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NASA Technical Memorandum 58209

Revised Estimates for Ozone Reduction By Shuttle Operation

A. E. Potter
Lyndon B. Johnson Space Center

May 1978

NASA

National Aeronautics and
Space Administration

Lyndon B. Johnson Space Center
Houston, Texas

Revised Estimates for Ozone Reduction
By Shuttle Operations

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CONTENTS

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SUMMARY

The Space Shuttle is boosted into orbit by a rocket engine fueled
with liquid hydrogen and liquid oxygen and by two large solid-fuel rocket
motors. The exhaust products from the solid-fuel rocket motors include
chlorine species (hydrogen chloride and chlorine), which are released into
the stratosphere during launch. Chlorine compounds are catalysts for the
decomposition of stratospheric ozone. This relationship has led to a con-
cern that Shuttle launches could reduce stratospheric ozone concentrations.

The effects of Shuttle exhaust products on stratospheric ozone have
been assessed by use of theoretical models of the stratosphere. In 1976,
five different modeling groups assessed the effect of Shuttle operations
on the ozone layer. An estimate of 0.2-percent ozone reduction for the
Northern Hemisphere at 60 launches per year was consistent with all the
model predictions. Since these calculations were made, the accepted rate
constant for the reaction between hydroperoxyl and nitric oxide to yield
hydroxyl and nitrogen dioxide, $HO_2 + NO \rightarrow OH + NO_2$, was revised upward by
more than an order of magnitude, with a resultant increase in the pre-
dicted ozone reduction for chlorofluoromethane (CFM) by a factor of ap-
proximately 2. New calculations of the Shuttle effect have been made with
use of the new rate-constant data, again by five different modeling groups.
The new value of the Shuttle effect on the ozone layer was found to be
0.25 percent. The increase resulting from the revised rate constant is
considerably less for Space Shuttle operations than for chlorofluoromethane
production, because the new rate constant also increases the calculated rate
of downward transport of Shuttle exhaust products out of the stratosphere.

INTRODUCTION

The Space Shuttle is boosted into orbit by a rocket engine fueled
with liquid hydrogen and liquid oxygen and by two large solid-fuel rocket
motors. The exhaust products from the solid-fuel rocket motors include
chlorine species (hydrogen chloride (HCl) and chlorine (Cl_2)), which are
released into the stratosphere during launch.

Chlorine compounds are catalysts for the decomposition of stratu-
spheric ozone (O_3). This relationship has caused serious concern over the
effect of chlorofluoromethanes on stratospheric ozone. Current predic-
tions (ref. 1) are that the CFM's may eventually reduce the ozone layer
by 11 to 16 percent. The chlorine species released into the stratosphere
by the Shuttle are also expected to reduce the ozone concentration, but
to a very much smaller extent.

The appendixes to this document were provided by the various modeling
groups who conducted research on Shuttle ozone reduction with 1977 models.

The following list specifies the author or authors of each appendix, together with their affiliations and the report date.

Appendix A - Richard S. Stolarski and Dixon M. Butler, NASA Goddard Space Flight Center (November 2, 1977)

Appendix B - John E. Nealy, NASA Langley Research Center (December 15, 1977)

Appendix C - R. C. Whitten and I. G. Poppoff, NASA Ames Research Center (February 14, 1978)

Appendix D - Donald J. Wuebbles, Lawrence Livermore Laboratory, University of California (December 13, 1977)

Appendix E - T. M. Donahue, R. Cicerone, and S. Liu, Space Physics Research Laboratory, University of Michigan (March 1, 1978)

INITIAL EVALUATION OF THE SPACE SHUTTLE EFFECT ON THE OZONE LAYER

The Space Shuttle effect on the stratospheric ozone layer was first evaluated in 1976 by using the stratospheric models available at that time (ref. 2). Five different modeling groups were asked to compute the effect of the Space Shuttle on the assumption of a launch rate of 60 flights per year. The results are shown in table I.

TABLE I.- PREDICTED OZONE REDUCTION FOR 60 SPACE SHUTTLE LAUNCHES PER YEAR (1976 MODELS)

Modeling group	Ozone reduction (hemispheric average), percent
NASA Ames Research Center	0.11
NASA Lyndon B. Johnson Space Center (JSC)	.2
Lawrence Livermore Laboratory, University of California	.26
Space Physics Research Laboratory, University of Michigan	.29
Harvard University	.2

A later calculation by a National Academy of Sciences committee provided a value of 0.15 percent (ref. 3).

The uncertainty of these predictions arises from two sources: systematic and random errors. Systematic errors can arise from the omission of an important reaction or from the use of reaction rates that are incorrect because of improper measurement techniques. These errors cannot be evaluated by statistical methods. Random errors, as represented by the experimental scatter in measured values of a reaction rate, can be evaluated statistically. Initial estimates of the random error of these model predictions resulted in an uncertainty factor of 3, high or low, at a 95-percent confidence level (ref. 2). All the model predictions are well within this range of uncertainty.

A value of 0.2 percent was chosen as the nominal value for the effect of the Shuttle on the ozone layer, on the basis of the 1976 model predictions and the range of uncertainty in the predictions.

In 1977, a systematic error was discovered. The rate of the reaction between hydroperoxyl and nitric oxide to yield hydroxyl and nitrogen dioxide, $HO_2 + NO \rightarrow OH + NO_2$, was actually 20 times faster than previously supposed because of incorrect measurement techniques used earlier (ref. 1, p. 17). This reaction is important in stratospheric chemistry because it affects the concentration of catalytically active chlorine by the reaction between hydroxyl and hydrogen chloride to yield water and atomic chlorine, $OH + HCl \rightarrow H_2O + Cl$.

The predicted ozone reduction produced by CFM's is almost doubled by this changed reaction rate (ref. 1). It is to be expected that the predicted Shuttle effect on the ozone layer will also be increased, perhaps by as much as a factor of 2.

REEVALUATION OF THE SPACE SHUTTLE EFFECT ON THE OZONE LAYER

To evaluate the effect of the new reaction rate, the same modeling groups were asked to repeat their calculations. However, in the period since the first calculations were performed in 1976, the JSC group had transferred to the Goddard Space Flight Center, the Harvard University group had moved to the National Oceanic and Atmospheric Administration and were unavailable for this calculation, and a new modeling group had appeared at the NASA Langley Research Center. A listing of the groups and the names of the individuals involved in the reevaluation follows.

Modeling group	Responsible individuals
NASA Ames Research Center	I. G. Poppoff and R. C. Whitten
NASA Goddard Space Flight Center	R. S. Stolarski and D. M. Butler
NASA Langley Research Center	J. E. Nealy
Lawrence Livermore Laboratory, University of California	D. J. Wuebbles
Space Physics Research Laboratory, University of Michigan	T. M. Donahue, R. Cicerone, and S. Liu

These groups all recalculated the effect of the Space Shuttle on the ozone layer, using the new reaction rate for $HO_2 + NO \cdot OH + NO_2$.

The new reaction rate affected not only the chemistry of the stratosphere but also the transport coefficients used to calculate the rate of loss of exhaust products from the stratosphere. This unexpected effect arises from the fact that vertical-transport coefficients are calculated from the vertical-concentration profiles of methane, which is produced in the troposphere and transported upward into the stratosphere, where it is destroyed by chemical reaction. The most significant stratospheric loss process for methane is oxidation by OH. Because the new reaction rate leads to an increased concentration of OH in the stratosphere, the stratospheric loss rate for methane must be revised upward to maintain methane concentrations at their observed values. This revision results in an increase of the vertical-transport coefficients.

The results of the model calculations by each of the five groups are summarized in table II.

Each modeling group prepared a brief report outlining its procedures and conclusions relative to Shuttle ozone reduction. All these are reproduced in their entirety in appendixes A to E of this report.

The hemispheric-average value from the NASA Ames Research Center group was estimated from its recent two-dimensional calculations, which gave the global distribution of ozone reduction. This group found that the hemispheric-average assumption overestimated the Northern Hemispheric effects and underestimated the Southern Hemispheric effects. A global average, whereby the ozone reduction occurs uniformly over the entire world rather than only in the Northern Hemisphere, was a much better fit to these results.

