbon tetrachloride production differ by 20 to 50 percent;** the main uncertainty here is provided by tropospheric transport and photochemistry, in particular, the concentration of OH and/or other reactive species which destroy these materials in the troposphere. The injection estimates for volcanic eruptions listed in Tables 2-6 and 2-7 are evidently quite poor. As far as cosmic ray effects go, data on the 1959 and 1960 SPEs are quite limited, but since the effects of SPEs (or of GCRs, for that matter) are not very large, this uncertainty is probably not very important. Finally, regarding nitrogen fixation, there

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*A very recent note by Stief et al. (1978) on the reaction of stratospheric formaldehyde with atomic chlorine to produce the relatively inert HCl suggests approximately a 10 percent reduction in sensitivity of stratospheric ozone to chlorine perturbations.

**This uncertainty is not very important since during the 1955 to 1975 time period the principal stratospheric effect of CCl_4 comes from the large pre-1950 injections (which are relatively well known), rather than from the small post-1950 injections where there is a major discrepancy.

are significant uncertainties in the nitrogen fixation by combustion, in the rate and product of denitrification, and, in particular, in the fate and budget of N_2O in the troposphere. Among all these factors, I think that the uncertainties in volcanic injections may well be of greatest significance in the present context.

Compared with these injections, the different factors discussed in Chapter 3 are far more uncertain and ill-defined, and limitations in our overall understanding may well affect overall predictions to a significant extent. In particular, if the estimates of solar UV variation shown in Fig. 3-2 apply, and if the corresponding predictions of an 8 percent ozone variation between solar minimum and maximum quoted in Section 3.1 are appropriate, then this is probably the biggest single time-varying effect during the 1955 to 1975 time frame.

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APPENDIX A

STRATOSPHERIC BURDENS OF NO_x, HO_x, ClX, ETC.

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STRATOSPHERIC BURDENS OF NO_x, HO_x, ClX, ETC.

For orientation, it is desirable to have estimates of the total stratospheric burden of the NO_x, HO_x, and ClX groups of molecules. The present estimates are very poor; they are based primarily on available experimental data, supplemented by current theoretical computations of Crutzen et al. (1978) and Wofsy (1978).* It should be noted that the stratospheric mean lifetime of HO_x is significantly shorter than those of NO_x and ClX, so the relative importance of HO_x, NO_x, and ClX perturbations is not simply proportional to the respective number of molecules injected.

For some of the more reactive species (OH, HO_2, Cl, ClO) we only have a daytime profile near 30° N latitude which is taken as a global mean. Thus, for NO_x and ClX species, the global burden is taken as this integrated profile multiplied by the surface area of the earth, $A_s = 5.11 \times 10^{14}$ m^2. However, for HO_x species which are produced by sunlight and have a mean lifetime less than 12 hours, we use only the sunlit fraction of the earth's surface area, $A_d = 1/2\ A_s$.

A.1 OXIDES OF NITROGEN

$NO_x = NO + NO_2$, $NO_y = NO_x + HNO_3$ (N_2O_5, etc., are sometimes included). Estimates for NO_y range from 4.4×19^{34} molecules (Johnston, 1975, p. 5-109), to 8.5×10^{34} (after Penndorf, 1977) or 15×10^{34} (COMESA, 1975, p. 26). We suggest $(4\text{-}15) \times 10^{34}$ as a plausible range.

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*Some of the numbers are written with three digits to minimize internal round-off errors: this does not imply significance.

A.2 OXIDES OF HYDROGEN

$HO_x = OH + HO_2$ (H_2O_2 should be included). For OH, we use Hudson (1977), p. 154, Fig. 28.

$$A_d \int_{11\ \mathrm{km}}^{50\ \mathrm{km}} [OH]\ dz = 1.1 \times 10^{32}\ \text{molecules} \tag{1a}$$

$$A_d \int_{50\ \mathrm{km}}^{70\ \mathrm{km}} [OH]\ dz = 0.4 \times 10^{32}\ \text{molecules (not included here)} \tag{1b}$$

Figure 1a from Crutzen et al. (1978) gives 0.95×10^{32} molecules, and Fig. 6b from Wofsy (1978) gives 1.5×10^{32} molecules, both for the stratosphere alone, i.e., 11 to 50 km altitude.

Measurements of HO_2 are currently being made by at least the Max Planck Institute and the University of Michigan groups, but I have not yet seen sufficient data to make an estimate, thus present model estimates:

$$A_d \int_{\text{tropopause}}^{50\ \mathrm{km}} [HO_2]\ dz = \begin{cases} 3 \times 10^{32} & \text{(CIAP, Monograph 1, p. 3-96, representative values)} \\ 6 \times 10^{32} & \text{(Crutzen et al., data from Fig. 1)} \\ 15 \times 10^{32} & \text{(Wofsy, data from Figure 6b)} \end{cases} \tag{2}$$

Those experimental numbers that I have seen support Crutzen's rather than Wofsy's numbers. Thus, one can say that current estimates for the $HO_x = OH + HO_2$ burden in the stratosphere lie in the range 7 to 16×10^{32} molecules, but evidently the reliability of these figures is not high. In fact, both the production and destruction rates of HO_x radicals in the stratosphere are very high, so that while the burden of HO_x is low, the injection of additional HO_x will affect the atmospheric photochemistry for only a relatively short time.

A.3 CHLORINE RADICALS

$\mathrm{ClX} = \mathrm{Cl} + \mathrm{ClO} + \mathrm{ClO\,NO_2} + \mathrm{HCl}$. HCl appears to be the most abundant species [see Sundararaman (1976), p. 12; Hudson (1977), p. 97], for which

$$A_s \int_{11\text{ km}}^{50\text{ km}} [\mathrm{HCl}]\, dz = 1.07 \times 10^{34} \text{ molecules} \qquad (3)$$

Three measurements of ClO have been reported by Anderson et al. (1977); they differ by about a factor of 10.

$$A_d \int_{11\text{ km}}^{50\text{ km}} [\mathrm{ClO}]\, dz = \begin{cases} 0.09 \times 10^{34} \text{ molecules} \\ \text{(largest value)} \\ 0.02 \times 10^{34} \text{ molecules} \\ \text{(smallest value)} \end{cases} \qquad (4)$$

The other species, $\mathrm{ClO\,NO_2}$ and Cl have not been measured in the stratosphere, and thus we are forced to rely on model calculations.

$$A_d \int_{\text{tropopause}}^{50\text{ km}} [\mathrm{ClO\,NO_2}]\, dz = \begin{cases} 4.8 \times 10^{32} \text{ molecules} \\ \text{(Crutzen, Fig. 1a)} \\ < 6 \times 10^{32} \text{ molecules} \\ \text{(Murcray et al., 1978,} \\ \text{upper-bound estimates)} \end{cases} \qquad (5)$$

$$A_d \int_{\text{tropopause}}^{50\text{ km}} [\mathrm{Cl}]\, dz = \begin{cases} 0.6 \times 10^{30} \text{ molecules} \\ \text{(Crutzen, Fig. 1a)} \\ 1 \times 10^{30} \text{ molecules} \\ \text{(Anderson et al.} \\ \text{smallest value)} \\ 5 \times 10^{30} \text{ molecules} \\ \text{largest value)} \end{cases} \qquad (6)$$

Thus, we conclude that the stratospheric burden of ClX lies in the range of $(1.0\text{-}1.2) \times 10^{34}$ molecules, with a large uncertainty.*

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* Fig. 11a of Crutzen et al. reports the burdens of HCl and ClO as 37×10^{32} and 3×10^{32} molecules, respectively, so that their mean burden of ClX would be 0.4×10^{34} molecules; Fig. 4 of Wofsy (1978) gives 0.7×10^{34} molecules.

A.4 SOME OTHER QUANTITIES

The stratospheric burden of water is listed as (1.6-2.2) x 10^{12} kg [cf. Oliver, 1977, pp. 4-9], or (5-7) x 10^{37} molecules. Regarding stratospheric aerosols, it is impossible to make a meaningful statement, since it is considered that occasional large volcanic eruptions are the principal source of this material. Thus, in 1972-1973, 4 to 5 years after the last significant explosive eruption (that of Fernandina in 1968), the global loading was of order 10^8 kg, but the eruption of Fuego in 1974 probably put (4-6) x 10^9 kg of aerosols into the stratosphere. See Appendix D for a more detailed discussion.

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APPENDIX B

STRATOSPHERIC INJECTION OF OXIDES OF NITROGEN AND OTHER MATERIALS BY ATMOSPHERIC NUCLEAR EXPLOSIONS

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STRATOSPHERIC INJECTION OF OXIDES OF NITROGEN AND OTHER MATERIALS BY ATMOSPHERIC NUCLEAR EXPLOSIONS

B.1 INTRODUCTION

Foley and Ruderman (1972) pointed out that the theory of the depletion of stratospheric ozone by oxides of nitrogen by the reaction chain

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

$$NO_2 + O \rightarrow NO + O_2 \qquad (2)$$

$$O + O_3 \rightarrow 2\ O_2 \qquad (3)$$

lends itself to verification by studying global ozone changes related to the Soviet atmospheric nuclear test series of 1961 through 1962.

Explicitly, an atmospheric nuclear explosion produces nitric oxide, mainly by heating air above 2000° K; during the cooling to ambient temperature, some 5000 to 10,000 tons of NO per Mt yield remains, and rises into the stratosphere for yields in the Mt range (see Section B.2).

For orientation on the scale of the bomb-induced perturbation, the largest single test series (in terms of total yield) was the Soviet series of Fall 1962, which accounted for some 180 Mt of total yield. In terms of the current estimates of NO production per Mt (see Section B.2, especially Table B-1), this would correspond to an injection of (0.7 to 2.7) x 10^{34} NO molecules in the stratosphere over a period of several months

(5 August to 25 December 1962). This injection in the northern polar cap of the stratosphere (injection at 75° N latitude) may be compared with the global loading of stratospheric NO_y (= NO_x + HNO_3), estimates of which range from (4-15) x 10^{34} molecules (see Appendix A). We see that the fractional enhancement of NO_x or NO_y in the northern polar cap region of the stratosphere was very large. In terms of the models of stratospheric ozone of the 1973 to 1974 time period, which emphasize control of its concentration by NO_x and also by HO_x (= OH + HO_2), a detectable reduction in stratospheric ozone might have been expected. The earlier (1973 to 1974) models predicted a maximum hemispheric ozone reduction of 8 to 10 percent, while the later ones predict 4 to 6 percent, cf Chang et al. (1977). The data analysis for total ozone gives 95 percent confidence interval bounds of a 3 percent variation in total ozone (J. K. Angell, private communication), while H. S. Johnston (private communication) finds that when a 10 percent pulse injection is applied to the ozone data with the Angell-Korshover (1973) smoothing, its effect disappears in the noise. Thus, one can best summarize the situation by remarking that while there is no real disagreement between predictions and observations, existing atmospheric data on nuclear explosions do not provide a statistically significant demonstration of the catalytic destruction of ozone by oxides of nitrogen.

To date, however, only one-dimensional model calculations have been made; two-dimensional models, with latitudinally and seasonally varying dynamics, may indicate space-time regions where the effects should be most apparent, so that a more critical comparison with the data could be undertaken, bearing in mind that after 1955 a ground-based network of some 45 to 90 Dobson spectrophotometers and M-83 filter ozonometers has been operational, supplemented from 1970 to 1977 by the backscattered ultraviolet (BUV) instrument on the Nimbus-IV satellite.

The present discussion describes the physics of NO_x production by atmospheric nuclear explosions (Section B.2), the altitude of injection as a function of yield (Section B.3), some other chemical factors (Section B.4) and a listing of all atmospheric thermonuclear explosions as a function of date, location, and yield (Section B.5). The result of Sections B.2 to B.4 provides a listing of bomb-produced NO_x injections as a function of position and time (Section B.6, especially Table B-12), which is intended to provide input data for two-dimensional computer codes of stratospheric photochemistry and dynamics.

B.2 NO_x PRODUCTION IN A NUCLEAR FIREBALL

A nuclear weapon emits a very large amount of energy in a very short time ($\sim 10^{-8}$ sec); 1 Mt = 10^{12} Kcal = 4.2×10^{15} joule. Most of the close-in action takes place very rapidly, thus in a time order of 1 sec, a "fireball" is formed, which is a mass of heated air ($\sim 10^6$ tons/Mt yield) heated to a temperature of order 6000° K. At temperatures of this order, the oxygen in air is fully dissociated and the nitrogen is partially dissociated. The total mass of the nuclear weapon is evidently very small compared to the mass of the heated air, as an energy of 1 Mt corresponds to the complete fission of 56 kg of fissionable material, while for fusion the mass is even lower, by a factor of almost three.

"The color of the (radioactive) cloud is initially red or reddish brown, due to the presence of various colored compounds (oxides of nitrogen, especially NO_2) at the surface of the fireball. These result from the chemical interaction of nitrogen, oxygen, and water vapor in the air at the existing high temperatures and under the influence of the nuclear radiations." (Glasstone and Dolan, 1977, #2.08, p. 29).

Nitric oxide (NO) is produced in the fireball principally by the rapid heating of air and subsequent "freezing" of the chemical equilibrium as the fireball cools, either by radiation, expansion, or mixing with cold air. The precise quantity of NO formed depends on the details of the chemistry and on the mixing processes: thus as the freezing temperature (assuming equilibrium in dry air at 0.1 atmosphere pressure) changes from 2000 to 1800^{o} K, the mole fraction of NO changes from 0.76 to 0.45 percent, corresponding to a change of NO production per Mt of yield (or 10^{6} tons of heated air) of (1.6 to 0.9) x 10^{32} molecules, or (8 to 4.5) kt. (See, e.g., Gilmore, 1974.)

A secondary mechanism for NO production comes from the ionization of air by gamma and X-rays, neutrons, and beta particles. This yields roughly one ion pair per 35 eV of energy, and 1.3 NO molecule per ion pair (e.g., Section E-3 of Appendix E), leading to 10 x 10^{32} NO molecules or 50 kt of NO per Mt of that fraction of the bomb's energy that comes out as ionizing radiation. However, only a small fraction of the bomb's energy is deposited as ionizing radiation,* so that this is not the primary mechanism for NO production.

It is clear that the estimates of NO production are subject to large errors. A comparison of the best current estimates is listed in Table B-1, and the conclusion from the work of Gilmore (1974) is that NO production per Mt of yield is (0.4 to 1.5) x 10^{32} molecules, or 2 to 8 kt.

This discussion corresponds to the production of NO in the first few seconds after the explosion, and before the "fireball" has begun its expansion and buoyant rise to its stabilization

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*For a fission weapon, about 15 percent of the energy comes out as (prompt and delayed) ionizing radiation, while for a thermonuclear weapon, significantly less ionization is produced, since this comes largely from the fission fragments. See Glasstone and Dolan (1977), pp. 6-8.

altitude, which typically takes some 10 min for a MT-yield explosion. Next, we shall discuss the process of cloud rise to stabilization, which is physically distinct from the initial phase of NO production.

TABLE B-1. CALCULATED NO PRODUCTION BY LOW-ALTITUDE NUCLEAR EXPLOSIONS[a,b]

NO Produced per Mt of Yield		Calculation Includes		
Molecules	kt	Shock	Late Fireball	Reference
0.5×10^{32}	3	x		Zeldovich and Raizer (1967)
0.3-2	1.5-10		x	Foley and Ruderman (1972)
0.17-1	1-5		x	Johnston et al. (1973)
0.3-1.5	1.5-8		x	Foley and Ruderman (1973)
1-2.5	5-12		x	Simons and Caledonia (1973)
1	5	x		Goldsmith et al. (1973)
0.4-1.5	2-8	x	x	Gilmore (1974)
0.6-1.1	3-5.5	x	x	COMESA (1975) (Section 6.3, p. 543ff)

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[a] The following are the principal mechanisms for NO production:

Shock heating and subsequent quick cooling of air: 3.5 kt NO/Mt yield.

Fireball heating of air and slower cooling by radiation, expansion, and mixing in of cold air: -1.5 to +4 kt NO/Mt yield.

Bombardment of air by ionizing radiation (betas, gammas, neutrons): < 0.5 kt NO/Mt yield (this is generally smaller than the other mechanisms). (See Gilmore, 1974.)

[b] It has been suggested that not all the NO produced actually rises to the stabilization height of the fireball, as a consequence of detrainment during the cloud rise. This is discussed in Section B.3.3.

B.3 CLOUD RISE AND STABILIZATION AS A FUNCTION OF YIELD

B.3.1 Air Versus Surface Bursts

If the height of burst, H, for a weapon of yield Y (Mt) is greater than

$$H_1 = 870\ Y^{0.4} \text{ (meters)}, \qquad (4)$$

then the fireball does not "touch the ground" and we speak of an *air burst*; if the height of detonation is very much less than H_1, the fireball interacts strongly with the ground and we call it a *surface burst*.

Many, but not all, thermonuclear explosions have been conducted in an air-burst mode, partly to minimize local radioactive fallout. For the present application we shall assume the following:

1. The cloud rise height as a function of yield is independent of whether we refer to a surface burst or an air burst.
2. The NO_x production per Mt of yield for a surface burst is half the value/range estimated in Section B.2 (see Table B-1). This choice is made in analogy with the estimate of Machta et al. (1963) that a surface burst produces half the C-14 per Mt of an air burst.

B.3.2 Cloud Rise

Figure B-1 is a sketch of the air circulation inside the rising fireball, and Fig. B-2 shows the cloud rise as a function of time, to indicate the phenomenology and scale of the rise. Figure B-3 shows the apparent surface temperature of a fireball as a function of time; from the discussion of Section B.2 we know that most NO formation is complete after the temperature drops below 2000° K so that NO_x production is complete before any significant cloud rise shown in Fig. B-2.*

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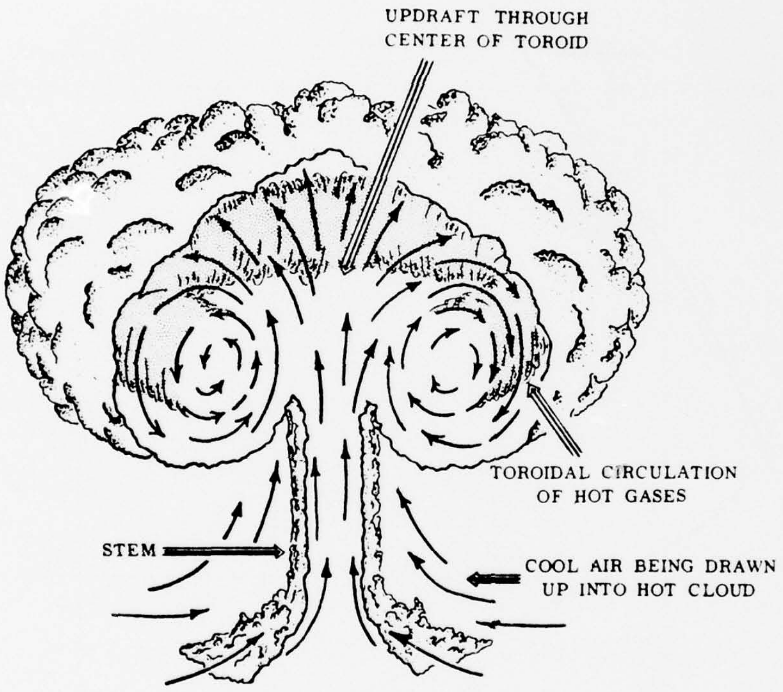
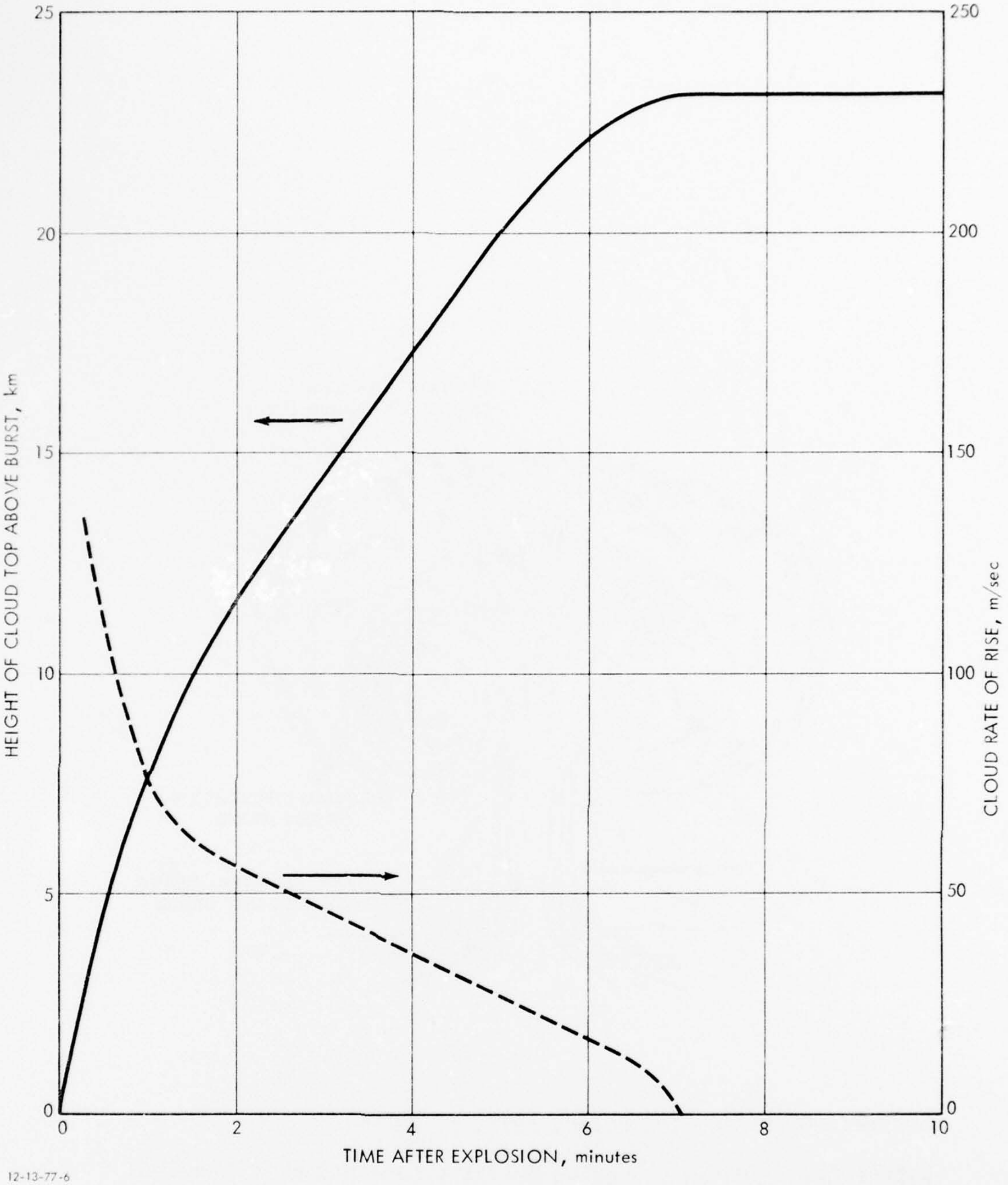
*The results of Fig. B-3 apply to a 20-kt explosion rather than to a 1-Mt explosion for which the time scale would be stretched out by a factor of several, say 2 to 10.



Source: Glasstone and Dolan, 1977, p. 29

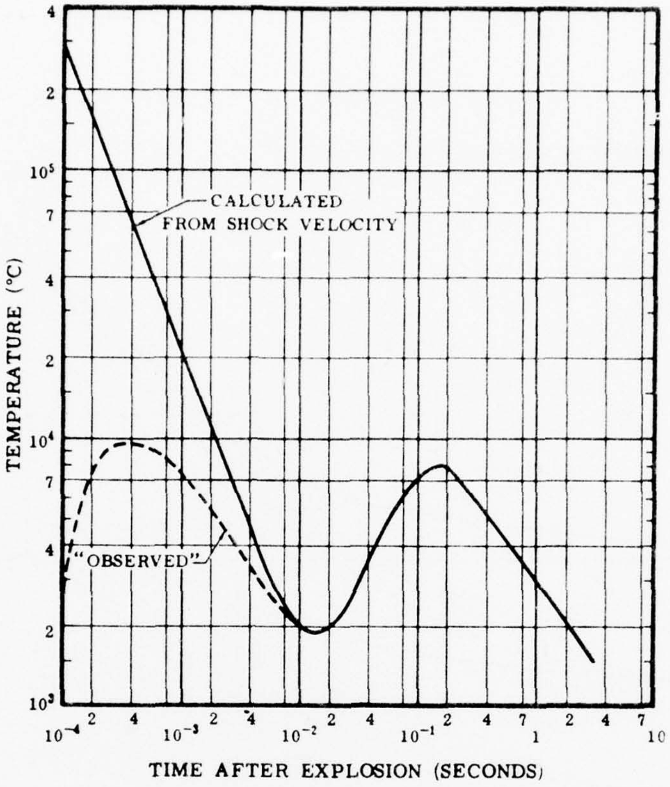
FIGURE B-1. Cutaway Showing Artist's Conception of Toroidal Circulation Within the Radioactive Cloud from a Nuclear Explosion.



12-13-77-6

Source: Glasstone and Dolan (1977), Fig. 2.12 and Table 2.12

FIGURE B-2. Height of Cloud Top and Rise Rate as a Function of Time After a 1-Mt Low Air Burst



Source: Glasstone and Dolan, 1977, Fig. 2.123, p. 69

FIGURE B-3. Variation of Apparent Fireball Surface Temperature with Time in a 20-kt Explosion

Note: After a 1-Mt explosion, the general behavior is the same, but the time scale is somewhat longer.

For this application, the primary interest is in the stabilization altitude of the nuclear cloud, since this indicates the altitude distribution at which the NO_x produced by the explosion is injected in the atmosphere. In Fig. B-4 we show the stabilization altitude as a function of yield, as debris;*

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*The fact that radioactive tracers are carried on aerosols which are subject to sedimentation (unlike gases) appears entirely immaterial, as sedimentation velocities are of order 100 m/month, which is 10^{-6} times the cloud rise velocity.

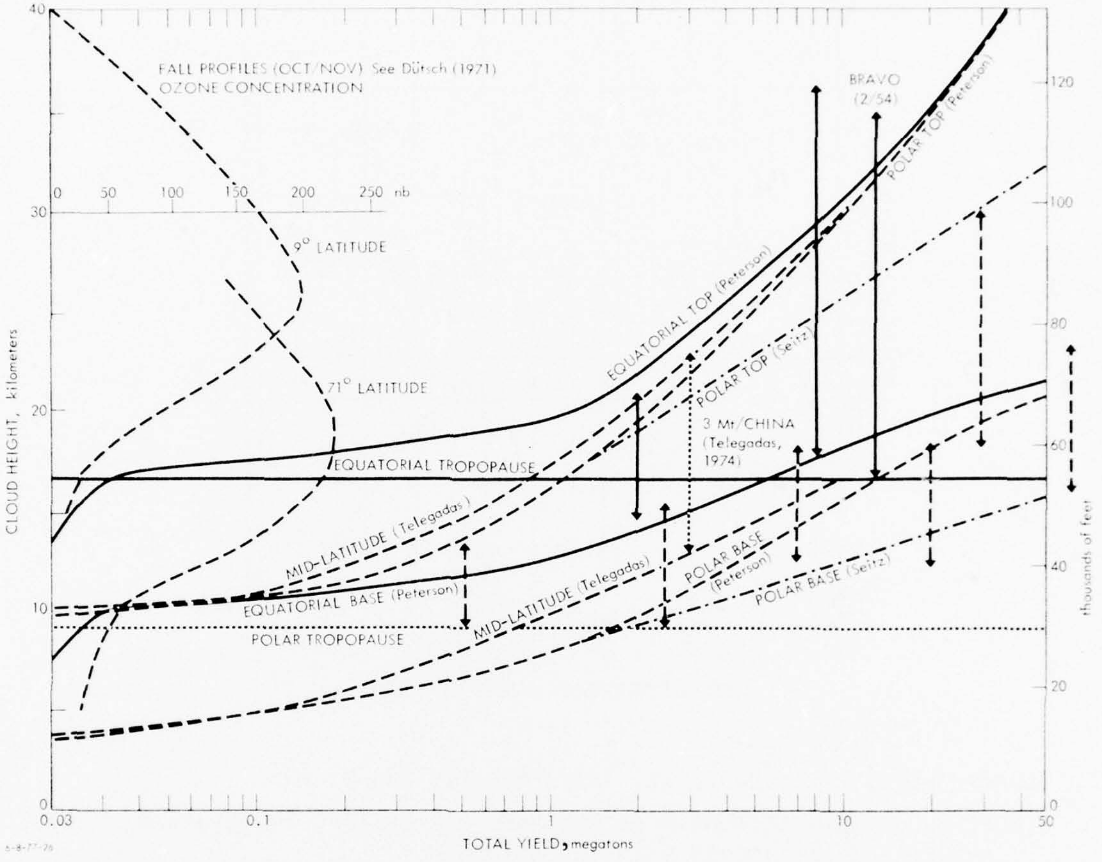

FIGURE B-4. Cloud Rise Height as a Function of Yield for Different Latitudes. U.S. tests were conducted at equatorial latitude (2 to 17° N), Chinese at mid-latitude (40° N), and Soviet at polar latitude (75° N). Peterson's (1970) curves are based on U.S. tests; all U.S. bombs had yields below 15 Mt. Thus, Peterson's equatorial curves for yields above 15 Mt as well as his polar curves are purely estimates. Estimates of Seitz et al. (1968) for individual U.S. (solid) and Soviet (dashed) explosions are shown as vertical lines. Dot-dash curves have been drawn by eye through Seitz' Soviet lines to provide an alternative to Peterson's polar case. Note the significant difference above Mt-yields. Some mid-latitude estimates of Telegadas (1977) are also shown, based on Chinese explosions. Within a given cloud the altitude distribution of NO_x shown in Table B-2 may be assumed. Representative ozone profiles for equatorial and polar latitudes are also shown.

