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**Computer Model Predictions of the Local Effects
of Large, Solid-Fuel Rocket Motors on
Stratospheric Ozone**

10 September 1994

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Prepared for

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A handwritten signature in cursive script, appearing to read "John R. Edwards", with a long horizontal flourish extending to the right.

J. Edwards
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Preface

This document is an updated version of a 1992 Aerospace technical report. This report includes additional computer model results for afterburning of Titan IV SRM plumes at tropospheric altitudes and a brief study of the dependence of chlorine plume chemistry on variations in chlorine-related chemical reaction rate constants.

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Contents

Preface	1
1. Introduction	7
2. Plume Flowfield Calculations	9
3. Local Ozone Depletion Analysis	17
4. Conclusions	21
5. References	23

Figures

1.	Cl density in plume (20 km)	11
2.	Cl ₂ density in plume (20 km)	11
3.	Geometry of residue calculation	12
4.	Chemical identity of chlorine in plume (20 km)	13
5.	Far-field chemical identity of chlorine as a function of altitude	13
6.	Effect of chemical rate constant variations on the production of Cl and Cl ₂	14
7.	Initial region of ozone depletion	19

Tables

1.	Calculated Exit plane Gas Mole Fractions for Titan IV SRM	9
2.	Chemical Distribution of Chlorine in Far Field of Plume	14
3.	Local Ozone Depletion Estimate	17

1. Introduction

The destructive effect of some chlorine compounds on stratospheric ozone has been recognized for nearly two decades.^{1,2} Chlorine atoms released from various chlorine-containing compounds by chemical and photolytic processes react rapidly and catalytically with ozone, reducing the protection provided to terrestrial objects against near-ultraviolet radiation. Some halogen-containing compounds are released into the stratosphere by natural processes. Man-made sources of chlorine include chlorofluorocarbon gases, which migrate unreacted through the troposphere to the stratosphere where ultraviolet photodissociation and reactions with O(¹D) atoms release active chlorine atoms. Slow upward migration through the troposphere and rapid lateral mixing in the stratosphere distribute terrestrially generated chlorine compounds globally. Regional depletions of ozone due to halogen cycles do occur, however, as the result of regional variations in stratospheric temperature, solar illumination, and wind patterns (e.g., antarctic ozone holes).

The solid-fuel rocket motors (SRMs) of heavy space launch vehicles inject large amounts of chlorine compounds directly into the stratosphere in a very localized volume. The Space Shuttle solid motors release a total of 70 to 80 tons of chlorine combined in various chemical compounds between the altitudes of 15 and 45 km. The Titan IV solid motors release approximately half as much chlorinated exhaust over approximately the same altitude range. In addition to chlorine compounds, the solid motors release a somewhat larger mass of micron-sized alumina particles.

The chlorine compounds and alumina ejected by large SRMs may have global, regional, and local effects on stratospheric ozone. When distributed globally, the total chlorine accumulation in the stratosphere due to several Space Shuttle and Titan IV launches per year is small compared to backgrounds from natural and other man-made sources. Computer models of the steady-state global effects of an annual rate of nine Space Shuttle and six Titan IV launches predict a very small reduction in the ozone column density (<0.1%) due to chlorine compounds and other SRM exhaust gases.³ Conclusions regarding the effects of micron-sized alumina particles are less certain because of the less well-understood heterogeneous chemistry. A somewhat larger depletion of ozone over the Northern Hemisphere has been predicted by a recent model of the effects of a nominal schedule of Space Shuttle and Russian Energiya launches.⁴

Prior to global mixing of the SRM exhaust gases through the stratosphere, transient regional increases in chlorine compound concentrations due to individual launches are predicted to persist for several days to several weeks.³ Regional ozone depletions on a distance scale of several hundred to a few thousand kilometers around the launch site and a time scale of several days to several weeks after an individual launch may be somewhat larger than the globally averaged, steady-state depletions caused by a nominal number of annual launches. Depletions on the regional scale are still probably no larger than a few percent of the normal ozone column density.

Launch-related ozone depletion on a short-term local scale may be more significant. A single aircraft-borne field measurement conducted by Loewenstein and Savage⁵ at an altitude of 18 km in the exhaust trail of a Titan III vehicle with large SRM strap-ons suggested a reduction of greater than 40% in the local ozone density. The horizontal spread of the exhaust gases 13 min after passage of the rocket was apparently a few kilometers, although the degree of ozone depletion over the entire region of the expanded exhaust is unclear. Current ozone observation satellites, such as the Total Ozone Mapping Spectrometer (TOMS) system, do not have the spatial resolution necessary to observe such highly localized depletions and, in fact, have not observed launch-related ozone variations.

