EXECUTIVE SUMMARY

Assessments of the current understanding of the stratospheric ozone layer and its depletion by natural and anthropogenic sources have been published in various joint reports from the World Meteorological Organization and the United Nations Environment Program. However, the effects of rocket exhaust on stratospheric ozone have not been updated in these assessments since 1991*(WMO [1991])*, and many questions have been left unanswered. The objective of this report is to compile and present current computer modeling calculations, laboratory data, and *in-situ* observations on the effects of rocket exhaust on stratospheric ozone. This report also describes the impact of deorbiting debris from satellites and launch vehicles on stratospheric ozone and compares this with the impact of meteorite debris. The information in this document is provided as a record of accomplishments and as a resource, and will serve as the current assessment report on the impact of rocket emissions and debris on stratospheric ozone.

Since the space program began in the late 1950's, space missions have been conducted using liquid propellants in a variety of launch vehicles. The requirement for instant readiness for the strategic missiles demanded that a storable type of fuel be used; that fuel was solid propellants. While all launch vehicle rocket engines produce effluents that may potentially affect the environment, effluents from solid rocket motors have received special scrutiny, since they contain chlorine, which is known to catalytically destroy ozone in the stratosphere. It is essential to understand the environmental effects of the effluents from solid rocket motors to: (1) be in compliance with the National Environmental Policy Act (NEPA) of 1969, and Executive Order 12114 - Environmental Effects Abroad of Major Federal Actions; (2) assist in maintaining current systems so that any deleterious environmental effects are minimized without affecting their reliability; and (3) assist in the design of new systems with improved performance that meet cost, reliability, and environmental requirements.

Studies performed by TRW, The Aerospace Corporation, and others have reported on several facets of launch vehicles that may have deleterious effects on stratospheric ozone. Among the U.S. launch vehicles addressed in this review are the Evolved Expendable Launch Vehicle (EELV), SEA Launch, Space Shuttle, and the Titan, Delta, and Atlas rocket platforms. While the primary focus of this work has been the effects of rocket exhaust, another area of concern reported on here is the effects of deorbiting space and meteorite debris on ozone. Also addressed in this review are potential alternative chemical propellants that may show diminished environmental impact. Ground-based sources of ozone depleting chemicals used in launch preparations are not included in this report.

The combustion of current conventional rocket fuels is known to produce chemical species that may be harmful to the environment in several ways, including destruction of stratospheric ozone. Solid-fuel rocket motor launch vehicles deposit chlorine directly in the stratosphere. Prudence, as well as consistency, requires that these sources should be evaluated under the same criteria as emission sources on the ground (for example, ozone depleting chemicals or ODCs) to determine their contributions, if any, to ozone depletion. The components of rocket exhaust (e.g., HCl, Al_2O_3, etc.) have not been listed as a Class I ODCs, and the Environmental Protection Agency (EPA) has made no move to reclassify them. However, this does not preclude them

being listed in the future, particularly if it were aggressively petitioned to do so *(SRS [1995])*. Accordingly, the terms ODC and ODP (Ozone Depletion Potential) will not be employed to describe the components of rocket exhaust, but instead the term PORS (Potential Ozone Reactive Species) will be introduced and used throughout the remainder of this report.

Assessment of the impact of space launch operations on the environment is now an integral part of launch operations and launch system acquisition. There are numerous published modeling studies dealing with the effect on the ozone layer by ozone reactive compounds that are exhausted into the stratosphere by solid rocket motors. Chlorine and chlorine oxides are present only in the exhaust of solid rocket motors 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. This is due in part to entrainment of ambient atmospheric oxygen, nitrogen, and hydrogen. There are also species such as alumina from solid rocket boosters and aerosol particulate and soot from LOX/Kerosene fuel in rocket exhaust. Particulate may promote heterogeneous reactions with ozone and ambient chlorine containing compounds *(Lohn et al., [1999])*.