TABLE B-2. INITIAL VERTICAL DISTRIBUTION OF RADIOACTIVITY OR NO_x ASSUMED WITHIN "MUSHROOM CAP" (see Fig. B-5)

Layer, Fraction of "Mushroom Cap" (from base to top)	Percentage of Activity Within Layer
$0 - \frac{1}{7}$	1
$\frac{1}{7} - \frac{2}{7}$	14
$\frac{2}{7} - \frac{3}{7}$	25
$\frac{3}{7} - \frac{4}{7}$	25
$\frac{4}{7} - \frac{5}{7}$	15
$\frac{5}{7} - \frac{6}{7}$	15
$\frac{6}{7} - \frac{7}{7}$	5

Source: Peterson, 1970

we may assume that the radioactivity is a tracer of cloud motion, and that the NO_x follows the cloud, with the exception of some possible detrainment, which will be discussed below. Peterson's analysis hypothesizes the distribution of radioactivity within the stabilized cloud as indicated in Table B-2. It refers to air bursts and shows some dependence on latitude; there is also some dependence on meteorological conditions, especially for kt-yield devices, where stabilization altitudes for different shots of the same yield may vary by as much as a factor of two.

Note that Peterson's estimates are based on U. S. data which cannot be relied upon above about 15 Mt* and which were always

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*The largest announced U. S. device tested was Bravo (28 Feb 1954), a 15-Mt surface burst fired at Bikini (11° N latitude). By contrast, the largest Soviet device was a 58-Mt air burst (fired at Novaya Zemlya, 75° N latitude, on 30 Oct 1961).

carried out (for large-yield devices) at equatorial latitudes; the estimates for polar latitudes are based on a correlation with atmospheric stability, and are clearly not as reliable as the estimates for equatorial latitudes. Here we may refer to the data of Telegadas (1974, 1976) on Chinese bombs (3 Mt, 40° N latitude) which come from airplane and balloon samples taken mainly over North America, a large fraction of the globe away in latitude so that the assumption of zonal average flow is crucial.

Here I use assignments of Seitz et al. of both weapon yield and cloud rise height for the Soviet bombs as shown in Fig. B-4, and thus draw the alternative curves for polar cloud height shown dot-dash,* which give significantly lower cloud heights than do Peterson's polar assignments. It is clear that this alternative assignment is not necessarily better than Peterson's, only different; and the difference gives merely a suggestion of the uncertainty of the cloud height assignment.

B.3.3 Detrainment?

The rising and expanding nuclear cloud is extremely turbulent, see e.g., Fig. B-1, and entrains a large quantity of air during its rise. One may ask whether any of the hot air, NO_x, and debris is "detrained" from the cloud and left behind while the rest of the cloud rises past it. Thus, Simons and Caledonia (1973) suggested that only 17 to 30 percent of the NO produced actually rises to the cloud stabilization height, while COMESA (1975), p. 555, estimates that about 80 percent of the NO produced rises to stabilization height.

During the U. S. "Dominic" nuclear test series of 1962, the stem left behind when a nuclear fireball rises was tested for radioactivity by flying an aircraft through the (visible) stem,

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*These curves have been drawn in by eye, i.e., there is no "objective" basis for them.

and it was established in "Project Stemwinder" that less than 1 percent of the total radioactivity is found in the stem 1 hour after detonation, see Ferber (1965). This suggests that no significant detrainment occurs, and thus we shall assume that all the NO_x produced rises to the stabilization altitude as shown in Fig. B-4 and Table B-2.

B.4 OTHER CHEMICAL FACTORS

In addition to oxides of nitrogen, atmospheric nuclear explosions may also deposit water and ozone in the stratosphere. These effects are estimated here.

B.4.1 Water

The stratosphere is very dry (3 to 4.5 ppmv of H_2O), whereas the troposphere, especially the tropical troposphere, can be very wet (10^3 to 10^4 ppmv of H_2O). Thus, large nuclear explosions can carry rather large amounts of water vapor into the stratosphere. I will show here that these quantities of water appear to be insufficient to make any significant change in stratospheric water vapor content, except locally, at very early times after the events (approximately 1 to 10 days). No attempt is made to give detailed estimates of the water-vapor addition for each event, but some guidelines are provided for a more detailed investigation.

From Eq. (4) we see that a 1-Mt "low air burst" will be detonated at about 1-km altitude. Table B-3 shows representative temperature and moisture contents at this altitude (assuming 50 percent relative humidity) for tropical summer and polar fall conditions which correspond, respectively, to U.S. and U.S.S.R. test conditions. Data are also shown for 4-km altitude, since the largest Soviet bomb was detonated at about that altitude. The final column in Table B-3 gives plausible estimates for the number of water molecules injected into the stratosphere per megaton of yield, assuming that the total mass of the fireball is 10^6 t/Mt as before, and that initial test conditions are representative of the total entrained air mass. Note that tropical explosions carry much larger quantities of water into the stratosphere than do polar explosions. Note also that the total water content of the stratosphere is roughly 2×10^{12} kg, 7×10^{37} molecules (e.g., Appendix A). We may approximate the water injected by the 1961 to 1962 series of atmospheric nuclear tests of 300 Mt by assuming an injection of 1×10^{32} H_2O molecules/Mt, which is approximately 1/2000 of the ambient stratospheric water loading. For time-dependent estimates, turn to Johnston (1977), who lists cloud volumes as a function of time after a 2-Mt test (from Christie, 1976). These volumes are shown in Table B-4 which also contains estimates of the fractional augmentation of local water content, assuming that the bomb-entrained water vapor is uniformly mixed in the stabilized (but growing) bomb cloud; thus eight days after the test there is only a 0.7 percent enhancement in stratospheric water vapor.

From these estimates, it can be concluded that detailed accounting of bomb-injected water vapor is not warranted; but if such calculations are considered desirable, the molecular ratios shown in Table B-5 can be used. These estimates are based on the water injection of Table B-4 and on an injection of 1×10^{32} NO_x-molecules/Mt.

TABLE B-3. POTENTIAL WATER TRANSPORT FROM THE TROPOSPHERE

(JI/S refers to Johnston Island--Summer (15° N. annual mean)
[NZ/F refers to Novaya Zemlya--Fall (75° N, ½ (Jan + July)]

Place/ Time	Height	T, °K	P, mbar	e_w, mbar*	s_w**	H_2O mols/Mt at 50% Saturation
JI/S	1 km	296	904.2	28.09	0.0321	3.33×10^{32}
NZ/F	1 km	264	889.5	3.097	0.00350	$0.364 \times 10^{32\dagger}$
JI/S	4 km	277	633	8.13	0.0130	1.35×10^{32}
NZ/F	4 km	251	598	0.850	0.0014	$0.15 \times 10^{32\dagger}$

Data from U.S. Standard Atmosphere, 1966 Supplements, Table 5.1
Smithsonian Meteorological Tables (6th Ed., 1958) p. 347f

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*e_w = saturation vapor pressure over water

**s_w = water molar (or volume) mixing ratio in air

†This is the saturation vapor pressure over ice rather than over water.

NOTE: If a 1-Mt air burst, detonated at 1-km altitude, picks up all its water at the height of detonation, then in the tropics it can carry (at 50 percent relative humidity) 3.33×10^{32} H_2O mols/Mt upward, say, into the stratosphere; in the polar region it can carry 0.36×10^{32} H_2O mols/Mt upward.

To avoid interaction of the fireball with the surface, i.e. to have an air burst, a higher yield burst has to be detonated at higher altitude, e.g., the 58-Mt Soviet bomb was detonated near 4 km; thus it would bring up, on the same scheme, only 0.15×10^{32} mols H_2C/Mt. Note, however, that if there happened to be a rain cloud at the place and time of detonation, so that the fireball brings up the cloud water as well as the atmospheric water vapor, the total water transport might be several times higher for, say, a 4-km detonation.

TABLE B-4. LOCAL WATER AUGMENTATION IN THE STRATOSPHERE FOLLOWING A 2-Mt TROPICAL TEST

Time, days	0	2	4	8
Volume (10^{21} cm^3)[a]	0.58	1.6	4.3	10
Air mass (10^{39} molecules)[b]	1.2	3.2	8.6	20
Background water (10^{33} molecules)[c]	5.4	14.4	38.7	90
Perturbation water (10^{33} molecules)[d]	0.67	0.67	0.67	0.67
Percent water augmentation	12	4.7	1.7	0.7

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[a] Johnston (1977), Table 2a

[b] Assuming 2 x 10^{18} mol/cm^3 (19 km)

[c] Assuming 4.5 ppmv

[d] Assuming a 2-Mt burst and 3.33 x 10^{32} mol/Mt

TABLE B-5. SUGGESTED STRATOSPHERIC H_2O INJECTION BY NUCLEAR TESTS

Type of Test	Ratio of H_2O Molecules/NO_x Molecule
U.S. (1 Mt)	3
U.S. (large)	1
Soviet (1 Mt)	0.4
Soviet (large)	0.2

B.4.2 Ozone and the NO/NO_2 Ratio

Johnston (1977) has estimated ozone production during nuclear tests as being in the range (-0.1 to +3.6) x 10^{32} molecules/Mt yield. This ozone production comes partly from chemical processes involving the injected NO_x production, which is (0.4 to 1.5) x 10^{32} molecules/Mt yield [see Gilmore (1974)]. Johnston also points out that at specified altitudes rather long times (from fractions of a year to almost two years) may be required for bomb-produced NO_x to destroy bomb-produced ozone.

This ozone injection is not a significant contributor to the long-term effect of nuclear tests, since one NO molecule presumably destroys a very large number of ozone molecules (of order 10^3, depending on the chemical model in current fashion) by the catalytic cycle of Eqs. (1 to 3)--see Section B.1. Thus, the possible injection of perhaps one ozone molecule along with each NO molecule is not a significant counter to process (1 to 3).

Further, there is a question as to whether the bomb-injected NO_x is injected in the stratosphere as NO or as NO_2. While this is significant on a short-term basis (cf. Johnston, 1977), for the long-term application of interest here it is not. (H. S. Johnston and F. M. Luther, private communications).

B.5 LISTING OF HIGH-YIELD ATMOSPHERIC NUCLEAR EXPLOSIONS, 1952 to 1976

The basic data source is U.S. DOE--see Glasstone (1964), Appendix B, updated by Cannon (1977), checked against the Swedish compilation of Zander and Araskog (1973), a more recent compilation of Carter and Moghissi (1977), and an informal compilation prepared by K. Telegadas (NOAA-ARL).

Here I provide a tentative assignment of effective yields for all listed high-yield atmospheric explosions. The procedure used to assign yields is the following:

1. If an "official" yield figure is quoted, that value is used.
2. For the older (1955 to 1958) Soviet series, Telegadas' total estimates divided by the number of H-bombs in the series are used.
3. For the 1961 to 1962 series, the values of Seitz et al. (1968) are used as base, but scaled to agree approximately with total announced yields (Federal Radiation Council, 1963). Thus, for the 1961 Soviet series, where Seitz et al. list a total of 97 Mt, I scale up 24 percent to give a total yield equal to the accepted

figure of 120 Mt; for the 1962 U.S. Pacific series, Seitz' total is 26 Mt, which is scaled up 42 percent to give the accepted total yield of 37 Mt; for the 1962 Soviet series, Seitz' values add up to the accepted figure of 180 Mt.

Table B-6 gives the locations of the various test sites and Table B-7 lists the yields and dates of thermonuclear explosions in the atmosphere: only those bombs are counted here that are likely to deposit some NO_x in the stratosphere, which means near-surface devices of Mt yield. "Intermediate" and lower yield devices are unlikely to affect the stratosphere because their clouds barely rise above the tropopause, while high-altitude explosions, which are detonated at altitudes of order tens of kilometers (see, e.g., Hoerlin, 1976) produce an effect on the mesosphere and thermosphere, but not on the stratosphere.

TABLE B-6. TEST SITES

U.S.A.	
Eniwetok (EN)	11° N, 162° E
Bikini (BK)	11° N, 165° E
Christmas Island (XI)	2° N, 157° W
Johnston Island (JI)	17° N, 169° W
U.S.S.R.	
Novaya Zemlya/Arctic (NZ)	75° N, 55° E
Siberia	52° N, 78° E
Semipalatinsk (SP)	50° N, 80° E
U.K.	
Christmas Island (XI)	2° N, 157° W
FRANCE	
Centre d'Experimentation du Pacifique (CEP), Tuamotu Archipelago	21° S, 137° W
CHINA	
Lop Nor (LN)	40° N, 90° E

TABLE B-7. ATMOSPHERIC THERMONUCLEAR EXPLOSIONS
(See Notes at End of Table)

Date	Country	Location	Name	Type	Yield, Mt DOE	Z & A	C & M	TELEGADAS	Other	Suggested
31 Oct 52	USA	EN:Ivy	Mike	Surface	10.4	10.4	10.4			10.4S
12 Aug 53	USSR	?		Atmos.	H	H	H	1		1
28 Feb 54	USA	BK:Castle	Bravo	Surface	15	15	15			15S
4 Aug 55	USSR	?		Atmos.	A	A	A	3		0.75
24 Sep 55	USSR	?		Atmos.	A	A	A			0.75
10 Nov 55	USSR	?		Atmos.	A	A	A			0.75
23 Nov 55	USSR	?		Atmos.	Mt range	Mt range	>1			0.75
20 May 56	USA	BK:Redwing	Cherokee	Air Drop	Several	Several	>1	17		2
27 May 56	USA	BK:Redwing	Zuni	Surface	3.5	3.5	3.53			3.5S
20 Jul 56	USA	BK:Redwing	Tewa	Barge	5	~5	5.01			5S
30 Aug 56	USSR	?		Atmos.	Large	Large	0.2-1	6		1.5
2 Sep 56	USSR	?		Atmos.	A	A	A			1.5
10 Sep 56	USSR	?		Atmos.	A	A	A			1.5
17 Nov 56	USSR	?		Atmos.	Large	Large	0.2-1			1.5
10 Apr 57	USSR	?			Large	Large	0.2-1	6		3
16 Apr 57	USSR	?			Large	Large	0.2-1			3
15 May 57	UK	XI:Grapple		Air Drop	Mt range	Mt range	>1	3		1
31 May 57	UK	XI:Grapple		Air Drop	Mt range	Mt range	>1			1
19 Jun 57	UK	XI:Grapple		Air Drop	range	range	>1			1
22 Aug 57	USSR	Siberia			Substantial	Substantial	>1	6		2
24 Sep 57	USSR	Arctic			Mt range	Mt range	>1			2
6 Oct 57	USSR	?			Substantial	Substantial	H			2
8 Nov 57	UK	XI:Grapple		Air Drop	Mt range	Mt range	>1			1
23 Feb 58	USSR	Arctic			Mt range	Mt range	>1	10		3
27 Feb 58	USSR	Arctic			Mt range	Mt range	>1			3
28 Apr 58	UK	XI:Grapple		Air Drop	Mt range	Mt range	>1	1		1
12 May 58	USA	EN:Hardtack	Koa	Surface	1.37	1.37	1.37	E		1.4S
28 Jun 58	USA	EN:Hardtack	Oak	Barge	8.9	8.9	8.9	E		8.9S
2 Sep 58	UK	XI:Grapple		Air Drop	Mt range	Mt range	>1	2		1
11 Sep 58	UK	XI:Grapple		Air Drop	Mt range	Mt range	>1			1
10 Oct 58	USSR	Arctic		Atmos.	Rel. large	Mt range	>1	26		1
12 Oct 58	USSR	Arctic		Atmos.	Large	Mt range	>1			3
15 Oct 58	USSR	Arctic		Atmos.	Large	Mt range	>1			3
18 Oct 58	USSR	Arctic		Atmos.	Large	Mt range	>1			3
20 Oct 58	USSR	Arctic		Atmos.	Large	Mt range	>1			3
22 Oct 58	USSR	Arctic		Atmos.	Large	Mt range	>1			3
24 Oct 58	USSR	Arctic		Atmos.	Large	Mt range	>1			3
25 Oct 58	USSR	Arctic		Atmos.	Rel. Large	Rel. Large	0.2-1			1

TABLE B-7. ATMOSPHERIC THERMONUCLEAR EXPLOSIONS (Cont. p. 2)

					Yield, Mt					
Date	Country	Location	Name	Type	DOE	Z & A	C & M	TELEGADAS	Other	Suggested
10 Sep 61	USSR	NZ		Atmos.	Order of Several Mt	Several Mt	>1		2.4(Seitz)	3
12 Sep 61	USSR	NZ		Atmos.	Several Mt	Several Mt	>1		2.4(Seitz)	3
14 Sep 61	USSR	NZ		Atmos.	Several Mt	Several Mt	>1		2.4(Seitz)	3
16 Sep 61	USSR	NZ		Atmos.	∿1	Mt Range	>1		0.5(Seitz)	1
18 Sep 61	USSR	NZ		Atmos.	∿1	Mt Range	>1		0.5(Seitz)	1
20 Sep 61	USSR	NZ		Atmos.	∿1	Mt Range	>1		0.5(Seitz)	1
22 Sep 61	USSR	NZ		Atmos.	∿1	Mt Range	>1		0.5(Seitz)	1
2 Oct 61	USSR	NZ		Atmos.	∿1	Mt Range	>1	120	0.5(Seitz)	1
4 Oct 61	USSR	NZ		Atmos.	Order of Several Mt	Several Mt	>1		2.4(Seitz)	3
6 Oct 61	USSR	NZ		Atmos.	Several	Several	>1		2.4(Seitz)	3
20 Oct 61	USSR	NZ		Atmos.	Several	Several	-		2.4(Seitz)	3
23 Oct 61	USSR	NZ		Atmos.	∿25	25	25		20(Seitz)	25
30 Oct 61	USSR	NZ		Air burst	58	58	58		55(Seitz)	58
31 Oct 61	USSR	NZ		Atmos.	Several	Several	>1		2.4(Seitz)	3
4 Nov 61	USSR	NZ		Atmos.	Several	Several	>1		2.4(Seitz)	3
2 May 62	USA	XI	Arkansas	Air burst	Low Mt	1-10	>1		2 (Seitz)	3
10 Jun 62	USA	XI	Yeso	Air burst	Low Mt	1-10	>1		2 (Seitz)	3
27 Jun 62	USA	XI	Bighorn	Air burst	Mt Range	>1	>1	32	8 (Seitz)	11
30 June 62	USA	XI	Bluestone	Air burst	Low Mt	1-10	>1		2 (Seitz)	3
11 Jul 62	USA	XI	Pamlico	Air burst	Low Mt	1-10	>1		2 (Seitz)	3
5 Aug 62	USSR	NZ			30	<30	30	D	30 (Seitz)	30
20 Aug 62	USSR	NZ			Order of Several Mt	Several	>1	D	7 (Seitz)	7
22 Aug 62	USSR	NZ			Low Mt	Mt Range	>1	D	3 (Seitz)	3
25 Aug 62	USSR	NZ			Order of Several Mt	Several	>1	D	7 (Seitz)	7
27 Aug 62	USSR	NZ			Several	Several	>1	D	7 (Seitz)	7
8 Sep 62	USSR	NZ			Mt Range	Mt Range	>1	D	1 (Seitz)	1
15 Sep 62	USSR	NZ			Several Mt	Several Mt	>1	D	7 (Seitz)	7
16 Sep 62	USSR	NZ			Several Mt	Several Mt	>1	D	7 (Seitz)	7
18 Sep 62	USSR	NZ			A few Mt	A few Mt	>1	D	3 (Seitz)	3
19 Sep 62	USSR	NZ			Multi-Mt	Multi-Mt	>1	D	24 (Seitz)	24
21 Sep 62	USSR	NZ			A few Mt	A few Mt	>1	D	3	3
25 Sep 62	USSR	NZ		Atmos.	Multi-Mt	Multi-Mt	>1	D	27 (Seitz)	27
27 Sep 62	USSR	NZ		Atmos.	<30	30	<30	D	24 (Seitz)	24
18 Oct 62	USA	J.I.	Chama	Air burst	Lot Mt	1-10	>1	C	2 (Seitz)	3
22 Oct 62	USSR	NZ		Atmos.	Several Mt	Several Mt	>1		7 (Seitz)	7
30 Oct 62	USA	J.I.	Housatonic	Air	Mt-range	>1	>1	C	8 (Seitz)	10
25 Dec 62	USSR	NZ		Atmos.	B	B'	B'		20, 3 (Seitz)	20, 3
17 Jun 67	China	Lop Nor		Air drop	∿3(H)	3(H)	∿3(H)	3		3

TABLE B-7. ATMOSPHERIC THERMONUCLEAR EXPLOSIONS (Cont. p. 3)

Date	Country	Location	Name	Type	Yield, Mt DOE	Z & A	C & M	TELEGADAS	Other	Suggested
24 Aug 68	France	CEP	Canopus	Balloon	Low Mt	2.5	<1(H)	4		2.5
8 Sep 68	France	CEP	Procyon	Balloon	Low Mt	1	<1			1
27 Dec 68	China	Lop Nor		Air drop	~3	3	~3(H)	3		3
29 Sep 69	China	Lop Nor		Air drop	~3	3	~3	3		3
30 May 70	France	CEP	Dragon	Balloon	Intermed.	0.1-1	1	2		1
3 Jul 70	France	CEP	Licorne	Balloon	Intermed.	1	1			1
14 Oct 70	China	Lop Nor		Air drop	~3	3	~3	3		3
14 Aug 71	France	CEP	Rhea		High	~1	0.2-1			1
26 Jun 73	China	Lop Nor		Atmos.	2-3	-	2.3			2.5
17 Nov 76	China	Lop Nor		Atmos.	4	-				4

NOTES: High-altitude explosions are excluded.

USSR SHOTS: Dates are sometimes date of AEC announcement rather than shot date.

Location is often not specified in the earlier events.

Type is generally not specified (i.e., air drop, balloon, surface, etc.) Thus one may assume that the effective NO_x production corresponds to the full yield rather than only 50% as for a surface-interactive burst.

Codes for locations listed on Table B-4.

Yield

DOE means Glasstone (1964), supplemented with Cannon (1977)

Z & A means Zander & Araskog (1973)

C & M means Carter & Moghissi (1976)

Telegadas means private communication, April 1977

Seitz means Setiz et al. (1968)

A dash(-) means yield not specified

A blank space means detonation not listed (typically, event after publication of reference)

A means "yield not specified: may not be thermonuclear"

H means "thermonuclear: yield not specified"

B means "AEC announcement: a number of atmospheric tests held 23-25 Dec. 1962, largest about 20 Mt, others low to a few Mt"

B' means "20 Mt; others listed without yield"

C means "Telegadas quotes 4 Mt for Chama + Housatonic"

S means "surface-interactive shot: rise height corresponds to yield quoted, NO_x injection should correspond to half the effective yield"

D means "Telegadas quotes total yield of 180 Mt for Soviet 1962 series, in agreement with Federal Radiation Council"

E means "Telegadas quotes a total yield of 28 Mt for US tests from 28 April to 26 July 1958"

Note that Federal Research Council (1963) lists total yields of 1962 tests as USA, 37 Mt; USSR, 180 Mt

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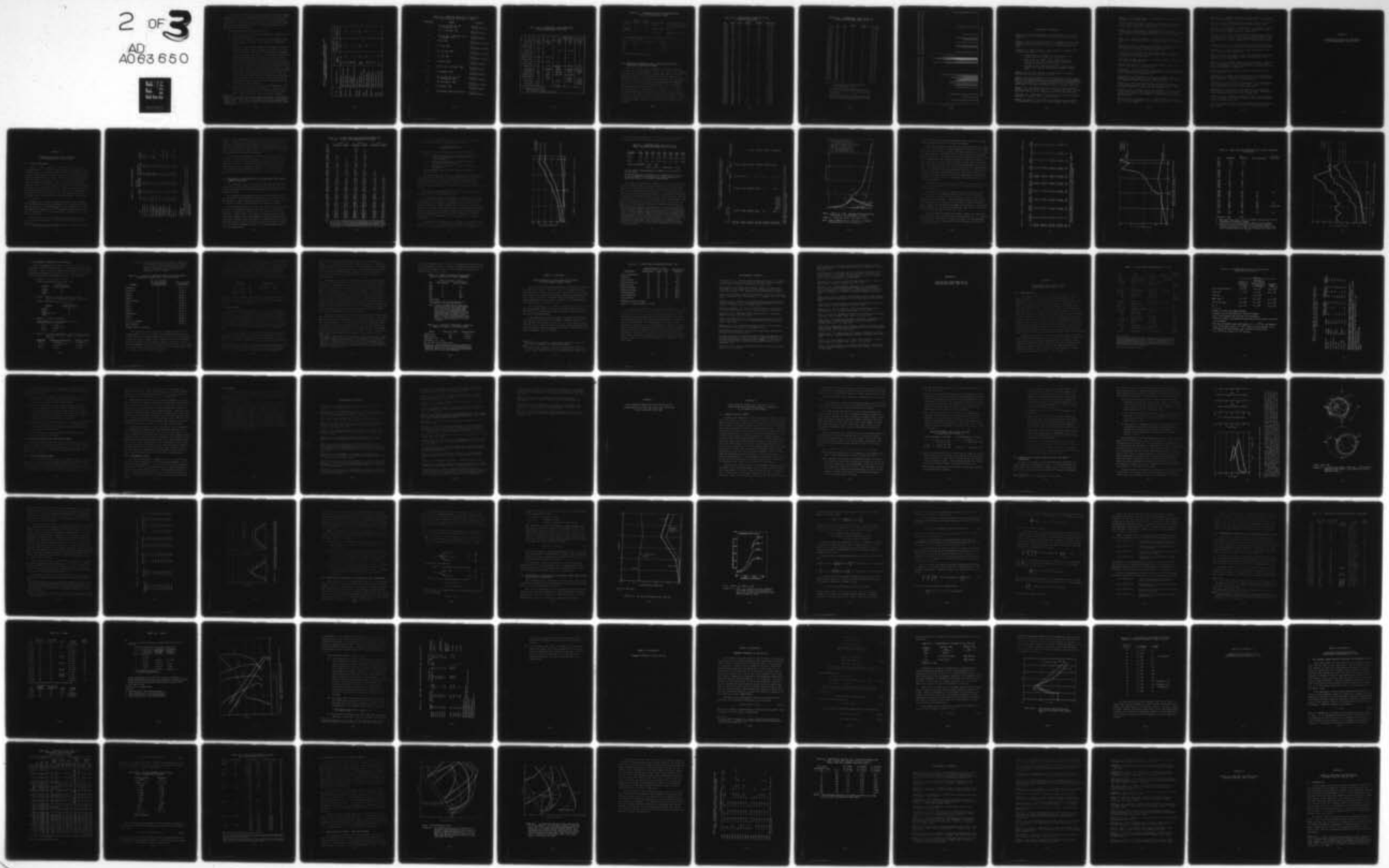

For general orientation, Table B-8 provides the total megatonnage of the various atmospheric test series, Table B-9 gives the groupings used by Seitz et al. (1968)* of the high-yield stratospheric injections for the 1961 to 1962 series, and Table B-10 gives an aggregated list of "intermediate-range" atmospheric nuclear explosions.

The following comments should be made:

a. These data are all taken from published information in the open literature.

b. The data are clearly incomplete and inconsistent--see the procedure of items 1 to 3 above for "assigning" yields.

c. There have been a large number of atmospheric nuclear explosions with energy significantly below 1 Mt, which tend to stabilize near the local tropopause according to current cloud rise models. They will not reduce the ozone level very much; in fact, as a result of the "smog" reactions they may even enhance the ozone level. Table B-11 is an attempt to put these various factors in context by correlating the mean size of explosions with their cloud altitude and thus with their effect on ozone; it is clear that while there have been very many "small" bombs, the overwhelming megatonnage and thus NO_x was carried by the "relatively few" H-bombs, and therefore it is not appropriate to concern oneself unduly with the production of ozone from the "small" bombs through the tropospheric smog reactions.

d. The overall division into "small," "intermediate," and "large" bombs is somewhat ambiguous. I have tried to count every announced event in one and only one category, except for sub-kt events, which are ignored.

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*Seitz et al. (1968) studied the global transport of radioactive debris (Sr-90) from the various high-yield tests in the 1961 to 1962 series. Thus, their assignment of injection heights and yields is of some relevance for the present injection of oxides of nitrogen.