TABLE II.- PREDICTED OZONE REDUCTION FOR 60 SPACE SHUTTLE LAUNCHES
PER YEAR (1977 MODELS)

Modeling group	Ozone reduction (hemispheric average), percent
NASA Ames Research Center	[a]0.28
NASA Goddard Space Flight Center	.26
NASA Langley Research Center	.24
Lawrence Livermore Laboratory, University of California	.27
Space Physics Research Laboratory, University of Michigan	.23

[a]Estimated for hemispheric average from a two-dimensional global prediction.

Because calculations are still preliminary, it was thought best to retain for now the original hemispheric-average assumption. However, it may prove necessary in the future to revise downward the predicted Shuttle effect, perhaps by as much as a factor of 2, if the validity of using a global-average effect instead of a hemispheric average is verified.

As discussed previously, the uncertainty of the prediction can be attributed to two possible types of error: systematic and random. The extent of the former depends on the correctness of the model formulation and is impossible to estimate quantitatively at this time. The ongoing national stratospheric research program is designed to establish the general validity of the models. The random errors are, however, susceptible to statistical analysis. The most recent results of this type of analysis specify the uncertainty at approximately a factor of 1.8 on the high side and 2.9 on the low side for a 95-percent confidence level (ref. 1).

SUMMARY OF RESULTS

The predicted ozone reduction values shown in the reevaluation section display a considerable degree of unanimity. A reasonable average or nominal value that represents all the model results well within the random uncertainty limits is 0.25 percent.

The predicted ozone reduction increased from its 1976 value of 0.2 percent to a new value of 0.25 percent with the new reaction rate. An increase by a factor of 2 might have been expected as a result of the chlorofluoromethane case, in which the effect of the new reaction rate was an approximate doubling of the percentage of ozone reduction. However, the increased transport coefficients resulting from the new reaction rate caused a reduction of the amount of Shuttle-exhaust chlorine retained by the stratosphere. This reduction partly compensated for the larger quantity of catalytically active chlorine resulting from the new reaction rate.

Lyndon B. Johnson Space Center
  National Aeronautics and Space Administration
    Houston, Texas, April 28, 1978
      383-85-00-00-72

APPENDIX A

CURRENT ASSESSMENT OF SHUTTLE OZONE DEPLETION

ON THE GODDARD SPACE FLIGHT CENTER (GSFC) ONE-DIMENSIONAL MODEL

Richard S. Stolarski and Dixon M. Butler
NASA Goddard Space Flight Center

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APPENDIX A

A reassessment of the Shu tle-ozone-depletion calculation has been run on the GSFC one-dimensiona. model. For the Dickinson-Chang eddy coefficient (curve B in fig. 10 of the CFM Workshop report, ref. 1) and the Shuttle source function listed below, a steady-state chlorine species (ClX)[1] content averaged over a hemisphere has been obtained that asymptotes to 0.084 part per billion by volume (ppbv) above approximately 40 kilometers. The source function was as follows.

Altitude band, kilometers	HCl source, molecules per cubic centimeter per second
12 to 14	0.610
14 to 16	.616
16 to 18	.542
18 to 20	.469
20 to 22	.443
22 to 24	.417
24 to 26	.378
26 to 28	.362
28 to 30	.348
30 to 32	.307
32 to 34	.253
34 to 36	.234
36 to 38	.193
38 to 40	.141
40 to 42	.094
42 to 44	.069
44 and upward	0

---

[1]ClX represent various chlorine species, collectively, including chlorine (Cl) and combinations of chlorine with other atoms or groups of atoms (such as hypoch rite (ClO), HCl, chlorine nitrate ($ClNO_3$)).

The efficiency of ClX for small depletions of the ozone column is 3.1 percent per 1 ppbv added ClX for the current chemistry (ref. 1). Thus, a value is obtained for the hemispherically averaged column ozone depletion - for 60 launches per year carried on indefinitely - of (0.084 ppbv) x (3.1 percent/ppbv) = 0.26 percent.

The Monte Carlo uncertainty model has also been run for a small perturbation in an attempt to assess the precision with which numbers can be quoted for ozone depletion. This procedure includes only uncertainties due to rate constants as evaluated in the CFM report (ref. 1). The runs were made with 1 ppbv added ClX. Smaller values could have been used, but because the range involved was linear, it was believed that the results would accurately project down to the ClX amounts for the Shuttle. The imprecisions found were all larger than those corresponding to the much larger CFM injections. The results on the high side of the central value were a factor of 1.45 for 1 sigma and 2.09 for 2 sigma. On the low side, factors of 1.80 for 1 sigma and 3.23 for 2 sigma were found. The asymmetries found for the CFM case remained and are thus due to saturation of the atmosphere in chlorine. Applying these factors to the central value of 0.26 percent yields a 1-sigma range of 0.14 to 0.38 percent and a 2-sigma range of 0.08 to 0.54 percent.

The end results for depletion of the ozone column are not much different from those in the Shuttle Workshop report (ref. 2) because of nearly cancelling changes. The efficiency of ClX for ozone depletion has approximately doubled, whereas the eddy coefficients used have increased, a change leading to less chlorine in the steady state. Thus, the Shuttle depletion has remained approximately the same, whereas the CFM depletion has doubled because it is relatively insensitive to the eddy coefficient.

APPENDIX B

RESULTS OF CALCULATIONS CONCERNING SPACE SHUTTLE EXHAUST

IN THE STRATOSPHERE

John E. Nealy
NASA Langley Research Center

1. The source of HCl used in the injection case was as follows.

Altitude, kilometers	HCl source, particles per cubic centimeter per second
15	0.464
20	.406
30	.307
35	.206
40	.157
43	0

This source function was used for altitudes (Z) in the following range: $13 \leq Z \leq 43$ kilometers. The coefficient and reaction rates were as recommended in reference 1. The model used for these calculations was one in which the stratospheric temperatures and local chemical reaction rates were coupled. The solar zenith angle was assumed to be constant at $45°$.

2. The percentage of ozone reduction was found to be 0.245 percent. Details are as follows.

Constituent	Ambient	Injection
O_3 column sum, molecules per square centimeter	1.1300E+19	1.1273E+19
$\Delta O_3/O_3$, percent	_____	-.245
O_3 at 46 kilometers, molecules per cubic centimeter	1.1695E+11	1.1660E+11
[2]Clx at 40 kilometers, ppbv	.807	.881
Clx at 46 kilometers, ppbv	.833	.907
$(\Delta O_3/O_3)/\Delta$Clx at 50 kilometers, percent per ppbv	_____	3
ClO at 34 kilometers, ppbv	.032	.329
$ClNO_3$ at 25 kilometers, ppbv	.215	.230
$ClNO_3$ at 31 kilometers, ppbv	.267	.288

---

[2]Elemental chlorine, with "x" designating a variable number of atoms that may comprise the species.

Constituent	Ambient	Injection
Oxides of nitrogen (NO_x) at 34 kilometers, ppbv	13.25	13.24
NO_x at 49 kilometers, ppbv	10.09	10.06
Nitrous oxide (N_2O) at 31 kilometers, ppbv	76.82	76.51
OH at 31 kilometers, radicals per cubic centimeter	5.85E+06	5.87E+06
OH at 40 kilometers, radicals per cubic centimeter	2.99E+07	2.99E+07

3. The calculations were iterated until species concentrations were constant to within 0.0001 and until temperatures were constant to within 0.1 K. The noise in the value of $\Delta O_3/O_3$ resulting from these calculations was estimated to be ± 0.03.

APPENDIX C

SPACE SHUTTLE ASSESSMENT - STRATOSPHERIC EFFECTS

R. C. Whitten and I. G. Poppoff
NASA Ames Research Center

APPENDIX C

The Ames two-dimensional (2-D) photochemical stratospheric model has recently been employed to reassess the ozone degradation by Space Shuttle launch vehicle emissions because of some important advances in connection with the photochemistry of stratospheric minor constituents. These new developments were (1) the discovery that chlorine nitrate can be an important reservoir for stratospheric active chlorine and odd nitrogen and (2) the measurement of a large rate coefficient, $(8.1 \pm 1.5) \times 10^{-12}$ cm^3/sec, for the important reaction (ref. 4)

$$NO + HO_2 \rightarrow NO_2 + OH \tag{C-1}$$

The large rate coefficient for reaction (C-1) leads to larger predicted OH concentrations - and thus to more active chlorine in the form of ClO and Cl - and to a somewhat reduced importance of chlorine nitrate to the odd-oxygen photochemistry. The net result is an increase by a factor of approximately 2 in the estimated efficiency of ozone destruction by active chlorine. In the calculations reported here, use was made of the chemical rate coefficients recommended in the NASA chlorofluoromethane report (ref. 1), a set of transport parameters very similar to those presented in a recent report by Whitten et al. (ref. 5), and the HCl deposition rates for Space Shuttle launch vehicles presented by Bowyer (ref. 6).