The atmospheric chemical transport computer models used in global and regional modeling studies do not have sufficient grid resolution to predict the transient response to individual launches on the time scale of a few hours, or distance scale of a few kilometers around the vehicle track. New models have begun, however, to address the local question. Recent computer model calculations of the local effects of the Space Shuttle SRMs by Karol et al.⁶ have suggested stratospheric ozone depletions of >80% within a kilometer of the vehicle track up to an hour or two after launch. Model calculations by Denison et al.⁷ for a smaller solid-fuel motor have suggested depletions of much smaller extent and duration. Other models that address the unusual chemistry and mass transport conditions in a stratospheric rocket-plume wake in a more detailed manner are being developed.^{8,9}

The requirements of a local ozone depletion model are considerably different from those of global and regional models. An understanding of the immediate effects of SRM exhaust gases on ozone density requires a consideration of hot plume chemistry and afterburning, transport and mixing of the exhaust trail into the ambient atmosphere over distances of several kilometers, and the subsequent short-term chemistry and photochemistry of the mixed exhaust and ambient gases. Assumptions about the chemical identity of exhaust species and the large-scale transport mechanisms that are adopted for global models may be inadequate, or misleading, in a consideration of more localized effects. A particular example is the chemical identity of the chlorine-containing compounds in the exhaust plume of a large SRM. Although it is frequently assumed that most chlorine released by SRMs is released as HCl, it has also been noted that chlorine atoms and molecules may be generated in SRM plumes^{6,7,10} and could generate local ozone depletions.^{6,7,11}

The primary objective of this study is to describe with model predictions the physical characteristics and chemical residue in the immediate exhaust plume of a large solid-fuel rocket motor, such as the Titan IV SRM. An important concern is the effect of afterburning on chlorine-containing compounds. The results are intended to provide a starting point for modeling the expansion and chemistry of the immediate exhaust plume from a diameter of several tens of meters a few seconds after vehicle passage to a diameter of several kilometers a few hours after launch. Although this subsequent expansion is not modeled in detail in this study, an estimate of the effect of the expansion and chlorine chemistry on local ozone density is possible. Regardless of the precise details of the expansion, the predicted presence of a large amount of free chlorine generated by afterburning in the SRM exhaust implies that for a daytime launch, a significant ozone depletion over a region at least a kilometer in diameter is created along the vehicle track.

2. Plume Flowfield Calculations

The initial stage of the Titan IV space launch vehicle consists of two strap-on solid-fuel rocket motors (SRMs), which burn through the troposphere and much of the stratosphere to an altitude of 40-50 km. The exhaust properties of the motors and the interaction of the plume with the ambient atmosphere have been calculated in this study with standard nozzle and plume flowfield computer codes.

Calculated gas mole fractions of chlorine compounds and other significant species at the nozzle exit plane of a Titan IV SRM are given in Table 1. The composition of aluminized solid-fuel rocket propellants is typically fuel rich. The highly reduced environment at the nozzle exit plane results in nearly all chlorine exiting the nozzle as HCl and in large mole fractions of H₂ and CO. The high levels of H₂ and CO are capable of supporting vigorous afterburning upon downstream mixing with the ambient atmosphere. Although HCl is the dominant chlorine-containing compound at the nozzle exit plane, this is not necessarily true in the downstream region of the plume, where vigorous afterburning of H₂ and CO may result in the conversion of HCl to other chlorine species.

It is typically assumed in global modeling of the impact of SRMs on stratospheric ozone that all exhaust chlorine is deposited as HCl. The assumption is reasonable for long-term global models since other exhaust chlorine compounds are ultimately converted in large part to the sink molecule HCl through a sequence of reactions with the ambient atmosphere. The distinction among chlorine compounds is critical, however, in the short term. Chlorine that emerges from the plume as HCl has little immediate impact on ozone since HCl does not react directly with ozone and photolyzes and reacts with ambient species very slowly. In contrast, the emergence of chlorine as Cl atoms or Cl₂ molecules would have an immediate impact on local ozone density. Cl₂ molecules are photodissociated rapidly in the daytime stratosphere, and Cl atoms react extremely rapidly with ozone. Thus, Cl and Cl₂, rather than HCl, are the potential agents of a short-term localized depletion of ozone.

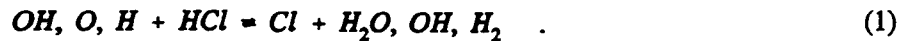
SRM plume properties downstream of the nozzle exit plane have been modeled using a standard plume flowfield computer code. The calculated flowfield is referred to here as the *immediate plume*. The immediate plume includes (1) a region of initial expansion of the exhaust gases from the motor nozzle, (2) a region of mixing with the ambient atmosphere and hot afterburning several hundred meters downstream of the motor, and (3) a region of cooling and further expansion that stretches a few kilometers downstream. The flowfield computer code accepts nozzle exit plane properties from the nozzle computer code (i.e., temperature, pressure, species mole fractions, gas and particle velocities, etc.) and propagates the exhaust flow into the ambient atmosphere. The code treats gas and particle dynamics, turbulent mixing with the ambient atmosphere, and plume chemistry.

Table 1. Calculated Exit Plane Gas Mole Fractions for Titan IV SRM

CO	:	0.27	CO ₂	:	0.02
H ₂	:	0.34	H ₂ O	:	0.12
HCL	:	0.15	Cl	:	1.0E-3
Cl ₂	:	1.2E-7	N ₂	:	0.08
NO	:	3.0E-4	NO ₂	:	0.

The flowfield computer code was run with a standard set of chemical reactions from the code data base that describe the primary afterburning of H₂, CO, and HCl with the ambient atmosphere. In order to form a more complete set of chlorine-related reactions and to investigate the formation of minor chlorine species in the plume, additional reactions and chemical species, including ClO, HOCl and ClOO, were added to the nominal reaction set. The added reactions were found to have a negligible effect on the formation of Cl and Cl₂ and to produce only small amounts of other chlorine compounds.