TABLE B-8. GENERAL ORIENTATION: ESTIMATED TOTAL YIELD OF VARIOUS ATMOSPHERIC NUCLEAR TEST SERIES

Time	Country/Location	Total Yield, Mt			
		Bauer Estimate		COMESA (1975) p. 566	Chang et al. (1977)
1952-54	USA (Tropical)	59	60	60	-
	USSR (Mid-High Latitude)	1			
1955-56	USA (Tropical)	19	28	28	20
	USSR (Mid-High Latitude)	9			
1957-58	USA (Tropical)	30	85	75	74
	UK (Tropical)	7			
	USSR (Mid-High Latitude)	48			
1959-60	Moratorium		0	0	0
1961-62	USA (Tropical)	37	340	334	335
	USSR (High Latitude)	300			
1963	Partial Test Ban Treaty		0	0	0
1967-68	France (Tropical)	4	10	11	0
	China (Mid-Latitude)	6			
1969-70	France (Tropical)	2	8	9	0
	China (Mid-Latitude)	6			
1971	France (Tropical)	1	1	1.6	-
1973	China (Mid-Latitude)	2-3	2-3	-	-
1976	China (Mid-Latitude)	4	4	-	-

TABLE B-9. INJECTION GROUPINGS OF 1961-1962 TEST SERIES USED BY SEITZ et al. (1968)

Injection	Dates	Location
1	10, 12, 14, 16, 18, 20, 22 September 1961	U.S.S.R. (Novaya Zemlya)
2	2, 4, 6 October 1961	U.S.S.R. (Novaya Zemlya)
3	20, 23, 30, 31 October 1961; 4 November 1961	U.S.S.R. (Novaya Zemlya)
4	2 May 1962	U.S.A. (Christmas Island)
5	10 June 1962	U.S.A. (Christmas Island)
6	27, 30 June 1962	U.S.A. (Christmas Island)
7	11 July 1962	U.S.A. (Christmas Island)
8	5 August 1962	U.S.S.R. (Novaya Zemlya)
9	20, 22, 25, 27 August 1962	U.S.S.R. (Novaya Zemlya)
10	8 September 1962	U.S.S.R. (Novaya Zemlya)
11	15, 16, 18, 19, 21, 25, 27 September 1962	U.S.S.R. (Novaya Zemlya)
12	18, 30 October 1962	U.S.A. (Johnston Island)
	22 October 1962	U.S.S.R. (Novaya Zemlya)
13	24 December 1962 (two tests)	U.S.S.R. (Novaya Zemlya)

TABLE B-10. INTERMEDIATE YIELD ATMOSPHERIC NUCLEAR EXPLOSIONS, 1962-1976

Date	Country	Location	Type	Number/Yield in kt		
				ERDA	Z & A	C & M
Nov 52	USA	EN:Ivy	Air Drop	1/(500)	1/500	1/(>200)
Jun 54	USA	BK:Castle	Surface	1/100	1/100	1/110
Aug-Nov 56	USSR	?	-	-	-	3
Apr	USSR	Various	-	-	-	3
Mar 58	USSR	NZ	-	3/(<1000)	3/(<1000)	10
Sep-Oct 61	USSR	SP	-	6	6	6
Sep-Nov 61	USSR	NZ	-	7	7	7
Apr-Jul 62	USA	XI:Dominic	Air Drop	17	17	17
Aug-Sep 62	USSR	NZ	-	2	2	2
Oct 62	USA	JI:Dominic	Air Drop	2	2	2
Oct-Dec 62	USSR	NZ	-	10	10	10
May 66	China	Lop Nor	Air Drop	1/(lower end of I Range)	1/(200-500)	1/(20-60)
Sep 66	France	CEP	Balloon/Barge	2(small)	2/(120,150)	low yield only
Oct 66	France	CEP	Barge	1(200-300)	1/(200-300)	1/(200-300)
Dec 66	China	Lop Nor	Tower	1/(few 100 kt)	1/300	1/(>200)
Jul-Aug 68	France	CEP	Balloon	2/(500,<1000)	2/(500,<1000)	2
May-Aug 70	France	CEP	Balloon	3	3(<20)	5
Jul 71	France	CEP	Balloon	1	1/(400-500)	1/(20-200)
Mar 72	China	Lop Nor	-	1/(20-200)	1/(20-200)	1/(20-200)
Jul 74	China	Lop Nor	-	1	-	1/(200-1000)
Sep 76	China	Lop Nor	-	1/(20-200)	-	-

NOTES: Notation is same as for Table B-5

Intermediate range is 20 to 1000 kt

This is a greater level of aggregation than in Table B-5

TABLE B-11. AGGREGATED EFFECTS OF BOMB-PRODUCED NO_x ON STRATOSPHERIC OZONE

Yield, Range	Total Megatonnage (1950-1976)	Total No. of Bombs* (1950-1976)	Altitude of Injection	Effect of Stratospheric Ozone
Low: 1-20 kt	~10	190	tropopause	Increases ozone by smog reactions, but is lost rapidly by rainout.
Intermediate: 20-1000 kt	~10	64	just above tropopause	Rather little.
High: $\gtrsim$1 Mt	~500	87	in stratosphere	Reduces ozone by catalytic cycle: long life time.

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*Note: The breakdown by countries is shown below. High-altitude explosions (height of burst above 10 km) are omitted.

Country	A-Bombs (1-20 kt)	I-Bombs (20-1000 kt)	H-Bombs (>1 Mt)
U.S.A.	124	21	14 (~145 Mt)
U.S.S.R.	35	28	55 (~360 Mt)
U.K.	11	--	7 (~7 Mt)
France	15	9	5 (~7 Mt)
China	6	6	6 (~18 Mt)

Note that high-altitude explosions are omitted.

B.6 SUGGESTED STRATOSPHERIC NO_x INJECTIONS DUE TO PAST ATMOSPHERIC NUCLEAR EXPLOSIONS

Table B-12 lists my best estimates of stratospheric NO_x injections due to atmospheric nuclear explosions. The estimates were derived by combining the various input data and models discussed previously. For orientation, Fig. B-5 shows the NO_x injection into the stratosphere by months from 1952 through 1976 in terms of megatons of effective yield using the conversion factor (0.5 to 1) x 10^{32} NO_x molecules/Mt. For the ambient stratospheric NO_x loading we use the value of 5 x 10^6 tons (as HNO_3) from A. J. Grobecker et al. (1974), p. 10. By far the most significant NO_x injections were the Arctic injections of 1961 to 1962, which exceed 10 percent of the global stratospheric NO_x loading for several months and thus might be expected to show observable effects on total ozone, at least at high latitudes.

TABLE B-12. STRATOSPHERIC INJECTION OF NO_x BY NUCLEAR EXPLOSIONS

Date	Country	Location	Effective Yield, Mt	NO_x Injection 10^{32} mols	Altitude Range, km
31 Oct 52	USA	EN	10.4S	5.2	8.3 - 30.7
12 Aug 53	USSR	?M	1	1	7.9 - 16.0
28 Feb 54	USA	BK	15S	7.5	19.1 - 32.8
4 Aug 55	USSR	?M	0.75	0.75	7.3 - 14.9
24 Sep 55	USSR	?M	0.75	0.75	7.3 - 14.9
10 Nov 55	USSR	?M	0.75	0.75	7.3 - 14.9
23 Nov 55	USSR	?M	0.75	0.75	7.3 - 14.9
20 May 56	USA	BK	2	2	13.2 - 21.7
27 May 56	USA	BK	3.5S	1.75	15.3 - 24.7
20 Jul 56	USA	BK	5S	2.5	16.3 - 26.5
30 Aug 56	USSR	?M	1.5	1.5	9.1 - 17.9
2 Sep 56	USSR	?M	1.5	1.5	9.1 - 17.9
10 Sep 56	USSR	?M	1.5	1.5	9.1 - 17.9
17 Nov 56	USSR	?M	1.5	1.5	9.1 - 17.9
10 Apr 57	USSR	?M	3	3	10 - 20.7
16 Apr 57	USSR	?M	3	3	10 - 20.7
15 May 57	UK	XI	1	1	12.5 - 19.5
31 May 57	UK	XI	1	1	12.5 - 19.5
19 Jan 57	UK	XI	1	1	12.5 - 19.5
22 Aug 57	USSR	Sib	2	2	9.3 - 24.3
24 Sep 57	USSR	Arc.	2	2	9.3 - 24.3
6 Oct 57	USSR	?M	2	2	9.3 - 24.3
8 Nov 57	UK	XI	1	1	12.5 - 19.5
23 Feb 58	USSR	Arc.	3	3	10 - 20.7
27 Feb 58	USSR	Arc.	3	3	10 - 20.7
28 Apr 58	UK	XI	1	1	12.5 - 19.5
12 May 58	USA	EN	14S	0.7	13.2 - 20.4
28 Jul 58	USA	EN	8.9S	4.45	17.5 - 28.9
2 Sep 58	UK	XI	1	1	12.5 - 19.5
11 Sep 58	UK	XI	1	1	12.5 - 19.5
10 Oct 58	USSR	Arc.	1	1	7.9 - 16.0
12 Oct 58	USSR	Arc.	3	3	10 - 20.7
15 Oct 58	USSR	Arc.	3	3	10 - 20.7
18 Oct 58	USSR	Arc.	3	3	10 - 20.7
20 Oct 58	USSR	Arc.	3	3	10 - 20.7
22 Oct 58	USSR	Arc.	3	3	10 - 20.7
24 Oct 58	USSR	Arc.	3	3	10 - 20.7
25 Oct 58	USSR	Arc.	1	1	7.9 - 16.0
10 Sep 61	USSR	NZ	3	3	10 - 20.7
12 Sep 61	USSR	NZ	3	3	10 - 20.7
14 Sep 61	USSR	NZ	3	3	10 - 20.7
16 Sep 61	USSR	NZ	1	1	7.9 - 16.0
18 Sep 61	USSR	NZ	1	1	7.9 - 16.0
20 Sep 61	USSR	NZ	1	1	7.9 - 16.0
22 Sep 61	USSR	NZ	1	1	7.9 - 16.0
2 Oct 61	USSR	NZ	1	1	7.9 - 16.0
4 Oct 61	USSR	NZ	3	3	10 - 20.7
6 Oct 61	USSR	NZ	3	3	10 - 20.7
20 Oct 61	USSR	NZ	3	3	10 - 20.7
23 Oct 61	USSR	NZ	25	25	13.0 - 26.9
30 Oct 61	USSR	NZ	58	58	15.7 - 29.7
31 Oct 61	USSR	NZ	3	3	10 - 20.7

TABLE B-12. STRATOSPHERIC INJECTION OF NO_x BY NUCLEAR EXPLOSIONS (Cont. p. 2)

Date	Country	Location	Effective Yield, Mt	NO_x Injection 10^{32} mols	Altitude Range, km
4 Nov 61	USSR	NZ	3	3	10 - 20.7
2 May 62	USA	XI	3	3	14.7 - 23.5
10 Jun 62	USA	XI	3	3	14.7 - 23.5
27 Jun 62	USA	XI	11	11	18.1 - 30.9
30 Jun 62	USA	XI	3	3	14.7 - 23.5
11 Jul 62	USA	XI	3	3	14.7 - 23.5
5 Aug 62	USSR	NZ	30	30	14.4 - 29.6
20 Aug 62	USSR	NZ	7	7	11.3 - 23.7
22 Aug 62	USSR	NZ	3	3	10 - 20.7
25 Aug 62	USSR	NZ	7	7	11.3 - 23.7
27 Aug 62	USSR	NZ	7	7	11.3 - 23.7
8 Sep 62	USSR	NZ	1	1	7.9 - 16.0
15 Sep 62	USSR	NZ	7	7	11.3 - 23.7
16 Sep 62	USSR	NZ	7	7	11.3 - 23.7
18 Sep 62	USSR	NZ	3	3	10 - 20.7
19 Sep 62	USSR	NZ	24	24	13.9 - 29.1
21 Sep 62	USSR	NZ	3	3	10 - 20.7
25 Sep 62	USSR	NZ	27	27	14.1 - 29.2
27 Sep 62	USSR	NZ	24	24	13.9 - 29.1
18 Oct 62	USA	JI	3	3	14.7 - 23.5
22 Oct 62	USSR	NZ	7	7	11.3 - 23.7
30 Oct 62	USA	JI	10	10	17.9 - 30.0
23 Dec 62	USSR	NZ	20	20	13.6 - 28.0
25 Dec 62	USSR	NZ	3	3	10 - 20.7
17 Jun 67	CHINA	LN	3	3	13.1 - 22.7
24 Aug 68	FRANCE	CEP	2.5	2.5	14.4 - 22.9
8 Sep 68	FRANCE	CEP	1	1	12.5 - 19.5
27 Dec 68	CHINA	LN	3	3	13.1 - 22.7
29 Sep 69	CHINA	LN	3	3	13.1 - 22.7
30 May 70	FRANCE	CEP	1	1	12.5 - 19.5
30 Jun 70	FRANCE	CEP	1	1	12.5 - 19.5
14 Oct 70	CHINA	LN	3	3	13.1 - 22.7
14 Aug 71	FRANCE	CEP	1	1	12.5 - 19.5
26 Jul 73	CHINA	LN	2.5	2.5	12.5 - 21.6
17 Nov 76	CHINA	LN	4	4	13A - 24.7

NOTES: For locations see Table 2.2 where identified, otherwise:

?M (USSR, 1953-1957) take 50-52°N, 78-80°E
Arc (USSR, 1958) take NZ: 75°N, 55°E

For effective yields, S denotes surface burst: height corresponds to actual yield. NO_x injection is half that of equivalent air burst.

For NO_x injection, see Table B-1. I suggest 1×10^{32} NO_x mols/Mt as a plausible choice.

For altitude range, see Fig. B-5. For equatorial bursts I suggest Peterson's (1970) curves, for polar bursts, Seitz (1968) curves as shown there. Table B-2 [from Peterson (1970)] is the recommended NO_x injection within the altitude range quoted here.

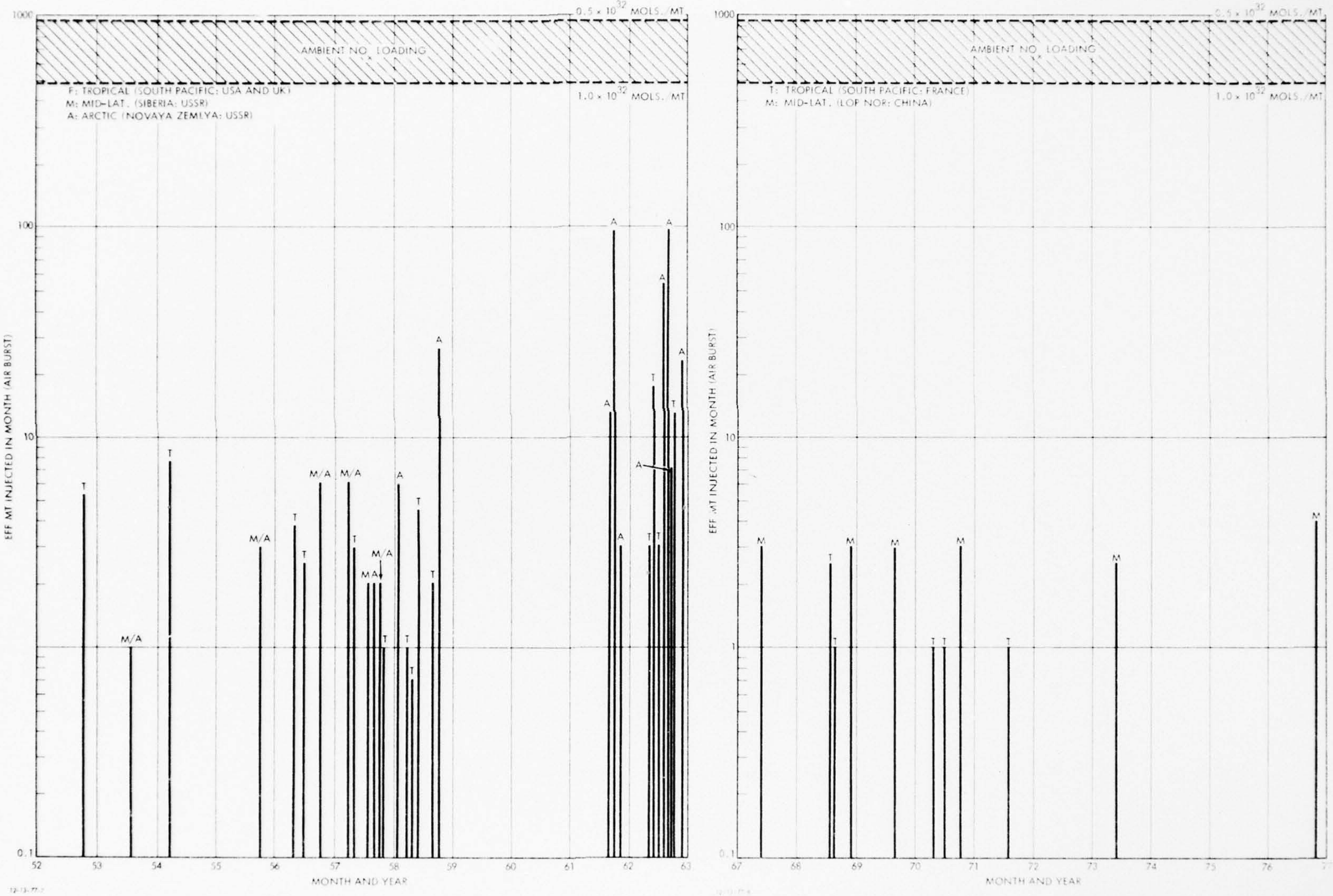

FIGURE B-5. NO_x Injected Into the Stratosphere by Nuclear Explosions

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APPENDIX C

ANTHROPOGENIC RELEASE OF HALOCARBONS IN THE ATMOSPHERE, 1955 TO 1975

APPENDIX C

ANTHROPOGENIC RELEASE OF HALOCARBONS IN THE ATMOSPHERE, 1955 TO 1975

C.1 SPECIES CONSIDERED

Table C-1 lists a number of chlorofluoro- and chlorocarbons which are of possible significance as a source of free chlorine atoms, or, more generally, of ClX (=Cl + ClO + HCl) in the stratosphere, and which may thus serve to reduce the concentration of stratospheric ozone. Bromine-containing molecules are discussed in Section C.4 below. The standard notation is used for chlorofluorocarbons: thus, in molecule FC-xyz, the hundreds digit "x" is the number of carbon atoms in the molecule minus one, the tens digit "y" is the number of hydrogen atoms in the molecule plus one, and the units digit "z" is the number of fluorine atoms in the molecule. The undesignated atoms are chlorine, and if x=0, the first digit is dropped. Thus, FC-11 is $C\,F\,Cl_3$, etc.

In Table C-1, I quote the mass of material that contains 10^{34} chlorine atoms, since, presumably, it is these atoms that deplete the ozone. For orientation, if the mixing ratio of the ClX species is q ppbv (= $q \times 10^{-9}$ molecules per "air molecule"). this corresponds to a total stratospheric loading of $q \times 2.47 \times 10^{34}$ molecules.*

Table C-1 also lists estimated tropospheric injection rates and mean tropospheric lifetimes for the species quoted to

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* This assumes a global 11-km tropopause and the number densities of U.S. Standard Atmosphere, 1976.

TABLE C-1. SPECIES CONSIDERED

Name	Formula	Molecular Weight	10^{34} Cl atoms contained in Following Mass of Material (10^9 kg)	Net Release in 1973		Tropospheric Lifetime (yr)
				(10^8 kg)	(10^{34} Cl atoms)	
FC-11 (Fluorocarbon 11)	$CFCl_3$	137.5	0.761	2.86^a	0.38	36 ± 8^b
FC-12 (Fluorocarbon 12)	CF_2Cl_2	121	1.005	4.35^a	0.43	50 ± 33^b
Carbon tetrachloride	CCl_4	154	0.640	0.82^c 0.42^e	0.13	d
FC-22 (Fluorocarbon 22)	CHF_2Cl	86.5	1.436	0.77^a	0.05	4.5^f
Methyl chloroform (1:1:1 trichloroethane)	CH_3CCl_3	133.5	0.739	3.40^g 3.24^e	0.46	1.4^f, 7.2 ± 1.2^b 8.0^h
Ethylene dichloride (1,2 dichloroethane)	$C_2H_4Cl_2$	99	0.822	5.65^e	0.69	-
Methylene chloride (dichloromethane)	CH_2Cl_2	85	0.706	3.46^e	0.49	0.2^f
Perchlorethylene (tetrachloroethylene)	C_2Cl_4	166	0.689	6.09^e	0.88	0.2^f, 0.4 ± 0.1^b
Trichlorethylene	C_2HCl_3	131.5	0.728	6.48^e	0.89	"a few days"[h]
Vinyl chloride (monochloroethylene)	C_2H_3Cl	62.5	1.038	3.52^e	0.34	-
Methyl chloride	CH_3Cl	50.5	0.838	0.08^e	0.01	0.4^f
Chloroform	$CHCl_3$	119.5	0.661	0.12^e	0.02	0.2^f, 1.7 ± 0.4^b
Ethyl chloride	C_2H_5Cl	64.5	1.071	0.15^e	0.01	-

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a. DuPont (1977)
b. Singh (1977)
c. Singh (1976)
d. i) "Order of several decades" - Galbally (1976)
ii) "35 to 50 years if there is no sink other than photolysis" - Rowland and Molina (1975)
e. A. D. Little (1975) pp I-6 and III-29
f. Luther et al. (1977) Table 20, pp 138. These estimates use a large OH concentration, i.e., may be too short by a factor of 5 to 10
g. *Neely and Plonka (1977)*
h. McConnell and Schiff

provide a crude estimate of their relative impact on the stratosphere. Evidently, a species with a small atmospheric injection rate and a relatively short lifetime in the troposphere is less likely to contribute to stratospheric chlorine than do FC-11 and FC-12, with relatively large injection rates and no established photochemical sinks in the troposphere.

The specific tropospheric lifetimes of various materials are due to reaction with OH radicals. There is a current controversy over whether the tropospheric concentration of these radicals is (1 - 3) x $10^6/cm^3$, which is the range of measured values, typically at midday, as against 4 x $10^5/cm^3$ on a diurnal average, which gives the range of 5 to 10 in effective tropospheric lifetimes shown in Table C-1 (see, e.g., Singh, 1977).

C.2 ANTHROPOGENIC EMISSION RATES OF CHLOROFLUORO- AND CHLOROCARBONS, 1955-1975

The production rates of halocarbons derived from different sources show some variation, and thus rather detailed explanations are presented of how the data given here are derived from earlier sources.

The emission rates present an even more complicated problem, which has been discussed by McCarthy et al. (1977) for the fluorocarbons. Again, detailed descriptions are included of how the present estimates were derived from "primary" sources.

For fluorocarbons FC-11, FC-12, and FC-22, the latest estimates for the global production and release rates are given in Table C-2. Explicitly, I have used the primary data as compiled by A. Grant (1977), who used as a data base the records of some 20 companies (plus subsidiaries) that reported production and/or release data [see Table 1 of McCarthy et al. (1977)]. The data of Grant (1977) for FC-11 and FC-12 have been analyzed by E. I. duPont de Nemours (1977) to provide worldwide production and release data.

TABLE C-2. GLOBAL PRODUCTION AND RELEASE RATES FOR FC-11, -12, and -22 THROUGH 1976 (in 10^6kg)

Year	FC-11		FC-12		FC-22	
	Production	Release	Production	Release	Production	Release
1931			0.5			
1932			0.1			
1933			0.3	0.1		
1934			0.7	0.2		
1935			1.0	0.2		
1936	0.1		1.7	0.4		
1937	0.1		3.1	0.6		
1938	0.1		2.8	0.9		
1939	0.1	0.1	3.9	1.8		
1940	0.2	0.1	4.5	1.7		
1941	0.3	0.1	6.3	2.3		
1942	0.3	0.1	5.9	2.9		
1943	0.4	0.2	8.2	3.5		
1944	0.4	0.2	16.7	4.7		
1945	0.4	0.3	20.1	6.1	0.1	
1946	0.7	0.6	16.6	11.9		
1947	1.3	1.2	20.1	19.0	0.1	
1948	3.0	2.3	24.8	22.2	0.2	
1949	4.5	3.7	26.1	24.2	0.3	0.1
1950	6.6	5.4	34.9	27.4	0.8	0.1
1951	9.1	7.5	37.0	30.8	1.0	0.2
1952	13.7	10.9	38.5	32.6	1.6	0.3
1953	17.6	14.9	48.2	37.0	2.2	0.4
1954	21.4	18.7	51.3	42.2	2.9	0.6
1955	27.0	23.2	60.3	47.5	3.5	0.8
1956	33.5	29.1	71.9	55.4	6.1	1.2
1957	35.3	32.8	77.9	63.1	6.4	1.1
1958	31.3	31.2	77.8	66.4	7.7	1.4
1959	37.9	32.3	92.5	73.9	11.4	2.7
1960	52.5	42.2	105.0	88.1	12.3	3.3
1961	63.9	54.1	114.7	98.6	12.3	3.6
1962	82.1	67.6	135.0	113.1	15.6	4.7
1963	98.0	82.6	154.0	132.5	17.8	5.7
1964	116.6	97.9	178.4	153.8	22.6	6.9
1965	129.1	111.7	199.2	173.6	25.4	8.2
1966	148.1	125.1	226.1	192.9	31.9	9.9
1967	167.8	141.9	253.5	217.6	37.8	12.5
1968	192.1	161.6	279.3	248.9	46.1	16.5
1969	227.3	187.0	310.0	271.1	56.6	20.6
1970	249.2	212.3	334.8	296.1	59.3	23.5
1971	275.5	233.2	356.3	317.7	65.2	26.5
1972	315.8	260.3	391.1	343.5	70.8	31.3
1973	359.5	295.6	434.7	378.0	77.4	36.1
1974	379.7	324.1	455.0	408.4	88.7	42.3
1975	326.5	314.9	396.1	396.3	74.4	47.6
1976	355.2	308.2	427.9	380.1	94.1	60.2

Note: For FC-11 and -12 the data from Table 5 of DuPont (1977). For FC-22, the production figures are from Grant (1977) corrected for global production as indicated in the text (Section 2). The FC-22 release figures are obtained from the production figures by multiplying by the release/production ratio from Table 7 of McCarthy et al. (1977) on a year-by-year basis; but for 1976 the 1975 ratio, 47.1/73.6 = 0.640, was used.

For FC-22, the production data are from Grant (1977) for the 20 primary companies, corrected by a factor

$$1 + \frac{11.5 + 9.9}{1858.9 + 11.5 + 9.9}$$

on an *annual* basis. The terms here are the following:

1858.9 = *cumulative* production of FC-22 by the 20 reporting companies from the start of production through 1976

11.5 = *cumulative* production of FC-22 estimated for Eastern Bloc countries

9.9 = *cumulative* production of FC-22 in India and Argentina

[These numbers come from Grant (1977), Schedules 4, 11, and 12.]

The release data for FC-22 are obtained from the production data obtained in this way, by multiplying them by the ratio of release/production on an annual basis from McCarthy et al. (1977), Table 7; except that for 1976 the correction factor used is from McCarthy et al. (1977) for 1975, which is 47.1/73.6 = 0.640.

The overall release data for FC-11, FC-12, and FC-22 are shown in Fig. C-1 as functions of time.

For the Soviet Bloc, the estimates of Schedule 12 of Grant (1977) have been used here. Presumably, these estimates should be updated by the new data of Borisenkov and Kazakov (1977) given in Table C-3, which indicate that U.S.S.R. production represents 2.5 percent of the world total in aggregate, as compared with 4.5 percent for the whole Eastern Bloc (including China), as the earlier estimate of Grant (1977) indicated. However, these quantities lie within the error bounds of the current estimates.

For purposes of comparison, the estimate of Schedule 12 of Grant (1977) for total Soviet Bloc production from 1950 to 1976 is FC-11, 172 x 10^6 kg; FC-12, 226 x 10^6 kg. Note that the

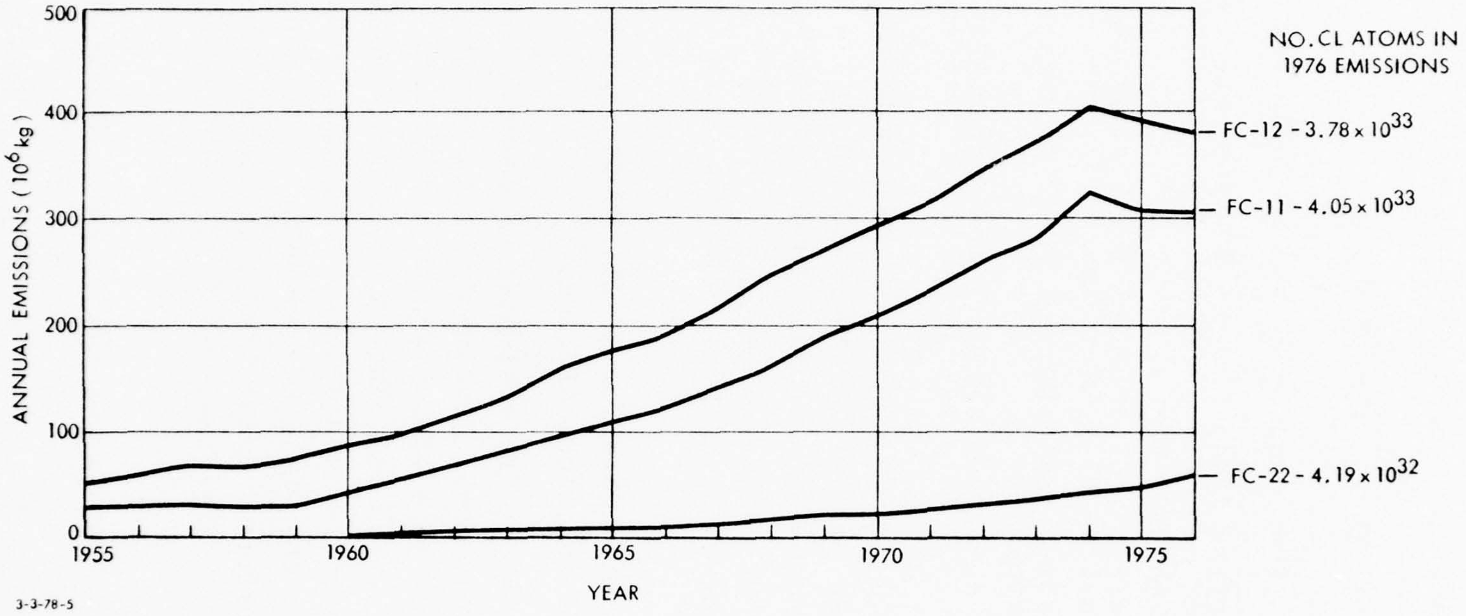

FIGURE C-1. Global Emissions of Fluorocarbons -11, -12, and -22 listed production figures for the U.S.S.R. are lower than the estimates for the Eastern Bloc, especially for FC-11.*

TABLE C-3. FLUOROCARBON PRODUCTION IN THE U.S.S.R. 1968-75 (BORISENKOV AND KAZAKOV, 1977) in 10^6 kg/yr

Compound	1968	1969	1970	1971	1972	1973	1974	1975
FC-11	1.4	2.2	2.5	2.9	3.6	4.0	6.1	7.4
FC-12	9.6	12.0	13.3	15.9	18.2	19.8	25.2	31.2
Total	11.0	14.2	15.8	18.8	21.8	23.8	31.3	38.6

Total for 1968-1975: FC-11 -- 30.1
FC-12 -- 145.1 Grand total -- 175.2

U.S.S.R. share in world production for 1968-75 is 1.3% for FC-11, 4.9% for FC-12.

