Effects of Launch Vehicle Emissions in the Stratosphere

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A plume dispersion and chemical kinetic model has been used to estimate the total impact of motors of different propellant types on stratospheric ozone. In previous studies, industry standard rocket motor performance and plume flowfield computer programs were used to model the chemistry in the rocket combustion chamber and expansion nozzle and also in the downstream afterburning region of the plume. Our model and the results of previous studies were used to follow the plume chemistry for up to a day as the plume dispersed into the ambient stratosphere. Several large motor-types were analyzed: two different solid-fueled motors without chlorine and one with chlorine, an amine/N_2O_4 fueled first stage, a kerosene/liquid oxygen (LOX) fueled first stage, and an l-H_2/LOX fueled engine with two nozzle variants. The modeled motors are based loosely on existing vehicles, but we varied several parameters to create hypothetical vehicles that may be viewed as prototypes of next-generation launchers. Two dispersion rates were used, a worst case and a best guess, based on published models. In the worst case, ozone depletion due to NO_x or other exhaust species was several orders of magnitude smaller than depletion due to chlorine in the exhaust. Depletion due to motors using LOX was minimal within 5 min of vehicle passage in all cases.

Nomenclature

A_R = ratio of surface area to gas phase volume, cm^{-1}
b = diffusion parameter, m/s
C_P = specific heat capacity at constant pressure, J/gK
H_i^m = enthalpy in mass units for species, J/g
i = chemical species index
m_i = molecular weight, g/mole
m_l = total mass in condensed phases, g
N = total number of chemical species
n_i^{phase} = moles produced by gas g (surface s), phase reactions per unit volume (area)
r = plume radius, m
T = temperature, K
t = time, s
t_0 = starting time for model calculation
V_R = ratio of condensed volume to gas phase volume
X_i = site fraction
Y_i = mass fraction
Γ_j = density of surface sites in surface phase j, cm^{-2}
δt = time interval, s
ν = species number density in plume, cm^{-3}
ρ = gas phase density, g/cm^3
σ_i = sites occupied by species
σ_p = cross-sectional area of plume, m^2

Introduction

ASSESSMENT of the impact of space launch operations on the environment is now an integral part of launch operations and launch system acquisition. Whereas most of this work focuses on ground-based operations, there have been several papers dealing with the effect on the ozone layer by chlorine released in the stratosphere by solid rocket motors.[1-11] Chlorine and chlorine oxides are only present in the exhaust of solid rocket motors (SRMs) such as those found on the Titan IV, the Space Shuttle, and many smaller launch vehicles. There are two other classes of compounds commonly found in rocket exhaust that can cause ozone destruction. These are the oxides of nitrogen and hydrogen, and they are present to some extent in the exhaust of every launch vehicle. There are also species such as alumina in solid rocket exhaust that may promote heterogeneous reactions with ozone and ambient chlorine containing compounds. To assess the environmental impact of launch vehicles, it is necessary to consider all of the ozone reactive compounds that are exhausted in the stratosphere and the effect of those compounds on ozone. The comparative impact of various launch vehicles calculated in this way, along with performance and cost figures, is a useful data set for launch planners and acquisition decision makers.

We model the time evolution of a point inside a dispersing plume from a launch vehicle in the stratosphere. We confine the discussion to 20-km altitude and look for the transient effect on the stratosphere. We look at a sampling of hypothetical large rocket motors loosely based on the following propulsion systems from existing launch vehicles: the Titan IV SRM boosters (T4/SRM), the Titan IV SRM upgrade (T4/SRMU), the Titan III B (T3B) first stage, the Delta core (Delta), the Space Shuttle main engine (SSME), and a hypothetical variant of the SSME (SSME mod). These motors span the range of currently used and proposed propellant types for large launch vehicles. The purpose is not to precisely characterize existing vehicles but to identify the differences expected for generic vehicles using different propellant types. Dispersion rates, discussed later, are scaled to the size of the T4/SRM to facilitate comparison.