As ambient oxygen is mixed into the plume exhaust gases, afterburning of H₂ and CO generates high temperatures and high local concentrations of OH radicals and O and H atoms. At a vehicle altitude of 20 km, the calculated peak local density of OH in the afterburning region is approximately 10 orders of magnitude greater than the normal background OH density. The high temperature and high density of reactive radicals created by afterburning provide an environment for the reaction of HCl and the release of chlorine atoms. Chlorine atoms may be generated readily by the reactions in Equation (1),



The reactions in Equation (1) are either exothermic, or nearly thermoneutral,¹² and are relatively fast at temperatures characteristic of the afterburning region (i.e., forward rate constants of 10⁻¹² to 10⁻¹⁰ cm³/s).^{13,14}

The calculated densities of Cl and Cl₂ produced by afterburning and subsequent recombination reactions are shown in Figures 1 and 2, respectively, for vehicle altitude of 20 km. The densities are shown as a function of (axial) distance down the plume centerline from the nozzle exit plane and (radial) distance off the centerline of the cylindrically symmetric plume. The amount of Cl and Cl₂ produced in the afterburning region of the plume is many orders of magnitude greater than the amount of any ambient species incorporated by mixing of the surrounding atmosphere into the immediate plume, with the exception of O₂ and N₂. Therefore, in the cooler post-afterburning region of the immediate plume, the reaction of Cl is largely limited to recombination to form Cl₂. For the 20 km altitude case, recombination of Cl is essentially complete less than 1 kilometer downstream, or 1 to 2 seconds after passage of the vehicle. Thus, a few seconds after passage, the SRM has left a far-field trail of Cl₂ in a cylinder several tens of meters in diameter, which is poised to spread into the surrounding stratosphere. The *far field* of the plume is used here somewhat loosely to identify the region of the immediate plume far enough downstream of the afterburning region that hot chemistry has ceased and plume temperatures have cooled substantially toward the ambient temperature (i.e., roughly 1 to 1.5 km downstream of the nozzle for the 20-km altitude case).

At the axial distance where afterburning chemistry is complete and temperatures have cooled, the radius of the plume is small compared to a radial distance that encompasses an amount of ambient ozone comparable to the amount of chlorine atoms and molecules generated in the plume. Thus, for purposes of estimating the effect of the subsequent expansion of the exhaust gases, it is reasonable to approximate the far-field exhaust trail of two SRM motors by doubling the residue left by a single motor.

It is necessary to determine the quantity of various chlorine compounds deposited in the far field of the SRM plume. The *residue* of a particular species is defined here as the number of molecules (or atoms) of the species per unit distance along the plume axis. Far enough downstream that the motor

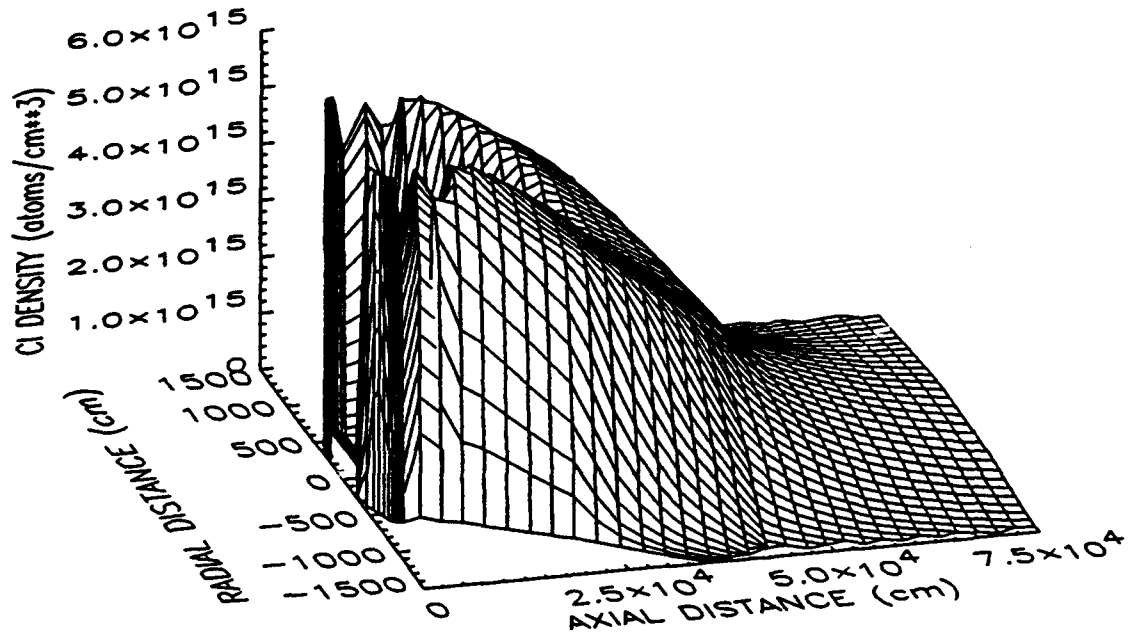


Figure 1. Cl density in plume (20 km).