Figure C-1 shows the buildup of the globally averaged ozone decrease as computed with the Ames 2-D model (curve A) and with a one-dimensional (1-D) model (curve B) in which the Dickinson-Chang diffusion profile was used (see the solid curve in fig. 18 of ref. 1). There are two notable features in the curves. First, the buildup predicted by the 1-D model is more rapid than that predicted by the 2-D model because of slower effective vertical transport in the latter model. At the end of 10 years, the buildup predicted by the 2-D model just begins to level out, whereas the ozone decrease predicted by the 1-D model begins to level out at the end of approximately 7 years. The 1-D model has also been employed to determine the time constant for recovery of the ozone layer to normal if Space Shuttle operations should cease; it proved to be approximately 3 years. A similar time constant calculation has not yet been made with the 2-D model; but on the basis of the buildup curves shown in figure C-1, it is estimated to be approximately 4.5 years. These values differ from those reported in the earlier assessment report; the change is attributed in part to the increased importance of active chlorine at altitudes below 25 kilometers, where vertical transport is slower, and in part to the use of the Chang-Dickinson eddy diffusivity (ref. 3). Secondly, figure D-17 of the original assessment report shows a marked seasonal variation that is not present in curve A; this point is discussed further in subsequent paragraphs.

Figures C-2 and C-3 show the ozone column reduction as a function of latitude for the four seasons during the 10th and 30th years, respectively, of Space Shuttle operations. Note the absence of a strong "corridor effect" at 30° N latitude in the summer, the presence of which was suggested in

figure D-16 of the original report. Again, the change in assessment is attributed to the greatly increased importance of relatively low-altitude active chlorine. Also note that the summer and fall hemispheric asymmetry has been greatly reduced. In fact, the strongest asymmetry is now predicted for winter rather than spring.

The ozone perturbation has been studied with the aid of a simple photochemical-equilibrium analysis to obtain further insight into the physics of the ozone perturbation. Here, the ozone concentration perturbation $\delta(O_3)$ is expressed in the form.

$$\delta(O_3) = \frac{\delta P - (O_3)\delta L}{L} \tag{C-2}$$

where the "δ" operator means "take the difference between ambient and perturbed values," P is the odd-oxygen-volume production rate,

$$P = 2J_1(O_2) + J_2(NO_2) + J_4(ClO) \tag{C-3}$$

and L is the odd-oxygen loss rate,

$$L = 2k_2(O) + k_4(NO) + k_5(OH) + k_8(Cl)$$

$$+ \left(\frac{J_3}{k_1(M)(O_2)}\right)\left(k_3(NO_2) + k_6(OH) + k_7(HO_2) + k_9(ClO)\right) \tag{C-4}$$

where O is atomic oxygen, O_2 is molecular oxygen, and M represents another molecule. The chemical reaction rate coefficients k_i and the photodissociation rates J_i are given in table C-I, and the species concentrations (X_i) are obtained from the 2-D model calculations. It is important to include in L all the terms shown in equations (C-1) and (C-2) if one is to obtain good quantitative agreement between the "photochemical equilibrium" values of $\delta(O_3)$ calculated by means of equation (C-2) and the values obtained from the model calculations. Attempts to compute $\delta(O_3)$ with a simpler form of δL

$$\delta L \sim k_9(ClO)(O) \tag{C-5}$$

did not yield satisfactory results below a 40-kilometer altitude. Furthermore, seasonal and latitudinal variations of $\delta(O_3)$ are due as much to the variations in L as to the variations in (Cl) and (ClO).

The close agreement of the model calculation of $\delta(O_3)$ with that obtained with the aid of equation (C-2) (see figs. C-4 and C-5) provides

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added confidence in the computations because it graphically demonstrates the close correlation between the distributions of minor species used in equation (C-2) and the local change in ozone concentration. Further, the good agreement existing between the calculated minor-species distributions and the distributions, both observed and calculated, obtained by other investigators serves to validate the ambient model (see ref. 7). Although the simple approach of equation (C-2) appears to be surprisingly good, one must remember that use of the 2-D model was necessary to predict the active-chlorine distribution and the distribution of the important minor species.

It has been proposed by Hofmann et al. (ref. 8) that the numerous small aluminum oxide particles emitted by Space Shuttle launch vehicle motors might act as seeds from which many new large particles could be grown in a supersaturated stratosphere, enough to significantly alter the optical properties of the aerosol layer. The Ames 1-D model of the stratospheric sulfate aerosol layer (ref. 9) has been used to make pertinent estimates of the corresponding aerosol layer change. With use of the estimated aluminum oxide particle size distributions and emission rates for the launch motors and on the assumption of 60 launches per year, a hemispherically and time averaged particle injection rate has been calculated as a function of height. With this injection rate, a prediction has been made of the large-particle mixing ratios shown in figure C-6 for steady-state conditions. (The result is also shown for 10 times the injection rate.) Note that it is the large particles that affect the planetary albedo and the climate. The effect of 60 launches per year on the aerosol layer is clearly small. Toon and Pollack (ref. 10) estimate the corresponding atmospheric temperature change to be less than 273.16 K (0.01° C).

TABLE C-I.- RATE COEFFICIENTS[a] USED IN EQUATION (C-2)

Reaction no.	Reaction	Value[b]
R1	$O + O_2 + M \rightarrow O_3 + M$	$1.1 \times 10^{-34} e^{520/T}$[c]
R2	$O + O_3 \rightarrow 2O_2$	$1.9 \times 10^{-11} e^{-2300/T}$
R3	$O + NO_2 \rightarrow NO + O_2$	9.1×10^{-12}
R4	$O_3 + NO \rightarrow NO_2 + O_2$	$2.1 \times 10^{-12} e^{-1450/T}$
R5	$O_3 + OH \rightarrow HO_2 + O_2$	$1.5 \times 10^{-12} e^{-1000/T}$
R6	$O + OH \rightarrow H^d + O_2$	4.2×10^{-11}
R7	$HO_2 + O \rightarrow OH + O_2$	3.5×10^{-11}
R8	$Cl + O_3 \rightarrow ClO + O_2$	$2.7 \times 10^{-11} e^{-257/T}$
R9	$ClO + O \rightarrow Cl + O_2$	$7.7 \times 10^{-11} e^{-130/T}$
J1	$O_2 + h\nu^e \rightarrow O + O$	5.9×10^{-8}; (f)
J2	$NO_2 + h\nu \rightarrow NO + O$	6.4×10^{-3}; (f)
J3	$O_3 + h\nu \rightarrow O + O_2$	5.5×10^{-3}; (f)
J4	$ClO + h\nu \rightarrow Cl + O$	4.5×10^{-3}; (f)

[a]Taken from reference 1.
[b]In units of sec^{-1} for unimolecular processes, $cm^3 sec^{-1}$ for bimolecular processes, and $cm^6 sec^{-1}$ for termolecular processes.
[c]T = temperature, K.
[d]H = atomic hydrogen.
[e]$h\nu$ = solar ultraviolet radiation.
[f]At zero optical depth.