Background

Hydrogen chloride (HCl) is a major combustion product of solid rocket boosters that use ammonium perchlorate oxidizer. As this gas leaves the motor, plume models[2,5,10] indicate that afterburning takes place, converting a substantial amount of the HCl to Cl and Cl_2 (21–65%, depending on altitude). The chlorine conversion occurs through reactions such as

$$OH + HCl \longleftrightarrow Cl + H_2O \tag{1}$$

$$H + HCl \longleftrightarrow Cl + H_2 \tag{2}$$

$$O + HCl \longleftrightarrow Cl + OH \tag{3}$$
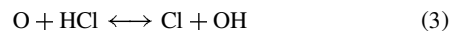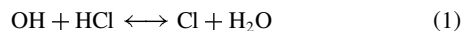
The chlorine so released will immediately react with ozone to begin a catalytic destruction cycle. The cycle represented by reactions 4–5 is fast when oxygen atoms are present (as at high altitudes). In the absence of oxygen atoms, cycle 6–10 is faster but requires either low temperature or high chlorine concentration to facilitate the chlorine oxide dimer formation[12]
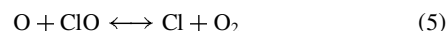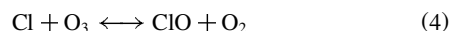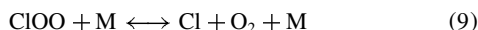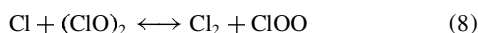
$$Cl + O_3 \longleftrightarrow ClO + O_2 \tag{4}$$
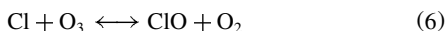
$$O + ClO \longleftrightarrow Cl + O_2 \tag{5}$$

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$$Cl + O_3 \longleftrightarrow ClO + O_2 \qquad (6)$$

$$ClO + ClO \longleftrightarrow (ClO)_2 \qquad (7)$$

$$Cl + (ClO)_2 \longleftrightarrow Cl_2 + ClOO \qquad (8)$$

$$ClOO + M \longleftrightarrow Cl + O_2 + M \qquad (9)$$

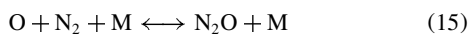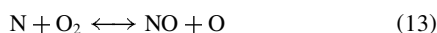$$Cl_2 + h\nu \longrightarrow 2Cl \qquad (10)$$
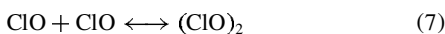
Cycle 6–10 is similar to that which causes the Antarctic ozone-depleted region, except that the chlorine oxide dimer forms because of the high concentrations of chlorine in the rocket plume (six orders of magnitude above background) and not because of low temperatures. Also, as we discovered in running this model, the principal route for generation of atomic chlorine from the dimer is not photolysis of the dimer (which is the route in the Antarctic) but the branched chain reaction of the dimer with atomic chlorine as shown in the given equations. Because the two reaction cycles shown regenerate atomic chlorine, these cycles will continue to destroy ozone until the Cl and ClO return to HCl by reactions with hydrogen containing molecules such as methane or hydrogen:

$$Cl + CH_4 \longleftrightarrow HCl + CH_3 \qquad (11)$$
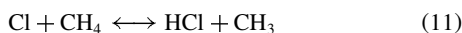
In the normal stratosphere, the Cl and ClO are typically converted to HCl by this process in a few minutes, with the HCl returning only very slowly to active form. In a rocket plume, however, there is sufficient Cl and ClO to deplete the methane and hydrogen concentration so that substantial local depletion of ozone may take place on short time scales. There is some early observational evidence that a local ozone-depleted region may be created in the wake of an SRM launch.[13] More recently, the Rocket Impacts on Stratospheric Ozone program has attempted to characterize the plume more precisely.[14−17]

NO_x (NO and NO_2) in the rocket exhaust can come from two different sources, depending on the motor used. NO_x can come from the propellant; nitrogen tetroxide (N_2O_4, or NTO) that is not fully reacted remains as NO or NO_2 in the plume. Similarly, nitrogen in the fuel, from the amine fuels or impurities in the hydrocarbon fuels, can be converted to NO_x upon oxidation. The second source of NO_x comes from afterburning, which occurs in essentially all rocket plumes in the lower stratosphere. As air mixes into the hot exhaust, nitrogen and oxygen from the ambient atmosphere can combine to create NO_x in regions of high flame temperature. Several of the important reactions in this process follow:

$$O + N_2 \longleftrightarrow NO + N \qquad (12)$$

$$N + O_2 \longleftrightarrow NO + O \qquad (13)$$

$$N + OH \longleftrightarrow NO + H \qquad (14)$$

$$O + N_2 + M \longleftrightarrow N_2O + M \qquad (15)$$

$$O + N_2O \longleftrightarrow NO + NO \qquad (16)$$

$$H + N_2O \longleftrightarrow NH + NO \qquad (17)$$

Once the NO_x is formed, it can react with ozone in a cycle similar to that for chlorine:

$$NO + O_3 \longleftrightarrow NO_2 + O_2 \qquad (18)$$
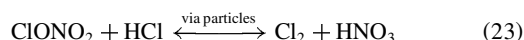
$$NO_2 + O \longleftrightarrow NO + O_2 \qquad (19)$$
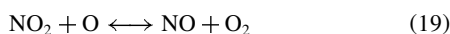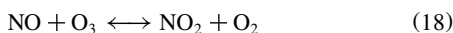
NO_x in the plume can also be converted into reservoir species by the following reactions. The NO_x conversion temporarily halts the ozone destruction cycle. As in the case of HCl, the reservoir species are only slowly converted back to active species and may be removed by mixing with the troposphere:

$$NO_2 + ClO + M \longleftrightarrow ClONO_2 + M \qquad (20)$$

$$NO_2 + OH + M \longleftrightarrow HNO_3 + M \qquad (21)$$

The exhaust from SRMs also contains solid aluminum oxide (and some aluminum oxychloride) particles, which may participate in heterogeneous reactions. At this time, several heterogeneous chemistry mechanisms that take place on the particles are being investigated. Some reactions that have been proposed are the direct destruction of ozone by surface catalysis,

$$2O_3 \xleftrightarrow{\text{via particles}} 3O_2 \qquad (22)$$
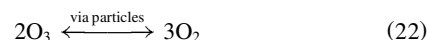
and the catalytic activation of reservoir compounds,

$$ClONO_2 + HCl \xleftrightarrow{\text{via particles}} Cl_2 + HNO_3 \qquad (23)$$

In the preceding reactions, particles include the alumina from the solid rocket exhaust. Reactions such as Eq. (23) are analogous to reactions that take place on polar stratospheric clouds to produce the Antarctic ozone-depleted region and may occur on sulfate aerosols from the Junge layer, but they are just beginning to be examined in the laboratory.[18] The potential effect of such chemistry, excluding sulfate aerosol, is included in the model.

Vehicles

To compare the amount of ozone destruction predicted by the computer models for different propellant types, several different rocket motors have been considered. Nozzle exhaust compositions and afterburning results were taken from two studies that employed standard nozzle and plume flowfield computer models to estimate the NO_x and ClO_x residue in various motor wakes.[10,19] In those motor designs, propellant compositions and other operational parameters were taken from available data for real motors and launch vehicles. Some hypothetical motors and trajectories were also considered to provide comparisons of potential launch systems of similar thrust and trajectory, differing only in basic propellant type. The parameters of those studies are briefly summarized next.

The two solid-fueled motors considered are the current seven-segment Titan IV strap-on booster T4/SRM and a scheduled upgrade T4/SRMU. These motors have a propellant composition of 16–19% aluminum (Al), 68% ammonium perchlorate (AP), and polymeric binders and catalysts (PBAN or HTPB). For simplicity, the altitude-dependent thrust of the motors is modeled as $\sim 1.6 \times 10^6$ lbf over the 0–20 km altitude region. Only the results at 20 km are relevant to the calculation of ozone destruction. The motors are modeled as single and isolated, although two strap-ons are in fact used during the initial Titan IV boost phase. The core vehicle can be safely ignored because those motors are not ignited until just before separation from the solid strap-ons. A typical operational trajectory, i.e., velocity vs altitude, was used for the T4/SRM, and a hypothetical Titan IV/Centaur trajectory was used for the T4/SRMU.

The propellants used in the first-stage T3B are an amine fuel and NTO (N_2O_4) oxidizer. The Aerozine-50 (A-50) fuel is a 50/50 mixture by weight of hydrazine and 1,1-dimethyl hydrazine. The two-motor, first-stage propulsion system of the T3B is modeled here as a single equivalent motor with a thrust of 520 klbf. The trajectory is a typical operational space-launch trajectory flown by the vehicle.

