ATMOSPHERIC ENVIRONMENTAL IMPLICATIONS OF PROPULSION SYSTEMS

Allan J. McDonald*
Robert R. Bennett**
Thiokol Space Operations
Brigham City, Utah

ABSTRACT

Three independent studies have been conducted for assessing the impact of rocket launches on the earth's environment.[1,2,3] These studies have addressed issues of acid rain in the troposphere, ozone depletion in the stratosphere, toxicity of chemical rocket exhaust products, and the potential impact on global warming from carbon dioxide emissions from rocket launches. Local, regional, and global impact assessments were examined and compared with both natural sources and anthropogenic sources of known atmospheric pollutants with the following conclusions:

- Neither solid nor liquid rocket launches have a significant impact on the earth's global environment, and there is no real significant difference between the two.
- Regional and local atmospheric impacts are more significant than global impacts, but quickly return to normal background conditions within a few hours after launch.
- Vastly increased space launch activities equivalent to 50 U.S. Space Shuttles or 50 Russian Energia launches per year would not significantly impact these conclusions.

However, these assessments, for the most part, are based upon homogeneous gas phase chemistry analysis; heterogeneous chemistry from exhaust particulates, such as aluminum oxide, ice contrails, soot, etc., and the influence of plume temperature and afterburning of fuel–rich exhaust products, need to be further addressed. It was the consensus of these studies that computer modeling of interactive plume chemistry with the atmosphere needs to be improved and computer models need to be verified with experimental data. Rocket exhaust plume chemistry can be modified with propellant reformulation and changes in operating conditions, but, based upon the current state of knowledge, it does not appear that significant environmental improvements from propellant formulation changes can be made or are warranted. Flight safety, reliability, and cost improvements are paramount for any new rocket system, and these important aspects cannot be compromised. A detailed environmental cost–benefit–risk analysis must be conducted before any new chemistry or changes in rocket operating conditions should be seriously considered for any future space or defense applications.

This paper presents a summary of the results of environmental assessments contained in these independent studies.

*Vice President and Senior Staff
**Scientist

INTRODUCTION

These studies were conducted to answer a basic question: As a result of increased space launch activities, will chemical rocket propulsion have a major impact on the earth's environment? This issue was first raised by environmentalists who were particularly concerned about the deposition of hydrogen chloride (HCl) from solid rockets into the atmosphere. HCl in the presence of water can form acid rain (hydrochloric acid) in the launch area as well as deposit a chlorine–containing gas directly into the ozone layer of the stratosphere. These issues were of sufficient concern that the original U.S. Air Force–NASA joint program office for the Advanced Launch System (ALS) would not consider solid rockets for that application unless the propellants were reformulated to produce less than one percent by weight of HCl in the exhaust plume, compared to the 21 percent for current propellants. As a result, several alternative propellants that were perceived to be more environmentally acceptable were formulated in the laboratory and tested in subscale motors under U.S. Air Force–sponsored "clean propellant" programs. Initially, existing solid propellant formulations were modified to reduce the HCl content in the exhaust plume; later formulations included totally new propellants that contained non–chlorine oxidizers (these propellants were referred to as "totally clean" propellants). All of these so–called "clean" propellants have some serious drawbacks in one or more important propellant characteristics: losses in performance (specific impulse or density); difficulties in processing and/or reduced physical properties and aging characteristics; humidity sensitivity; increased safety hazards during propellant processing or use; limited ballistic tailoring; and reduced bonding capability. Moreover, many have significant increases in costs over contemporary solid propellants using ammonium perchlorate (AP) as the oxidizer. The chemistry of solid rocket propellants is the single most important factor in determining the performance, safety, reproducibility, reliability, and cost of a solid rocket propulsion system. Departing from a well–established experience base, along with the lack of understanding of the real environmental impact of chemical rocket exhaust, dictated the need to fully examine this issue before changes in solid rocket propellant chemistry were warranted.