A 2-D MODEL
B 1-D MODEL

OZONE COLUMN REDUCTION, percent

.1

.05

B

A

LAUNCHES PER YEAR

60

50

40

30

20

10

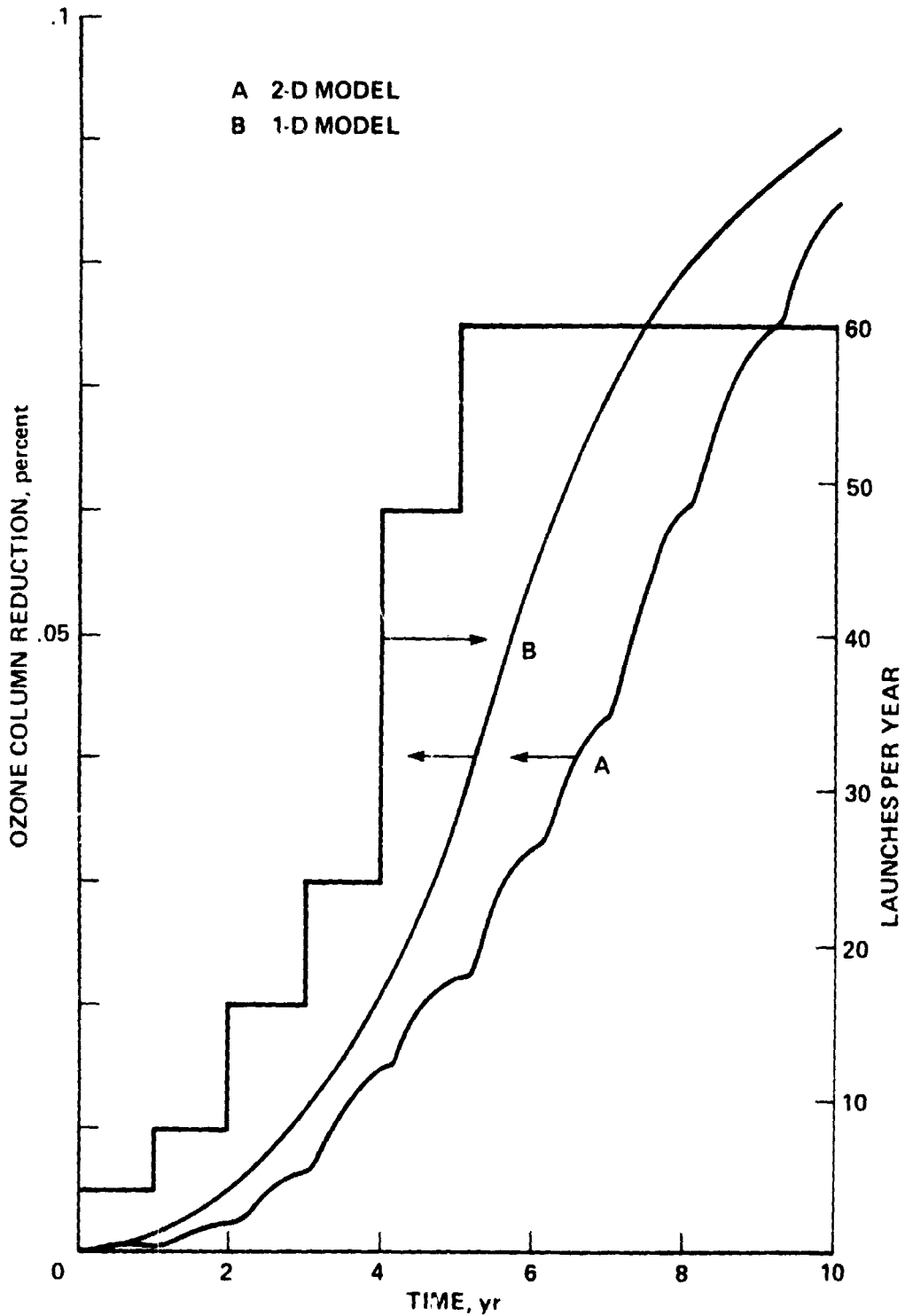0   2   4   6   8   10

TIME, yr

Figure C-1.- Time dependence of the globally averaged ozone reduction.
Curve A - Ames 2-D model; curve B - an Ames 1-D model (the 1-D predicted
ozone reduction after 20 years was approximately 0.11 percent). Also
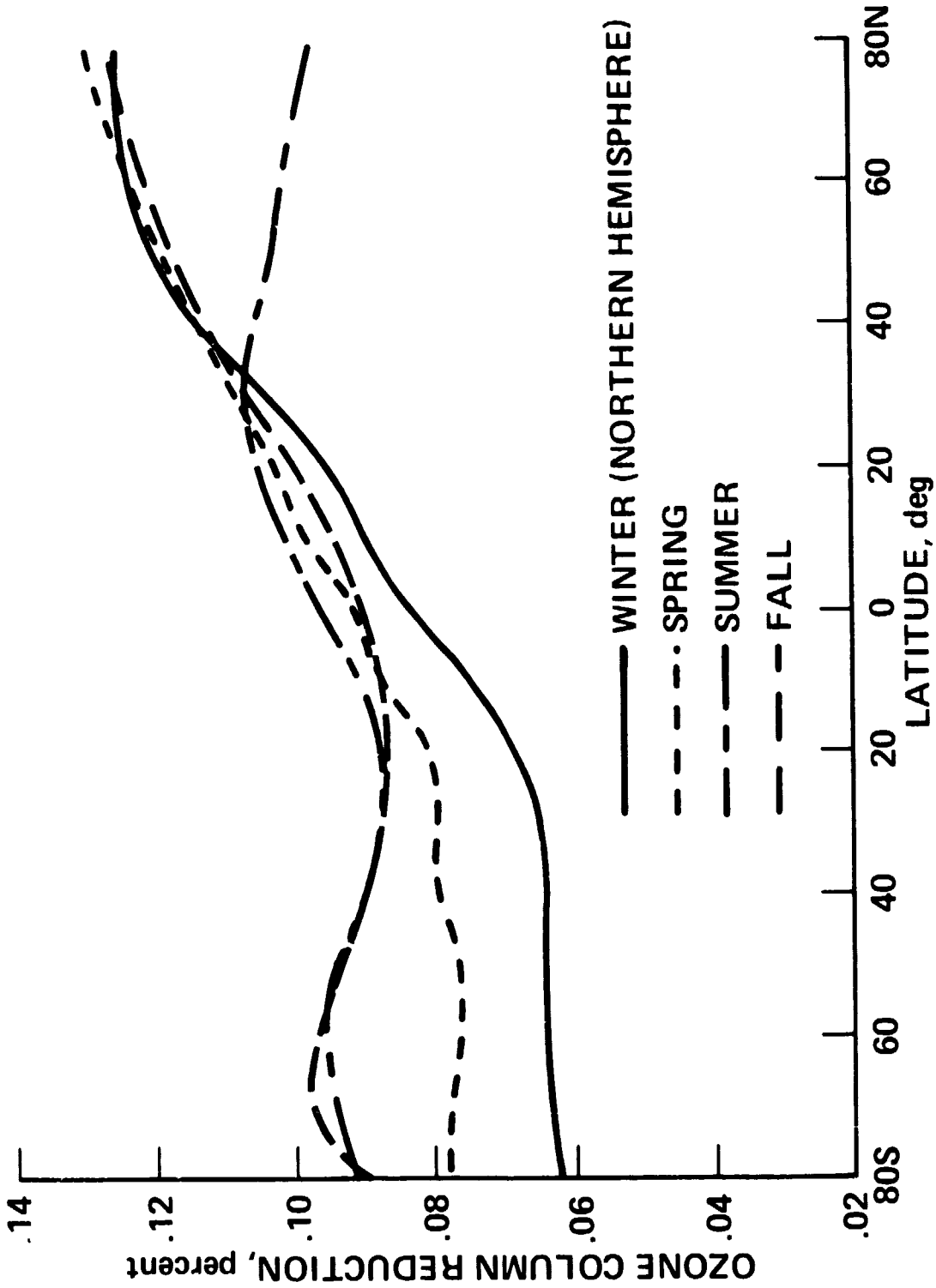shown is a candidate Space Shuttle launch schedule.