The core stage of the Delta space launcher (Delta core) is a 270,000-lbf-thrust motor using kerosene (RP-1) and liquid oxygen (LOX) propellants. In practice, at low altitude, the core stage is surrounded by several large solid-fueled, strap-on boosters, creating a very complicated plume structure. For purposes of comparing ozone destruction by motors of specific fuel types, the Delta core stage is modeled here as a hypothetical isolated motor (with no solid strap-ons) on a trajectory that is the same as the T3B. The plume chemistry derived here for the Delta core is not intended to represent the chemistry of a core stage in the presence of strap-ons but rather a hypothetical launch vehicle consisting only of the RP-1/LOX core motor.

The SSME is a 520,000-lbf-thrust motor propelled by liquid hydrogen (l-H_2) and LOX. The Space Shuttle actually employs a cluster of three SSME motors, with solid strap-ons at low altitude. For the results presented, however, a single isolated SSME motor is modeled on the same trajectory as the T3B. The purpose of this model, like that of the Delta core, is to compare motors of similar thrust and trajectory but with different specific propellant types.

The results of this model are, therefore, relevant to an evaluation of a moderate-thrust, l-H_2/LOX-fueled space launcher but are not intended to model the plume chemistry of SSME engines in the normal low-altitude configuration with adjacent large solid-fueled boosters.

A modified version of the SSME was also considered as an alternate model for the l-H_2/LOX-fueled first stage of a moderate-sized space launch vehicle.[19] The nominal SSME motor may not be designed optimally for stand-alone operation from ground level because in the Space Shuttle configuration, large strap-on, solid-fueled motors provide most of the boost at low altitude. The exit-plane gas pressure of the SSME is low and more appropriate for operation at higher altitude following SRM separation. Therefore, a modified version (SSME-mod) was modeled as a better representation of a stand-alone, 0.5×10^6 lb thrust space launcher. The modification to the motor consisted of shortening and reshaping the nozzle to achieve an area expansion ratio of 35, as compared with the exit-plane-to-throat area ratio of 77.5 for the actual SSME. The modification resulted in an exit-plane lip pressure greater than 1 atm and an exit-plane gas temperature higher than the temperature for the actual SSME.

Nozzle and Flowfield Computer Models

The exhaust residues of the motors considered were taken from model calculations.[10,19] In those studies, standard computer codes were used to model the production of NO_x and other exhaust gases in the motor/nozzle and afterburning flowfield of rocket motors that burn typical liquid and solid propellants.

The standard model codes proceed from the starting point of thermodynamic equilibrium in the motor combustion chamber upstream of the throat. Relative fuel and oxidizer flows are specified along with chamber pressure, and the equilibrium temperature and chemical composition in the combustion chamber are computed from a thermodynamic database. From the throat through the nozzle expansion, however, chemical kinetic mechanisms are employed to model the changing chemical composition as the exhaust expands and cools. The nozzle codes ultimately predict chemical composition at the end (exit plane) of the expansion nozzle.

In typical estimates of the chemical composition of rocket exhaust, the flow of a chemical species into the ambient atmosphere is taken as the flow at the exit plane of the rocket nozzle. This approach, however, neglects the chemistry that may occur downstream of the vehicle in the hot afterburning region of the plume. At altitudes below 20 km, most rocket plumes afterburn strongly on mixing of the underoxidized rocket exhaust with oxygen from the atmosphere. Depending on the altitude and the abundance of unoxidized fuel fragment species, very high temperatures may be reached downstream of the motor in a region of vigorous afterburning, where NO_x and ClO_x species may be generated or consumed. Recent models of the conversion of HCl to other chlorine-containing species in the afterburning region of solid-fueled rocket motors illustrate the importance of afterburning chemistry.[10]

The residues calculated[10,19] and used in this study include the altitude-dependent contribution of the plume afterburning, as calculated by standard plume flowfield models augmented by an expanded ClO_x and NO_x reaction set.

Stratospheric Plume Computer Model

The computer model is based on the SURFACE CHEMKIN,[20−22] which has been described previously.[23,24] Our alterations will be described in more detail. We have used a similar version of this program to model a tropospheric spill of rocket oxidizer (N_2O_4) and to model HCl in the ground cloud from an SRM. Comparisons with field data for the two previously modeled cases are quite favorable.[23,24]

The plume model is adiabatic; this is a better description of the plume than an isothermal model because the heat transfer rates are slow compared to evaporation/condensation and chemical reaction. CHEMKIN calculates the enthalpy of each species in the model. As species are created or destroyed through reaction, they add or subtract energy from the plume; mixing with the air also affects the energy balance. This net change in energy is divided by the heat capacity of the plume to obtain the temperature change for each

integration step. This energy conservation equation is included as a governing equation, or constraint, for SURFACE CHEMKIN.