It was decided to examine the environmental impact of all rocket propellants, both solid and liquid. Table I lists the propellant combinations that were examined and the major exhaust products from these propellants. The first propellant in the table is the standard solid rocket propellant used in all space launch vehicles incorporating solid rocket boosters (SRBs) today; all current space launch solid propellants use a rubber binder containing aluminum as the primary fuel and AP as the oxidizer. The second formulation in the table is a "clean" propellant that replaces a portion of the AP oxidizer with sodium nitrate. As this propellant burns, most of the

Propellant System	Major Exhaust Products
Ammonium perchlorate . Aluminum	HCl, Al_2O_3, CO_2, CO*, N_2, H_2*, H_2O
Ammonium perchlorate . Sodium nitrate Aluminum	NaCl, Al_2O_3, CO_2, CO*, N_2, H_2*, H_2O
Ammonium perchlorate . Magnesium	MgO, $MgCl_2$, CO_2, CO*, N_2, H_2*, H_2O
Ammonium nitrate .... Magnesium or aluminum	Al_2O_3 or MgO, N_2, CO_2, CO*, H_2*, H_2O
Liquid oxygen ..... Liquid hydrogen	H_2O, H_2*
Liquid oxygen ..... Hydrocarbon	CO*, CO_2, hydrocarbons, H_2O
N_2O_4 ..... Dimethylhydrazine	N_2, NOx, CO*, CO_2, H_2O

*Mostly consumed during afterburning

Table I.
Chemical Propulsion Components
and Exhaust Species

HCl produced is scavenged inside the combustion chamber to form sodium chloride (NaCl), common table salt, as a combustion product rather than HCl. The third propellant is also a "clean" propellant and is sometimes referred to as the "Maalox rocket." This propellant replaces the aluminum fuel with magnesium to produce the oxide of magnesium metal (MgO) rather than aluminum oxide. Magnesium oxide in the presence of water forms magnesium hydroxide, which is a strong base. Magnesium hydroxide is the primary ingredient in Maalox for neutralizing stomach acid (which is also HCl). The magnesium oxide in the rocket exhaust neutralizes the HCl in the plume as it mixes with the water in the ambient air and the water that is produced as part of the combustion process, forming a magnesium chloride ($MgCl_2$) salt in place of HCl. The fourth propellant is referred to as a "totally clean" propellant because it replaces all of the AP oxidizer with an ammonium nitrate oxidizer to prevent any chlorine–containing compounds from being formed. There are several candidate nitrate oxidizers available, and many more energetic nitrate oxidizers are in laboratory development, but the exhaust gas chemistry produced is quite similar to the one shown in the table. The last three propellants are all–liquid rocket propellants used in various space launch vehicles; the simplest chemistry is produced from liquid hydrogen and liquid oxygen that forms water as the primary combustion product with considerable free hydrogen (H_2) present, as the engines are generally run fuel–rich for improved reliability and performance. It should be noted that all of the propellant combinations produce large quantities of water and most produce carbon monoxide (CO); carbon dioxide (CO_2), and free hydrogen (H_2) in the exhaust plume. The storable bipropellant system using nitrogen tetroxide (N_2O_4) and unsymmetrical dimethylhydrazine (UDMH) also produces free nitrogen and oxides of nitrogen. The environmental impact assessment that was made assumed that all of the hydrogen and carbon monoxide produced below an altitude of 25 kilometers was converted to water and carbon dioxide as a result of afterburning with the ambient air.

STRATOSPHERIC OZONE DEPLETION

Figure 1 depicts the various atmospheric zones surrounding the earth. The stratosphere located approximately 13 to 50 kilometers above the earth is particularly important to our environment because it contains a low concentration of ozone (O_3) that acts as a protective shield from damaging ultraviolet radiation from the sun.