Figure C-2.- Computed relative ozone column reduction as a function of latitude during the 10th year of Space Shuttle operations, with use of the Ames 2-D model.
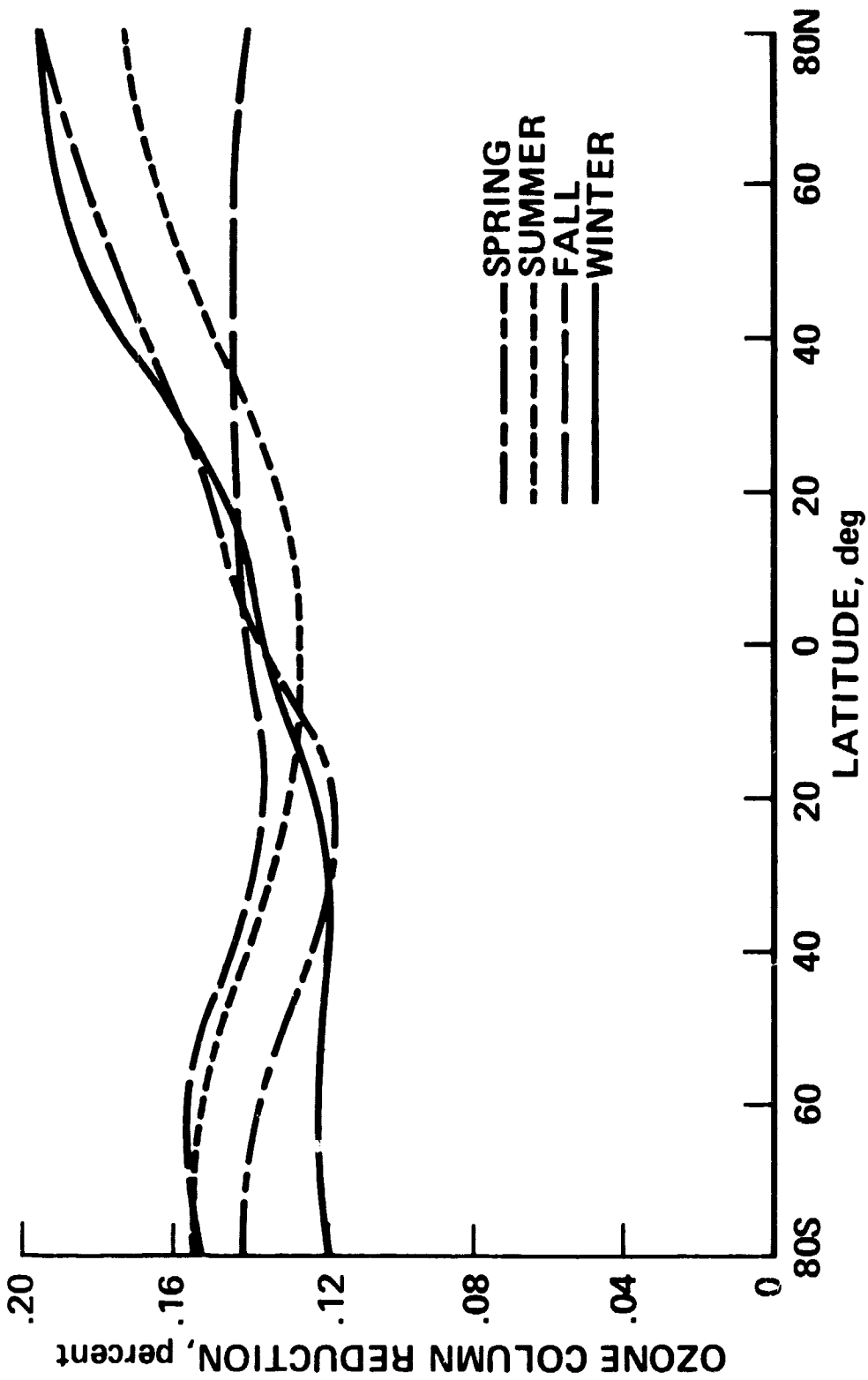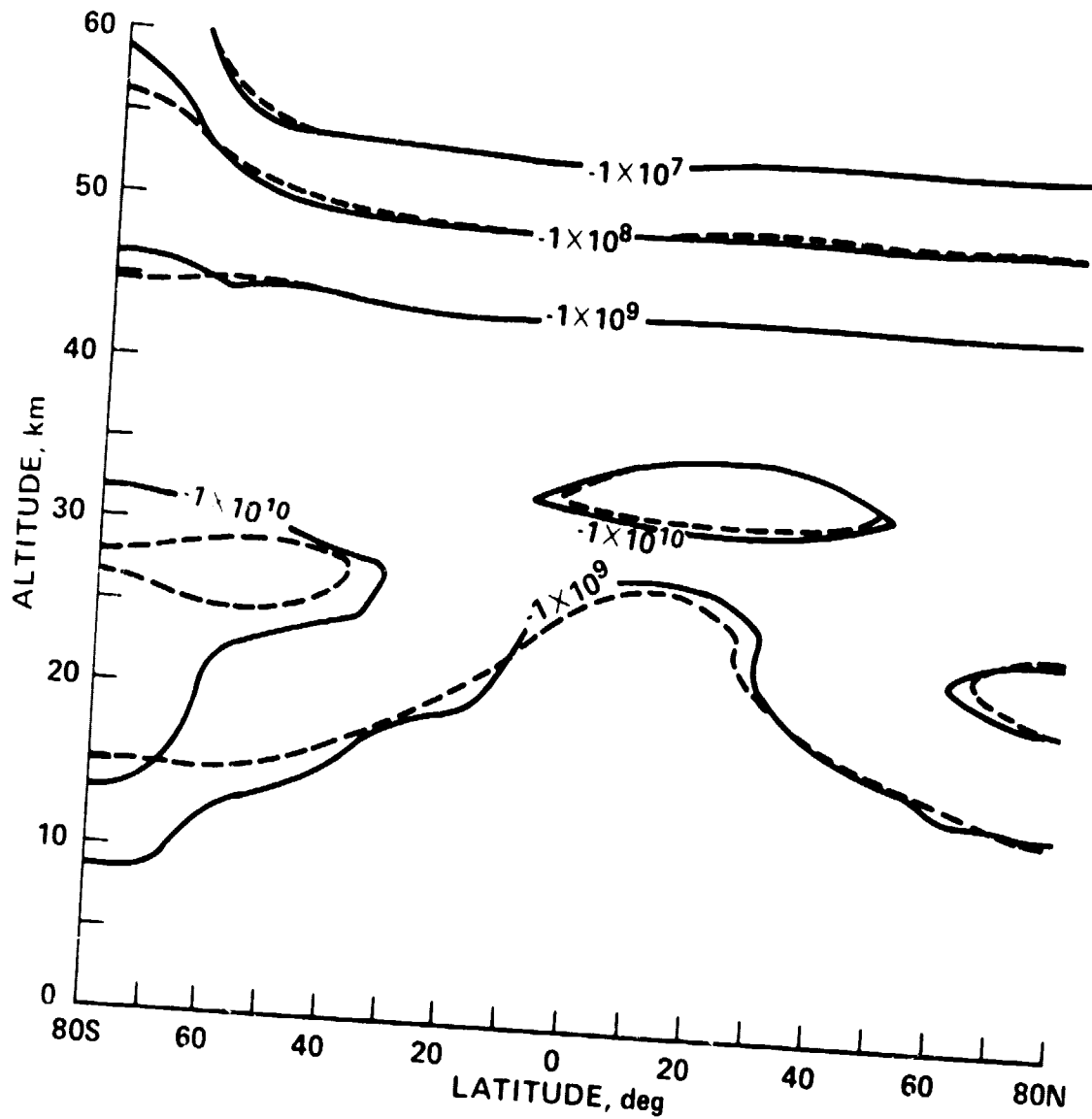
Figure C-3.– Computed relative ozone column reduction as a function of latitude during the 30th year of Space Shuttle operations, with use of the Ames 2-D model.
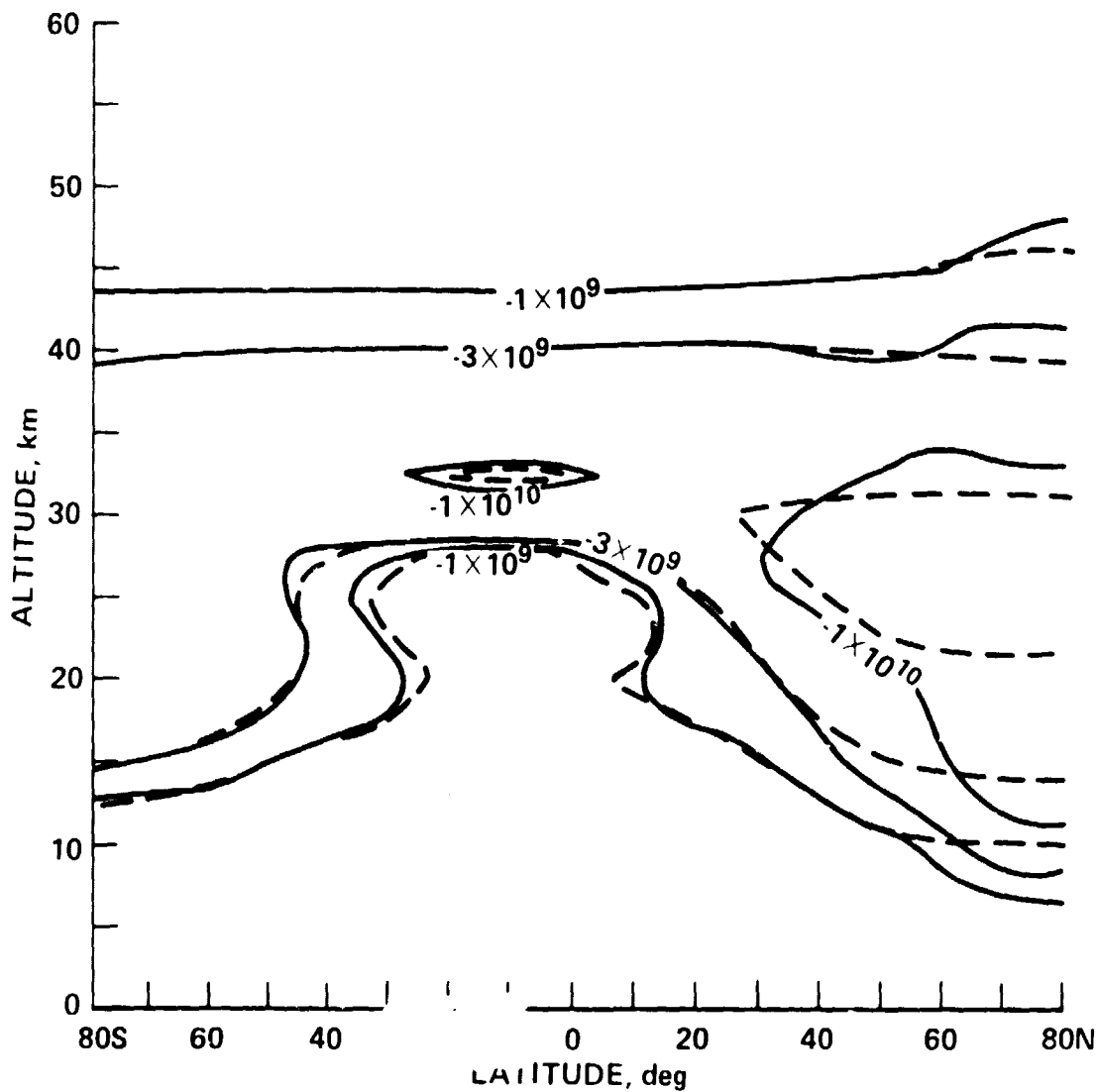
(a) Winter in the Northern Hemisphere.