The governing equation for temperature is based on conservation of energy and is included here for reference:

$$\frac{\partial T}{\partial t} =$$

$$\left[\sum_{i=1}^{N} H_i^m m_i \left(\frac{\partial n_i^g}{\partial t} + \frac{\partial n_i^s}{\partial t} A_R + \frac{\partial n_i^l}{\partial t} V_R \right) \middle/ \left(C_p^g \rho + C_p^l m_l \right) \right]$$

$$+ \left[(T^{Air} - T) \frac{\partial \sigma_p}{\sigma_p \partial t} C_p^{Air} \middle/ \left(C_p^g \rho + C_p^l m_l \right) \right] \quad (24)$$

The preceding equation describes the change in the plume temperature with time. The numerator in this equation is the total enthalpy change for the plume; here N is 34. The product $H_i^m m_i (\partial n_i^g/\partial t)$ represents the heat gained or lost to the plume due to the production (or consumption) of a particular chemical species in gas phase reactions. The rate of species production from surface reactions $\partial n_i^s/\partial t$ is normalized by A_R. The term $(T^{Air} - T)(\partial \sigma_p/\sigma_p \partial t) C_p^{Air}$ represents the heat required to bring ambient air, which is mixing into the plume, to the same temperature as the plume gases. The superscript Air refers to quantities in the undisturbed air outside the plume. The denominator in the preceding equation represents the specific heat of the plume and is made up of the specific heat of the gas phase and condensed phase portions. The heat capacity of the surface phase is negligible and is ignored.

The remaining constraints are based on conservation of mass and are broken down into separate equations for each species in each phase. The governing equation for gas phase species is

$$\frac{\partial Y_i}{\partial t} = \frac{m_i}{\rho} \left(\frac{\partial n_i^g}{\partial t} + \frac{\partial n_i^s}{\partial t} A_R + \frac{\partial n_i^l}{\partial t} V_R \right) + \left(Y_i^{Air} - Y_i^g \right) \frac{\partial \sigma_p}{\sigma_p \partial t} \quad (25)$$

The first term in this equation is the molar changes due to reaction converted to a mass fraction, and the second term is the effect of dilution on plume species. This equation has a similar structure to the numerator of the first governing equation.

The equation for surface species in terms of site fraction is similar. There is also a correction for coverage; large molecules could occupy several sites, but all of the species in this model are small molecules with $\sigma_i = 1$. Only one surface phase is used in our model. There is an equation like the following for each surface species:

$$\frac{\partial X_i}{\partial t} = \left(\frac{\partial n_i^s}{\partial t} + \frac{\partial n_i^l}{\partial t} \frac{V_R}{A_R} \right) \frac{\sigma_i}{\Gamma_j} \quad (26)$$

This complete set of constraints is used in solving the differential equations from the kinetics for each time step in the simulation.

The model includes 34 chemical species, some 100 gas phase chemical and photochemical reactions, and two heterogeneous reactions. All of the important stratospheric reactions of nitrogen, hydrogen, oxygen, and chlorine containing molecules are included; the sources for the rates used are shown. Heterogeneous reactions, including direct loss of ozone on alumina, and catalysis of the reaction of chlorine nitrate with HCl are included as described in the results. Details of the parameters for this are given in a previous report.[6]

Exhaust Plume Dispersion

The model is formulated as a two-bin system, consisting of a plume bin that slowly mixes with the surrounding stratosphere and a stratosphere bin that is assumed to be infinite, i.e., concentrations of species in the overall stratosphere are assumed not to be perturbed by the plume. The composition used for the ambient stratosphere is based on recent measurements.[25] Interbin transport is described by a simple dilution function, which gives the plume concentration as a function of time. The dispersion (dilution) of the plume appears to be the most poorly understood part of this phenomenon at this time. Previous models of dispersing plumes[2,6,26] have used widely varying dispersion rates. In a previous report, we studied several different rates of dispersion to understand the coupling between the chemistry and the dispersion.[6] The ozone-destroying reactions are

second order in the concentration of chlorine-containing species; therefore, the ozone impact of SRMs is highly dependent on the dispersion rate. NO_x-based ozone destruction, being first order in NO_x, should depend less strongly on dispersion rate, and the relative impact of different motors should be even less dependent on dilution. The relative ozone impact of rockets whose exhaust contains only NO_x, compared to rockets that produce both NO_x and chlorine in the exhaust, will still depend on dispersion rate.