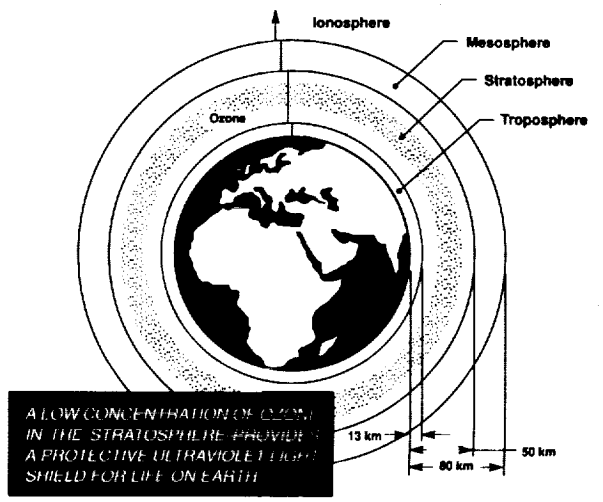

Fig. 1. Stratospheric Ozone Effects

Figure 2 presents the chemical and photochemical processes that are important in the formation of ozone from molecular oxygen in the stratosphere and the reactions associated with ozone destruction.[4] The process is very dynamic in that ozone is continuously being produced and destroyed by naturally occurring photochemical processes in the stratosphere.

Ozone Production

$$O_2 \xrightarrow{h\upsilon} 2O$$
$$O + O_2 + M \longrightarrow O_3 + M$$

Ozone Destruction

$$O_3 \xrightarrow{h\upsilon} O + O_2$$
$$O_3 + O \longrightarrow 2O_2$$
$$Cl + O_3 \longrightarrow ClO + O_2$$
$$ClO + O \longrightarrow Cl + O_2$$
$$H + O_3 \longrightarrow HO + O_2$$
$$HO + O \longrightarrow H + O_2$$
$$OH + O_3 \longrightarrow HO_2 + O_2$$
$$O + HO_2 \longrightarrow OH + O_2$$
$$NO + O_3 \longrightarrow NO_2 + O_2$$
$$NO_2 + O \longrightarrow NO + O_2$$
$$Br + O_3 \longrightarrow BrO + O_2$$
$$BrO + O \longrightarrow Br + O_2$$

Fig. 2. Natural Stratospheric Ozone Pathways

Figure 3 summarizes the naturally occurring ozone–depleting chemistries into nitrogen, hydrogen, oxygen and chlorine.[4] It is important to note that all are catalytic cycles in that the ozone–depleting species is regenerated such that it can re–enter the cycle to destroy additional ozone molecules. The asterisk on the chart reflects those ozone–depleting chemistries that are affected by rocket propulsion, i.e., nitrogen, hydrogen, and chlorine. It is interesting to note that chlorine chemistry is responsible for the least amount of ozone destruction. The reason chlorine chemistry has been of most concern is because it is the one that human activity has contributed to most.

	25 to 30 km Altitude (%)	Total Stratosphere (%)
Nitrogen*		
$NO + O_3 \rightarrow NO_2 + O_2$ $NO_2 + O \rightarrow NO + O_2$	70	32
Hydrogen*		
$OH + O_3 \rightarrow HO_2 + O_2$ $O + HO_2 \rightarrow OH + O_2$	10	26
$H + O_3 \rightarrow HO + O_2$ $HO + O \rightarrow H + O_2$		
Oxygen		
$O + O_3 \rightarrow 2O_2$	10	23
Chlorine*		
$Cl + O_3 \rightarrow ClO + O_2$ $ClO + O \rightarrow Cl + O_2$	10	19

* Relevant to chemical propulsion exhaust

Fig. 3. Relative Importance of Various Catalytic Stratospheric Ozone Depletion Cycles

Analysis of more recent data obtained from aircraft flying in the lower part of the stratosphere has cast some doubt on the predominance of nitrogen oxide reactions to ozone destruction in the lower stratosphere.[5] In the spring of 1993, for the first time, atmospheric researchers were able to obtain data from an instrument–laden aircraft that observed all the important families of radicals that affect ozone, i.e., chlorine, bromine, nitrogen, and hydrogen. A new instrument measured hydroxyl (OH) and hydroperoxyl (HO_2) radicals as the aircraft crisscrossed the stratosphere. The data obtained indicated that the hydrogen radical family may be a more important natural loss process for ozone than the nitrogen oxide cycles. These conclusions were also supported by more recent computer models that include heterogeneous chemistry; computer models used in the past based upon homogeneous chemistry alone predicted that nitrogen oxides were the predominant ozone destruction mechanism.