In 1974-75 about 45% of the total U.S.S.R. production of FC-11 and FC-12 was consumed in the manufacture of consumer chemicals, as against 50% in the U.S.A. and 80% in Great Britain.

For carbon tetrachloride, different estimates for production and release rates are shown in Table C-4. The values of Singh et al. (1976) come from Fig. C-2 which shows that most U.S. (and in fact global) emissions of $C\,Cl_4$ occurred in the 1940s; in fact, the integrated burden of atmospheric injections of carbon tetrachloride from the start of production to 1955 is 1.33×10^9 kg, or 2.07×10^{34} Cl atoms, which corresponds to 16 years of injection at the 1973 injection rate of 81×10^6 kg. Thus, if the atmospheric lifetime of carbon tetrachloride is

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*Dr. F. A. Bower (duPont) comments that (1) the data quoted by Borisenkov and Kazakov apply to the U.S S.R. only, while the Grant estimates apply to the whole Eastern Bloc, including the U.S.S.R., East Germany, Poland, Czechoslovakia, Rumania, Bulgaria, and the People's Republic of China, (2) these data will presumably give rise to slight changes in future estimates of A. Grant and Co., and that, (3) the ratio of FC-11 to FC-12 as estimated by Grant does seem irregular when compared with Borisenkov and Kazakov. Item (3) needs clarification, even though its effect on total worldwide emissions is not likely to be significant.

TABLE C-4. GLOBAL PRODUCTION AND RELEASE RATES OF CARBON TETRACHLORIDE THROUGH 1976 (in 10^6kg/yr)

Year	Production	Release			
(Source:	Galbally (1976)	Galbally (1976)	Singh et al.* (1976)	Parry (1977) Table 2	Little (1975) (Annex A; USITC after 1974)
1914	5	5	-	-	-
1934	30	27	31	36	-
1939	51	46	54	61	-
1941	69	62	63	80	-
1943	99	89	75	117	-
1945	108	97	76	105	-
1946	82	74	75	78	-
1947	113	102	73	109	-
1950	109	88	62	83	-
1955	145	60	52	83	11
1956	156	60	-	81	12
1957	170	59	-	80	13
1958	171	54	-	69	13
1959	206	58	-	77	15
1960	216	55	50	62	15
1961	229	50	-	47	15
1962	297	53	-	61	19
1963	-	-	-	66	21
1964	-	-	-	62	21
1965	408	62	62	45	24
1966	-	-	-	72	26
1967	-	-	-	89	28
1968	-	-	-	93	30
1969	-	-	-	114	35
1970	-	-	78	123	40
1971	-	-	-	96	40
1972	904	78	-	79	40
1973	998 (950, Little, 1975)	90	-	53	42
1974	- (1014, Little, 1975)	-	94	-	40
1975	- (907, USITC & App. A)	-	-	-	36
1976	- (857, USITC & App. A)	-	-	-	34

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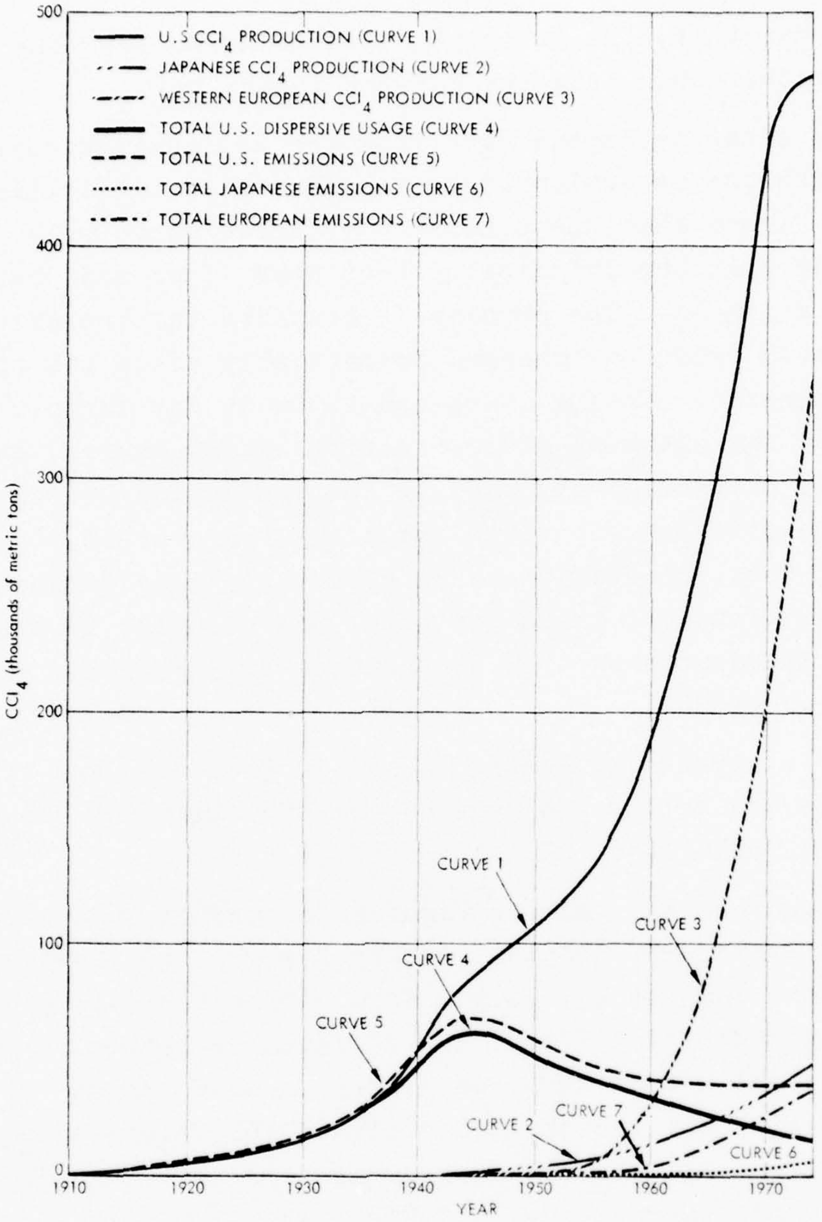
*Release rates from U.S., W. Europe, and Japan have been read from Fig. 1 of Singh et al. (1976), added and multiplied by 1.1 to account for global production (see Fig. 2 of Singh et al., 1976). The figures may be interpolated.



Source: Singh et al., 1976. Copyright 1976 by the American Association for the Advancement of Science.

FIGURE C-2. Production and Emission Trends for CCl_4

Note: Singh recommends using 1.1 times (U.S. + European + Japanese emissions) for Global Emissions.

longer than this, the principal effects arise from the existing burden rather than from the current injections.

The other estimates come from the sources indicated in Table C-4. With the exception of the estimates of Little (1975), which are much lower than the others, they agree quite well. All workers agree that the principal effect comes from past rather than current releases. The problem is that the pattern of use of carbon tetrachloride has changed dramatically since its toxicity was recognized. In the 1940s and 1950s it was largely used dispersively (as cleaning fluid, in fire extinguishers, etc.), but now it is overwhelmingly used in the production of fluorocarbons. Thus, the difference between assuming 3 percent or 5 percent release of total production makes a very large difference in the estimate. Further, there are also uncertainties in production, especially outside the U.S.A. [perhaps ± 20 percent; see also Altshuller (1976)].

The suggested estimate, listed in Table C-5 and in Fig. C-3, is simply the arithmetic mean of all the different values recorded in Table C-4.

Production and release figures for methyl chloroform are shown in Table C-6, listing release figures from Dow Chemical Co. (Neely and Plonka, 1978), from Little (1975), and from McConnell and Schiff (1978). The differences between the various estimates are not as large as in the case of carbon tetrachloride. Again, the recommended estimate for releases is the arithmetic mean of all the values recorded for that year in Table C-6. This is shown in Table C-6 and Fig. C-3.

For the other chlorocarbons listed in Table C-2, the emission rates are given in Table C-5, using the data of A. D. Little (1975) and the procedure of Annex A; in Fig. C-4 the principal anthropogenic global emissions in this category are shown as a function of time.

TABLE C-5. GLOBAL ATMOSPHERIC RELEASE RATES OF CHLOROCARBONS, 1955-76 (in 10^6kg/yr)

Year	Carbon Tetrachloride	Methyl Chloroform	Ethylene Dichloride	Methylene Chloride	Perchlor-ethylene	Trichlor-ethylene	Vinyl Chloride	Methyl Chloride	Chloroform	Ethyl Chloride
1955	52	8	31	49	154	453	35	.5	2	-
1956	51	12	37	63	160	496	39	.6	3	14
1957	48	20	49	63	170	485	41	.7	3	13
1958	47	21	47	59	161	423	45	.6	2	12
1959	50	30	70	75	175	516	64	1.0	4	12
1960	46	36	77	75	180	506	68	1.2	4	12
1961	41	38	83	77	194	443	69	1.5	4	11
1962	47	56	108	96	276	511	86	1.6	5	12
1963	48	51	109	99	280	528	94	1.7	5	13
1964	48	57	134	119	316	531	106	1.9	6	15
1965	48	73	149	141	370	624	132	2.7	8	15
1966	54	133	220	178	400	689	164	3.4	9	15
1967	62	131	241	175	460	703	159	4.0	9	14
1968	65	161	292	202	549	744	195	4.4	9	13
1969	75	170	367	244	548	856	245	5.9	11	15
1970	80	186	454	268	610	877	266	6.1	12	15
1971	73	214	460	267	608	738	285	6.3	11	14
1972	71	246	477	314	633	613	334	6.6	12	13
1973	61	387	565	346	609	648	352	7.9	12.4	14.6
1974	67	356	470	394	630	622	375	6.7	15	15
1975	54	319	485	331	586	420	276	5.3	13	13
1976	51	401	489	356	577	453	373	5.5	14	15

Note: Data for carbon tetrachloride come from Table C-4, and for methyl chloroform from Table C-6. In each case, we list here the arithmetic mean of all the release figures quoted in the approximate table. All the other figures come from Little (1975) using the analysis of Annex A to this Appendix.

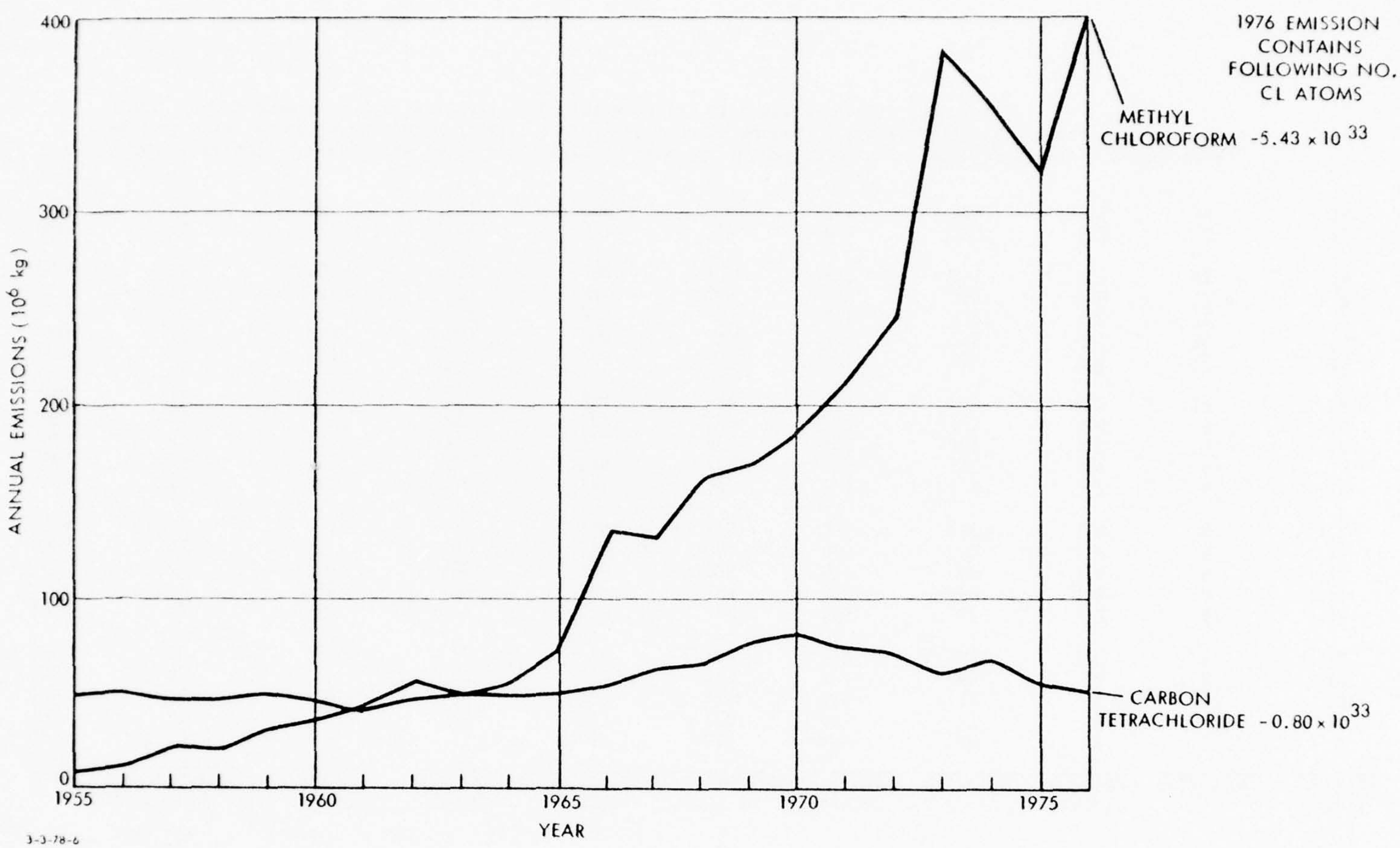


FIGURE C-3. Global Emissions of Carbon Tetrachloride and Methyl Chloroform, 1955-1976

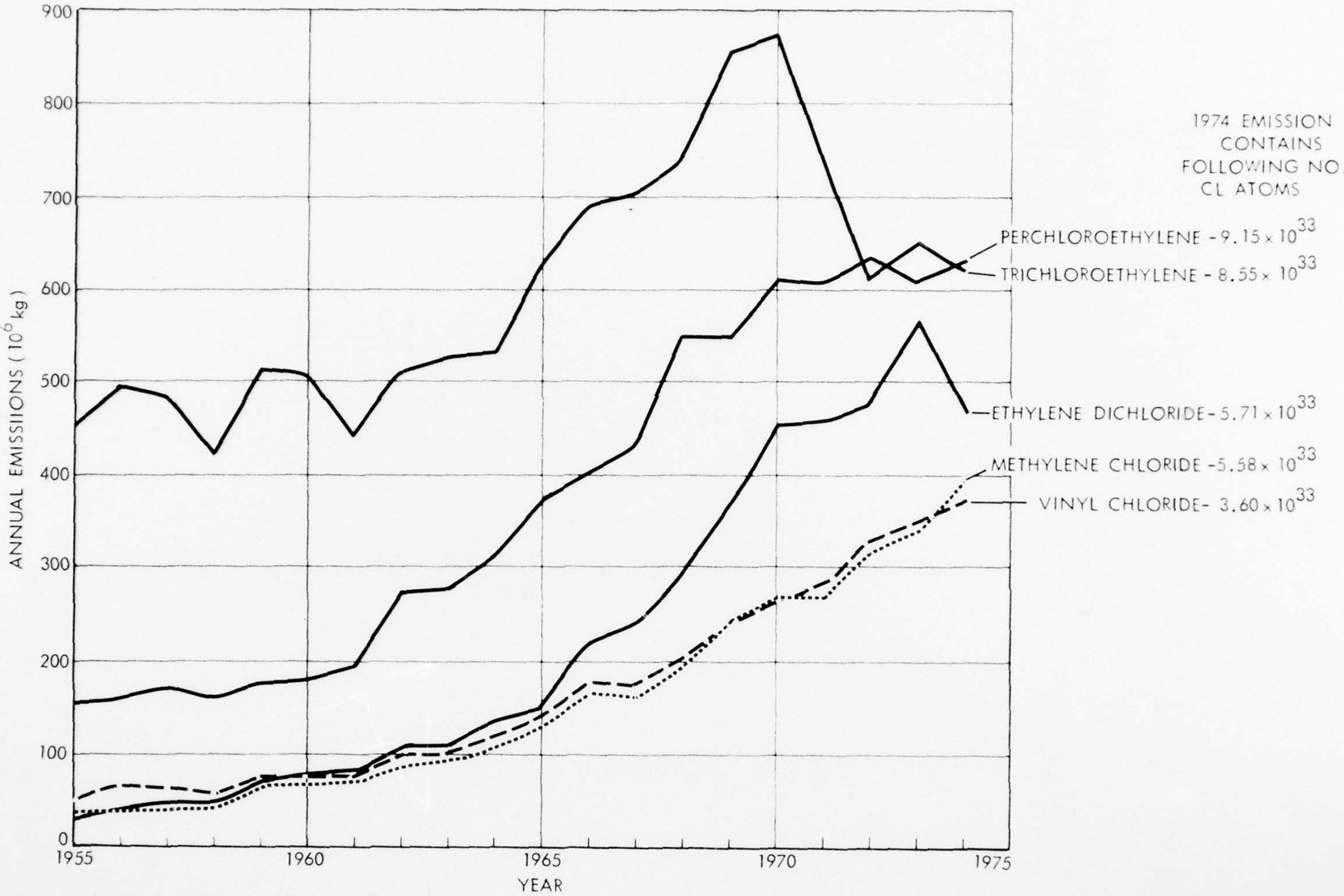
TABLE C-6. GLOBAL PRODUCTION AND RELEASE RATES OF METHYL CHLOROFORM (in 10^6 kg/yr)

Year	Production	Dow Chemical[a]	A.D. Little, Inc.[b]	McConnell and Schiff[c]
1951	0.1	0.1	-	
1952	0.2	0.2	-	
1953	1.0	1.0	-	
1954	3	3	-	
1955	8	8	-	
1956	14	12	-	
1957	21	20	-	
1958	22	21	-	
1959	32	30	-	
1960	38	36	-	
1961	40	38	-	-
1962	59	56	-	-
1963	58	51	-	-
1964	64	57	-	-
1965	83	73	-	-
1966	116	109	144	147
1967	146	131	-	-
1968	158	145	177	-
1969	168	148	192	-
1970	181	155	217	-
1971	191	167	222	253
1972	267	230	261	-
1973	350	340	324	396;407;466
1974	390	363	349	-
1975	374	365	272	-
1976	438	416	373	413
Cumulative:	3222	2975		

a. Neely and Plonka (1978), Table 1, estimated by the Corporate Product Department of Dow Chemical Company

b. Little (1975), using the procedure of Annex A of this Appendix

c. McConnell and Schiff (1978) quote various estimated production figures for some years; I convert to release by multiplying by the ratio release/production for that year from Neely and Plonka (1977)



Source: Data of A.D. Little (1975); analysis of Annex A.

FIGURE C-4. Global Emissions of Various Chlorocarbons

C.3 LATITUDINAL DISTRIBUTION OF EMISSIONS

For a two-dimensional computer code, it is necessary to estimate the latitude distribution of anthropogenic halocarbon emissions. The A. D. Little (1975) and A. Grant (1977) reports provide the following data, which are not strictly comparable; these are used here to provide an initial best estimate.

1. Source: A. D. Little, p. II-9

   World fluorocarbon production, 1973

Region	Percent of Global Production
U.S.A.	44
Europe	41
Japan	8
Other	7

2. Source: Bureau of Domestic Commerce Estimate (from U.S. International Trade Commission)

   World fluorocarbon production, 1973

Region	Percent of Global Production
U.S.A.	48
Europe	35
Japan	9
Communist Bloc	4
Other	4

3. Source: A. Grant, Schedule 7

   Total production of fluorocarbons, ratio southern/northern hemisphere

FC-11	0.035	0.039
FC-12	0.042	
FC-22	0.035	

4. Source: A. Grant, Schedules 1, 11, 12, total production, 1931 to 1976, fraction of global production

Substance	"India and Argentina"		"Eastern Bloc"	
FC-11	0.00093	0.0015	0.048	0.045
FC-12	0.0018		0.043	
FC-22	0.0054		0.0062	

5. Source: Table C-7 [from A. Grant (1977), Schedule 1 for listing of primary countries, Schedules 11 and 12 for others] lists the countries where fluorocarbons are produced, together with the effective range of latitudes assigned to each country.

TABLE C-7. LISTING OF COUNTRIES PRODUCING FLUOROCARBONS, INCLUDING LATITUDE RANGE TO BE CONSIDERED

COUNTRY	NO. OF COUNTRIES OR SUBSIDIARIES IN TABULATION*	LATITUDE RANGE CONSIDERED
Argentina	1	35-41 S
Australia	2	28-39 S
Brazil	2	5-33 S
Canada	1	42-48 N
France	2	42-50 N
Great Britain	2	50-55 N
India	-	8-32 N
Italy	1	39-45 N
Japan	4	33-45 N
Mexico	1	15-20 N
Netherlands	2	51-53 N
Spain	2	35-43 N
U.S.A.	6	30-48 N
U.S.S.R./COMECON	-	40-60 N
West Germany	2	47-54 N

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*Grant (1977), Schedule 1

From the data quoted in items 1 through 4 above, and including Table C-7, it is clear that the primary production of fluorocarbons is in the latitude range of 30 to 55° N, which includes the U.S.A., Europe, Japan, and most of U.S.S.R./COMECON. Bearing in mind that the category "other, 7 percent" in item 1 includes COMECON at about 4 percent--see item 3, this would leave 2.5 percent unaccounted for; and this may be compared with item 3, 4 percent in the Southern Hemisphere.

The difference between these items should not be considered significant. Taking into account the difference between production, sale/consumption, and emission figures, the difference between integrated production and production rate (per annum), and the difference between the different chemicals listed in Table C-1,[*] I recommend the following two options for the latitude distribution of emissions of all halocarbons considered here.

Option I		Option II	
50 to 60° N	5%	30 to 55° N	96%
30 to 50° N	90%	30 to 40° S	4%
30° N to 30° S	2%		
30 to 40° S	3%		

where the emission should be distributed uniformly within each relevant latitude band. Option I is recommended as primary, with Option II as an alternative.

C.4 BROMOCARBONS

It has been suggested by Wofsy et al. (1975) that bromine injections into the stratosphere can also reduce the concentration of stratospheric ozone. For the present catalog, this is unlikely to be important because the major source of stratospheric bromine is presumably natural--cf. Wofsy et al. (1975)--and the relevant anthropogenic production was relatively small during the 1955 to 1975 time period and has not changed very much.

The largest single use of bromine--representing perhaps 60 percent of global production--is ethylene dibromide (1, 2 dibromoethane) used as a scavenger in leaded gasoline. The bromine (or equivalently chlorine) is added so that the lead (from

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[*] For chlorocarbons, there are estimates of the breakdown of 1973 emissions into the categories "U.S.," "Europe" and "Other"--see A. D. Little (1975), p. III-29, but these do not differ drastically from the present estimates for fluorocarbons.

tetraethyl lead used as anti-knock agent) will be scavenged as $PbBr_2$, etc., rather than deposited inside the engine. Like most other bromides, this lead bromide will be exhausted as fine particles which are mostly washed out by precipitation or else fall to the ground by sedimentation, rather than being transported out of the "planetary boundary layer"* to enter the "free troposphere."

Approximately 2 percent of man-made ethylene dibromide, as well as most man-made methyl bromide, are used as soil and grain fumigants. Some fraction of these materials enters the atmosphere unchanged and so supplements the natural sources of bromine from seaweed, etc., in the free atmosphere. In the atmosphere, ethylene dibromide and methyl bromide will react rather slowly with OH, presumably with lifetimes comparable to those of corresponding chlorocarbons (see Table C-1, where lifetimes of order 0.2 to 0.4 years are listed). Thus, the relative contribution of these bromocarbons to stratospheric bromine will be comparable to the relative contribution to stratospheric chlorine of materials like ethylene dichloride and methyl chloride, rather than that of materials like FC-11 and FC-12.

Table C-8 lists industrial production figures for methyl bromide and ethylene dibromide for the time period 1955 to 1976, and Table C-9 lists my best estimate of sources of bromine that enter the free atmosphere. It is clear that the total man-made source of bromine is not only relatively small, but also its variation over the 1955 to 1975 time period is relatively small within any reasonable error or variation in the natural source. At present, while a constant ground-level source of $(950 \pm 250) \times 10^6$ kg

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*The lowest 1-km portion of the earth's atmosphere in which large day-night temperature variations occur, and in particular, rapid transfer of water occurs between the atmosphere and land/sea. Most air pollution processes take place in the boundary layer, and only a small fraction of air pollutants ever rise above this region to enter the "free troposphere" which lies above and outside the boundary layer.

Br./yr is appropriate in a model of atmospheric bromine, including its potential effects on ozone, no significant variation in this source appears to have occurred during the interval of interest here, 1955 to 1975.

TABLE C-8. WORLD INDUSTRIAL PRODUCTION OF METHYL BROMIDE AND ETHYLENE DIBROMIDE

	Annual Production (in 10^6 kg)	
Year	Methyl Bromide	Ethylene Dibromide
1955	5	-
1960	5	120*
1965	8	-
1970	13	190
1972	16	205
1974	13	190
1976	16	160**

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*Early 1960s

**The decrease is genuine, associated with increasing U.S. use of unleaded gasoline.

Note: E. Bauer's estimates, based on data from the Bureau of Mines; the U.S. International Trade Commission; and Kirk-Othmer (1965), Vol. 3, pp. 763-772. Most primary data listed are for U.S. production, and have been scaled on the assumption that U.S. production represented 75 percent of worldwide production in 1960, 70 percent in 1973. Errors of at least 10 to 20 percent are probable, i.e., not all figures listed are significant. "Ethylene dibromide" is 1, 2, dibromoethane.

TABLE C-9. POTENTIAL ATMOSPHERIC SOURCES OF BROMINE IN 1975 (in 10^6 kg Br./yr)

Source	Wofsy et al. (1975)	Present Estimate
Natural Source	900	900[a]
Methyl Bromide	100	12 to 14[b]
Ethylene Dibromide	100[c]	4 to 5[b]

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[a] From Wofsy et al. (1975)

[b] Dr. Wm. Hunt, private communication

[c] Wofsy et al. (1975) assume that 50 percent of bromine from ethylene dibromide can enter the lowest atmosphere in inorganic form. However, Dr. Wofsy in a private communication stated that most of it will be washed out, and a negligible fraction ($\lesssim$ 1%) will enter the stratosphere.

ANNEX A TO APPENDIX C

PRESENT ANALYSIS OF DATA FROM LITTLE (1975) TO OBTAIN ANNUAL RELEASE RATES*

Little (1975) quoted estimated world chlorocarbon emissions for 1973 (Table CA-1). They also list U.S. production from 1960-74--see pp. II-13, -14, *op. cit.* In general, U.S. production rates are about half worldwide production rates--see Table CA-1; Little, for 1973, estimates annual worldwide ratios of emission/production to be equal to annual U.S. emission/production ratios--see p. III-27, *op. cit.*

Here I supplement U.S. production figures for 1955 to 1960 from Kirk-Othmer (1965), Vol. 5, pp. 107-201, and for 1975 to 1976 from U.S. International Trade Commission figures (Reports 804 and 833, respectively).

I also assume, (1) that the ratio of annual world production rate/U.S. production rate remains constant from 1955 to 1974 (at the ratios given in Table CA-1 for each chemical species),** and (2) that the ratio of annual world emission/annual world production remains constant from 1955 to 1974 at the 1973 ratios estimated by Little (1975).