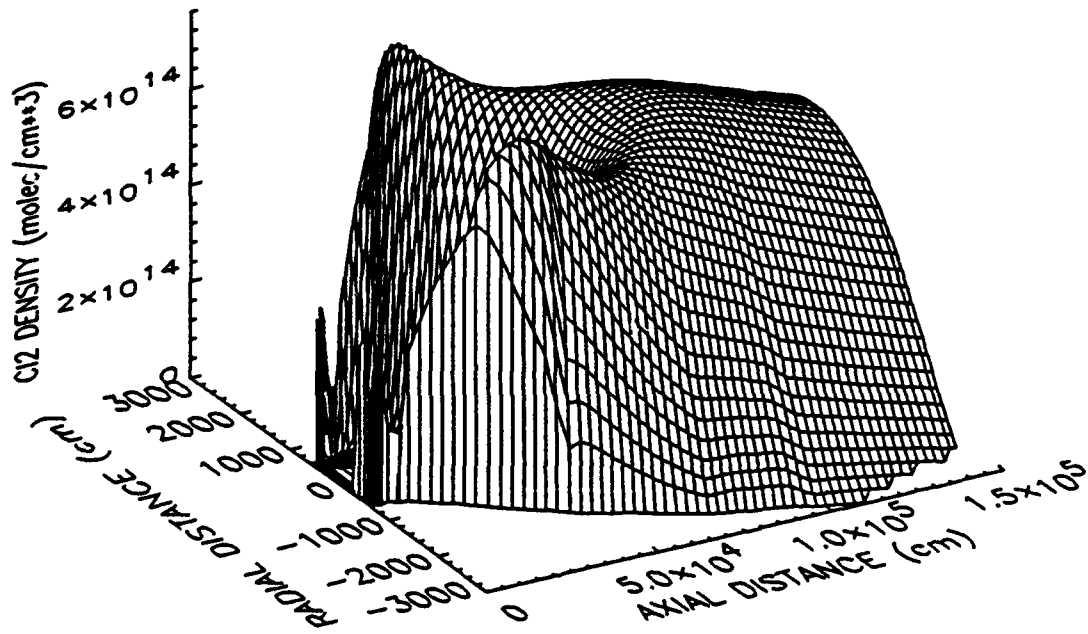


Figure 2. Cl₂ density in plume (20 km).

exhaust is at rest with respect to the ambient atmosphere, the residue is the number of molecules (atoms) left behind per unit distance along the vehicle track. The residue at a given axial distance downstream is the integral of the number density of the species over a plane perpendicular to the plume axis at the axial location. The residue of species A at axial station z is given by

$$N_A(z) = 2\pi \int_0^{\infty} n_A(z,r) r dr \quad , \quad (2)$$

where $n_A(z,r)$ is the number density of species A at the axial and radial coordinates z and r, respectively. Figure 3 illustrates the geometry of the residue calculation. Figure 4 shows the fraction of total chlorine predicted to appear in each of the gaseous chlorine compounds as a function of axial station for the 20-km altitude plume. The sum of the fractions appearing as Cl and Cl₂ is also shown. The distinction between Cl atoms and Cl₂ molecules is not important for modeling the effects on ozone for a daytime launch since Cl₂ is rapidly photodissociated to Cl. The fractions appearing as ClO, HOCl, and ClOO are close to zero.

Plume flowfields and chlorine compound residues have been calculated for the Titan IV SRM over the altitude range of 0.5 to 40 km. Figure 5 shows the fraction of total chlorine deposited as HCl, Cl, and Cl₂ in the far field of the plume as a function of altitude. Other gaseous chlorine-containing compounds are of negligible abundance. For stratospheric altitudes of interest, the distribution of chlorine among the different chlorine-containing compounds in the far field of the plume is listed as a function of altitude in Table 2. The far-field fractions of free chlorine (i.e., Cl plus Cl₂) are very similar to the results calculated by Denison et al.⁷ for a much smaller solid-fuel motor at altitudes of 18 and 30 km.

The effect of uncertainties in the rate constants used in the chemical data base for these calculations was briefly investigated by varying selected chemical rate constants in the flowfield code. Only rate constants involving chlorine chemistry were varied, including those in Equation (1). A sensitivity

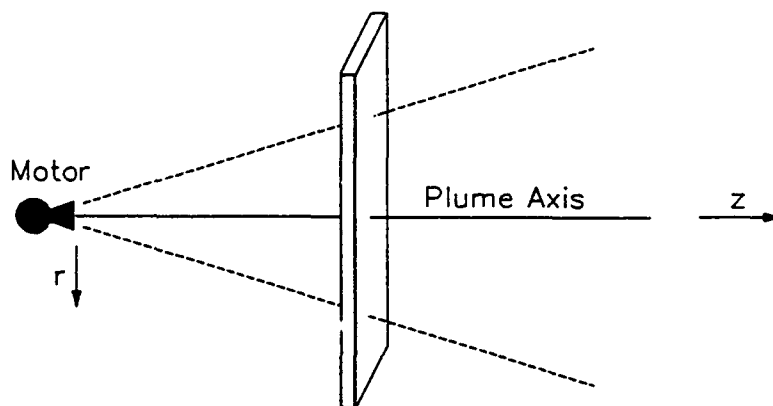


Figure 3. Geometry of residue calculation.