Validation of computer models is essential to understanding the full ramifications of rocket exhaust on the atmosphere, and this validation is accomplished by laboratory investigations and by *in-situ* measurements of SRM exhaust plumes. In the Laboratory Measurements chapter of this report, chemical processes and yields are described. Heterogeneous processes are discussed, including rocket exhaust laboratory simulations, chlorine activation reaction dynamics, and reaction probability determinations for ozone depleting chemical reactions involving the effects of sulfuric acid vapor, the adsorption of water vapor on the surface of alumina, and the aerosol chemistry of aluminum oxide and nitrogen oxide.

The modeling results on the impacts of SRM exhaust products on stratospheric ozone are validated further with *in-situ* observations of the exhaust plume. Stratospheric ozone measurements are described. A variety of plume measurement campaigns are described, including RISO, the Rocket Impacts on Stratospheric Ozone experiment. Also described are a variety of plume measuring techniques, including specific ozone and aerosol measurements, LIDAR remote sensing, measurements of plume dispersion via electronic imaging, Total Ozone Mapping Spectrometer (TOMS) satellite observations, and a new instrument with the acronym High Resolution Ozone Imager (HIROIG) which may be used to study the plume chemistry in a local plume environment.

Local Effects on Ozone Depletion

Rocket launches have the potential to affect the atmosphere both in an immediate, episodic manner, and in a long-term, cumulative manner. When the stratosphere is affected immediately after launch, the perturbation occurs along or near the flight trajectory. Emissions from some types of launch vehicles significantly perturb the atmosphere along the launch trajectory at an approximate range of 10 kilometers or less from the rocket passage. Ozone concentration is temporarily reduced, an aerosol plume may be produced, and combustion products such as chlorinated compounds, alumina, NO_x, and reactive radicals can temporarily change the normal chemistry along the vehicle path.

Rocket launches can have a significant local effect on the stratosphere by reducing ozone substantially within the expanding exhaust plume up to 2 hours after launch. An ozone hole is observed within this plume and found to increase in size during this period. Ozone concentrations recover to background levels as time passes and ozone back-fills into the hole by diffusive processes. The extent of the hole depends on the quantity of emissions released and the thrust (size) of the launch vehicle. The time for this hole to refill to ambient ozone levels was 3000 seconds at 15-20 km and 6000 seconds at 40 km, based on measurement *(Ross et al., [1997])* and modeling *(Lohn et al., [1999])* studies.

It was long thought that hydrogen chloride, a relatively inactive form of chlorine, was the only SRM chlorine containing emission species. Calculations and laboratory experiments *(WMO [1991, 1995])* have shown that chlorine is present also as Cl_2 or Cl radical. This is significant, because, while hydrogen chloride primarily adds to the global chlorine burden and, hence the global ozone depletion, the extremely active Cl (Cl_2 photolyzes rapidly to Cl) can participate in immediate, local destruction of ozone.

The process of ozone destruction is controlled by the rate at which plume species diffuse into the ambient atmosphere and by the reaction of ozone with chlorine (with ClO as a product) and the subsequent reproduction of chlorine by photoreactions, and reactions associated with chlorine chemistry. These model simulations of dramatic ozone losses in the first couple of hours after launch have been corroborated by measurements taken after the launch of a variety of SRM vehicles, namely Titan III, Titan IV, and Space Shuttle *(Ross [1997], Jackman [1998], Lohn et al., [1999], McKenzie [1998], WMO [1991]).*

Global Effects on Ozone Depletion

In addition to local effects, the effluents from rockets may have long term or global impacts on stratospheric ozone. These potential global impacts derive from the relatively long lifetimes of alumina particulate and chlorine (primarily as HCl) in the stratosphere. Although rocket motor emissions appear to represent a small fraction of the total anthropogenic impact on stratospheric chemistry, prudence requires a careful evaluation of this impact, particularly on stratospheric ozone *(Ko [1999], WMO [1991]).*

Jackman *et al., [1998]* carried out detailed stratospheric modeling calculations of ozone depletion caused by a launch rate of nine Space Shuttle launches and three Titan IV launches per year using the reaction probability measurement of $ClONO_2$ with HCl on alumina surfaces by Molina *[1999]*. Their results indicate that the effect on the annually averaged global total ozone is a decrease of 0.025% by the year 1997; about one-third of this decrease results from the SRM-emitted alumina and the remaining two-thirds results from the SRM-emitted hydrogen chloride. These results were confirmed independently by the modeling efforts of both Lohn *et al., [1999]* and Ko *et al., [1999]*.