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*This is not necessarily a satisfactory analysis, but it is objective in terms of the limited data base.

**Galbally (1976) estimates the U.S./Global production ratio for CCl_4 as 90 percent in 1955 and 50 percent in 1972; the Little (1975) figure for 1973 is 50 percent--see Table CA-1.

TABLE CA-1. ESTIMATED WORLD CHLOROCARBON EMISSIONS, 1973

Chlorocarbon	Regional Percent of Total[a]			World Emissions (10^6 kg)
	United States	Europe	Other	
Carbon tetrachloride	50	40	10	41.7
Chloroform	50	40	10	12.4
Ethyl chloride	55	30	15	14.6
Ethylene dichloride	35	40	25	565.2
Methyl chloride	60	35	5	7.9
Methyl chloroform	60	30	10	324.2
Methylene chloride	55	30	15	346.4
Perchloroethylene	45	45	10	609.0
Trichloroethylene	30	55	15	648.3
Vinyl chloride	25	40	35	351.6

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[a] Rounded to nearest 5 percent.

Source: A. D. Little (1975), p. III-29

For carbon tetrachloride and methyl chloroform there exist other estimates--see Section C.2, especially Tables C-4 and C-6. In Figs. C-3 and C-4 I compare different estimates for emission rates of these two species, and conclude that the various estimates agree quite well for methyl chloroform, but not for carbon tetrachloride. The disagreement for carbon tetrachloride is unlikely to be very significant, since it is the burden of pre-1955 injections rather than the annual injections thereafter that are probably most important for the present atmospheric loading of this material, but the deviations between these different estimates does raise a warning flag about possible errors in the present estimates of atmospheric emission rates.

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APPENDIX D

STRATOSPHERIC INJECTIONS DUE TO VOLCANIC ERUPTIONS, 1955 TO 1976

APPENDIX D

STRATOSPHERIC INJECTIONS DUE TO VOLCANIC ERUPTIONS, 1955 TO 1976

D.1 DATA AND MODEL

A listing of major volcanic eruptions from 1955 to 1976 is given in Table D-1. The list is not complete--Dr. S. Self (Dartmouth College) is preparing a much more comprehensive listing--see, e.g., Barbera and Self (1978)--but it probably includes all eruptions that sent major amounts of material into the stratosphere. Table D-2 lists the suggested stratospheric injection due to the major eruptions of Mt. Agung in 1963. We show the estimates of Cadle et al. (1976, 1977) based, ultimately, on some unpublished estimates of Lamb (see Mitchell, 1970), adjusted to agree with the mass of fine dust estimated by Mossop (1964), and also those of Self (private communication) which are based solely on volcanic parameters, in particular on the report of Zen and Hadikusumo (1964). In view of the very limited data base and the different methods used, the relatively good agreement of these two data sets must be considered rather satisfactory.

Regarding the height of injection, we may assume that for a given eruption the material is distributed uniformly between the tropopause and an observed maximum height. Values for these heights are listed in Table D-3 for the largest volcanic eruptions; once again, we may note the very limited data base. Reference should be made to Fig. 4 of Lamb (1970), to Friend (1972), and especially to Wilson et al. (1978).

TABLE D-1. MAJOR EXPLOSIVE VOLCANIC ERUPTIONS, 1955-76

Date	Volcano	Position	Severity [a]	Stratospheric Input? [b]
Jun 1955	Puyehue (and Ranco), Chile	$40-41^{\circ}$ S, 72° W	2 (0.3 km^3 tephra)	No
30 Mar 1956	Bezymianny, Kamchatka	56° N, 160° E	1 (1 km^3 tephra)	Yes
21-24 May 1960	Puyehue (etc), Chile	$39-45^{\circ}$ S, $72-73^{\circ}$ W	3	Yes
1962	Tokati	43° N, 143° E		Probable, but small
17 Mar and 16 May 1963	Agung, Bali	8.5° S, 115.5° E	1-2	Yes
12 Nov 1964	Sheveluch, Kamchatka	56.4° N, 161° E	1 (1 km^3 tephra)	??
28 Sep 1965	Taal, Luzon	14° N, 121° E	3	Yes
1966	Redoubt, Alaska	60.5° N, 153° W		Probable
1966	Kelud	8° S, 112° E		Probable, but small
12 Aug 1966	Awu, Celebes	3.5° N, 125.5° E	2 ($\sim$ 3 km^3 dust)	Yes
4-7 Dec 1967	Deception Island	63° S, 60.5° W	3	No
1967-68	Redoubt and Trident			No
11-12 Jul 1968	Fernandina Is., Galapagos	0.5° S, 72° W	2 ($\gtrsim$ 1 km^3 ?)	Yes
5-6 May 1970	Hekla, Iceland	64° N, 19.5° W		Yes
1970	Deception Island			No
1971	Mt. Hudson, Chile	46° S, 73° W		Probable
1972	Alaid, Kurile Islands	51° N, 155° E		Probable
23 Jan-16 Feb 1973	Helgafell, Iceland	63.5° N, 20.3° W		No
1974	ApiSian	8° S, 119° E		Probable
10-23 Oct 1974	Fuego, Guatemala	14.5° N, 91° W	2+	Yes
1975	Plosky Tolbuchik, Kamchatka	56° N, 160° E		Probable but small
23 Jan 1976	Augustine, Alaska	59.4° N, 153.4° W	3	Yes, but small

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[a] A qualitative measure of the overall magnitude of the eruption (not necessarily its stratospheric injection!), see Sapper (1927) and Lamb (1970). 1 is biggest, 2 is an order of magnitude smaller, 3 is an order of magnitude smaller yet, in terms of either mass or volume of material moved. Note that no successful scaling has been achieved in that the volume of material injected, the energy released, and the amount and chemical composition of gases emitted are not simply related. It is likely that only studies of individual eruptions will have success in predicting their stratospheric injection, in terms of the total mass and composition.

[b] From S. Self, private communication, May 1978.

TABLE D-2 STRATOSPHERIC SOURCE FUNCTION OF THE AGUNG ERUPTION CLOUD

	Mass, kg		
	Estimate of Cadle et al. (1977)	Estimate of S. Self (private communication, May 1978)[a]	Suggested Value[b]
Total erupted material[c]	5×10^{12}	1.4×10^{12}	2.6×10^{12}
Fine ash[d]	1×10^{10}	9×10^{9}	9.5×10^{9}
Total gas	-	2.9×10^{10}	-
Water vapor[e]	1.2×10^{11}	2.2×10^{10}	5.1×10^{10}
Total S as H_2SO_4[f]	1.8×10^{10}	2.1×10^{9}	6.1×10^{9}
HCl[g]	1.2×10^{9}	7.3×10^{8}	9.4×10^{8}

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[a] Based on 17 March and 16 May eruptions.

[b] Geometric mean of the Cadle et al. and Self estimates.

[c] Most of this material does not enter the stratosphere.

[d] Cadle et al(1977) do not specify the particle size; Self refers to particles < 2 μm diameter.

[e] The mean stratospheric water vapor loading is ~ 2×10^{12} kg, see Appendix A.

[f] 5.1×10^{9} kg H_2SO_4 contain 3.3×10^{34} S atoms so that presumably $(3\text{-}6) \times 10^{34}$ OH radicals are consumed in the formation of sulfuric acid.

[g] 9.4×10^{8} kg HCl contain 9×10^{33} molecules.

TABLE D-3. A RECOMMENDED LIST OF STRATOSPHERIC INJECTIONS DUE TO MAJOR VOLCANIC ERUPTIONS FROM 1955-1975, SCALED IN TERMS OF THE AGUNG INJECTION OF TABLE D-2[a]

Date of Eruption	Volcano	Latitude	Magnitude of Injection Relative to Agung			Maximum Height of Injection, kg			Local Tropopause Height, km[e]
			b	c	d	b	c	d	
30 Mar 1956	Bezymianny	56° N	(1)	2	1.4	45	47	47	9.5
21-24 May 1960	Puyehue	40° S	-	0.5	0.2	-	18	18	11.5
17 Mar, 5 May 1963	Agung	8.5° S	1.0	1.0	1.0	52	23	23	16.3
12 Nov 1964	Sheveluch	56° N	(1)	-	(0.3)	(25)	-	(25)	9.8
12 Aug 1966	Awu	3.5° N	0.3	-	0.1	(20)	-	(20)	16.5
11-12 Jun 1968	Fernandina	0.5° S	0.3	-	0.1	(20)	22[f]	22	16.3
10-23 Oct 1974	Fuego	14.5° N	0.2	0.5	0.3	20	19	19	16

---

[a] Preliminary estimate. Material injected should be distributed uniformly between the local tropopause height and the maximum height of injection. Numbers in parentheses are especially uncertain.

[b] Estimate extracted by E. Bauer from diverse published and unpublished sources, in particular, Lamb (1970), Friend (1972), and private communication, and Cadle et al. (1976, 1977).

[c] Private communication from S. Self, April 1978 - computed from Wilson et al. (1978).

[d] Revised estimate using b and c.

[e] Source: Crutcher and Davies, 1969.

[f] Observed.

In Table D-3, we also list recommended source functions for the major eruptions between 1955 and 1975. The following comments should be noted:

- Uncertainties in absolute injected amounts by a factor 2 to 5 (up or down) exist, but the ratios quoted in Table D-3 may have a smaller uncertainty.
- The S/Cl ratio differs drastically between different types of eruptions. For Icelandic and Hawaiian eruptions (effusive, not explosive) the ratio is of order 10 to 20:1, while for Central American volcanoes, which are more explosive, the ratio is of order 1:1. [See Anderson (1975), Stoiber and Rose (1973)].
- The average gas composition used by S. Self is 75 percent H_2O, 15 percent CO_2, 5 percent SO_2, 2.5 percent HCl, 2.5 percent others, but evidently large variations from this mean composition occur.
- In particular, for Bezymianny and Sheveluch there is very little data available.

D.2 POSSIBLE INFLUENCES ON STRATOSPHERIC OZONE

The stratospheric injections due to the Agung eruption, as listed in Table D-3, should be compared with the "normal" stratospheric loading of the relevant materials. This is done now for each component in turn. (See also Stolarski and Butler, 1977, Turco et al., 1978.)

D.2.1 Aerosols/Sulfuric Acid

In the lower stratosphere there is normally a region of fine particles, the density and composition of which is quite variable. Typical loadings in nonvolcanically perturbed times (e.g., 1972 to 1973, prior to the eruption of Agung) are of order of one particle of radius $\gtrsim 0.15\ \mu m$ per cm^3, with a vertical extent of 5 km centered about 18 to 20 km, the so-called "Junge layer" [cf. Cadle et al., 1975]. This corresponds to 5×10^9 particles/m^2-column, or a global loading of order 10^8 kg (if each particle has radius 0.15 µm and a density of 2 to 3 gm/cm^3).

Stratospheric aerosols are generally considered to be made up of a mixture of impure sulfuric acid (including some ammonium sulfate) and of silicates, i.e., fine volcanic ash. The relative amount of these materials found by different observers at different times and places varies significantly. Table D-3 lists a current estimate of the stratospheric loading due to the Agung eruption, with comparable amounts of sulfuric acid and silicates, and a total mass injection of order several times 10^{10} kg. This is consistent with the current concept that explosive volcanic eruptions are the major source of the Junge aerosol layer.

Regarding the effect of this injection on the stratosphere, it is generally considered that stratospheric aerosols of volcanic origin affect the climate [cf., e.g. Oliver (1976)], but it is possible that they may also affect the stratospheric photochemistry; thus, Cadle, Crutzen, and Ehhalt (1975) discuss heterogeneous reactions that may take place on the stratospheric aerosols. Also, if the sulfur enters the stratosphere as SO_2 which is there oxidized to sulfuric acid by reaction with OH radicals, locally and for a time of order a month this oxidation of SO_2 may also provide a significant loss mechanism for the OH radicals, and could thus affect the local ozone concentration.

D.2.2 Hydrochloric Acid

The total stratospheric loading of ClX = Cl + ClO + HCl + ClO NO_2 is approximately 1×10^{34} molecules worldwide (6×10^8 kg as HCl)--see Appendix A. Thus we see that the stratospheric injection of HCl due to the present model of Agung is almost as large as the global loading of ClX. This might be expected to show an effect, either by reducing the ozone through the catalytic ClX-O_3 cycle or else by trapping HO_X and NO_X as HOCl and $HONO_2$.

D.2.3 Water

The normal stratospheric loading of water is quoted as (1.6 to 2.2) x 10^{12} kg--see Appendix A--so that the eruption of Agung presumably led to a 5 to 7 percent enhancement of global stratospheric water vapor.

We see that at the injection levels postulated by Cadle et al. (1976, 1977), a major volcanic eruption, such as that of Agung, would be expected to produce significant effects on the stratosphere, although the specific effects are subject to much uncertainty. Angell and Korshover (1976) find an increase in total ozone--as well as a change in the quasibiennial oscillation--occuring shortly after the eruption of Agung. A number of workers have presented annual mean volcanic injections [e.g., Cicerone (1975), Ryan and Mukherjee (1975)], which is appropriate in asking for sources and sinks of ClX, aerosols, etc., but evidently not for the present purpose.

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APPENDIX E

TIME-DEPENDENT PRODUCTION OF NO AND OH IN THE STRATOSPHERE RESULTING FROM COSMIC RAY IONIZATION IN THE 1955-1975 TIME FRAME

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E.1 INTRODUCTION AND SUMMARY

Ruderman and Chamberlain (1975) and Nicolet (1975), enlarging on an earlier calculation of Warneck (1972), pointed out that galactic cosmic rays (GCR) produce ionization in the stratosphere which leads to increased NO production as a result of ion chemistry, with subsequent effects on stratospheric ozone. The GCR intensity is modulated by the solar wind and thus varies with the 11-year sunspot cycle, leading to an 11-year oscillation in NO_x (= $NO + NO_2$) production with its maximum at sunspot minimum. Crutzen et al. (1975)--see also Heath et al. (1977)--pointed out that some large solar flares produce bursts of high-energy protons, the solar cosmic rays; these "Solar Proton Events" (SPE) also produce ionization in the stratosphere/mesosphere that would be expected to affect NO and hence stratospheric ozone. SPEs occur mainly near (but not at) sunspot maximum. Both GCRs and SPEs are modulated by the geomagnetic field and thus their effects are maximized at high geomagnetic latitudes, where charged particles of relatively low energy, momentum, or "rigidity" can penetrate most easily into the earth's atmosphere.

There are also other sources of atmospheric ionization which may exhibit some time-dependence, such as X-rays, EUV (in particular Lyman-alpha, 121.6 nm), auroral electrons, etc., which all lead to ionization at altitudes above 60 to 80 km. At these altitudes, there is very little ozone, and the lifetime of NO_x is so short that all the NO produced as a result of ionization will be destroyed photochemically before it can move down to altitudes where there is a significant amount of ozone (mainly below 35 km).

Two other effects which have been considered are the following:

a. relativistic electron precipitation (REP) events (Thorne, 1977, 1978), which can be shown to be small in the altitude range of interest here, below 45 km--see Figs. E-7 and EB-2.

b. high energy GCRs (above 0.1 to 0.3 GeV) produce chlorine isotopes 36, 38, 39 in the atmosphere through nuclear reactions with atmospheric argon (see Lal and Suess, 1968). While these Chlorine isotopes do undergo chemical reactions (Rowland, 1978) and thus can affect the ozone, the total number of atoms produced is so small ($\lesssim 10^{-10}$ times the number of HO_X or NO_x molecules produced by GCRs) that its effect on ozone will be negligible.

Here we summarize all currently known time-dependent sources of ionization in the stratosphere which, by producing either oxides of nitrogen ($NO_x = NO + NO_2$) or oxides of hydrogen ($HO_x = OH + HO_2$), would be expected to have produced time-varying reductions in stratospheric ozone during the 1955 to 1975 time period.

The conclusions of this discussion are the following:

- One ion pair produces, on the average, 1.3 NO molecules, and 2.0 OH radicals (see Section E.3 and Fig. E-5).
- The largest and principal time-varying effects of (solar and galactic) cosmic ray ionization on ozone occurs in the polar cap regions of high geomagnetic latitude $\Lambda \gtrsim 60°$ to $65°$, which are shown in Fig. E-2. Also see Table E-1 and Fig. E-3 for an effective representation in terms of geographic latitude θ for use in a two-dimensional photochemical/dynamic model of ozone.

- At high latitudes, most of the ozone lies below 25 to 30 km (see Fig. E-1).
- Because of the altitude variation of photochemical lifetimes for NO and OH, and also the characteristic times for vertical diffusion, NO produced below approximately 45 km can affect the bulk of the ozone, but because of its relatively short lifetime, the OH radical is most unlikely to diffuse far enough (say, $\gtrsim$ 1 km) to affect ozone other than locally (see Annex A to this Appendix).
- The ionization profile due to GCRs may be expressed as a function of both time (relative to the year YM of GCR maximum, i.e., solar sunspot minimum) and of latitude (where we distinguish between the polar cap region, defined in terms of the curves C_o of Fig. E-2 (or $\Lambda > 60°$) and the rest of the earth, i.e., curve "$1-C_o$" (or $\Lambda < 60°$) as follows:

IONIZATION PROFILE DUE TO GCRs IN TERMS OF EQUATIONS OF SECTION E.4

High Geomagnetic Latitude, C_o	Low Geomagnetic Latitude, $1-C_o$
$z > 20$ km, Eq (9)	$z > 31$ km, Eq (12)
$15 \text{ km} < z < 20$ km, Eq (10)	
$10 \text{ km} < z < 15$ km, Eq (11)	$18 \text{ km} < z < 31$ km, Eq (13)

- The ionization profile due to SPEs may be taken as uniform with latitude over the polar caps defined in terms of the inner curves C_i of Fig. E-2, or equivalently, for geomagnetic latitudes $\Lambda \gtrsim 65°$. The altitude profile of ionization due to SPEs is shown in Section E.5, Fig. E-7.
- The overall magnitude of the effect of GCRs and SPEs may be represented as follows:

-- At solar sunspot minimum, the total number of ion pairs produced by GCRs in the stratosphere over both polar caps ($\Lambda \gtrsim 60°$), as well as the total number of ion pairs produced in the stratosphere over lower latitudes ($\Lambda \lesssim 60°$) each exceed the appropriate number of ion pairs produced at sunspot maximum by approximately 6×10^{32} ion pairs per year (see Section E.4).

-- A large SPE produces $\sim 20 \times 10^{32}$ ion pairs (see Table E-3).

-- During the 1955 to 1975 time frame, there have been just three major series of SPEs that should be considered from the standpoint of ozone depletion, namely those of May-July 1959, November 1960, and August 1972 (see Table E-3 and Fig. E-7).

-- The Soviet atmospheric nuclear test series of Fall 1961 (the largest ever, corresponding to 180 Mt total yield) injected $(70 \text{ to } 270) \times 10^{32}$ NO molecules into the stratosphere.

-- The global stratospheric loading of NO_y (= NO + NO_2 + HNO_3) is of order $(4 \text{ to } 15) \times 10^{34}$ molecules.

-- The global stratospheric loading of HO_x radicals (= OH + HO_2) is of order $(7 \text{ to } 16) \times 10^{32}$ molecules, but with very large uncertainties.*

E.2 PENETRATION OF IONIZING RADIATION INTO THE EARTH'S ATMOSPHERE

We have to consider X-rays and gamma-rays, electrons and heavy particles, principally protons. All electromagnetic ionizing radiation of wavelengths longer than 0.3 nm is absorbed above 80 km, and the overall intensity of X-rays of wavelength

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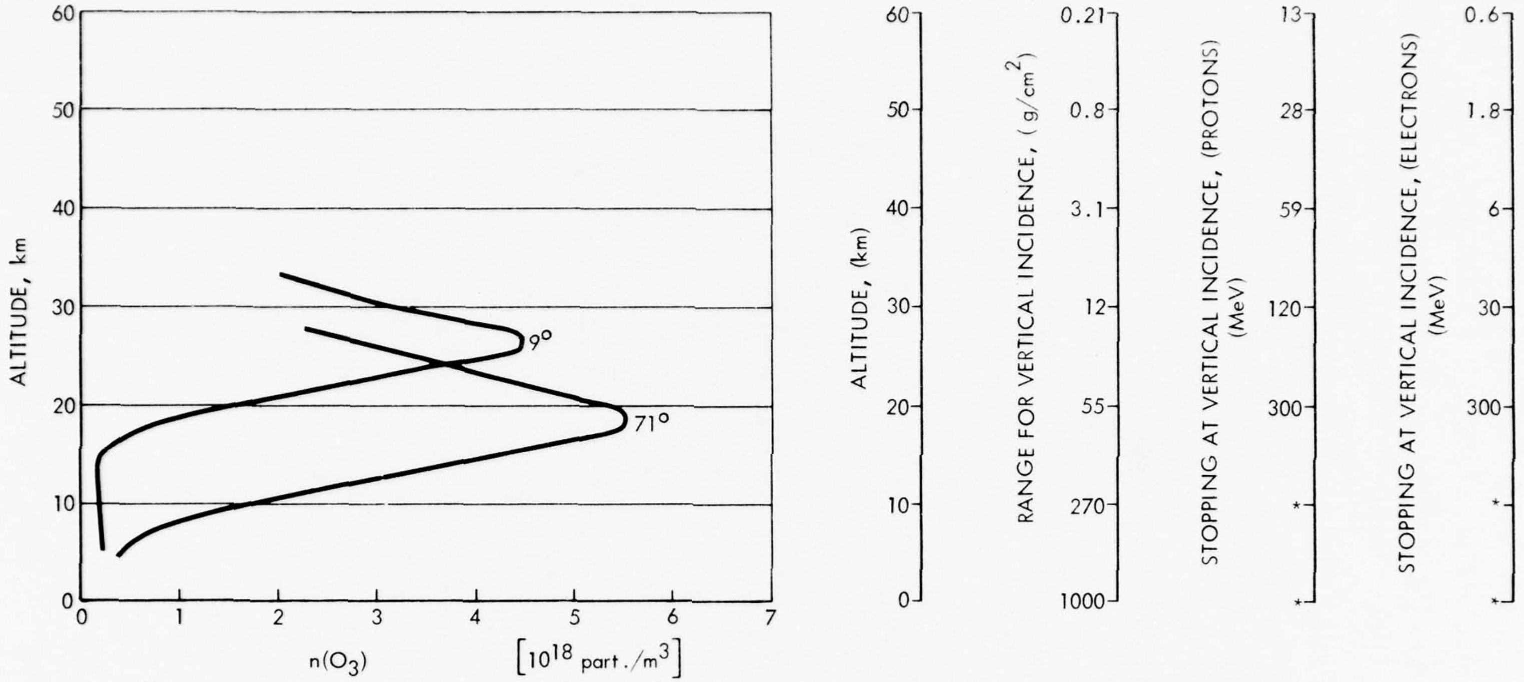
*See Appendix A for a discussion of this point.

less than 0.3 nm is so low that this again may be ignored in the present context. Regarding particulate radiation, Fig. E-1 shows the effective penetration depth of electrons and protons for vertical incidence. The following points should be noted:

- For oblique incidence, the actual penetration depth is slightly less than the value shown. Thus, the penetration depth is reduced by about 5 km for angles of incidence greater than 60°, and by 10 km for angles of incidence greater than 80° (see Reid, 1974).
- For charged particles, the energy loss due to ionization (average, 35 eV/ion pair in air) maximizes during the last portion (say, 1 to 2 scale heights) of the path [cf. Fermi (1950, p. 33)].
- For protons at energies in excess of 100 MeV, nuclear collisions are a significant source of energy loss through the production of "stars" and "showers." The physics here is significantly different [cf. Fermi (1950, p. 215)].

The ionization in the atmosphere leads to NO and OH species, which in turn affect the ozone. For a discussion of NO and OH production, see Section E.3. The next question is whether the NO and OH molecules produced by ionization at a given, relatively high altitude z_1 can get down to where the ozone is. See Fig. E-1, which shows that at low and mid-latitudes this is mainly below 40 km, while at high latitudes it is mainly below 30 km. High (geomagnetic) latitudes are particularly significant because the earth's magnetic field deflects charged particles away from lower geomagnetic latitudes, but not from the polar cap regions in which the flux of charged particles is approximately equal to the flux in free space.

Figure E-2 shows the polar cap regions that are particularly affected by cosmic rays, both solar and galactic. The inner closed curve C_i corresponds roughly to geomagnetic latitude $\Lambda >$



*DENOTES THAT NUCLEAR RATHER THAN IONIZING COLLISIONS PREDOMINATE.

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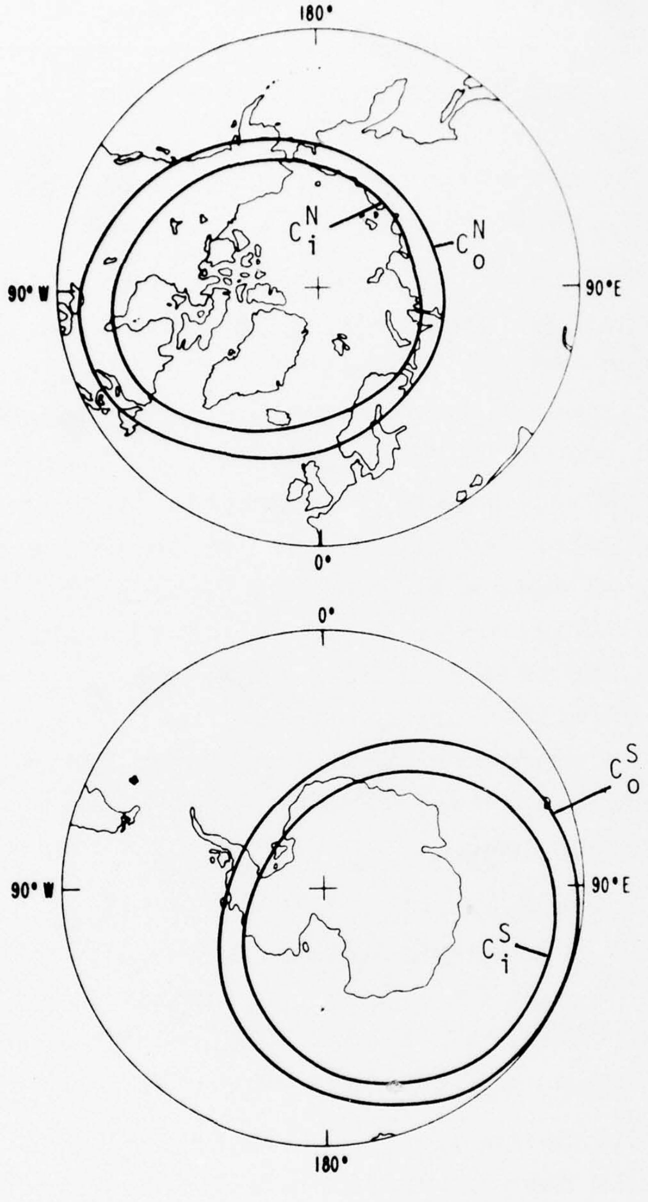
FIGURE E-1. General Orientation. We show height profiles for ozone (Fall, Latitudes 9° and 71°, both from Dütsch (1971), and also the range and penetration height both at vertical incidence, for electrons and protons (from Valley, 1965, p. 17-24) and Davidson (1971, p. 5-6). Note that there is more ozone at high than at low latitudes, and that it lies at lower altitudes. Regarding penetration of protons and electrons, at vertical incidence at 20 MeV, proton will penetrate down to 55 km, while at 20 MeV, electrons will penetrate down to 32 km. For energies above approximately 300 MeV, protons lose energy by nuclear collisions in the atmosphere rather than by ionization, giving rise to "stars" or "showers". Thus, it is not apparent how far the primary proton penetrates, although some of the ionization of 1 to 10 GeV particles does get down to sea level.



Source: Reid, 1974

FIGURE E-2. The Northern and Southern "Polar Caps." SPE effects are important inside curves C_i, while GCR effects are most important inside C_o.

65° (total area 4.8×10^{13} m^2 in both hemispheres); this is the region in which solar protons produce the biggest effect.* The outer curve C_o, which corresponds approximately to geomagnetic latitude $\Lambda > 60°$ (total area 6.9×10^{13} m^2) is that over which the galactic cosmic ray flux has its plateau value, and should thus be used for GCR effects.

There is a question of how these curves C_i should be modeled in a two-dimensional photochemical/dynamic model which uses geographic latitude as one parameter. Of course, there is no very simple correlation between geographic and geomagnetic latitude. The following procedure is suggested. Let the polar caps be divided into annular zones of geographic latitude having 5-deg width,** i.e., going from 60 to 65°, 65 to 70°, etc. For each annular zone, we ask, what fraction f_j ($j = i,o$) of the area of the zone lies inside curve C_j of Fig. E-2. Table E-1 and also Fig. E-3 show the area A of each zone, the f_j (K = north,south), and also the effective area, weighted by f_j^{K}, that should be used here. Note the asymmetry between Northern and Southern Hemispheres; the effects extend from 40 to 90°, but maximize in the 60 to 70° latitude range.

Note in Table E-1 that $\Sigma f_i^{(N+S)}A = 5.8 \times 10^{13}$ m^2, whereas the area of the polar caps defined as $\Lambda > 65°$ is 4.8×10^{13} m^2, while $\Sigma f_o^{(N+S)}A = 7.9 \times 10^{13}$ m^2 as against 6.9×10^{13} m^2 for $\Lambda > 60°$. This difference arises because of the zonal asymmetry of the actual polar caps shown in Fig. E-2.