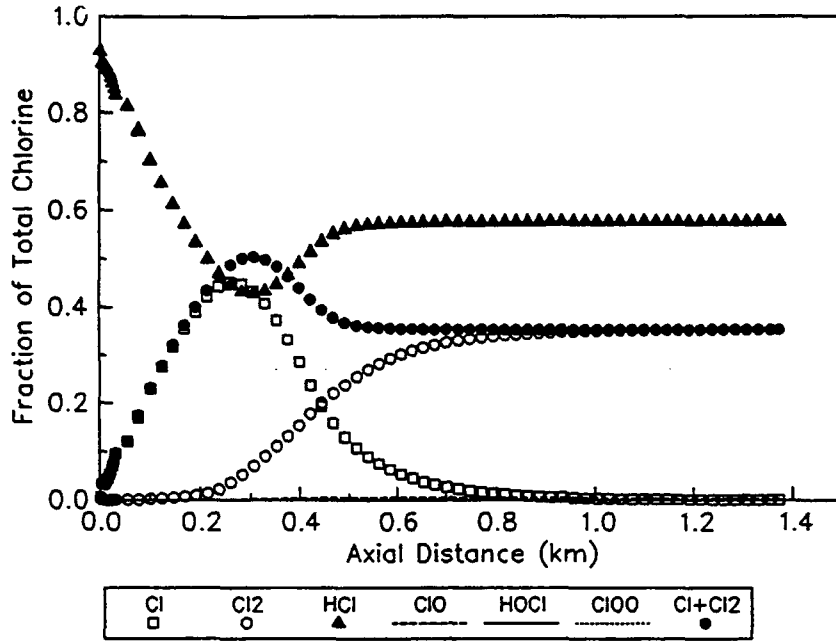


Figure 4. Chemical identity of chlorine in plume (20 km).

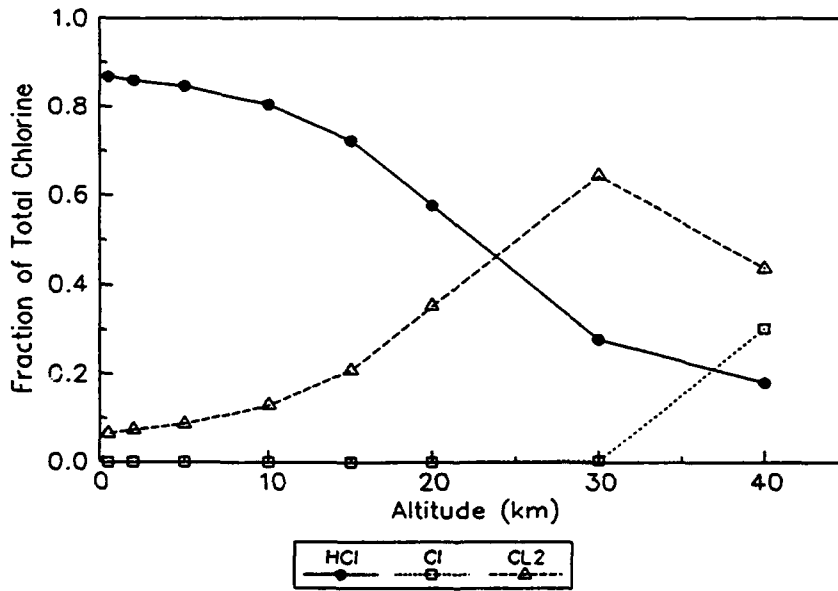


Figure 5. Far-field chemical identity of chlorine as a function of altitude.

Table 2. Chemical Distribution of Chlorine in Far Field of Plume^a

Motor Altitude (km)	Percent of Total Chlorine ^b					
	Cl	Cl ₂	HCl	ClO	HOCl	ClOO
15	0.01	21.0	72.2	0.2	2x10 ⁻⁸	1x10 ⁻³
20	0.1	35.3	57.6	0.4	8x10 ⁻⁹	2x10 ⁻³
30	0.4	64.5	27.7	0.8	7x10 ⁻⁸	1x10 ⁻³
40	30.8	43.4	17.7	1.5	4x10 ⁻⁶	2x10 ⁻³

^a Determined at downstream (axial) distances of 1.1, 1.4, 5.5, and 6.9 km for motor altitudes of 15, 20, 30, and 40 km, respectively.

^b Note that 6.6% of total chlorine is in Fe and Al compounds.

analysis first determined the sign of the effect of individually altering each rate constant on the conversion of HCl to Cl and Cl₂. An estimate of the maximum production of Cl and Cl₂ by afterburning was then obtained by running the flowfield code with the rate constants for reactions that enhanced free chlorine production increased by a factor of 5, and the rate constants for reactions that depressed free chlorine production reduced by a factor of 5. An estimate of the minimum production of Cl and Cl₂ was obtained by the inverse adjustment of rate constants. Since the rate constants for the most important reactions, including those in Equation (1), are known reasonably well,^{13,14,15} a variation of the values used in the computer calculations by a factor of 5 includes any reasonable uncertainties over the temperature range of interest. The minimum, nominal, and maximum fractions of total exhaust chlorine deposited in the far field of the plume as free chlorine (i.e., Cl atom or Cl₂ molecule) are shown in Figure 6 as a function of altitude.