Potential long-term effects utilizing solid rocket propellants include a global reduction in stratospheric ozone, an increase in the chlorine loading of the stratosphere, and an increase in the particulate burden. Based on the modeling efforts of Jackman *et al., [1998]* and others, the global implications appear to be extremely minor at current launch rates, but are nonetheless real and long-lived.

In-Situ Measurement Studies

In-situ measurement results clearly suggest that SRM launch vehicles produce transient ozone loss following launch. A comparison of *in-situ* data to recent modeling efforts has confirmed that the models only slightly underestimate both the size and the duration of the region of ozone removal in the wake of large and medium launch vehicles. However, even when such reductions occurred, the reduction in column ozone was found to exist over an area a few kilometers by a few tens of kilometers and was generally much smaller. The local-plume ozone reductions decrease to near zero over the course of a day, and the regional effects were smaller than could be detected by TOMS satellite observations.

Laboratory Studies

Laboratory investigations by Disselkamp *[1999]* assessed the uptake of NO and NO_2 onto the surface of Al_2O_3. These reactions have two potential implications in atmospheric chemistry. First, a decrease in atmospheric NO_x concentrations could enhance the catalytic destruction of ozone by halogen species. Considering that the ambient stratospheric NO_x concentration was approximately 10 ppbv (parts per billion volume), or $2.5x10^{10}$ molecules/cm^3, it would take an Al_2O_3 particle density of 640 particles/cm^3 to deplete all the NO_x species. Aluminum oxide chemistry is not expected to be important in the exhaust plume because the particulate concentration is far too low to be significant in comparison with the homogeneous chlorine chemistry. A second potential atmospheric implication of this chemistry was to consider the uptake of halogen species onto the surface of aluminum oxide particles. Disselkamp *[1999]* suggests that the uptake of active halogen species by aluminum oxide to liberate NO would have the effect of increasing the ozone concentration by reducing the contribution of halogen catalyzed ozone destruction. There is no evidence to date to support this hypothesis; additional studies are needed to characterize this halogen chemistry.

The reaction probability (γ) for the reaction of $ClONO_2$ with HCl on alumina surfaces was measured by Molina *[1999]*. The result was $\gamma = 0.02$ under conditions similar to those which would be encountered at mid-latitudes in the lower stratosphere. The result is in good agreement with other published measurements on alumina and on glass surfaces conducted with larger reactant concentrations. The reaction was found to be nearly zero-order in HCl, and the mechanism was dependent on the presence of absorbed water layers not on the detailed nature of the refractory oxide surface itself. Furthermore, it was determined that a significant fraction of the injected alumina surface area would be catalytically active and would remain unaffected in the stratosphere by sulfuric acid vapor. The time required for the alumina particulate to be covered by a monolayer of sulfuric acid was estimated at 8 months, assuming an accommodation coefficient of 0.1. Finally, coalescence with stratospheric sulfuric acid aerosols would most likely be unimportant for the alumina particles larger than about 0.1 μm in diameter before they settle out of the stratosphere. For particle distributions less than 0.13 μm, the mass-weighted atmospheric lifetime is about 0.3 years with or without sedimentation and collision removal, because reactivity for particles smaller than 0.13 μm is small. These results were confirmed by 3-D model calculations of Ko *et al., [1999]*.

Propellants

A methodology for the systematic removal of PORS from rocket plume exhaust streams using alternate propellants is presented. The changes to launch vehicles vary from a minimum of a reformulated conventional solid propellant containing ammonium perchlorate, but with afterburning suppressant chemicals added, to a completely reformulated solid propellant that incorporated nitrate/carbonate oxidizers, to new engines based on fluorine oxidizers or redeveloped engines burning conventional liquid propellants. Reformulated solids with afterburning suppressants could be implemented as a direct response to Cl_2 production; conventional liquid engines utilizing LOX/LH_2 and/or LOX/RP-1 could be implemented to remove HCl; and fluorine systems (solids and/or gels) could be implemented to eliminate H_2O and CO_2.