The dispersion rate of Watson et al.[26] is the slowest at early times and gives the largest ozone impact. The basis of the Watson et al. dispersion is beyond the scope of this paper, except to say that it was intended as a model of rocket effluent diffusion on a global scale. The nature of the ozone depletion considered here is more local and short term in nature than the phenomena considered by Watson et al. We include results based on the Watson et al. dispersion as a worst-case scenario and to illustrate the effect of dispersion rate on the chemistry. The functional form of the dilution factor for the Watson et al. case follows:

$$\frac{1}{\nu}\frac{\partial \nu}{\partial t} = -\frac{0.0053}{1 + 0.0019t} \qquad (27)$$

The rate of Denison et al.[2] is the fastest, partly because it models the effluent of a very small vehicle. The rate used by Denison et al. is size dependent; this makes the dispersion vehicle dependent and quite steeply time dependent. The distribution of Beiting[27] is essentially the same as that of Denison et al.[2] with some corrections for vehicle size. Both of these models are based in part on short-term ($t < 600$ s) observation of visible exhaust plumes. The functional form for the diffusion of the number density in the plume is[18,27,28]

$$\nu(r, t) = \nu_0(t_0/t)^2 \exp\{-(1/b)[(r/t) - (r_0/t_0)]\} \qquad (28)$$

where the diffusion parameter $b = 1.75$ m/s. Our model is one dimensional, assuming a constant concentration in a plume radius, and this concentration decreases through a dilution factor given by

$$\frac{1}{\nu}\frac{\partial \nu}{\partial t} = -\left(\frac{2}{t} - \frac{r_0}{bt^2}\right) \qquad (29)$$

For an expanding plume, $t > r_0/2b$, and the time axis must be redefined, i.e., $t \rightarrow t - r_0/2b + t_0$. The hot-plume flowfield model[10,19] follows the plume for approximately 2 s, at which point the radius

of the plume is about 25 m. We assume these values for t_0 and r_0 in this approach.

For most of the calculations, we will use this approach as our best guess of the true dilution factor. We treat all vehicles as if the initial plume were the size of the initial Titan IV plume. This gives the relative impact of different motors and propellant types for similar lift capacities. In addition, there is not enough data on dispersion rates to find an accurate model for each vehicle size. In all of the runs, we include 0.01% helium in the initial plume as a tracer to show the rate of dilution. The natural abundance of helium is omitted from the stratospheric bin for simplicity.

Results and Discussion

The output from the nozzle and hot-plume flowfield calculations[10,19] is used as input for our model based on SURFACE CHEMKIN from Sandia National Laboratories. The relative NO_x mass flux ratios for each vehicle is shown in Fig 1. The composition of the ambient stratosphere is taken from Ref. 25.

The concentrations of O_3 are calculated using the model for each launch vehicle at an altitude of 20 km for the Beiting[27] and Watson et al.[26] dilution factors. The results are shown in Figs. 2 and 3. The relative ozone impact for each vehicle is nearly independent of the dilution rate, but the absolute impact is strongly dependent on dilution. The ozone depletion is both deeper and longer lived when we use the dispersion model of Watson et al.[26] The vehicles using LOX as a propellant, with either l-H_2 or kerosene, destroy the least ozone. There is not a significant difference among the LOX vehicles, but the next launcher (solid propellant without chlorine) destroys between 3 and 20 times as much ozone, depending on the dispersion model. There is a similar difference between the vehicles using hypergol propellants and solid propellants (when chlorine is ignored). The largest ozone impact is from SRMs when the effects of chlorine are included; these destroy between 3 and 200 times as much ozone as the T3B, depending on dispersion and the timescale of interest. The T3B destroys the most ozone if only NO_x is considered. Because the effect of the NO_x chemistry is orders of magnitude less severe than that of the chlorine chemistry, further refinements of the nozzle and flowfield codes to better quantify NO_x production may be unnecessary, unless they result in orders of magnitude greater NO_x production.