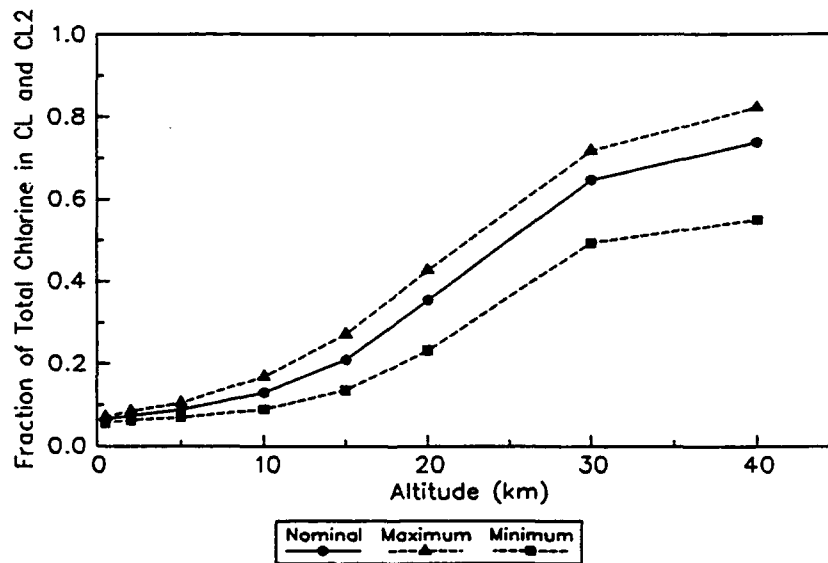


Figure 6. Effect of chemical rate constant variations on the production of Cl and Cl₂.

The abundances of other exhaust gas species have also been modeled through the SRM afterburning region. According to the nozzle code calculations (i.e., Table 1), a very small amount of NO_x is initially present at the nozzle exit plane of the Titan IV SRM. The flowfield code has been run with additional NO_x reactions and additional relevant species added to the standard afterburning reaction set. Very little NO_x was found to be produced by afterburning. The computer-modeled amounts of NO_x are insignificant compared to the amounts of chlorine atoms and molecules generated by afterburning. It is suggested by these modeling results that NO_x chemistry, as well as the simple thermolysis of entrained ambient ozone, make contributions to *local* ozone depletion that are small compared to the effect of the chlorine atoms and molecules.

3. Local Ozone Depletion Analysis

A precise description of the local effects of the expansion of the far-field SRM exhaust gases into the ambient stratosphere beginning a few seconds after vehicle passage requires a model for plume/ambient mixing and chemistry that is beyond the scope of this study. Some local effects, however, are fairly obvious. A simple, semi-quantitative estimate of the short-term effects of the expansion of the SRM exhaust for a daytime launch is discussed here.

The flowfield computer model calculations predict a large conversion of HCl, which is the major chlorine-containing compound at the SRM nozzle exit plane, to Cl and Cl₂ as a result of afterburning. The fraction of the total chlorine exhaust deposited in the stratosphere as free chlorine (i.e., Cl and Cl₂) is predicted to range from ~20% at an altitude of 15 km to ~70% at an altitude of 40 km. The mass of free chlorine deposited per cm of vehicle path as Cl and Cl₂ is given in Table 3 as a function of altitude. The density of free chlorine in the far-field plume is orders of magnitude greater than the ambient density of ozone, or any ambient species other than N₂ and O₂. The exhaust gas must expand to a diameter of a few kilometers in order to encounter an amount of ozone (or other trace ambient gases) equivalent to the free chlorine residue.

The relevant reactions of the first phase of the exhaust gas expansion and ozone depletion are given by Reactions (3) to (5),

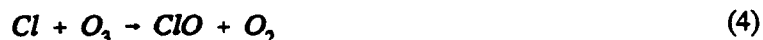


Table 3. Local Ozone Depletion Estimate

Altitude (km)	Cl + Cl ₂ Residue ^a (gm/cm)	Alumina Residue ^a (gm/cm)	Ambient O ₃ Density (molec/cm ³)	D _{depl.} ^b (km)
15	3.28	21.7	2.1x10 ¹²	1.0-1.8 ^c
20	4.28	16.8	5.5x10 ¹²	1.1-1.3 ^c
30	5.70	12.2	3.1x10 ¹²	2.0
40	4.93	9.2	4.3x10 ¹¹	5.0

^a Mass deposited in far field of plume per cm of vehicle track (2 SRMs).

^b Diameter of ozone depletion cylinder. Assumes complete photolysis of Cl₂ and 1:1 destruction of O₃ by Cl atoms.

^c Smaller of the two values includes the estimated effect of Reaction (5), which may be significant at the lowest altitudes. Larger of the two values does not include the effect.

For typical daytime illumination, the photodissociation rate of Cl_2 is calculated to be $\sim 0.14 \text{ min}^{-1}$ at an altitude of 40 km and is nearly the same throughout the stratosphere. The rate of Reaction (4) ranges from 5 to 45 s^{-1} over the 15- to 40-km altitude region for normal ambient densities of ozone. Reaction (5) is a potential sink for Cl and has a rate that decreases from 3.7 to 0.13 min^{-1} for normal ambient CH_4 densities as altitude increases from 15 to 40 km. The density of CH_4 is much less than the density of O_3 above 20 km, and the effect of Reaction (5) on the initial ozone depletion process is probably significant only below $\sim 20 \text{ km}$.