Figure 4 pictorially represents the differences between an all–liquid propulsion system and the Space Shuttle, which uses both solid rocket and liquid propulsion. The exhaust products of interest—HCl, H_2O, and H_2—deposited in the troposphere by either vehicle are of little concern because H_2 afterburns to H_2O, and both HCl and H_2O are quickly removed by raining out in the troposphere. Approximately two–thirds of the exhaust produced from the Space Shuttle SRBs is deposited in the troposphere, and the remainder is exhausted into the stratosphere where the boosters burn out. It is also important to note that the exhaust products produced—H_2O, H_2, and HCl—do not react directly with ozone;

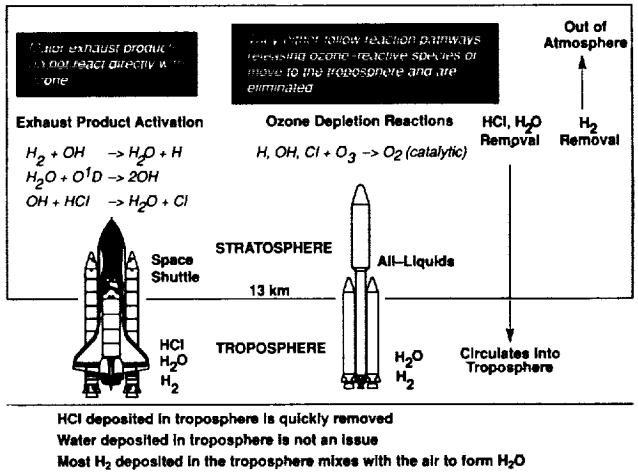

Fig. 4. Mechanisms of Potential Effect of Rocket Exhaust on Ozone

the ozone–reactive species (H, OH, Cl) must be released from the molecules in the plume before any ozone destruction can occur. Much of the HCl and water deposited into the lower portion of the stratosphere is removed by circulation into the troposphere, and considerable hydrogen deposited in the upper stratosphere is removed by escaping into the mesosphere.

Figure 5 depicts the molar concentration of important exhaust gases and where they are deposited from the Space Shuttle SRBs and the Space Shuttle main engines (SSMEs). Ozone–reaction chemistry is controlled by the molar concentration of the reacting species and the chemical reaction kinetics associated with releasing the reactive species and its subsequent reaction with ozone. It was assumed that all of the rocket exhaust produced in the stratosphere stayed there to react with ozone and none of it circulated into the troposphere or escaped into the mesosphere. It should be noted from Fig. 5 that, even though the SRBs do generate a considerable amount of HCl, from a molar basis, water and hydrogen are the major exhaust products. Even though the SSMEs produce only water and hydrogen, the SRBs, because of their much higher thrust level, deposit nearly as much water and hydrogen into the stratosphere as the SSMEs; most of the SSME exhaust is deposited above the stratosphere.

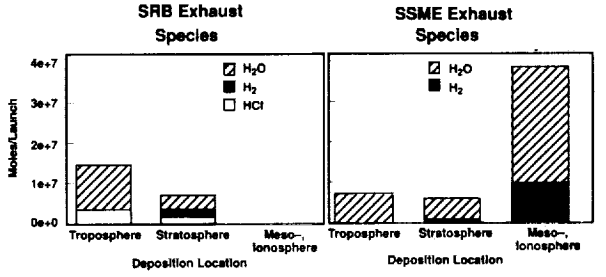

Fig. 5. Space Shuttle Exhaust Species

Much of the environmental concern with solid rocket motors was a by–product of associating solid rocket–produced HCl with chlorofluorocarbons (CFCs). Figure 6 presents a schematic representa-