Which dispersion model is most realistic can only be determined by measurements. The only published in situ measurement of O_3
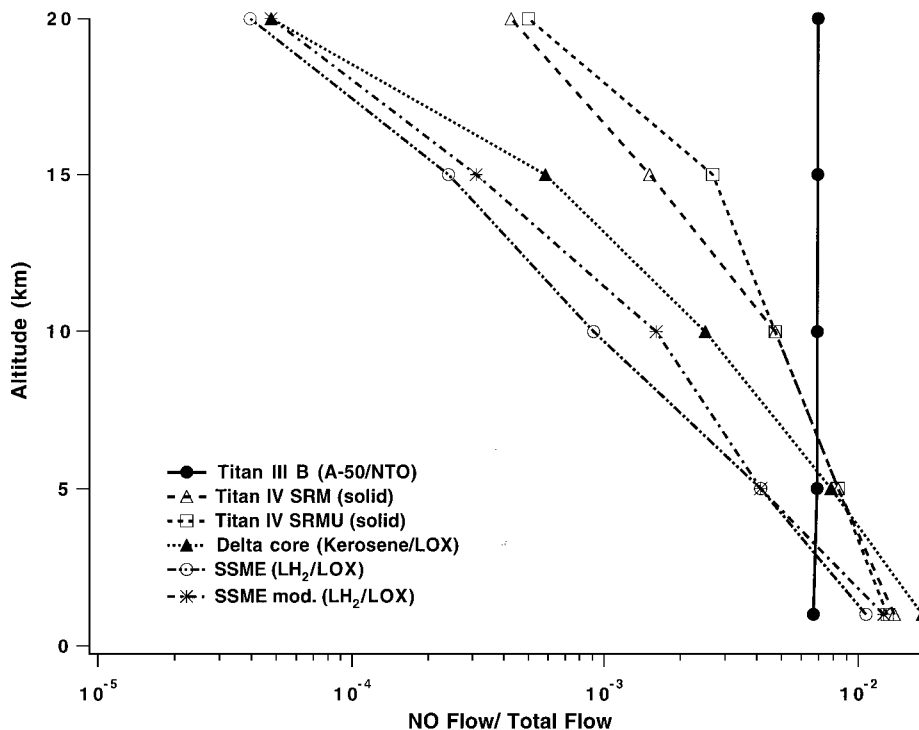

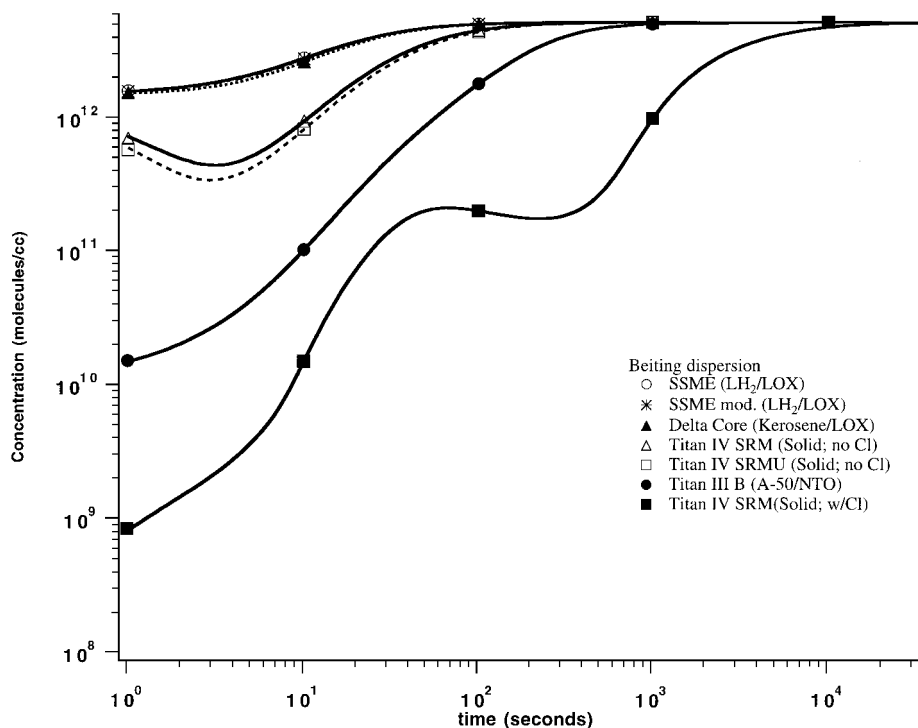Fig. 1 NO_x as a fraction of the total mass flow.