Among launch vehicles utilizing the following propellants LOX/LH_2, LOX/RP-1, NTO/Amine, solid, and solid with chlorine, Brady *et al., [1997]* concluded that LOX vehicles generated the least amount of ozone depletion (a hole which lasted less than 5 minutes) and that solid rocket motors with chlorine generated the most ozone destruction (a depleted region which persisted for 3 to 10 hours, depending on dilution parameters).

Deorbiting Space and Meteorite Debris

A discussion of the impact on stratospheric ozone from deorbiting debris is presented. Consideration of the individual studies assessed in this document leads to the conclusion that the physical and chemical phenomena associated with deorbiting debris and meteoroids do not have a significant impact on global stratospheric ozone. The reasons are twofold: slow reaction rate and low particle density. However, it was noted that a large deposition of particles in the

stratosphere due to volcanic eruptions could have a significant impact on the local ozone column density. The effect of meteoroids on the stratospheric ozone layer also was investigated. The meteoroid population for micron to millimeter size objects was found to be comparable to the orbital debris flux. Meshishnek *[1995]* presented data from the Interplanetary Dust Experiment (IDE) which measured impact fluxes on six sensors on the Long Duration Exposure Facility (LDEF). The LDEF sensors measured impacts due to particles greater than roughly 0.2 μm and up to 100 μm in diameter. There was no way to differentiate between debris and micrometeoroid impacts; however, the vast majority (>80%) of the particle impacts were presumed to be from debris since the sensors must have been in the 25-μm and below range, where debris clearly dominates *(Meshishnek [1995]).* To the extent that they are comparable, it may be concluded that meteoroids pose little or no threat to global stratospheric ozone.

Summary

Depletion of stratospheric ozone locally within the exhaust plume of a launch vehicle is real as measured by *in-situ* and other field techniques, but is short-lived. On a global scale, depletion of ozone from a rocket launch is calculated in theoretical models, but is found to be well below the detection limits of current measurement techniques. Should the frequency of rocket launches using solid propellants increase (i.e., from both commercial and government launches on a global scale), the extent of ozone depletion will increase. As the United States and other governments move toward more reliable and more "ozone friendly" propellants in its rocket programs, the levels of global ozone depletion will be minimized.

Perhaps the single most important parameter in modeling stratospheric ozone depletion by rocket exhaust plumes is the rate of dispersion in an expanding plume parcel. The plume expansion rates measured in the fly-through of a NASA WB57F aircraft *(Ross et al., [1997]),* as well as that determined by LIDAR *(Dao et al., [1997])* and electronic imaging *(Beiting [1999])* of several different launch vehicles are in reasonable agreement with modeling efforts *(Brady et al., [1997], Beiting [1999], Denison et al., [1994], Lohn et al., [1994], Watson et al., [1978]).* As explained in Beiting *[1999],* the WB-57 and LIDAR observations cannot measure the aggregate plume dispersion; they can detect the existence of parcels at later times and the parcels can have a higher concentration of PORS than that inferred from the aggregate dispersion rate. To understand the spatial extent of the plume as a function of time, the aggregate dispersion rate should be used. Higher concentrations of PORS than predicted by the aggregate dispersion rate will exist in parcels – as noted by LIDAR *(Dao et al., [1997])* and WB-57 aircraft *(Ross et al., [1997]).* The models give reasonable answers when correct dispersion rates are used in them. Watson *et al., [1978]* and Lohn *et al., [1994]* calculated diffusion constants for large scales. The model of Brady *et al., [1997]* uses an experimental value for the diffusion parameter and will give correct concentrations for the correct parameters – which may vary greatly depending on atmospheric conditions and altitude. Again, all of the differences between modeling efforts and *in-situ* measurements may be explained if each plume parcel is expanding at its own rate, a complexity which must be incorporated into future modeling efforts.

Future Work

      Despite the conclusions presented in this report, there are still opportunities for further work. These opportunities include increased fidelity in the models employed, thorough assessments of potential alternative propellants, the effect of deposition of large amounts of water in the stratosphere, more detailed *in-situ* assessments, and deployment of the HIROIG instrument for monitoring the local effects of rocket exhaust in locations which are geographically inaccessible or have restricted access.