HCl in the far-field plume has a negligible effect on local short-term ozone depletion since HCl does not react directly with O_3 . The release of chlorine from HCl occurs primarily through Reactions (6) and (7),



For typical daytime illumination, the photodissociation rate of HCl is 0.48 day^{-1} at an altitude of 40 km and decreases rapidly with decreasing altitude.¹⁶ The rate of Reaction (7) increases from 0.016 to 1.3 day^{-1} for normal ambient OH densities as altitude increases from 15 to 40 km. Other reactions of plume-generated HCl, Cl, and Cl_2 are probably negligible during the initial ozone depletion process because of the small densities of other reactive ambient species.

The first phase of the local depletion of ozone due to chlorine in the SRM exhaust gas is straightforward. The precise gas dynamic description of the turbulent mixing and expansion of the exhaust gases from the initial far-field plume diameter of several tens of meters out to a diameter of a few kilometers may be complex, but is not particularly critical with respect to the overall qualitative result. The initial chemistry is relatively simple, and the reactions are fast compared to any estimate of the expansion rate. As the exhaust gases expand, Cl and Cl_2 are consumed by Reactions (3) and (4). At the lowest altitudes of 15 to 20 km, Reaction (5) must also be considered. The diameter of the cylinder around the vehicle track that contains an amount of O_3 equal to the amount of chlorine deposited in the far-field plume as either Cl or Cl_2 is listed in Table 3 as a function of altitude. Regardless of the exact time scale of the initial expansion process, the minimum result of the first phase of the exhaust gas expansion and reaction is estimated to be the essentially complete depletion of ozone in the cylinder with diameter D_{depl} .

The time scale for the first phase of the ozone depletion process can be estimated. Mixing in the stratosphere is often described by a pseudo diffusion coefficient that is dependent on the distance scale of the mixing. Using a pseudo diffusion coefficient for horizontal mixing of $\sim 80 \text{ m}^2/\text{s}$ for a distance scale of a few kilometers,¹⁷ the horizontal expansion of the exhaust gases to a diameter of $\sim 1 \text{ km}$ is estimated to require less than 1 hour. Vertical diffusion is slower than horizontal diffusion in the stratosphere. The region of ozone depletion an hour or two after passage of a Titan IV vehicle on an inclined trajectory through the stratosphere is depicted in Figure 7. The effect of horizontal shearing winds is not considered in the schematic display. Such winds would probably distort the idealized, symmetric shape of the region of depletion.

Following the initial expansion of the exhaust gases to a dimension of a few kilometers and the complete consumption of Cl and Cl_2 by ozone, the dynamics and kinetics of the problem become more complex. The ClO molecule generated in Reaction (4) does not react rapidly with O_3 , if at all.

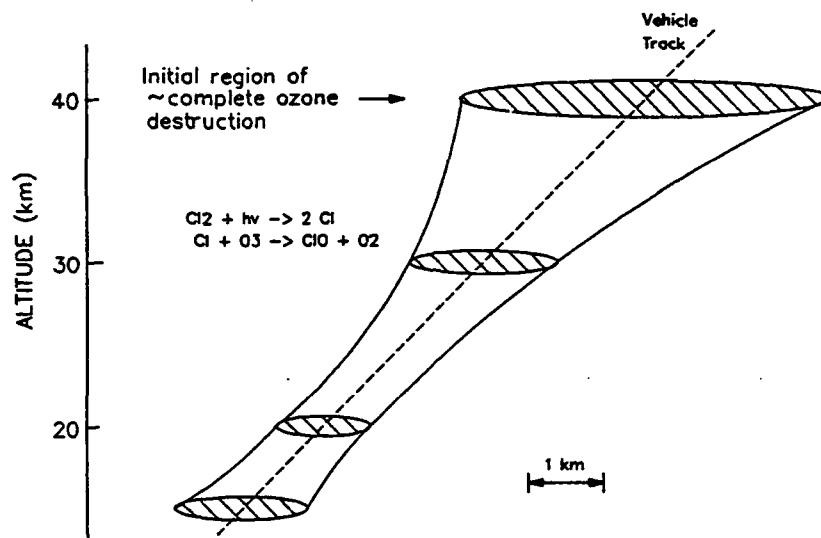


Figure 7. Initial region of ozone depletion. Note that the horizontal scale of the ozone "hole" is expanded around the vehicle track relative to the vertical altitude scale for clarity.

Relevant stratospheric gas-phase reactions of ClO are given in Equations (8) to (10),



For typical daytime illumination, the radiative predissociation rate of ClO is 3.3 h^{-1} at an altitude of 40 km and decreases to 0.13 h^{-1} at 20 km.¹⁶ To a first approximation, the photodissociation of ClO leads to no net reduction of ozone since the destructive reaction of the released chlorine atom with O_3 is balanced by the rapid recombination of the O atom with O_2 to form O_3 . Reactions (9) and (10) are dominant in the lower and upper stratosphere, respectively. Reaction (9) results in no net loss of ozone since NO_2 is rapidly photodissociated, and the released O atom recombines to form O_3 . Reaction (10) is the primary process for the gas-phase release of Cl from ClO in a cycle that does lead to continued, catalytic destruction of ozone in the upper stratosphere. The rate of Reaction (10) increases from 0.001 to 1.9 min^{-1} for normal ambient O atom densities as altitude increases from 15 to 40 km. The ambient density of O atoms is, however, several orders of magnitude smaller than the density of O_3 in the 15- to 40-km altitude range. Thus, Reaction (10) cannot sustain a significant *local* depletion of O_3 . No reaction that rapidly regenerates large amounts of free chlorine from ClO during the first phase of the expansion process is immediately obvious.