Fig. 2 Stratospheric ozone concentration in plume using the dispersion rate of Beiting.[27]
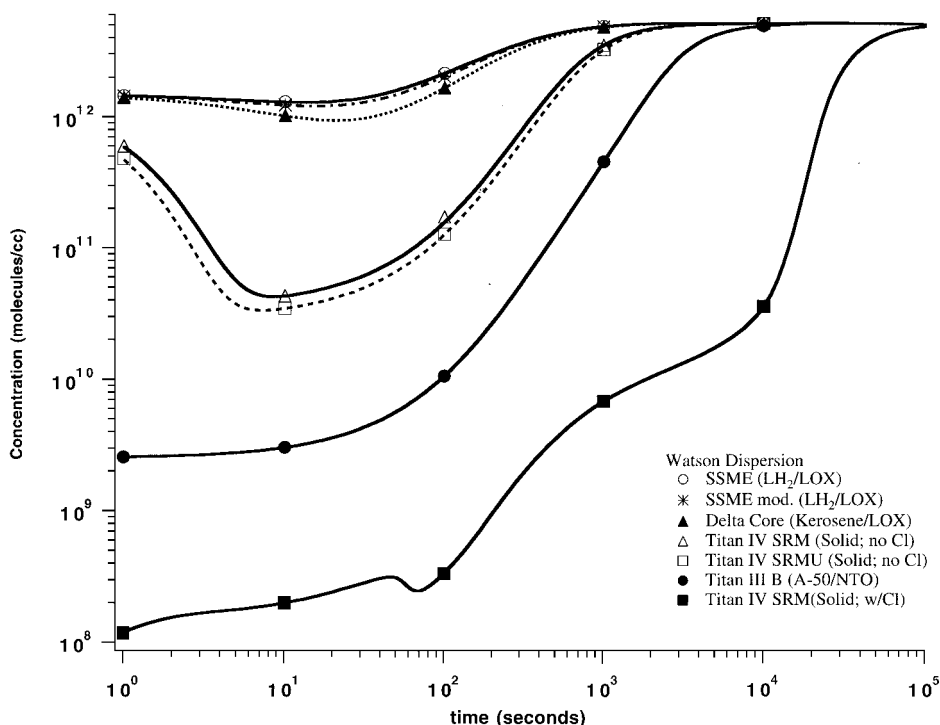

Fig. 3 Stratospheric ozone concentration in plume using the dispersion rate of Watson et al.[26]

concentration in an SRM (Titan III C) plume found a 40% decrease from the ambient value about 700 s after vehicle passage at an altitude of 18 km (Ref. 13). Comparing this result to the T4/SRM (solid; w/Cl) trace in Figs. 2 and 3, the Beiting[27] dispersion agrees more closely with the data but still shows too much depletion. A still faster dispersion rate than Beiting's should give better agreement with the Pergament et al.[13] observation, but more experimental data are needed to justify such a change.[14-17] We can also conclude that, based on the model, the observed depletion is more likely due to chlorine in the SRM exhaust than NO_x, contrary to what was originally suggested.[13] Field measurements should clarify this

issue.[14-17] For LOX vehicles in Figs. 2 or 3, the ozone-depleted region persists (greater than 10% ozone depletion) for less than 5 min; for the SRMs with chlorine, the depleted region persists for 3–10 h, depending on the dilution parameters.

Conclusions

We have used a model based on chemical kinetics and dispersion to estimate the atmospheric impact of launch vehicles. Our results indicate that the stratospheric impacts of rockets can be classified by the oxidizer used, the fuel being less important. SRMs with chlorine-containing propellant exert the greatest impact on ozone

by far. The vehicles using hypergolic propellant, N_2O_4 oxidizer, show the greatest impact from NO_x-based chemistry. Vehicles with LOX propellant using any fuel have the least impact. We have also demonstrated that dispersion of the gas plume represents the greatest uncertainty in modeling this system. Further refinement of the model awaits field data.

Acknowledgment

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