Figure C-4.- Isopleths of local ozone concentration change after 30 years of Space Shuttle operations. The broken curves represent results obtained from the full model calculation; the solid curves represent results obtained by using the simple approach of equation (C-2).

(b) Summer in the Northern Hemisphere.
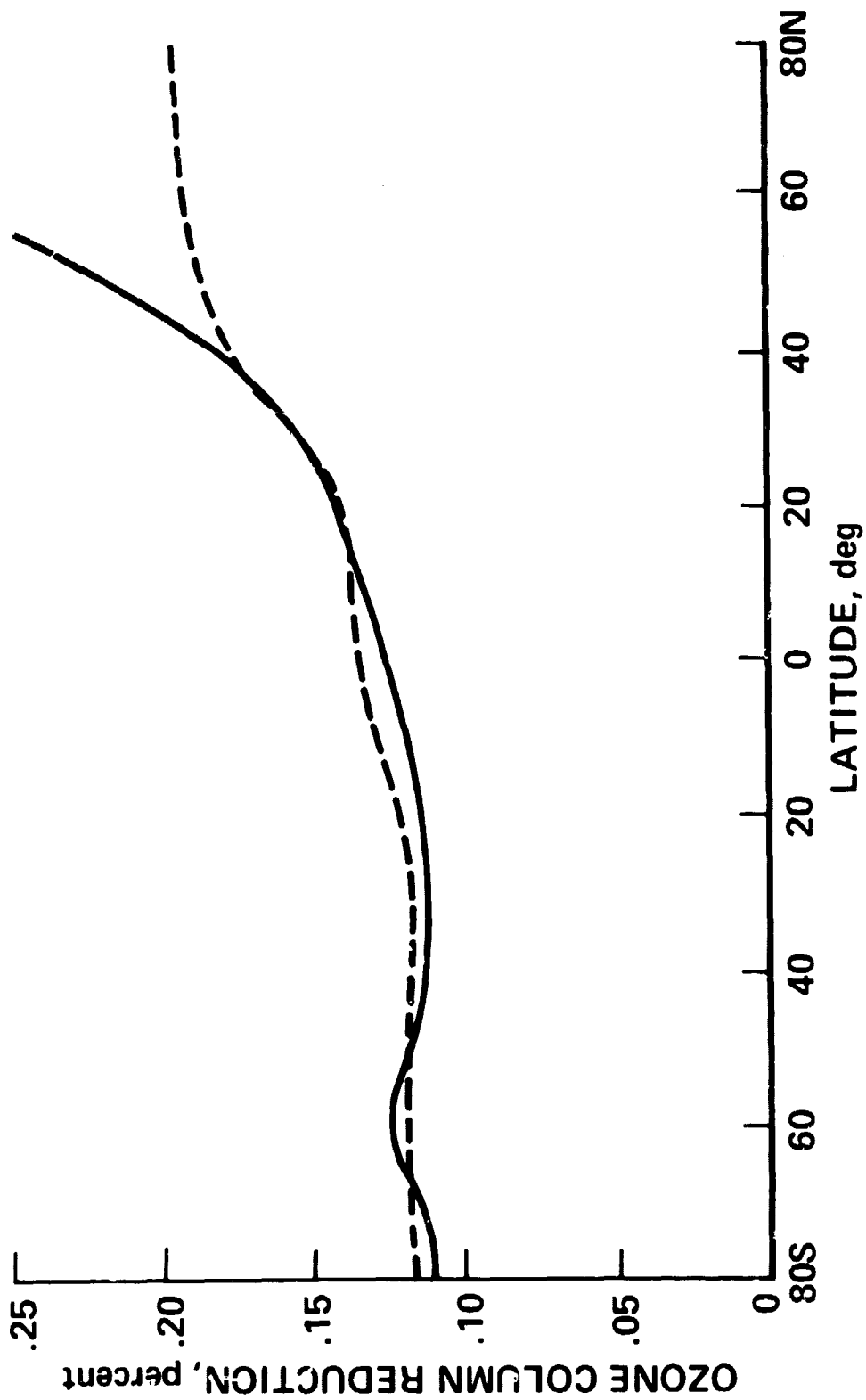
Figure C-4.- Concluded.