The second phase of the local ozone depletion problem involves the expansion of the exhaust gases from a diameter of a few kilometers around the vehicle track to larger, but still relatively local, dimensions. The major chlorine-containing compound at the beginning of the second phase of the expansion is ClO. A large number of slow reactions are potentially important in the second phase of the expansion. The high densities of several unusual species in the initial ozone hole may result in

some chemistry that is not typically considered important in the unperturbed mid-latitude ambient stratosphere. Photolytic and chemical reactions involving the ClO dimer may release Cl atoms, providing a catalytic cycle that enlarges the region of ozone depletion.⁸ The second phase of the expansion requires a sophisticated model of turbulent mixing and chemistry in order to obtain even rough estimates of ozone depletion. Such models are being developed,^{6,7,9} but are probably not yet comprehensive enough to provide a final (computer model) answer. *It is unclear whether the second phase of the plume gas expansion is characterized by a slow, continuing depletion of O₃ due to ClO chemistry, or by a cessation of ozone destruction and a refilling of the initial hole by mixing.*

The heterogeneous chemistry of alumina particles is not considered here in the estimate of local ozone depletion, but may be important. The alumina residue of the two SRMs of a Titan IV is given in Table 3 as a function of altitude. Assuming 1- μ m-diameter particles, the residue of alumina at an altitude of 20 km corresponds to $\sim 6.4 \times 10^5$ particles/cm³ within the ~ 40 -m diameter of the far-field plume, or 1.0×10^3 particles/cm³ after expansion of the plume to a diameter of 1 km. A typical plume gas molecule would collide with alumina particles at the rate of ~ 200 s⁻¹ in the far field of the immediate plume and ~ 0.4 s⁻¹ in the 1-km-diameter expanded plume. Given the typically large sticking coefficients of H₂O, HCl, and some other plume molecules, the potential exists for significant heterogeneous chemistry on the time scale of the local expansion of the exhaust gases. The potential for heterogeneous aqueous chemistry is increased by the presence of large amounts of H₂O in the afterburned exhaust of the Titan IV SRMs. In the case of the Space Shuttle, the simultaneous burning of the core liquid-fuel motor increases the density of water in the plume.

The temperatures of μ m-sized alumina particles in the immediate plume were also calculated by the plume flowfield computer code and were found to cool rapidly downstream of the afterburning region. Thermolytic destruction and other reactions of O₃ on hot alumina particles within the near field and afterburning regions of the plume are clearly negligible compared with the effects of the chlorine-based gas-phase reactions. Heterogeneous reactions far downstream in the plume at long times and low to moderate temperatures are probably more relevant to the ozone depletion problem. To the extent that such heterogeneous reactions are understood, future models of the second phase of the local ozone depletion problem should include heterogeneous chemistry.

4. Conclusions

The computer models used in this study predict that afterburning in the plume of the Titan IV (and presumably other large) solid-fuel rocket motors converts a large fraction of HCl exhaust gas into Cl and Cl₂. The fraction ranges from ~20% of the total chlorine exhaust at a vehicle altitude of 15 km to ~70% at an altitude of 40 km.

Photodissociation of Cl₂ and the rapid chemical reaction of chlorine atoms is predicted to lead to a significant local depletion of ambient ozone along the vehicle track. The chemistry of the initial phase of the process is fairly simple and allows an estimate of the magnitude of the initial effect for a daytime launch. Nearly complete depletion of ozone is predicted over a region approximately 1 to 2 km in diameter along the vehicle track at altitudes of 15 to 20 km. The predicted region of depletion is approximately 4 to 5 km in diameter at an altitude of 40 km. The time scale for this first phase of expansion and chlorine/ozone chemistry is estimated to be on the order of 1 hour.

Compared to the effects produced by chlorine chemistry, the effects of NO_x gas-phase reactions and heterogeneous reactions on alumina particles are estimated to be small during the first phase of the ozone depletion process. On a longer time scale, the large residue of alumina particles may be an important source of ozone-related heterogeneous chemistry.

The initial, rapid reaction of chlorine with ozone in the first phase of the exhaust gas expansion produces the less reactive ClO molecule. The gas dynamics and complex chemistry of the subsequent second-phase expansion of ClO and other exhaust gases cannot be approximated adequately by a simple model. It is unclear whether the initial ozone hole continues to expand as the result of continuing chlorine-based chemical reactions, or is closed by the inward diffusion of ambient ozone in a non-destructive environment.

The complicated second phase of the local ozone depletion problem requires improved analytical models for the expansion and reaction of exhaust gases over the distance scale of a few kilometers to a few hundred kilometers and the time scale of an hour to a few days. Beyond the distance scale of a few hundred kilometers and the time scale of a few days, regional and global models of stratospheric ozone chemistry become relevant.

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