A tentative discussion of the penetration of NO_x and HO_x from 40 to 60 km down to where the bulk of atmospheric ozone is

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* Dr. D. J. Hofmann (private communication) has pointed out that during an SPE the geomagnetic field is distorted so that the protons can penetrate to lower latitudes than normally. This is an effect of several degrees [see, e.g., Zmuda and Potemra (1973)] which is unlikely to be of primary importance in the present context.

** A 5-deg interval is used here simply because it appears roughly consistent with the overall data, that is, using finer intervals is not justified.

TABLE E-1. EFFECTIVE AREA OF THE POLAR CAPS C_i AND C_o OF FIG. E-2

Geographic Latitude Range, deg	Area of Annulus A, 10^{13} m^2	Northern Hemisphere		Southern Hemisphere		Effective Area, 10^{13} m^2			
		f_i^N	f_o^N	f_i^S	f_o^S	Af_i^N	Af_o^N	Af_i^S	Af_o^S
40 to 45	1.635	0	0	0.038	0.157	0	0	0.06	0.26
45 to 50	1.508	0	0.042	0.150	0.290	0	0.06	0.23	0.44
50 to 55	1.355	0.052	0.167	0.249	0.365	0.07	0.23	0.34	0.49
55 to 60	1.201	0.186	0.331	0.335	0.450	0.22	0.40	0.40	0.54
60 to 65	1.022	0.384	0.602	0.438	0.528	0.39	0.62	0.45	0.54
65 to 70	0.869	0.660	0.896	0.503	0.653	0.57	0.78	0.44	0.57
70 to 75	0.665	0.910	1.000	0.625	0.875	0.61	0.67	0.42	0.58
75 to 80	0.486	1.000	1.000	0.861	1.000	0.49	0.49	0.42	0.49
80 to 85	0.281	1.000	1.000	1.000	1.000	0.28	0.28	0.28	0.28
85 to 90	0.102	1.000	1.000	1.000	1.000	0.10	0.10	0.10	0.10

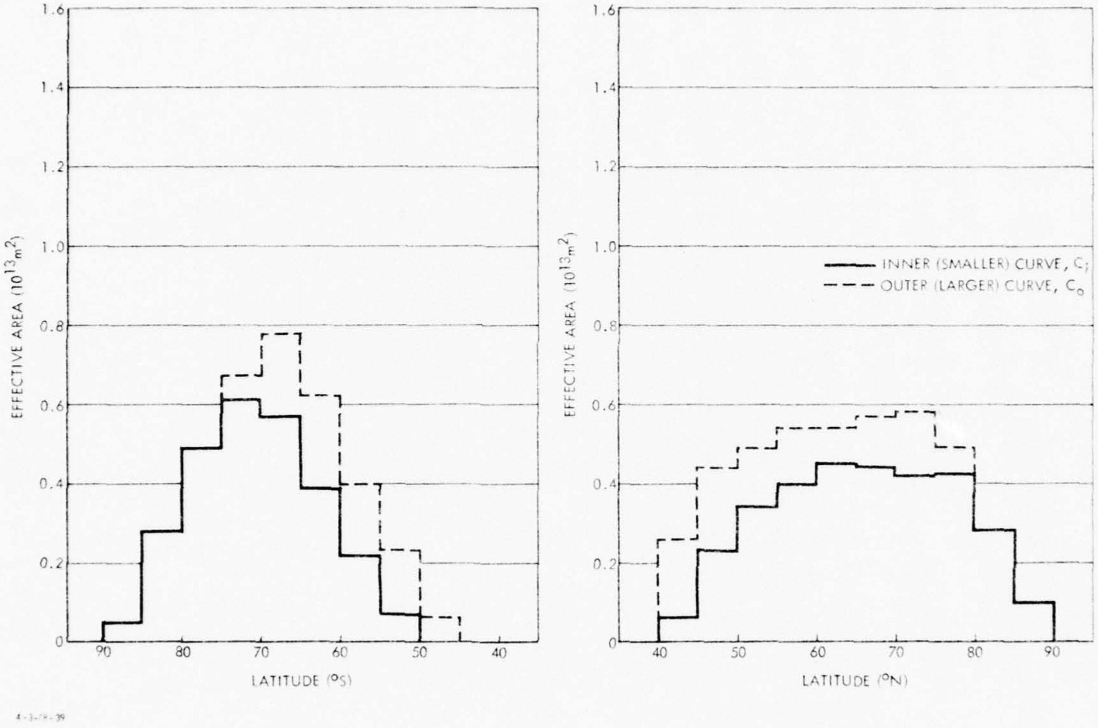

FIGURE E-3. Latitude-Weighted Areas of Polar Caps C_i and C_o of Fig. E-2 in Northern and Southern Hemisphere.

located is given in Annex EA; this suggests that HO_x radicals are destroyed so rapidly by photochemistry that they cannot be transported through significant vertical distances ("significant" here means more than a few kilometers). NO_x molecules are also destroyed very rapidly above about 45 km, but at lower altitudes their photochemical lifetime is so long that they can be transported downward to where they can affect the bulk of the ozone.

Thus, we conclude that ionization produced above 45 km is only of local significance in affecting atmospheric ozone, but ionization produced at lower altitudes will affect the ozone on an overall basis. Accordingly:

- Primary solar electromagnetic radiation is not significant because it produces ionization principally above 80-km altitude.

- Solar protons of energies 100 MeV or greater are found in relatively large solar proton events (formerly known as PCA from their effects on ionospheric radio propagation). The large SPEs are relatively rare and quite complex processes, which are discussed in Section E.5.

- Galactic (as distinct from solar) cosmic rays (GCRs) have energy in the 1 to 10 GeV range (1 GeV = 10^9 eV), and show a modulation with solar activity, having a maximum at solar minimum. These processes are discussed in Section E.4.

E.3 PRODUCTION OF NO AND OH BY IONIZATION IN THE STRATOSPHERE

When protons or other ionizing particles travel through the middle atmosphere, they lose energy and produce ions at the canonical rate of 35 eV/ion pair. As a result of charge transfer and ion-molecule reactions, the ions actually observed are not those formed initially, which are N_2^+, N^+, O_2^+, and O^+, but rather those of lowest ionization potential, which are NO^+ in dry air and and also H_3O^+, $H_5O_2^+$, etc. (hydrated protons) in the actual atmosphere, which contains 1 to 10 ppmv of water vapor.

The principal ions in the lower mesosphere are H_3O^+ and $H_5O_2^+$ [cf., e.g., Heicklen (1976, p. 127) and Ferguson (1975) for a review of stratospheric ion chemistry]. There are no detailed results on stratospheric ions, although observations from a balloon at 27 to 32 km indicate mass numbers 73+, 91+, 109+, which correspond to $H^+(H_2O)_n$, for n = 4, 5, 6--see Olson et al. (1977).

The NO and OH molecules are produced by a variety of reactions. Some currently accepted schemes are the following:

NO. The source of odd nitrogen is impact dissociation or dissociative ionization of atmospheric N_2 by fast (10 to 100 eV) secondary electrons produced from the incident protons

$$N_2 + e^- \begin{array}{l} \nearrow N_2^+ + 2e^- \qquad \text{(a)} \\ \rightarrow N^+ + N + 2e^- \qquad \text{(b)} \\ \searrow 2N + e^- \qquad \text{(c)} \end{array} \Bigg\} \qquad (1)$$

followed by the reactions

$$N_2^+ + e^- \rightarrow 2N \text{ (some atoms are excited)} \qquad (2)$$

$$N^+ + O_2 \begin{array}{l} \nearrow N + O_2^+ \qquad \text{(a)} \\ \searrow NO^+ + O \qquad \text{(b)} \end{array} \Big\} \qquad (3)$$

$$NO^+ + e^- \rightarrow N + O \text{ (some atoms are excited)} \qquad (4)$$

$$N + O_2 \rightarrow NO + O \qquad (5)$$

$$N + O_3 \rightarrow NO + O_2, \qquad (6)$$

which produce NO. There is also the destruction reaction for odd nitrogen

$$N + NO \rightarrow N_2 + O \qquad (7)$$

Different versions of this scheme give the following number of NO_x molecules/ion pair:

1.4 (factor 2)	Dalgarno (1967)
1.2 - 1.3	Frederick (1976)
1.5	Crutzen, Isaksen, and Reid (1975)

<u>OH</u>. After the initial ion formation, charge transfer and ion-molecule reactions lead to the formation of O_2^+, then O_4^+, and then either to (H_3O^+ + OH), or else to H_3O^+. OH, which reacts with another H_2O to make $H_5O_2^+$. Thus, one OH radical is produced in the formation of the hydrated hydronium ion. The ion is neutralized by dissociative recombination which yields yet another OH radical,

$$H_3O^+ + e^- \rightarrow OH + H_2. \tag{8}$$

This is the scheme of Swider and Keneshea (1973), who find two OH radicals/ion pair; Frederick (1976) uses a different scheme but, again, predicts two OH radicals/ion pair in the stratosphere/mesosphere below 60 km.

In the present context, following M.G. Heaps (1978b) as described by Fig. E-4, we suggest that one should assume that 1.3 NO molecules and 2.0 OH radicals are produced per ion pair at the altitudes of interest here, i.e., below 45 km.

E.4 STRATOSPHERIC IONIZATION DUE TO GALACTIC COSMIC RAYS (GCRs): VARIATION WITH SOLAR CYCLE*

The ionization rate Q (ion pairs $cm^{-3}s^{-1}$) due to GCRs shows considerable variation due to latitude, as well as solar sunspot cycle, as is illustrated in Fig. E-5.

The latitude dependence can be simplified such that for the polar cap regions (corresponding to those geographic latitudes for which the magnetic latitude $\Lambda > 60°$--see also Fig. E-2 and

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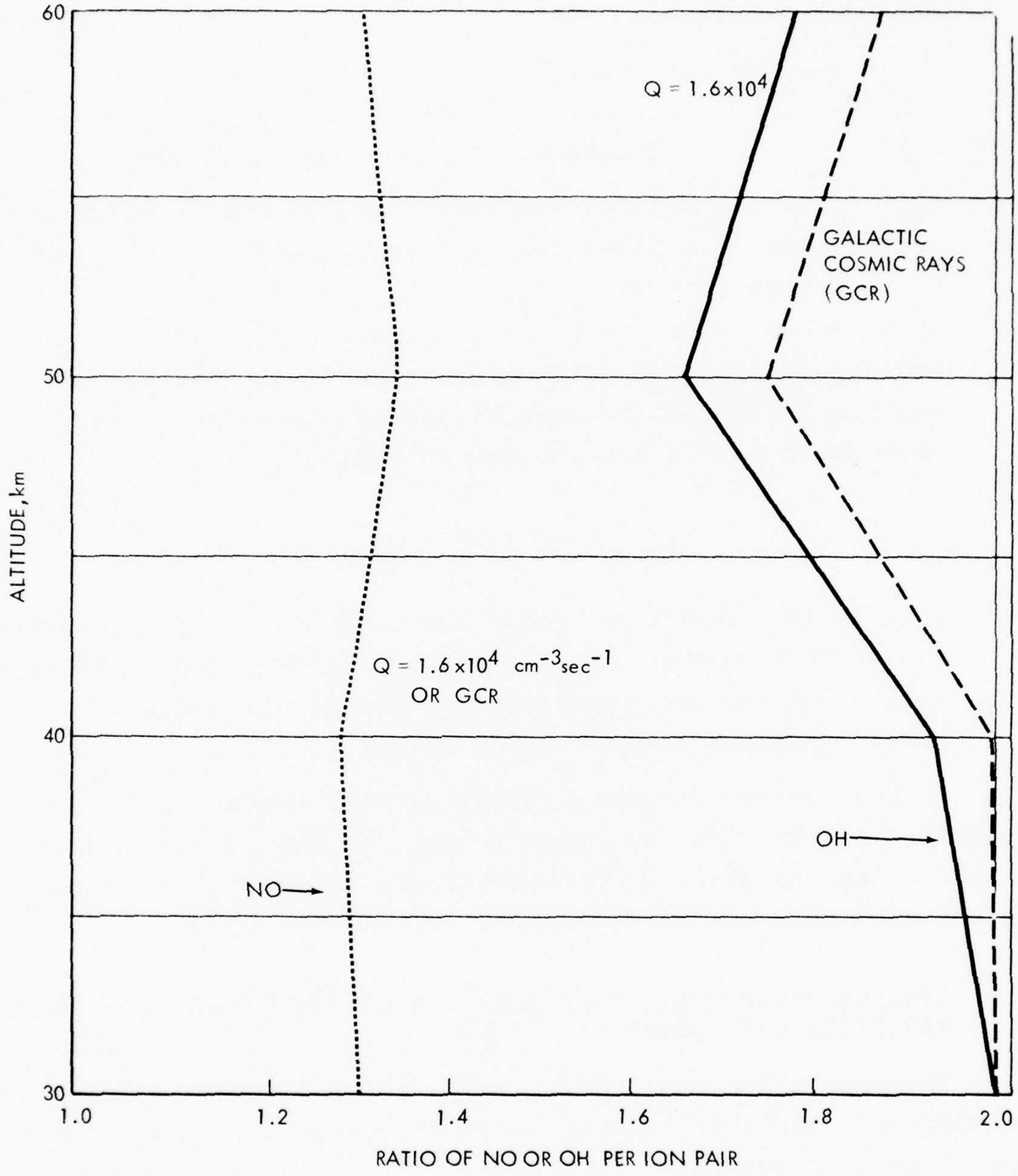
*This section has been extensively revised by M.G. Heaps.



Source: M.G. Heaps, 1978 b

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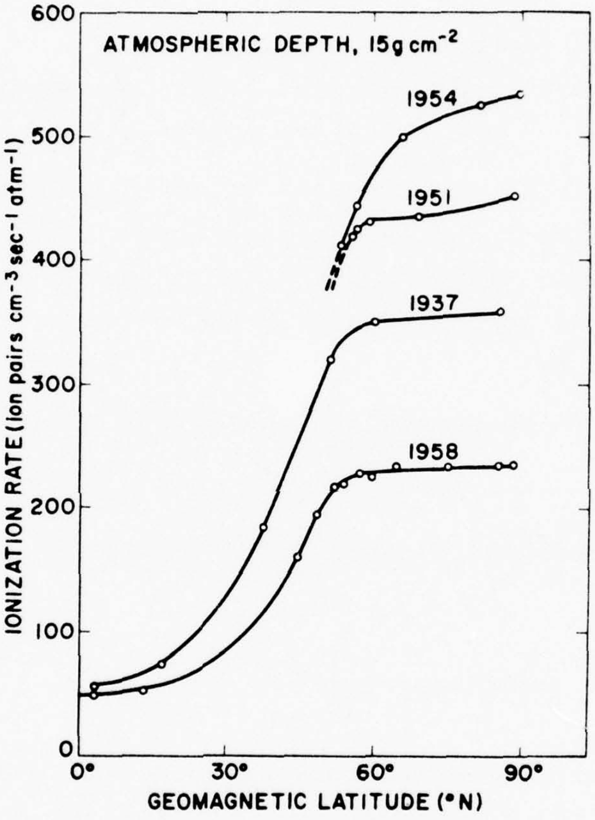
FIGURE E-4. NO and OH Production Per Ion Pair.



Source: Valley, ed., 1965, p. 17-25

FIGURE E-5. Cosmic ray ionization rates per atmosphere of air near the top of the atmosphere as a function of latitude for various years (from Neher and Anderson [1962]).

related discussion) the ion pair production rate may be represented as (Heaps, 1978a)

$$Q = \left[C + D\cos\left\{\left(\frac{2\pi}{P}\right)(\text{YM-year})\right\}\right]p \tag{9}$$

(Heaps, 1978a) where C = 0.38, p = 0.13, p = pressure (mbar) at the altitude of interest, and YM = 1954, 1965, and nominally 1976 (year of GCR maximum, i.e., solar sunspot minimum)

year = current year of interest
P = period: 9 years going down from YM
13 years going up from YM

Over the polar cap regions the value of Q depends linearly on pressure as shown in Eq (9) down to about 20 km (∿ 50 mbar) (see Fig. 1 in Heaps, 1978a), but then increases at a much slower rate down to approximately 15 km and actually begins to decrease below 15 km.

Below 20 km these approximations may be used over the polar caps

$$Q = \left[2.6 + 0.8\cos\left\{\left(\frac{2\pi}{p}\right)(\text{YM-year})\right\}\right]p^{0.5} \text{ (15-20 km, 50-110 mbar)} \tag{10}$$

$$Q = \left[70 + 21\cos\left\{\left(\frac{2\pi}{p}\right)(\text{YM-year})\right\}\right]p^{-0.2} \text{ (10-15 km, 110-250 mbar)} \tag{11}$$

At middle and low latitudes corresponding to $\Lambda < 60°$ (or, lying outside curves C_o of Fig. E-2) the ionization rate above 31 km may be expressed as (Heaps, 1978a)

$$Q = (A + B\sin^4\Lambda)p \text{ (above 31 km, } p \leq 10 \text{ mb)} \tag{12}$$

(Heaps, 1978a) where A = 0.046, B = 0.75 for a solar sunspot minimum and B = 0.51 for a solar sunspot maximum. A quasi-sinusoidal variation with solar sunspot cycle similar to that expressed in Eq (9) may be inferred, but there is no extensive lower latitude data to confirm this.

At lower latitudes the ionization rate due to GCRs actually increases faster than the ambient pressure in the 31-18 km range such that

$$Q = (A + B \sin^4 \Lambda) p_o^{\gamma} p^n \quad (18\text{-}31 \text{ km}, 10\text{-}70 \text{ mbar}) \tag{13}$$

where $p_o = 10$ mbar, $n = 0.8 + 0.6 \cos\Lambda$ and $\gamma = 1 - n$. A and B are the same as in Eq (11).

In the 15-18 km range the ionization rate may again be approximated as proportional to the pressure and Eq (11) may be used again if it is multiplied by the factor γ^{n-1}.

The ionization rates given in Eqs (9) to (13) can be integrated over the volume of the stratosphere to yield a total ion pair production for solar sunspot maximum (i.e., cosmic ray minimum), which should serve as a baseline and integrated again for solar sunspot minumum to obtain the difference in production over the solar cycle.

Over the polar cap regions a nominal tropopause level shall be taken as 10 km, which shall serve as a lower boundary on the spatial integration. Using the values of Q from Eqs (9) to (11) one has

$$\int_0^{1\text{ yr}} \int_0^{\pi/6} \int_0^{2\pi} \int_{z_o}^{z_t} Q(r^2 dr \sin\alpha d\alpha d\phi)dt = \int_t \int_{C_o} QdVdt \tag{14}$$

for total yearly production, which yields

$$\int_t \int_{C_o} QdVdt = 6.5 \times 10^{32} \text{ ion pairs/yr}$$

for the total ion pair production in the stratosphere over each polar cap for a solar sunspot minimum (i.e., GCR maximum), and

$$\iint_{C_o} QdVdt = 3.4 \times 10^{32} \text{ ion pairs/yr},$$

for a solar sunspot maximum.

The middle and low latitude regions also contribute appreciably to the total ion pair production because of the much larger surface area involved, even though the ionization rate is reduced. For these lower latitudes a nominal tropopause level of 15 km is chosen to serve as the lower bound on the spatial integration. Using the values from Eqs (12) and (13) over the appropriate altitude range, one has

$$\int_0^{1\text{ yr}} \int_{\pi/6}^{\pi/2} \int_0^{2\pi} \int_{z_o}^{z_t} Q(r^2 dr \sin\alpha d\alpha d\phi) dt = \int_t \int_{(1-C_o)} QdVdt \qquad (15)$$

for the total yearly production over middle and low latitudes. Here, $\int_{(1-C_o)} dV$ means the integration goes over a hemisphere but excludes the polar cap.

$$\iint_{t\ (1-C_o)} QdVdt = 13 \times 10^{32} \text{ ion pairs/yr},$$

the total ion pair production in the stratosphere over a hemisphere (0 to 60°) for a solar sunspot minimum (i.e., GCR maximum).

$$\int_t \int_{(1-C_o)} QdVdt = 10 \times 10^{32} \text{ ion pairs/yr}$$

for the solar sunspot maximum.

Thus, one can see that the total stratospheric ion pair production over both polar caps during a GCR minimum is on the order of 7×10^{32} ion pairs/yr, with a total global stratospheric production on the order of 27×10^{32} ion pairs/yr. These values represent the "baseline" values. During a solar sunspot minimum (GCR maximum) an additional 6×10^{32} ion pairs/yr are produced over the polar caps, with an additional total global production of 12×10^{32} ion pairs/yr.

When one adopts the odd-nitrogen/ion pair production ratio of 1.3, the baseline values for odd-nitrogen production become

8.8×10^{32} NO/yr	stratospheric production over both the polar caps during GCR minimum
8.1×10^{32} NO/yr	additional polar cap production during GCR maximum
3.5×10^{33} NO/yr	total global stratospheric production during GCR minimum
1.6×10^{33} NO/yr	additional global production during GCR maximum

Considering a total stratospheric loading of $(4 \text{ to } 10) \times 10^{34}$ NO_x molecules, the additional production over the polar caps during GCR maxima should be a slowly varying perturbation of < 2 percent/yr, with a total global perturbation < 4 percent/yr.

With an odd-hydrogen/ion pair production ratio of 2.0 below 30 km, the baseline and additional values of odd-hydrogen become

1.4×10^{33} OH/yr	stratospheric production over the polar caps during GCR minimum
1.2×10^{33} OH/yr	additional polar cap production during GCR maximum
5.4×10^{33} OH/yr	total global stratospheric production during GCR minimum
2.4×10^{33} OH/yr	additional global production during GCR maximum

The annual production of OH due to GCRs is still smaller than the production rate from the action of sunlight and $O(^1D)$ on H_2O.* Therefore, the global effect on loading is still likely to be a perturbation of a few percent, although the potential effect in the winter polar stratosphere may be much larger. The HO_x loading over the winter polar cap may even double due to the enhanced ionization during a GCR maximum.

E.5 STRATOSPHERIC IONIZATION DUE TO SOLAR PROTON EVENTS (SPEs)

In contrast to galactic cosmic rays, which are a very steady source of ionization, modulated principally by the 11-year solar cycle, solar proton events are highly variable impulsive events resulting from some (but not all) solar flares. For orientation, Table E-2 lists major SPEs during the time frame 1956 to 1972.** Here "major" refers to a Shea-Smart index (defined in footnote of Table E-2) greater than X20.

In fact, the Shea-Smart index has significant limitations for the present application because different solar flares produce significantly different numbers and energy distributions of high energy protons--see Annex B to this Appendix, item 1.

Given the total spectrum for a given SPE (see Annex B to this Appendix, item 1), it is possible to calculate the time-integrated ionization due to the event. Figure E-6 shows this for a number of major events.*** Next, we ask which SPEs should

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*Note that while the estimated HO_x loading of the stratosphere is only (7 - 16) x 10^{32} molecules (see, e.g., Appendix A) the lifetime of HO_x is so short (less than 30 min above 40 km--see Table EA-1) that the effect on these *annual* production rates is relatively small.

**No major events were recorded in 1955, and there were no major events during 1973 to 1975.

***It also shows the ionization due to relativistic electron precipitation (REP) events (Thorne, 1977, 1978) which occur approximately 3 to 4 percent of the time. Their contribution is evidently not very important.

TABLE E-2. SIGNIFICANT SOLAR PROTON EVENTS, 1956-1973

DATE	SHEA & SMART RATING^{a,1}	PEAK FLUX RATING (>30 Mev)^{b,2}	GLE (%)	PCA (dB)	FLARE CAUSING^{c}
23 Feb 56	X34	3&	4550 (c) 9000 (d)	13 (c,b,d)	3
31 Aug 56	X21	-	3 (c,d)	4.9 (c,b,d)	3
13 Nov 56	X30	NL	-	5.4 (c,d)	2&
22 Jun 57	X30	3&	3 (c,d)	4.9 (c,b,d)	?
3 Jul 57	X30	-	-	6-9.2 (c,b,d)	3+
29 Aug 57	X30	2&	-	8.2-9 (c,d)	?
31 Aug 57	X30	NL	-	4.9-5 (c,d)	3
2 Sep 57	X30	NL	-	7.2-9 (c,d)	2&
21 Sep 57	X30	NL	-	5.1 (c,d)	3
20 Oct 57	X30	-	-	5-7.8 (c,b,d)	3+
10 Feb 58	X30	-	-	3.2-12 (c,b,d)	2+
25 Mar 58	X30	3&	-	10-12 (c,d)	?
7 Jul 58	X40	3&	-	>15-23.7 (c,b,d)	3+
16 Aug 58	X40	2&	-	12.1->15 (c,b,d)	3+
22 Aug 58	X30	2&	-	>10-10.6 (c,b,d)	3
26 Aug 58	X40	3&	-	16.6 (c,b,d)	3
22 Sep 58	X30	NL	-	4-5 (c,d)	2
10 May 59	X40	3&	-	>15-22 (c,b,d)	3+
10 Jul 59	X40	3&	-	>15-20 (c,b,d)	3+
14 Jul 59	X40	4&	-	>15-23.7 (c,b,d)	3+
16 Jul 59	X42	4&	10 (c) 5 (d)	>15-21.2 (c,b,d)	3+
30 Mar 60	X30	1&	-	3-7 (c,b,d)	2
29 Apr 60	(1)30	2&	-	11.2-14 (c,d)	2+
4 May 60	(1)24	2&	290(c) 175(d)	3.4-5 (c,b,d)	3
6 May 60	(1)40	1&	-	8.7->15 (c,b,d)	3+
3 Sep 60	221	2&	4.5 (c,d)	2.5-4 (c,b,d)	2+
12 Nov 60	444	"5"&	135 (c) 100 (d)	>14->22 (c,b,d)	3+
15 Nov 60	443	3&	88 (c) 150 (d)	>22 (c,b,d)	3
20 Nov 60	(3)32	3&	8 (c) 7 (d)	3-8 (c,b,d)	2

TABLE E-2. (cont)

DATE	SHEA & SMART RATING[a,1]	PEAK FLUX RATING (>30 Mev)[b,2]	GLE (%)	PCA (dB)	FLARE CAUSING[c]
12 Jul 61	(2)40	2&	-	17-20 (c,b,d)	3
18 Jul 61	333	3&	24 (c)	8.7-10 (c,b,d)	3+
20 Jul 61	(1)22	2&	7 (c)	5 (c,b)	3
26 Sep 63	(1)30	0&	-	3-4.6 (c,b,d)	3
7 Jul 66	121	1&	2.5 (c)	2-2.5 (c,b)	2B
2 Sep 66	230	2&	-	12-14 (c,b,d)	3B
28 Jan 67	133	1&	{21 (c) 20 (d)}	7 (c,b,d)	?
23 May 67	330	1&	-	11 (c,b,d)	3B
9 Jun 68	230	1&	-	6.5 (c,b,d)	3B
29 Sep 68	121	1&	{1.4 (c) 2 (d)}	1.7 (c,b)	2B
31 Oct 68	230	1&	-	5.5 (c,b,d)	3B
1 Nov 68	230	NL	-	4-5.9 (c,d)	2N
18 Nov 68	233	2&	{14 (c) 13 (d)}	12.5 (c,b,d)	1B
5 Dec 68	230	1&	-	4.7 (c,b,d)	?
25 Feb 69	123	1&	{16 (c) 15 (d)}	2.1 (c,b)	2B
30 Mar 69	112	1&	{8.8 (c) 5 (d)}	1.3 (c,b)	?
11 Apr 69	330	2&	-	>12 (c,b,d)	N
2 Nov 69	330	2&	-	14.5 (c,b,d)	N

No Shea and Smart[a] or Svestka and Simon[c] rating after December 1969.

DATE	SHEA & SMART SYNTHESIZED RATING	PEAK FLUX RATING (>30 Mev)[b,2]	GLE (%)	PCA (dB)
24 Jan 71	233	2&	29 (d)	11-8 (b,d)
1 Sep 71	223	2&	16 (d)	4.2 (b,d)
4 Aug 72	443	4&	15 (d)	{720 (sic!b) ≥ 60 (d)}
7-8 Aug 72	242	2&	8 (d)	15.6 (d)

TABLE E-2. (cont)

NOTE:

Shea and Smart's ratings are listed below. Only events greater than (X20) are given in this table.