Fig. C-5. - Computed ozone column reduction for winter in the Northern hemisphere. The broken line represents the full model calculation; the solid line represents the results obtained with equation (C-2).
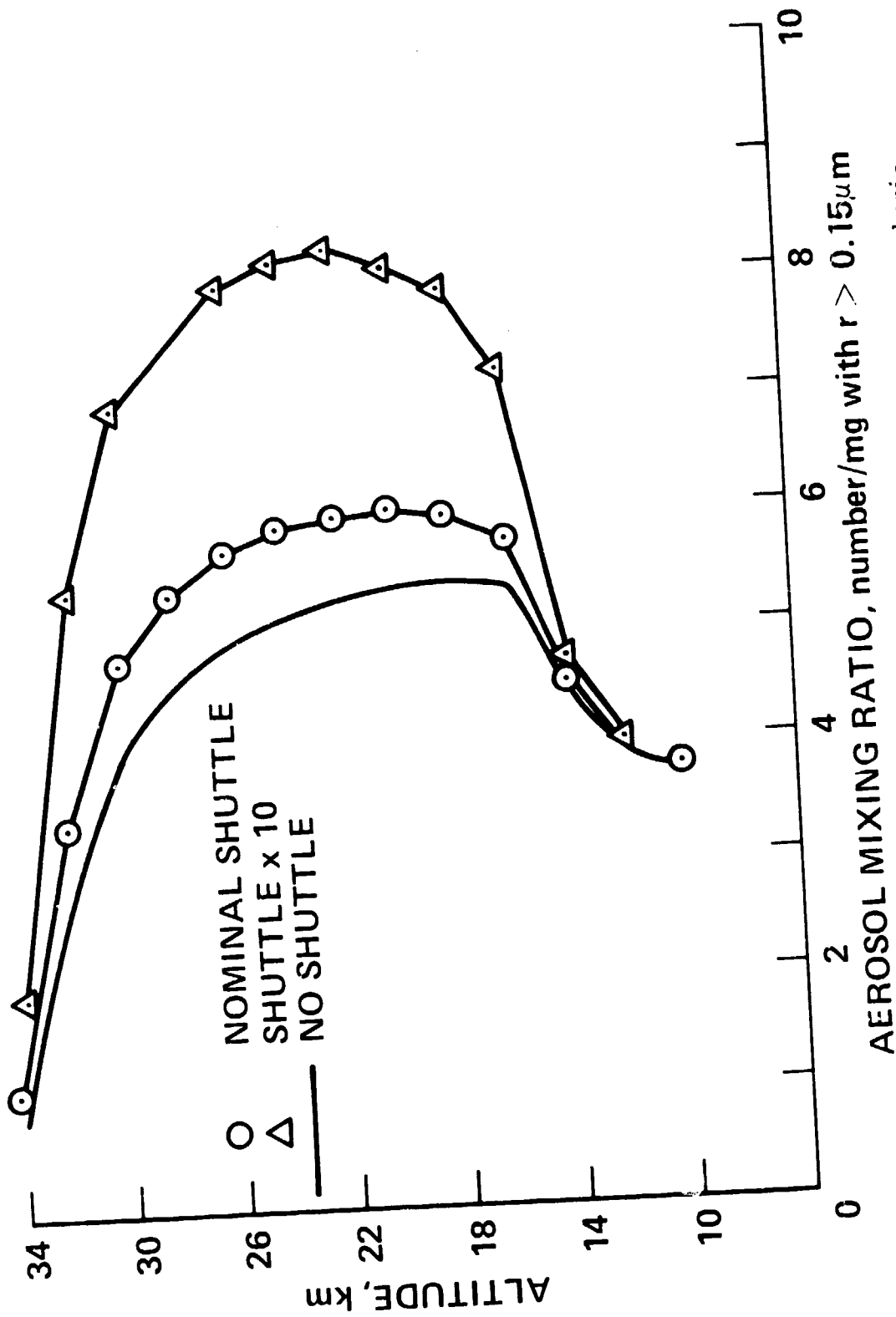
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Figure C-6.- Calculated large-particle mixing ratios in the stratospheric aerosol layer with and without aluminum oxide particle deposition by Space Shuttle rocket engines.

APPENDIX D

A REEXAMINATION OF POTENTIAL SPACE SHUTTLE EFFECTS

ON THE STRATOSPHERE

Donald J. Wuebbles
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A REEXAMINATION OF POTENTIAL SPACE
SHUTTLE EFFECTS ON THE STRATOSPHERE

Donald J. Wuebbles

ABSTRACT

The potential effects of the space shuttle on stratospheric chemistry is examined. Assuming 60 space shuttle flights per year, a calculated reduction in total ozone of 0.27 percent was derived. This corresponds to a 5% increase in stratospheric odd chlorine.

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A REEXAMINATION OF POTENTIAL SPACE
SHUTTLE EFFECTS ON THE STRATOSPHERE[*]

Donald J. Wuebbles

INTRODUCTION

In 1976, for the NASA Workshop on the Space Shuttle, we studied the
ffect of HCl in the exhaust of the space shuttle on the stratosphere.
Using an assumed value of 60 space shuttle flights per year, the LLL one-
dimensional transport-kinetics model calculated a 0.25% reduction in total
ozone at steady state.

Since these calculations were performed, numerous changes have occurred
in the measured values of chemical reaction rates important to stratospheric
chemistry. Probably the most important of these changes has been the
measurement of the rate of $HO_2 + NO \rightarrow OH + NO_2$ by Howard and Evenson (1977).
This reaction was found to have a rate approximately 20 times faster than
previously estimated, with a measured room temperature value of 8×10^{-12}
cm^3/sec. In addition there have been a number of smaller but nonetheless
significant changes to other reaction rates (due to new measurements or
estimates), particularly to reactions involving chlorine species. Details
of these changes can be found in Chang et al. (1977). Because of these
changes to model chemistry, it is useful to reexamine the potential strato-
spheric effects from future utilization of the space shuttle.

Beside emissions of approximately 60,000 kg per flight (based on NASA estimates) of HCl into the stratosphere, there are also other exhaust products to be considered. There are expected to be approximately 260,000 kg per flight of H_2O, 130,000 kg per flight of CO, and 4,200 kg of NO emitted in the exhaust. Aluminum oxides emitted in the exhaust may also be important to particulate formation but will not be further considered here. Water vapor and carbon monoxide are important minor constituents in the stratosphere with mixing ratios by volume of approximately 4-5 ppm for H_2O and 30 ppb for CO. This is to be compared with approximately 1.6 ppb of total odd chlorine, ClO_x (Cl, ClO, $ClONO_2$, and HCl), calculated for the present atmosphere in the model. Assuming 60 flights per year for the shuttle, emissions of HCl lead to approximately a 5% increase in ClO_x. Nitrogen oxide emissions are approximately 15 times smaller than the HCl emission, while the natural NO_x (NO, NO_2 and HNO_3) concentrations are approximately 8-10 times larger than the ClO_x concentration. Therefore, the NO emissions from space shuttle should be insignificant relative to the natural concentrations. The emissions of H_2O and CO from the space shuttle are much larger than that of HCl, but their ambient concentrations are also much larger such that the space shuttle should not be as significant perturbation to water vapor and carbon monoxide.

MODEL RESULTS

The effect of chlorine emissions from the space shuttle has been tested with the model by using the hemispherically averaged HCl source function shown in Figure 1. This source function is based on data provided by NASA assuming 60 shuttle flights per year. There are also emissions below 10 km,

but these are in the troposphere, where it is assumed that the HCl is rapidly removed from the atmosphere by heterogeneous or rainout processes.

The model used was the LLL one-dimensional time-dependent transport-kinetics model of the troposphere and stratosphere. The chemistry in the model is essentially that recommended by the recent evaluation in the NASA report on Chlorofluoromethanes and the Stratosphere (Hudson, 1977). Atmospheric vertical transport is parameterized in the model using the representation developed by Chang (1976). Other processes and features important to the model have been described in previous LLL reports.

The calculated concentrations of atmospheric species derived for current levels of chlorofluoromethanes ($CFCl_3$ and CF_2Cl_2) were the initial conditions in the model for this study. The model was then run to steady state ($\sim$20 years of model time) using the assumed space shuttle HCl emission rate in Figure 1. At steady state, there was found to be a reduction in total ozone of 0.27%. This resulted from an increase in atmospheric ClO_x of 0.08 ppbv, a 5% increase in stratospheric odd chlorine. The calculated changes in local ozone are shown in Figure 2. The maximum change of approximately 1% occurs near 40 km. This is probably too small to have a significant impact on stratospheric circulation or climate.