Solar Proton Event Classification System (Smart and Shea, 1971)

	First digit	Second digit	Third digit
Digit	>10 MeV proton *flux* $(cm^2\ s\ ster)^{-1}$	Daylight polar cap absorption *at 30 MHz*	Sea level neutron monitor increase
-2	10^{-2}-$<10^{-1}$	-	-
-1	10^{-1}-$<10^{0}$	-	-
0	10^{0}-$<10^{1}$	No increase	No increase
1	10^{1}-$<10^{2}$	<1.5 *dB*	<3%
2	10^{2}-$<10^{3}$	1.5-<4.6 dB	3-<10%
3	10^{3}-$<10^{4}$	4.6-<15 dB	10-<100%
4	$\geq 10^{4}$	≥ 15 dB	≥ 100%

X = *measurements not available*
() = the digit is uncertain or implied

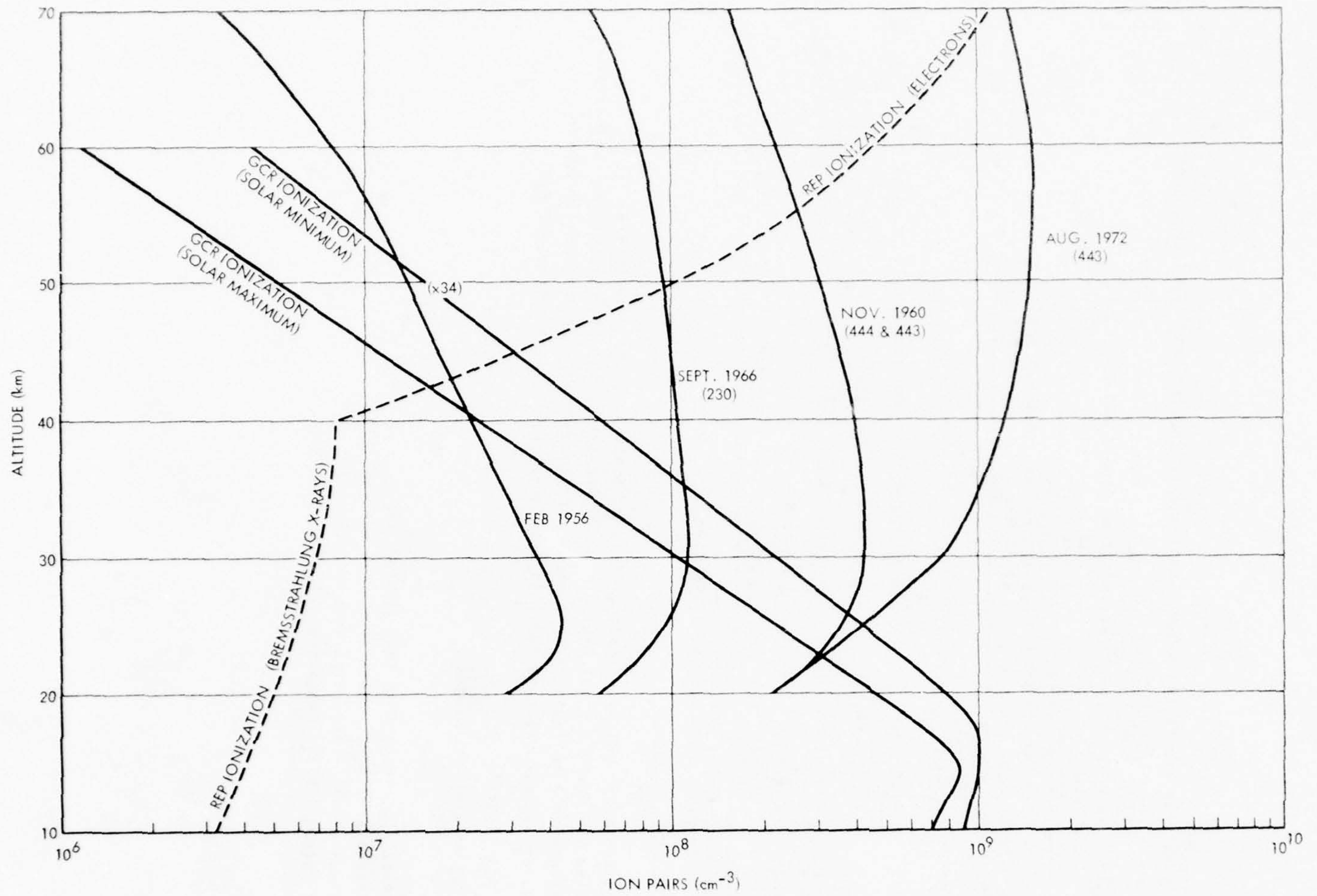
2. The Sauer and Stonehocker peak *flux* rating (Ref. b, Table 1, p. 5) used here is analogous to Shea and Smart's first digit, i.e., 3 for a flux 10^3 -10^4 protons/cm^2 -sec-ster. We write 3& instead of 3 to indicate that *Sauer and Stonehocker's flux refers to proton* energy >30 MeV, as against Shea and Smart's index which refers to energies >10 MeV.

NL - means "event not listed"

A dash (-) means "no enhancement quoted"

References:

a. Shea and Smart (1977) - data from 1955 through 1969
b. Sauer and Stonehocker (1977) - data from 1956 through 1972
c. Svestka and Simon (1975) - data from 1955 through 1969
d. Pomerantz and Duggal (1974) - data from 1942 through 1973



Sources: Crutzen, Isaksen and Reid (1975), Thorne (1978), and Reid private communication.

4-30-78-41

FIGURE E-6. Total Ionization Profiles due to Some SPEs and the Total Annual Ionization Due to GCRs.

be considered. Some details are reviewed in Annex B to this Appendix, where item 2 presents some general factors, while item 3 explains one method of calculating the total ionization due to protons of energy above 100 MeV. Table E-3 summarizes the results and indicates those events which ought to be considered as contributing at least several times 10^{32} ion pairs below 45 km or so.

The following comments should be made:

(a) The estimates for total ionization due to Reid, and those made here for the events between 1956 and 1960, use a slightly different treatment of the same data. Reid provides the various altitude profiles of ionization shown in Fig. E-6, while in item 3 of Annex B to this Appendix we simply compute the total energy carried by protons of 100 MeV or more (which penetrate down to perhaps 32-km altitude) and estimate the total ionization from the standard factor of 35 eV/ion pair in air. The agreement between the November 1960 events is excellent (17 vs 13.7, for the number of ion pairs in units of 10^{32}); for the February 1956 event the two estimates differ by a factor of 2.7, but it is clear that this was a much smaller event overall.

(b) We suggest that the ionization profile for the May-July 1959 events should be scaled from that for the November 1960 event by multiplying by a scale factor proportional to the respective ionization, which is

$$\frac{(4.8 + 1.7 + 5.7 + 6.1)}{(8.2 + 5.5)} = \frac{18.3}{13.7} = 1.34 \; .$$

(c) The events of February 1956, May 1960, and September 1966 are so small that they can probably be ignored;*

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*Using the scaling of (b) above, the May 1960 event is approximately one-eighth times as large as the February 1956 event.

TABLE E-3. SOME LARGE SOLAR PROTON EVENTS AND THEIR IONIZATION

Event Date	Shea-Smart Index	Peak Flux >30 Mev (part/cm^2 sec ster)[a]	GLE (%)[b]	Rigidity Spectrum[c]		Total No. of Ion Pairs ($\times 10^{32}$)		Suggested Ionization used for this event
				J_o (part/cm^2 sec ster)	P_o (Mv)	Reid[d]	This work[e,f]	
23 Feb 56	X34	6,200	4550-9000	140	300	0.74[g]	1.99	Event shown
10 May 59	X40	7,000	0	30,000	65	-	4.80	1.34 * profile for November 1960 (see text)
10 July 59	X40	4,000	0	7,800	90	-	1.71	
14 July 59	X40	11,000	0	35,000	68	-	5.72	
16 July 59	X42	17,000	0	3,200	125	-	6.14	
4 May 60	(1)24	200	175-290	6.7	280	-	0.25	Negligibly small: $\frac{0.25}{1.99} = 0.126 \times$ Feb 56 event
12 Nov 60	444	120,000	100-135	1,100 3,400	280 185	17	8.2	Event shown
15 Nov 60	443	6,000	88-150	250 3,300	375 120		5.5	
2 Sep 66	230	150	0	-	-	2.5	-	Event shown
2 Nov 69	330	737	0	-	-	-	-	---
4 Aug 72	443	21,000	15	-	-	25	-	Event shown

---

[a] From Sauer and Stonehocker (1977)

[b] From Svestka and Simon (1975); Pomerantz and Duggal (1974)

[c] From Freier and Webber (1963)--see Table D.3 and Eq. (D.3), where J_o and P_o are defined

[d] In Crutzen, Isaksen and Reid (1975)

[e] See Appendix D, item 3

[f] Three figures are not significant

[g] G.C. Reid, private communication, Dec. 1977

I have no calculations for the November 1969 event, which was certainly smaller than the other events listed.

(d) In conclusion, the events of summer 1959, November 1960, and August 1972 should probably be taken into account, although their effects on NO_x--and probably also on ozone--is certainly less than that of the largest individual nuclear test series (see, e.g., Appendix B).

ANNEX A TO APPENDIX E

DOWNWARD TRANSPORT OF NO_x AND HO_x

ANNEX A TO APPENDIX E

DOWNWARD TRANSPORT OF NO_x AND HO_x*

The question discussed here is the following. NO_x and HO_x are produced by ionization throughout the stratosphere and mesosphere, and they will affect the ambient ozone at the altitude of production. However, much ionization occurs at relatively high altitudes (above 60 km) while most of the ozone lies at relatively low altitudes (below 25 km), and so whether the NO_x and HO_x will affect the bulk of the ozone depends on the relative rate of transport as compared to photochemical destruction. These factors are compared here in a very crude way. The conclusion is that below about 45 km the photochemical lifetime of NO_x is sufficiently long that this material can be transported down to where the ozone is, but at higher altitudes NO_x is destroyed so very rapidly that transport is simply too slow. Overall, the lifetime of HO_x is so short that vertical transport of this species is never significant.

Throughout the stratosphere, and up to at least 60 km altitude, NO is produced principally by the reaction

$$N_2O + O(^1D) \rightarrow 2\ NO\ . \qquad \text{(EA-1)}$$

There are a number of photochemical reactions which shuffle "odd nitrogen" = $N + NO + NO_2$, in particular

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*I should like to thank Dr. J. Zinn (LASL) for providing the information on chemical production and destruction mechanisms and lifetimes used here.

$$\begin{aligned} NO + h\nu &\rightarrow N + O \\ N + O_2 &\rightarrow NO + O \\ N + O_3 &\rightarrow NO + O_2 \end{aligned} \qquad \text{(EA-2)}$$

$$\text{Net:} \quad N + O_3 + h\nu \rightarrow NO + 2\,O$$

$$\begin{aligned} NO + O_3 &\rightarrow NO_2 + O_2 \\ NO_2 + h\nu &\rightarrow NO + O \\ NO_2 + O &\rightarrow NO + O_2 \end{aligned} \qquad \text{(EA-3)}$$

$$\text{Net:} \quad NO + NO_2 + 2\,O_3 + h\nu \rightarrow 2\,NO + 2\,O + 2\,O_2$$

and combining these

$$\begin{aligned} N + O_3 + h\nu &\rightarrow NO + 2\,O \\ NO + NO_2 + 2\,O_3 + h\nu &\rightarrow 2\,NO + 2\,O + 2\,O_2 \\ N + NO &\rightarrow N_2 + O \end{aligned} \qquad \text{(EA-4)}$$

$$\text{Net:} \quad 2\,N + NO_2 + 2\,O_3 + 2\,h\nu \rightarrow NO + 3\,O + 2\,O_2 + N_2$$

so that we get

$$3 \text{ odd nitrogen} \rightarrow 1 \text{ odd nitrogen} \qquad \text{(EA-5)}$$

principally by the reaction

$$N + NO \rightarrow N_2 + O \qquad \text{(EA-6)}$$

HO_x is made and destroyed principally by the reactions

$$O(^1D) + H_2O \rightarrow 2\,OH \qquad \text{(EA-7)}$$

$$OH + HO_2 \rightarrow H_2O + O_2 \qquad \text{(EA-8)}$$

The characteristic lifetimes for both NO_x and HO_x are given in Table EA-1.

TABLE EA-1. PHOTOCHEMICAL LIFETIMES OF NO_x AND HO_x*

Altitude, km	Lifetime of NO_x, sec	Lifetime of HO_x, sec
"high"	"shorter"	-
52	3×10^5 (= 3.5 days)	1600 (30 min)
40	7×10^7 (2 yr)	1000 (20 min)

---

*Source: J. Zinn

Transport is crudely represented by a one-dimensional "eddy diffusivity" profile; in fact, the magnitude of the transport coefficient in the 40- to 60-km altitude range is not well established, but the general character of transport is that vertical transport is relatively fast in the 40- to 60-km range but much slower below 25 km where the ozone is. Figure EA-1 shows some currently used eddy diffusivity profiles.

Note that K is small in the altitude range from the tropopause to about 30 km, but large at both lower and higher altitudes. That is, transport is slow between the tropopause and 30 km, but fast at both lower and higher altitudes. To make a quantitative estimate of the overall rate of vertical transport is beyond the scope of this study, but a qualitative estimate can be made as described below.

From dimensional considerations, transport through a distance Δz near altitude z takes a time Δt

$$\Delta t \sim (\Delta z)^2/a\bar{K} \qquad \text{(EA-9)}$$

where $\overline{K}$ = mean eddy diffusivity at altitude z, and a ∿ 2 is a numerical constant. Thus, using the Wofsy 1975 K-profile of Fig. EA-1 and 5-km steps for Δz, one obtains the results of Table EA-2, which show that transport in the mesosphere is very fast (∿ 1 week), slower in the upper stratosphere (months), very low in the lower stratosphere (years), and fast in the troposphere (∿ 1 week).

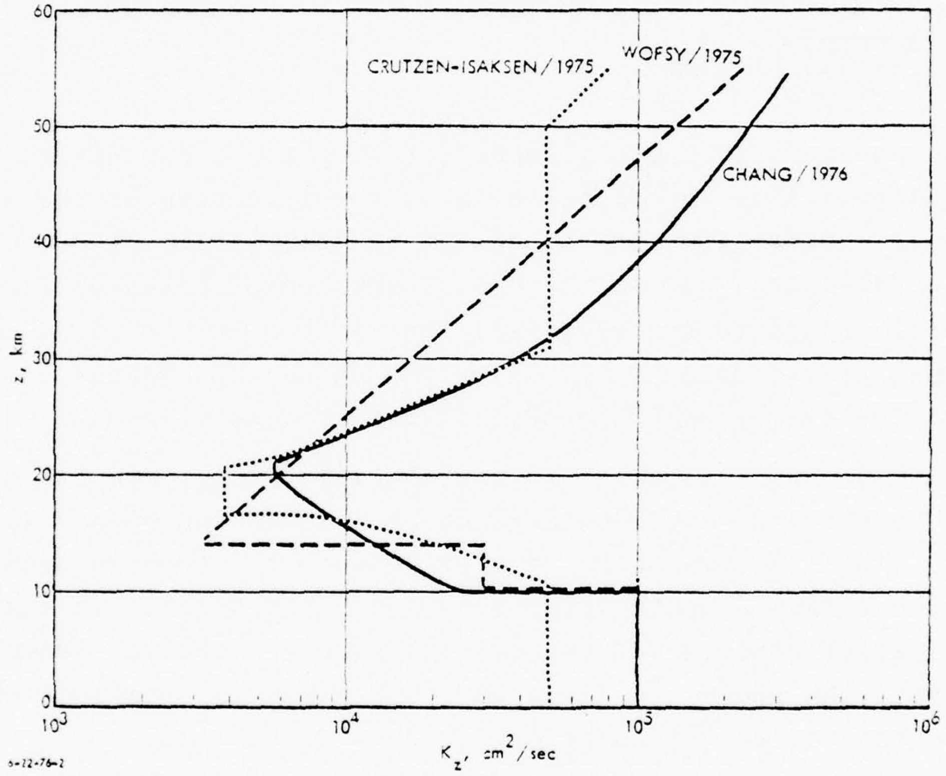


FIGURE EA-1. Three Recent Eddy Diffusivity Profiles (From Bauer and Gardner, 1977)

TABLE EA-2. REPRESENTATIVE DIFFUSION TIME STEPS THROUGH 5-KM HEIGHT INTERVALS [FROM EQ. (EA-9)]

Altitude z, km	$\bar{K}$, cm^2/sec	t, days	
60	2.5×10^5	6	
55	2×10^5	7	
50	1×10^5	14	stratopause
45	6×10^4	24	
40	3×10^4	48	
35	2×10^4	70	
30	1×10^4	140	
25	7×10^3	210	
20	5×10^3	290	
15	3×10^3	20	(through 1 km)
14	3×10^4	30	(through 4 km)
10	1×10^5	14	tropopause
5	1×10^5	14	
0			

We thus see that the photochemical lifetime of HO_x is so short that vertical transport of this species grouping is certainly not significant in the present context. For NO_x, things are more complex; evidently, above about 45 km the photochemical lifetime is so short that downward transport is not significant, but at lower altitudes vertical transport has to be taken into account.

ANNEX B TO APPENDIX E

SELECTED TOPICS RELATED TO THE STRATOSPHERIC IONIZATION DUE TO SPEs

ANNEX B TO APPENDIX E

SELECTED TOPICS RELATED TO THE STRATOSPHERIC IONIZATION DUE TO SPEs

1. THE INTEGRAL ENERGY/RIGIDITY SPECTRUM FOR DIFFERENT EVENTS

Table EB-1 shows the energy spectra of a number of large SPEs over the 1956 to 1961 time frame. Note the large difference between the ratios of integrated intensities in excess of 30 MeV vs 100 MeV for the different events (last two columns). Note also with reference to Fig. E-1 that only particles with energies in excess of 180 MeV can penetrate at vertical incidence down to 25 km, which is near the upper limit of the ozone layer at high latitudes. Also, from Tables E-2 and E-3 we see that relatively few of the events contain significant numbers of 1 to 10 GeV protons which give rise to a "Ground Level Enhancement" (GLE).

It is customary to characterize high-energy particles in terms of their magnetic rigidity P, which is a measure of their ability to penetrate into the atmosphere through the geomagnetic field which acts as a magnetic analyzer, removing charged particles of low rigidity from the flux incident on the top of the atmosphere. Magnetic rigidity is defined as

$$P = pc/q \qquad \text{(EB-1)}$$

where P = momentum, q = charge of the particle, and c = speed of light. P is customarily measured in volts (actually in GV), corresponding to the fact that pc is measured in eV, and q in units of the electron charge e; it is related to the kinetic energy K of the particle through the relativistic relation

TABLE EB-1. SOME MAJOR SOLAR COSMIC RAY OBSERVATIONS DURING 1956-1961 (After McDonald, 1963)

Solar Flare Data							Cosmic Ray Data							
					Maximum Radio Emission		Onset or Rise Time (h)		Decay Time (h)		Peak Flux (no. cm^{-2} sec^{-1})		Integrated Intensity (no. cm^{-2})	
Date		Importance	Heliographic Position (deg)	Optical Maximum (UT)	(*)	(UT)	$>$ 30 MeV	$>$ 100 MeV	$>$ 30 MeV	$>$ 100 MeV	$>$ 30 MeV	$>$ 100 MeV	$>$ 30 MeV	$>$ 100 MeV
1956	Feb 23	3+	N22 W74	0340	20,000	0341	6-8	3-4	30	16	6,200	5,000	6.5×10^8	3.2×10^8
1957	Jan 20	3+	S25 W30	1120							2,000- 3,000	100- 200	3×10^8	10^7
	Mar 23	3+	S14 E78	1005	10,000	1004			(40)	(20)	1,200- 1,500	≈ 50	2×10^8	5×10^6
	Jul 7	3+	N25 W08	0115	2,000	0112			32	16-20	1,500- 2,000	≈ 80	3×10^8	7×10^6
1958	Aug 16	3+	S14 W50	0440	6,200	0442	10		18		200		2×10^7	
	Aug 22	3	N18 W10	1448			10-12	3-4	20	8-12	500	20	5×10^7	1×10^6
	Aug 26	3	N20 W54	0027	6,700	0025	≈ 9		(12)		1,100		5.3×10^7	
	May 10	3+	N23 E47	2118	10,000		18-22	12-18	22	10-14	6,000- 8,000	1,000	7×10^8	7.5×10^7
1959	Jul 10	3+	N22 E70	0222	15,000	0224	30-40	18-20	40	20	4,000	1,200	8.8×10^8	1.0×10^8
	Jul 14	3+	N16 E07	0349	6,300	0352	16-20	12-18	18	9-12	10,000- 12,000	1,200	1.1×10^9	6.3×10^7
	Jul 16	3+	N08 W26	2145	6,500	2200	12-14	4-5	30	18	16,000- 18,000	1,500	8.1×10^8	1.3×10^8
	Apr 1	3	N12 W10	0859			2-3	< 1	12	4-6	50	6	2.7×10^6	1.5×10^5
	Apr 5	2+	N10 W61	0245	≈ 8,000	0203			12		40		2×10^6	
	Apr 28	3	S05 E34	0130			8-10	3-4	18 24	8	300	20	2.5×10^7	7×10^5
	May 4	3+	N14 W90	1020			2-3	< 1	8	4	200	40	7×10^6	7×10^5
1960	Sep 3	3	N18 E88	0110	12,000	0108	12-16	7-9	32	26	240	60	4×10^7	7×10^6
	Nov 12	3+	N27 W02	1329	10,000	1329	12-16	8-10	18-24	14-18	12,000	2,500	1.4×10^9	3.5×10^8
	Nov 15	3+	N30 W32	0221	14,000	0227	10-16	3-5	16-20	8-12	6,000	2,400	5.2×10^8	1.2×10^8
	Nov 20	3	N28 W113	2020			3-4	≈ 1	10-16	4-6	1,000	4,000	6×10^7	6×10^6
	Jul 11	3	S06 E32	1700	2,500		8-10	4	22-26	18	20	3	2×10^6	3×10^5
	Jul 12	3+	S07 E22	1030	7,500		8-12	6	16-20	12	120	15	1.0×10^8	1.6×10^6
1961	Jul 18	3+	S06 W60	1010	5,000		6-10	2-3	24	12	2,500	600	2.1×10^8	4.8×10^7
	Jul 20	3+	S07 W90	(1600)	2,500		4-6	1.5	6-8	3	300	70	9×10^6	1.2×10^6
	Sep 28	3	N14 E30	2223									2.2×10^5	9.7×10^4

* Units of 10^{-22} W m^{-2} (cps)$^{-1}$ at 3 to 10 kMcps.

Source: Valley -1965, pp. 17-20.

$$(K + M_o c^2)^2 = p^2 c^2 + M_o{}^2 c^4 \qquad \text{(EB-2)}$$

where M_o = rest mass of particle (0.9382 GeV for protons, 0.5110 MeV for electrons). Thus, the relation of rigidity and kinetic energy for protons is given in Table EB-2.

TABLE EB-2. RELATION BETWEEN RIGIDITY AND KINETIC ENERGY FOR PROTONS*

Kinetic Energy, GeV	Rigidity, GV
$p^2/2M_o$ ($\rightarrow$ 0)	pc ($\rightarrow$ 0)
0.0053	0.10
0.21	0.20
0.125	0.50
0.433	1.00
1.000	1.70
1.27	2.0
2.205	3.0
3.0	3.825
10.0	10.9
20.0	20.9
pc ($\rightarrow \infty$)	pc($\rightarrow \infty$)

---

*See Eq (EB-2).

The integral energy spectrum of solar protons is generally described by an exponential expression in terms of the rigidity of the form

$$J(> P) = J_o \exp(- P/P_o), \qquad \text{(EB-3)}$$

where J(> P) is the flux of particles with rigidity greater than P, expressed in protons/cm^2-sec-ster. A list of J_o and P_o values for a number of large SPEs is given in Table EB-3.

TABLE EB-3. INTEGRAL EXPONENTIAL SPECTRA FOR SOLAR PROTONS--EQ (D-3)

Event Date	Optical Flare Max., UT	Time of Measurement, UT		J_o Protons/cm^2-sec-ster	P_o, MV
23 Feb. 56	0342	1930	23 Feb.	140	300
10 May 59	2118	0500	12 May	30×10^3	65
		0520-0915	12 May	18×10^3	70
		1335-1750	12 May	2.8×10^3	66
10 July 59	0222	0755-1625	11 July	7.8×10^3	90
		1225-2345	12 July	2.1×10^3	90
14 July 59	0349	1330-1555	15 July	35×10^3	68
16 July 59	2145	1200	17 July	3.2×10^3	125
		1555-1935		1.1×10^3	113
		1400	18 July	800	90
		1350-1640		2.8×10^3	70
		1445	20 July	300	66
4 May 60	1020	1630	4 May	6.7	280
		1700-0200	5 May	5.8	235
12 Nov. 60	1329	1930	12 Nov.	1100	280
		2000		1250	240
		0200	13 Nov.	3400	185
		0800		3400	155
		1305		3000	120
		1830-2000		2800	95
		2230		1000	105
		0500	14 Nov.	1000	95
15 Nov. 60	0221	0500	15 Nov.	250	375
		1130		320	240
		1030-1230		285	175
		2130		3300	120
		0930	16 Nov.	1000	100
		1430-1730		300	100
		1800	2 Aug	6	178
		2100	2 Aug	11	130
4 Aug 72	0640[a]	0600	4 Aug	5.4×10^4	32
		0900	4 Aug	7.8×10^3	96
		2100	4 Aug	3.63×10^5	84
		0600	5 Aug	2.6×10^4	70
		0600	6 Aug	7.5×10^3	57
7 Aug 72	1534[b]	0600	7 Aug	3.9×10^3	49
		0600	8 Aug	9.1×10^3	65
		0600	9 Aug	1.58×10^4	40
		0000	10 Aug	220	63

Source: Results through November 1960 from Freier and Webber, 1963.

[a] G.C. Reid, private communication. These data for J_o and P_o are computed and analyzed from flux data at 10, 30, 60 MeV. Thus, the higher energies are not reliable. Note that the Aug 72 flares had a very large flux of relatively low energy protons.

[b] McMath region 11976 produced a number of large solar flares between 1 Aug and 11 Aug, in particular 8 giving a large optical (Hα) signal, 6 with large 10-cm radio noise, and 10 with large 1-8A X-ray flux--see Hakura (1972). We list the Hα maxima of the two class 3B flares.

2. IONIZATION DUE TO SPEs: GENERAL COMMENTS

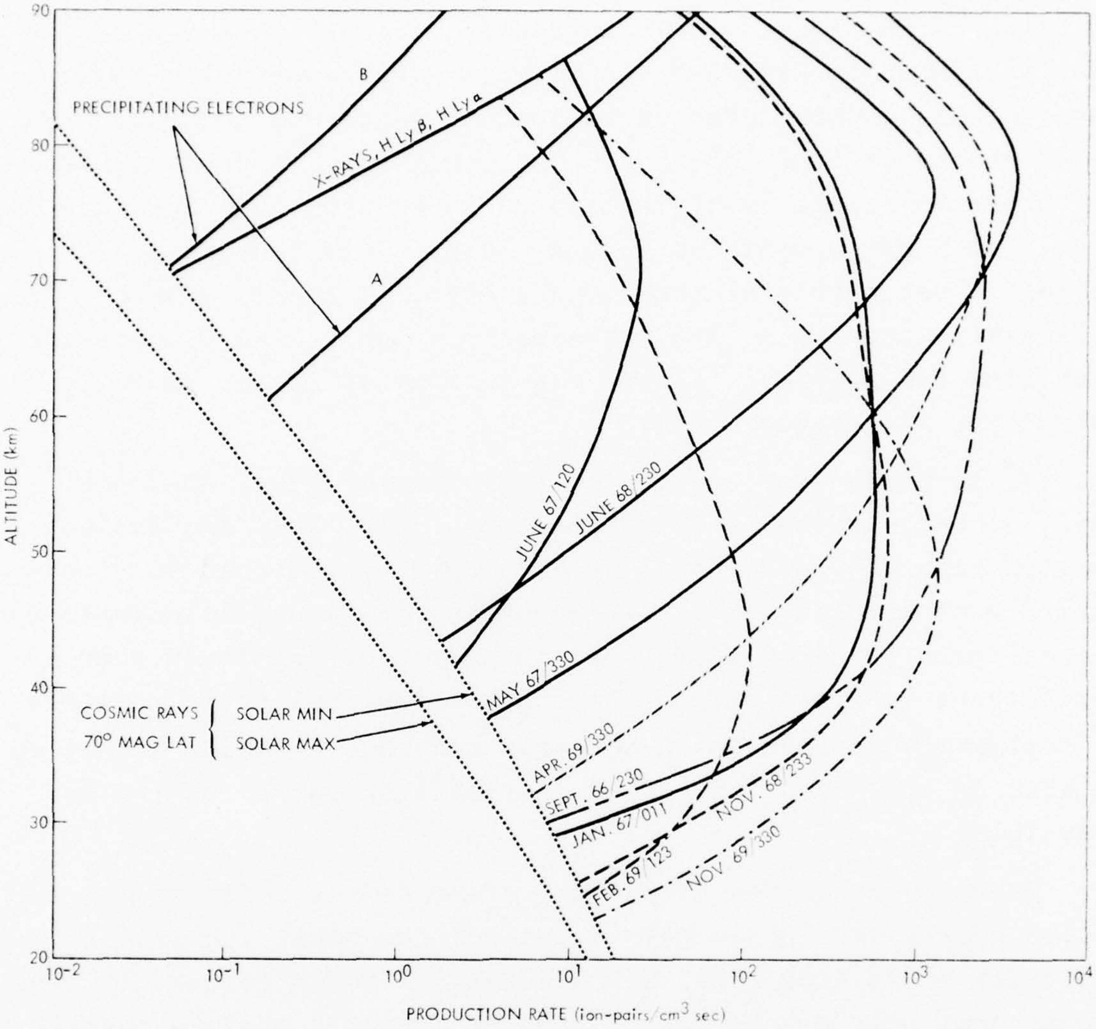
Given the integral spectrum J(> P) of Eq (EB-3) and the duration of the event, it is possible to compute the ionization profiles shown in Fig. E-7 for several events--see also Figs. EB-1 and EB-2, which compare ionization rates due to SPEs, GCRs, and a number of other sources. The ionization rate of an SPE (or other transient event) has to be integrated over its duration, which may extend for several days. This integration is evidently not a trivial task as the spectrum J(> P) changes significantly--see Table EB-3 where we show how J_o and P_o decrease with time for numerous events e.g., those of 10 May 1959, 16 July 1959, 12 November 1960.

It is clear that the ionization rates of Figs. EB-1 and EB-2, as well as the total ionization of Fig. E-7, are subject to significant errors; thus, in Fig. EB-2 we see that the ionization rate profile due to the November 1969 event calculated by two different workers differ by two orders of magnitude over a significant altitude range. I do not think that it is possible to estimate the error in these estimates, but a factor 2 to 3 up or down in the total ionization profile such as Fig. E-7 seems plausible.

Overall, it is not clear that there is any definite correlation between the Shea-Smart index and the total ionization, say below 45 km (see Figs. E-7 and EB-1). Nevertheless, it does appear that only a very few of the largest SPEs produce more than 10^{32} ion pairs in the middle stratosphere, and thus we shall restrict consideration to the events listed in Table E-3.

3. IONIZATION DUE TO SPEs: SOME CALCULATIONS

H.W. Dodson has computed the solar proton flux at various times following 17 solar flares, using the data compiled by Freier and Webber (1963). In Table EB-4 we show the flux for protons of energy greater than 20 MeV, and in Table D-5 we give her averaged conversion factors for energies > 50 and > 100 MeV.



Source: Zmuda and Potemra (1972).

FIGURE EB-1. Ion production rates due to different SPEs and also due to some other D-Region sources which are defined in Zmuda and Potemra (1972). Note that there is no obvious correlation between the Shea-Smart index and the ionization profile for these relatively small events.

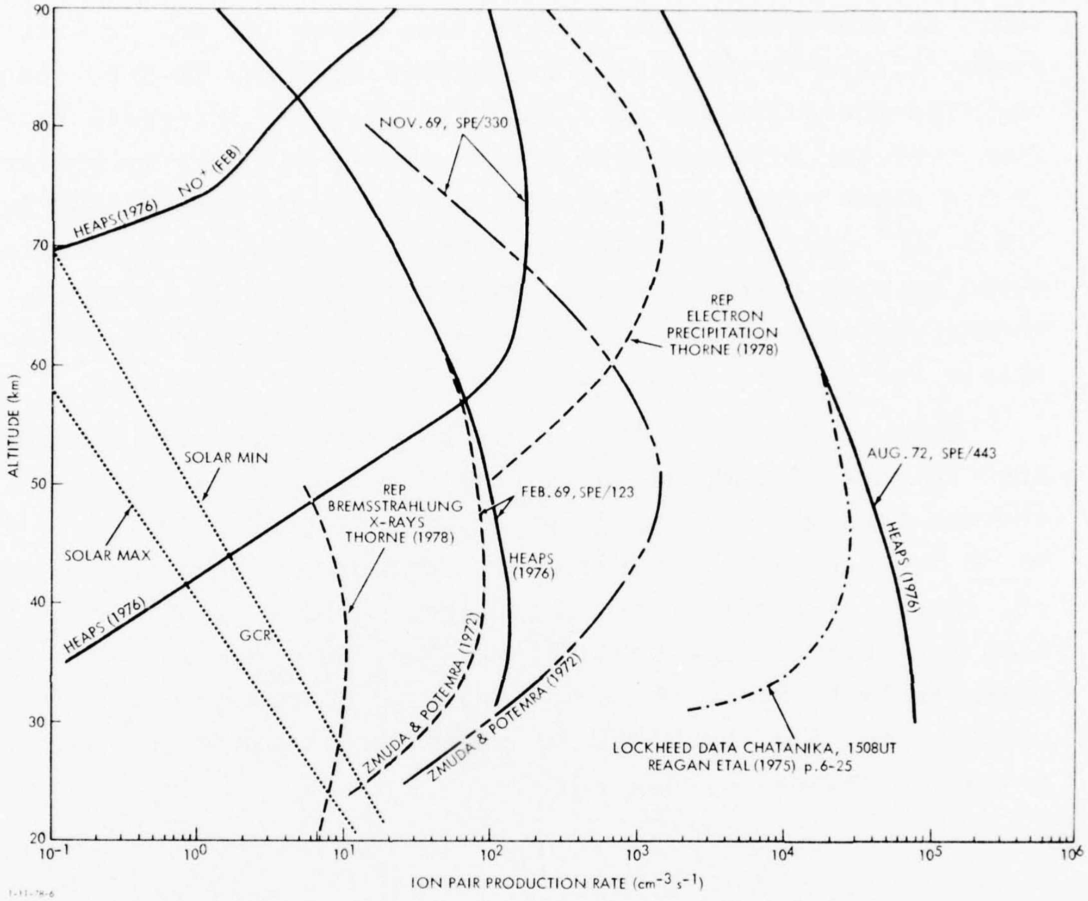


FIGURE EB-2. Ion production rates due to SPEs, and also those due to GCRs and REPs. Two different estimates are shown for each of the 3 SPEs listed to indicate the difference in ion production rate estimates made by different authors, which presumably gives a measure of the uncertainty in our quantitative understanding of the effect. (Note that the data of Heaps as listed do not extend below 30 km). The sources used are indicated on the figure.

From Fig. E-1 we see that for vertical incidence, protons of energy 20 MeV penetrate down to 54-km altitude, of energy 50 MeV down to 42 km, and of energy 100 MeV down to 32-km altitude. Thus, we arbitrarily ask for the flux above 100 MeV for the events listed in Table E-2; use Tables EB-4 and EB-5 to obtain the flux above 100 MeV as a function of time; integrate this flux over the time duration of the event; multiply by the area of the polar caps, here defined from curve C_1 of Fig. E-2 as 4.8×10^{17} cm^2; and obtain the total number of ion pairs produced by each event by multiplying by $10^8/35$ (i.e., average energy/proton = 100 MeV, average energy/ion pair = 35 eV) to obtain the results shown in Table E-3.

This is clearly a very crude procedure, and one can argue that in view of the transport considerations of Annex EA, all protons that get down to 35 to 38 km (i.e., of energies to 65 to 85 MeV) and which thus deposit most of their energy below 45 km, should be considered. The present choice makes some correction for oblique incidence and has the advantage that for the November 1960 events it is in very good agreement with Reid's calculation, and thus lends itself to the scaling procedure suggested in context of Table E-3.

TABLE EB-4. SOLAR PROTONS $(cm^2\text{-}sec)^{-1}$ OF ENERGY GREATER THAN 20 MeV AT VARIOUS TIMES FOLLOWING 17 SOLAR FLARES

	Time From Beginning of Flare, hr							
Date	3	12	24	48	72	96	120	144
2/23/56	10^3	5×10^3	10^3	10^3	2×10^2			
8/29/57	10^2	2×10^3	5×10^2	$< 1 \times 10^2$				
7/7/58	50	5×10^3	3×10^4	$< 3 \times 10^2$				
8/22/58	$< 1 \times 10^2$	3×10^3	2×10^3	5×10^2	1×10^2	< 10		
5/10/59	< 10	1×10^4	2×10^4	2×10^4	3×10^3	1×10^3	5×10^2	2×10^2
7/10/59	< 100	5×10^2	1×10^4	2×10^4	6×10^3	3×10^3	$< 10^3$	
7/14/59	$< 3 \times 10^3$	2×10^4	3×10^4	3×10^3	$< 10^3$			
7/16/59	5×10^3	5×10^4	1×10^4	1×10^3	3×10^2	1×10^2	30	
4/29/60	20	3×10^2	3×10^3	1×10^2	< 20			
5/4/60	5×10^2	50	50	< 30				
5/6/60	50	5×10^2	1×10^3	1×10^3	< 10			
9/3/60		1×10^2	2×10^2	2×10^2	50	∿ 20		
11/12/60	3×10^3	5×10^4	3×10^4	3×10^3	$< 10^3$			
11/15/60	3×10^3	2×10^4	3×10^4	2×10^3	1×10^3			
7/12/61	2×10^2	1×10^3	2×10^4	2×10^3	3×10^2	30	10	
7/18/61	5×10^2	3×10^3	2×10^3	5×10^2	2×10^2	50	20	10
9/28/61	2×10^2	3×10^2	2×10^2	2×10^3	20	10		

Source: Table reportedly compiled by H.W. Dodson; provided by E.W. Hones. For basic data, see Svestka and Simon (1975).

TABLE EB-5. CHARACTERISTIC RIGIDITY, $P_o(t)$, AND RATIOS OF PROTON FLUXES > 3 MeV, > 50 MeV, AND > 100 MeV, TO THAT > 20 MeV FOR VARIOUS TIMES IN AN "AVERAGE" SOLAR PROTON EVENT

Time After Beginning of Flare, hr	P_o, t	$\frac{Q(> 3\text{ MeV})}{Q(> 20\text{ MeV})}$	$\frac{Q(> 50\text{ MeV})}{Q(> 20\text{ MeV})}$	$\frac{Q(> 100\text{ MeV})}{Q(> 20\text{ MeV})}$
3	250	1.9	0.60	0.37
12	160	2.2	0.43	0.21
24	130	2.9	0.36	0.13
48	100	3.5	0.29	0.07
72	85	4.0	0.25	0.06
96	80	4.9	0.22	0.04
120	70	5.7	0.19	0.032
144	60	9.0	0.13	0.016

Source: Table reportedly compiled by H.W. Dodson; provided by E.W. Hones. For basic data, see Svestka and Simon (1975).

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APPENDIX F

CHANGES IN INDUSTRIAL AND AGRICULTURAL NITROGEN FIXATION, 1955 TO 1975

APPENDIX F

CHANGES IN INDUSTRIAL AND AGRICULTURAL NITROGEN FIXATION, 1955 TO 1975

F.1 INTRODUCTION

It was suggested by Crutzen (1974) and McElroy (1974) that the increased use of commercial nitrogen fertilizer, and also nitrogen fixation resulting from fossil fuel combustion, may lead to a reduction in stratospheric ozone. As the chemically fixed nitrogen (this means nitrogen present in molecules such as ammonia, amines, amino acids, etc., or nitrates, as distinct from the very stable and inert molecule N_2) is denitrified (i.e., as the compound breaks up to produce various end products, including in particular N_2), some fraction of the nitrogen appears as nitrous oxide N_2O, rather than as N_2. The fraction is normally in the range 5 to 20 percent, with 6 percent as a current best estimate--see CAST (1976).

The global cycle of atmospheric fixed nitrogen is not well known. Table F-1 lists various current estimates of sources of fixed nitrogen, but the sinks of nitrous oxide, which are by far the largest atmospheric components of fixed nitrogen, are not known. There may be a sink on the ground [see Brice et al. (1977)],* but there is no presently known sink of N_2O in the free troposphere.

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*Brice et al. (1977) find a diurnal variation in N_2O concentration at the ground in England, and from this infer a sink of N_2O. However, J.M. Bremner and A.M. Blackmer (see Denitrification Seminar, 1977) do not observe this diurnal variation near Ames, Iowa. See also Freney, Denmead and Simpson (1978) and Cicerone et al. (1978).

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A CATALOG OF PERTURBING INFLUENCES ON STRATOSPHERIC OZONE, 1955--ETC(U)
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TABLE F-1. SOURCES OF FIXED NITROGEN, ca 1975
[Units, 10^9 kg nitrogen = Mt(N)]

	CAST (1976)	Crutzen (1976)	McElroy et al. (1976)	Hahn and Junge (1977)	Liu et al. (1977)
Land Biological Fixation	149	> 175	170	180	200
Marine Biological Fixation	1	0.05-100	10	85	40
Fixation by Commercial Fertilizer	39 + 18	40	40	40	40
Fixation Due to Combustion, etc.	20	37	40	-	20
Fixation Due to Lightning	10	10	10	?	10
Net Fixation	237	> (260-360)	270	305	310

Note: Overall sinks are not understood. Thus, Hahn and Junge (1977) state that there is a discrepancy of 80 to 300 Mt(N)/yr.

The total stratospheric sink amounts to 13 Mt(N)/yr due to reactions (1) and (2) in the text.

CAST (1976) breaks up the "Land Biological Fixation" item as follows: agricultural items, legumes 35, nonlegumes 9, grassland 45, forest 50, unused land 10. The item "Fixation by Commercial Fertilizer" includes use as fertilizers 39, industrial uses 11, inefficiencies (losses) 7.

In the stratosphere, N_2O reacts with excited oxygen, $O(^1D)$ and is subject to photodissociation.*

$$N_2O + O(^1D) \begin{array}{l} \nearrow 2\ NO\ (\sim 50\%) \qquad (1a) \\ \searrow N_2 + O_2\ (\sim 50\%) \qquad (1b) \end{array}$$

$$N_2O + h\nu\ (\lambda < 230\ nm) \rightarrow N_2 + O(^1D) \qquad (2)$$

Reaction (1a) is the principal source of stratospheric NO. Roughly 80 percent of N_2O reaching the stratospheric is destroyed by reaction (2)--cf. Schmeltekopf et al. (1977).

It should be noted that NO formed in this way, by reaction (1a), is likely to be formed at relatively high altitudes ($\gtrsim 30$ km) because $O(^1D)$ is produced at high altitudes in the stratosphere and above by photodissociation of ozone (and of O_2) and is quenched somewhat by collision. Because of these relatively high altitudes of formation, the NO produced in this way will destroy ozone by the "well-known" catalytic cycle:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (3a)$$

$$\underline{NO_2 + O \rightarrow NO + O_2} \qquad (3b)$$

$$\text{net} \quad O + O_3 \rightarrow 2\ O_2 \qquad (3c)$$

There are, however, important interactions with the HO_x and ClX cycles, so that the net effect of N_2O injection on total ozone is uncertain--see Section F.3.

---

*The reaction $N_2O + O(^3P) \rightarrow N_2 + O_2$ has a temperature dependence $e^{-14000/T}$, i.e., is only significant at high temperatures such as in combustion, but not in the atmosphere.

After nitrogen is fixed, there is a delay time before the N_2O produced in denitrification actually affects stratospheric ozone. This time delay is the sum of three terms, namely, a time constant t_1 for denitrification, a time constant t_2 for transport and mixing in the troposphere, and t_3, a time constant for stratospheric photochemistry as a function of N_2O flux through the tropopause.

The denitrification time constant t_1 depends on how the material is used, and may range from a few months to many years (see Denitrification Seminar, 1977). Evidently, t_1 must be related to the time for recycling of CO_2 in plants, and here a representative estimate (Keeling, 1973, p. 307) is that two-thirds of agricultural fixed carbon is recycled in approximately one year, giving an effective recycling time for carbon of about 1.5 years.

Estimates for the tropospheric "turnover" time t_2 range from 5 to 200 years (cf. Johnston, 1977), but a current "best estimate" is 8 to 12 years (see, e.g., Hahn and Junge" 1977, and Goldan et al., 1978). Thus, even if the time constant t_3 for stratospheric photochemistry is short, there is still a significant delay between the time at which fixed nitrogen is produced or used at the ground, and the time when the N_2O resulting from denitrification can actually affect the stratosphere.

Anthropogenic nitrogen fixation comes from three principal sources, namely:

- Industrial nitrogen fixation, mainly as ammonia by Haber synthesis and also as ammonium salts formed as a by-product in coke production.
- Combustion, which leads to the production of oxides of nitrogen (NO, also NO_2)--essentially NO is formed in equilibrium when air is heated above 2000° K and then "freezes in," i.e., is not decomposed, as the air cools.
- The large-scale agricultural production of plants having nitrogen-fixing bacteria in their root systems,

principally legumes (cf. Evans and Barber, 1977) results in a significant amount of biological nitrogen fixation.

In each of these instances the nitrogen compound is either denitrified directly or else is taken up in plants (as proteins, amino acids, etc.) or in industrial products (such as nylon or other plastics); oxides of nitrogen formed by combustion are transformed into nitric acid, which is washed out of the atmosphere by rainfall and is, in turn, taken up in the biosphere.

Here we review time-dependent changes in anthropogenic nitrogen fixation during the 1955 to 1975 time frame (in Section F.2) in order to provide a basis for estimating the effect of the resulting N_2O on global ozone. However, the brief discussion in Section F.3 indicates that only a very small and somewhat uncertain change in total ozone could have occurred over the 1955 to 1975 time period.

F.2 CHANGES IN ANTHROPOGENIC NITROGEN FIXATION, 1955 to 1975

F.2.1 Industrial Nitrogen Fixation

Worldwide nitrogen production is shown in Table F-2, while Table F-3 shows nitrogen fertilizer production and consumption with a coarse indication of the latitude distribution of both production and consumption. Overall fixed nitrogen production has been rising at a very rapid rate--12 percent per annum from 1955 to 1970, or 10 percent per annum from 1955 to 1975.

The following points should be noted:

- In view of the long turnover time t_2 of N_2O in the troposphere, as compared to the time it takes for material to be distributed uniformly throughout the atmosphere (approximately 1 to 2 years), the latitude variation is unlikely to be significant.
- At this point, I am unable to recommend a unique value of t_1, the delay between the production of fixed nitrogen

TABLE F-2. WORLD ANNUAL INDUSTRIAL PRODUCTION OF FIXED NITROGEN, 1955 TO 1975*

Year Ending 30 June	Annual Fixed Nitrogen Production (10^9 kg nitrogen)
1950-1954 (avg)	5.40
1955	7.30
1956	8.07
1957	8.65
1958	9.49
1959	11.80
1960	12.87
1961	13.97
1962	14.81
1963	17.11
1964	19.39
1965	21.86
1966	24.49
1967	28.69
1968	32.14
1969	35.89
1970	38.78
1971	41.15
1972	43.00
1973	46.72
1974	48.44
1975	49.53

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*This is essentially all produced as ammonia, either by Haber (or other) synthesis, or as a by-product in coking plants. However, South American guano production is also included in the statistics. It was approximately 2 percent of global production in 1959 and tends to decrease both absolutely and relatively with time. Agricultural nitrogen fixation (e.g., in soybeans or alfalfa) is not included, nor is nitrogen fixation in combustion.

Source: U.S. Bureau of Mines, Minerals Yearbook--various years, data kindly provided by Dr. R.J. Foster

TABLE F-3. GLOBAL PRODUCTION AND CONSUMPTION OF FERTILIZER NITROGEN, 1953 TO 1974

	1953 to 1954	55/6	57/8	60/1	64/5	66/7	70/1	72/3	74/5
Global Production (10^9 kg N)	5.57	6.69	7.17	13.27	17.36	21.91	32.94	37.87	42.21
Latitude Distribution									
30° to 60° N	0.921	0.934	0.931	0.943	0.911	0.913	0.905	0.879	0.873
0° to 30° N	0.021	0.023	0.025	0.037	0.068	0.070	0.079	0.099	0.103
0° to 30° S	0.008	0.009	0.008	0.008	0.009	0.008	0.010	0.013	0.015
30° to 60° S	0.057	0.043	0.035	0.012	0.021	0.009	0.006	0.009	0.008
Global Consumption (10^9 kg N)	5.52	6.26	6.85	12.95	17.14	21.58	31.71	35.73	38.85
Latitude Distribution									
30° to 60° N	0.923	0.883	0.865	0.888	0.814	0.808	0.779	0.774	0.777
0° to 30° N	0.062	0.087	0.106	0.088	0.147	0.162	0.183	0.181	0.181
0° to 30° S	0.008	0.023	0.019	0.019	0.030	0.025	0.031	0.036	0.034
30° to 60° S	0.007	0.008	0.011	0.004	0.009	0.005	0.007	0.009	0.008

Source: U.S. Bureau of Mines, Minerals Yearbook. I wish to thank Dr. R.J. Foster for providing the information.

Note: Data from the U.S.S.R. and China are not included until 1960-1961.

Guano from Chile and Peru is included; its absolute as well as relative importance decreases monotonically with time.

The latitude assignment is somewhat arbitrary, as follows:

30° to 60° N	Canada, U.S.A., U.S.S.R., East and West Europe, Japan, Korea, Mideast (Turkey, Lebanon, Syria, Iraq, Iran, Israel), one-half China
0° to 30° N	One-half China; India (including Pakistan, Sri Lanka, Bangladesh); Southeast Asia (Burma, Thailand, Malaysia, Vietnam, Philippines); Mexico, Central America, Caribbean, Colombia, and Venezuela; North Africa (Egypt, Morocco, Algeria, Tunisia, Sudan)
0° to 30° S	Indonesia, Central and South Africa, Brazil, Peru, Ecuador
30° to 60° S	Australia, Argentina, Chile, Oceania

and the eventual appearance of N_2O. Putting $t_1 = 0$ gives an instantaneous response, which is certainly not correct, but provides an upper bound to the ozone changes.

- It is clear that most of the world's supply of anthropogenically fixed nitrogen is still both produced and consumed in the latitude range of 30 to 60° N, which represents the developed countries (see Table F-3).
- Note the discrepancy between global production figures in Table F-2 (which lists total fixed nitrogen, estimated by U.S. Bureau of Mines), and in Table F-3 (which lists only fixed nitrogen used in fertilizer, estimated by U.N. Agencies). In the U.S.A. (and to some extent in other developed countries), 25 percent of fixed nitrogen is used for applications other than as fertilizer (explosives, resins, fibers, plastics, and animal feeds), so that the figures in Table F-2 (which are larger than those of Table F-3) should be used.
- Note the discrepancy between production and consumption figures of Table F-3; the difference is due to stockpiling, possibly to diversion to nonfertilizer use, and possibly also due to errors in the figures.

F.2.2 The Combustion Source of Fixed Nitrogen

The four estimates for this quantity listed in Table F-1 range from 20 to 40 Mt(N)/yr,* with an arithmetic mean of 29 Mt(N)/yr. U.S. combustion emissions in 1975 are 2.2×10^{10} kg NO_2/yr, or 6.7 Mt(N)/yr (data kindly provided by C.O. Mann, U.S. EPA). Assuming that the U.S. represents 25 percent of worldwide use of fossil fuel, and presumably 25 percent of NO_x emissions, this corresponds to a global combustion source of 27 Mt(N)/yr, in excellent agreement with the above values. We shall use the 29 Mt(N)/yr value for 1975 as a recommended estimate.

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*1 Mt(N) = 10^6 metric tons of nitrogen, or 10^9 kg

The global production of fossil fuel has increased by a factor 2.7 between 1960 and 1971, corresponding to an annual growth rate of 5 percent (data from Perry and Landsberg, 1977); data from SCEP, 1970, p. 303, between 1950 and 1967 correspond to an annual growth rate of 4.5 percent. Assuming an annual growth rate of emissions of 5 percent, since these, presumably, track the worldwide use of fossil fuel, gives an estimated combustion source of 10.9 Mt(N)/yr in 1955.

F.2.3 Agricultural Source of Fixed Nitrogen*

During the 1955 to 1975 time frame, the total U.S. acreage of soybeans has almost tripled, from 19 to 54 million acres, or 7.7 to 22 million hectares. Assuming a median nitrogen fixation rate of 75 kg/hectare-year, this being the middle of the range 57 to 94 kg/hectare-year quoted by Evans and Barber (1977), leads to a change in biological nitrogen fixation resulting from this change of U.S. soybean production of 0.6 Mt(N) to 1.7 Mt(N)--numbers which are not insignificant, but still are less than 4 percent of industrial or combustion fixation taken separately.

Nitrogen fixation rates in kg/hectare-year are 57 to 94 for soybeans, and 128 to 600 for alfalfa, with other legumes generally lying between these limits (see Evans and Barber, 1977). The U.S. acreage of alfalfa has remained approximately constant, at 27 million, which would correspond to an annual rate of nitrogen fixation of (1.3 to 1.6 x 10^9 kg); the acreage of other clovers (timothy, lespedeza, etc.) has been declining slightly, and both the acreage and the nitrogen fixation is lower than those for soybeans and alfalfa. I do not have any statistics on non-U.S. acreage of these crops, but the U.S. is the biggest factor here.**

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* Dr. A.S. Newman (USDA) suggested this additional source, and Mr. Floyd Rolf (USDA) kindly provided the acreage figures.

** Chinese acreage of soybeans has not been changing rapidly, from 8 million hectares in 1970 to 9.2 in 1976. Brazil, the second largest exporter of soybeans (after the U.S.) had 6.4 million hectares planted in 1976, up from only 1.3 in 1970.

F.3 AN UPPER-BOUND ESTIMATE OF OZONE REDUCTION IN 1955 TO 1975 DUE TO TIME-DEPENDENT ANTHROPOGENIC NITROGEN FIXATION IN THIS TIME PERIOD

In 1975, a reasonable estimate of annual nitrogen fixation due to commercial fixed nitrogen production is 49.5 Mt(N) (see Table F-2), with an additional source of strength 29 Mt(N) due to combustion (see Section F.2.2). During the 1955 to 1975 time frame, the growth rate of commercial fixed nitrogen production was 10 percent per annum, while that of fossil fuel, and so presumably also of the combustion source, was 5 percent per annum.

Thus, in 1955, the nitrogen fixation due to commercial production was 7.4 Mt(N), and that due to combustion was 10.9 Mt (N). During the 20-year time period 1955 to 1975, the total nitrogen fixation due to commercial production was approximately 440 Mt(N) and that due to combustion was 370 Mt(N), or an increase in production of 450 Mt(N) over the rate of production at the initial (1955) rate.

In Table F-4 we list best-estimate nitrogen fixation rates during this time period, based on the present assumptions, to be inserted in numerical models.

TABLE F-4. ESTIMATE OF ANTHROPOGENIC NITROGEN FIXATION RATE, 1955 TO 1975 (units: Mt(N)/yr)

	1955	1960	1965	1970	1975
Commercial Production	7.4	11.9	19.1	30.7	49.5
Combustion	10.9	14.0	17.8	22.7	29.0
Total*	18.3	25.9	36.9	53.4	78.5

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*Effect of soybeans and other leguminous crops (see Section F.2.3) is not considered.

Let us now ask for the anthropogenic production of nitrous oxide due to this nitrogen fixation. Allowing for a denitrification factor of 6 percent (see CAST, 1976, p. 15), this being the fraction of fixed nitrogen that goes to make N_2O rather than

N_2 on denitrification, indicates an anthropogenic production of 49 Mt(N) as N_2O during this time period, of which 27 Mt(N) represents the increase over production at the 1955 rate, which we may call the time-varying part. This may be compared with a total atmospheric burden of nitrogen in N_2O of 1700 Mt(N) (see Hahn and Junge, 1977). Thus, assuming uniform mixing, the fraction of N_2O that is of anthropogenic and time-varying origin due to this 20-yr injection is 0.015.

Now the predicted effect on ozone due to a doubling of stratospheric N_2O is a decrease between 0 and 9 percent (see Crutzen and Howard, 1977).* If the change in ozone is a linear function of the change in N_2O, the predicted maximum decrease in ozone due to a 1.5 percent increase in N_2O is 0.14 percent.

These estimates represent an upper bound insofar as the times for denitrification, t_1, for mixing in the troposphere, t_2, and for formation of NO by reaction (F.1a), t_3, have all been ignored and also that none of the N_2O formed as a result of anthropogenic activity is lost to unknown sinks. In Section F.1 we see that $(t_1 + t_2) \sim 10$ yr, so that the predicted effects would occur with this delay, and correspondingly averaged out over a longer time and so even smaller.

F.4 CHANGES IN ATMOSPHERIC N_2O DURING THE 1955 TO 1975 TIME FRAME

If the effects on ozone of anthropogenic nitrogen fixation during the 1955 to 1975 time frame are to be significant, one would certainly expect to detect a change in atmospheric nitrous

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*Note, however, that at least some models using current (January 1978) chemistry predict that an increase in stratospheric N_2O will lead to an increase in stratospheric ozone (F. Luther, private communication to R.C. Oliver, January 1978). I have not seen published references showing this result. It is of interest also that, using CIAP (1974) chemistry, the predicted effect on ozone due to a doubling of stratospheric N_2O was a 19 percent decrease [see Vupputuri (1974)].

oxide. Pierotti and Rasmussen (1977) have reviewed the atmospheric measurements of N_2O between 1949 and 1976. While there are differences between different observers and between different methods of measurement, and while there has been no intercomparison of calibrations between the different experiments, there is no clear evidence of any long-term trend over the period as a whole.

The following points should be noted:

- Local measurements taken both in Germany and in Massachusetts over the period 1966 to 1968 show a definite increase of perhaps 20 percent over this 2 to 3 year period [see Schutz et al. (1970), Hahn and Junge (1977)], but no comparable effect is apparent in the rest of the data.
- H. Craig and R.F. Weiss [see report on GEOSECS, Science, 195, 166 (1977), also Denitrification Seminar (1977)] compared shipboard samples of N_2O taken at various times and find that the average concentration for equivalent sites in the Pacific had increased by 4 ppb/decade, or 0.15 percent per annum.
- Goldan et al. (1978), in reporting even more recent measurements, indicate that measurements of N_2O will be made on a continuing basis; from their careful measurements (which, however, only extend over a 6-month time frame), they are able to rule out changes in N_2O greater than 4 percent per annum.

In conclusion, it must be stressed that the present discussion is limited to the 1955 to 1975 time frame; it appears that current anthropogenic injections of fixed nitrogen are probably too small to have a detectable effect on stratospheric ozone, but this, clearly, could not continue to be the case indefinitely if nitrogen fixation rates continue to grow exponentially.

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