The calculated change in total ozone is very similar to that computed previously in 1976. Based on calculations of the effect of chlorofluoro-methanes on the stratosphere, a doubling in the computed effect on ozone would have been expected from the change in the rate for HO_2 + NO (Hudson, 1977). However, other changes to model chemistry since the previous calculations have compensated for this. In particular, reductions in the rates

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for the reactions $ClO + O \rightarrow Cl + O_2$ and $OH + HCl \rightarrow H_2O + Cl$ have occurred. The rate for $ClO + NO \rightarrow Cl + NO_2$ has increased slightly. The N atom sink (Duewer, et al., 1977) for nitrogen oxides has been reduced in importance due to rate changes. In addition, the previous calculations had a smaller background ClO_x concentration because ClO_x was derived from CH_3Cl and CCl_4 only and did not include the extra chlorine resulting from present levels of $CFCl_3$ and CF_2Cl_2. The additional ambient chlorine should reduce slightly the computed effects of an HCl injection.
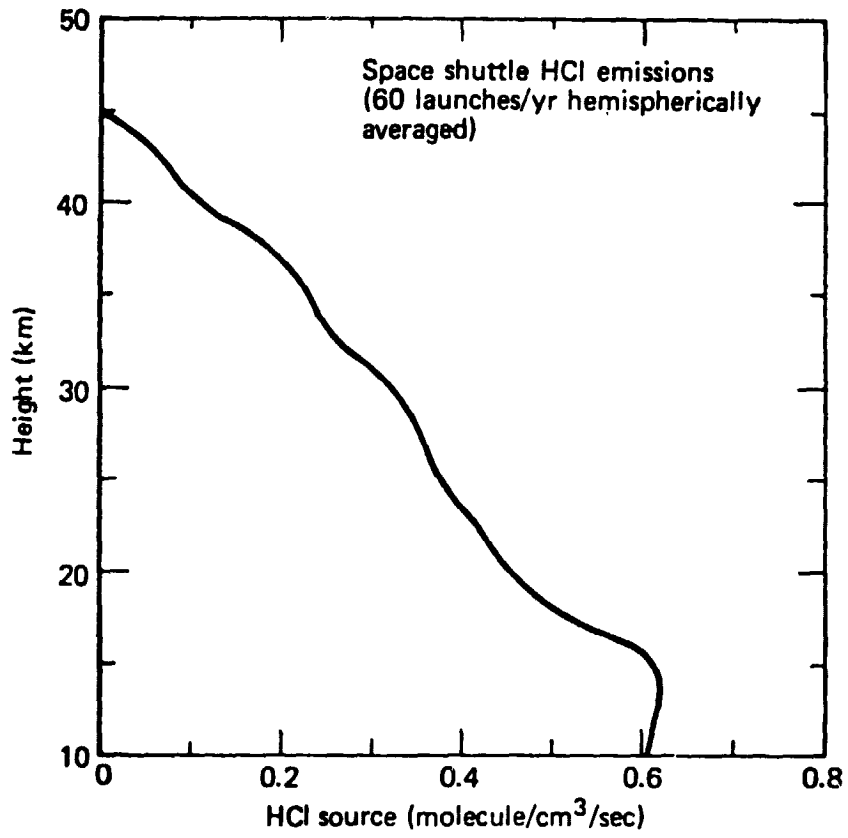
FIGURE 1

Hemispherically averaged HCl emission rate in the stratosphere for an assumed 60 space shuttle flights per year.
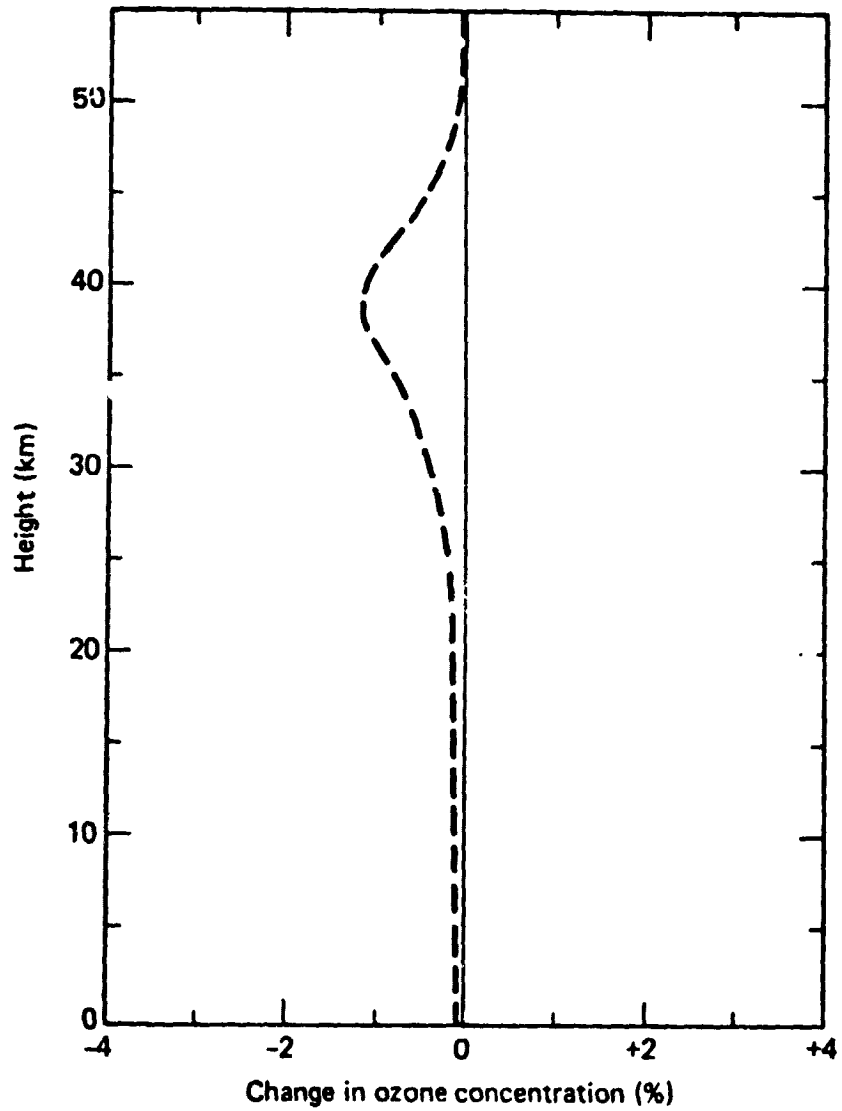
FIGURE 2

Percent changes in local ozone at steady
state resulting from space shuttle
calculations.

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APPENDIX E

EFFECT OF SPACE SHUTTLE LAUNCHES ON STRATOSPHERIC OZONE

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APPENDIX E

On the assumption that 60 Shuttle launches per year will inject HCl at a representative rate in the Northern Hemisphere in 2-kilometer intervals, beginning at 10 kilometers and ending at 44 kilometers, according to the following schedule -

Altitude, kilometers	HCl molecules per cubic centimeter per second
10 to 12	0.605
12 to 14	.610
14 to 16	.616
16 to 18	.542
18 to 20	.469
20 to 22	.443
22 to 24	.417
24 to 26	.378
26 to 28	.362
28 to 30	.348
30 to 32	.307
32 to 34	.253
34 to 36	.234
36 to 38	.193
38 to 40	.141
40 to 42	.094
42 to 44	.069

with a zero value above 44 kilometers and a zero value in the Southern Hemisphere, and on the assumption of a background ClX mixing ratio of 2.3 ppbv, the ClX mixing ratio has been calculated to increase to 2.37 ppbv and the ozone column above 10 kilometers to decrease from 1.0643×10^{19} to 1.06194×10^{19} molecules/cm^2 in the Northern Hemisphere. This decrease is a change of -0.23 percent. The eddy diffusion coefficient profile used was 2×10^5 cm^2/sec at 0 to 8 kilometers, decreased to 4.6×10^3 cm^2/sec at 14 kilometers, and then increased to 8.4×10^3 cm^2/sec at 20 kilometers, 3.06×10^4 cm^2/sec at 30 kilometers, 8.4×10^4 cm^2/sec at 40 kilometers,

7×10^5 cm^2/sec at 50 kilometers, 1.1×10^6 cm^2/sec at 60 kilometers and 1.7×10^6 cm^2/sec above 70 kilometers. The key rate constants used, in cubic centimeters per second, were as follows.

8×10^{-11}	for $HO + HO_2 \rightarrow H_2O + O_2$
$8 \times 10^{-14} \exp(-1275/T)$	for $O_3 + HO_2 \rightarrow HO + 2O_2$
2.5×10^{-12}	for $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
8×10^{-12}	for $NO + HO_2 \rightarrow NO_2 + HO$

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