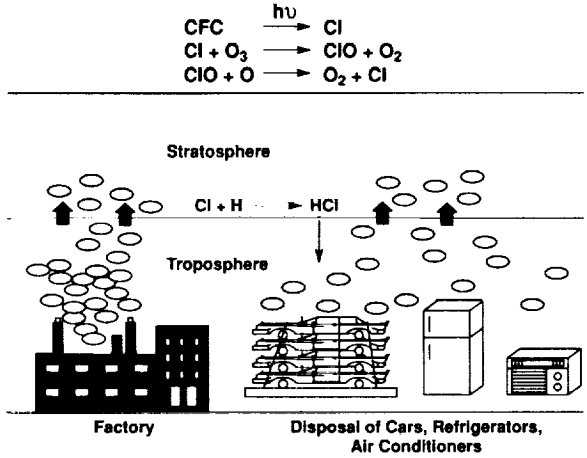

Fig. 6. Effects of CFCs on Ozone

tion of the CFC problem. CFCs are very chemically stable compounds used in refrigeration, air conditioning systems, aerosol products, and many cleaning solvents. These compounds are man-made chemicals that were designed to be chemically inert for the intended applications. As a result, there are no natural processes in the troposphere that will break down these chemicals until they reach the stratosphere, where photolysis by ultraviolet radiation releases chlorine atoms from the CFCs. The released chlorine then enters into a catalytic ozone destruction cycle. One of the major problems with CFCs is the long life and tremendous reservoir of these materials in discarded automobiles, refrigerators, air conditioners, etc., that provide a source of these chemicals to eventually enter the stratosphere for hundreds of years. Unlike HCl, which is washed out and removed as the stratospheric air circulates into the troposphere, CFCs are inert to most chemical processes in the troposphere. It is interesting to note from Fig. 6 that the chlorine released in the stratosphere from CFCs is eventually removed by the reaction of chlorine with stratospheric methane to form HCl, which can then circulate to the troposphere and be removed. As can be seen from Fig. 6, there is a significant difference between CFCs and HCl from solid rocket exhaust. In fact, *the formation of HCl* is the *primary removal process for chlorine atoms released from CFCs* in the stratosphere. Conventional wisdom indicates that all CFCs that are released to the atmosphere will eventually make it to the stratosphere, and will remain in the stratosphere until their chlorine is released by photodissociation from sunlight (a process that cannot be avoided) in the form of active chlorine (Cl) atoms; the released chlorine atoms will continue to catalytically destroy ozone until the chlorine is tied up in a reservoir specie or can be removed by forming HCl. However, HCl deposited directly into the stratosphere from rockets must undergo a chemical reaction before the ozone-destroying chlorine atoms can be released. HCl is not subject to photodissociation. As a result, some of the HCl deposited directly into the stratosphere may never release any chlorine before it has the opportunity to circulate back into the troposphere where it is readily rained out. Furthermore, HCl is a naturally occurring chemical in the earth's atmosphere, with a large natural reservoir of HCl in the troposphere and stratosphere in contrast to the unnatural molecules of CFCs that were engineered by man.

Figure 7 is a projection of the cumulative global stratospheric chlorine burden in parts per billion (ppb) over a 75-year time frame from 1979 to 2054, assuming that the Montreal Protocol ban on the production of Class I ozone depleting chemicals (ODCs) is effective by 1996 as planned.[6] Superimposed on this chart is the contribution to stratospheric chlorine in the form of hydrogen chloride from all rocket launches which represents a steady-state contribution of chlorine from HCl of approximately 0.003 ppb. This assumes a world launch rate of solid rockets equivalent to one Space Shuttle launch every month.[7] This launch rate represents a constant 40 percent increase in HCl deposited in the stratosphere from solid rocket launches over what was actually achieved in 1993.

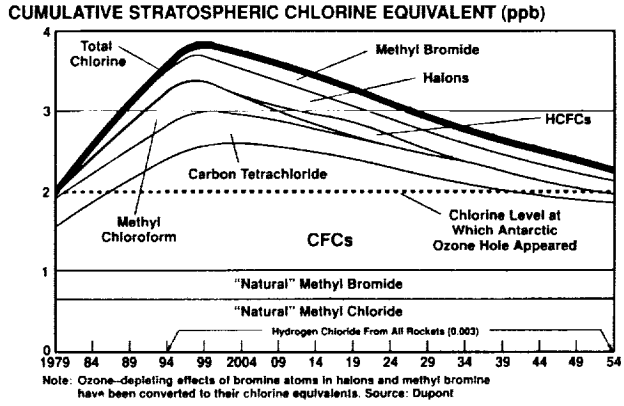

Fig. 7. Levels of Chlorine in Stratosphere Will Decrease Slowly Under Montreal Protocol

Figure 8 depicts the relative annual contributions from various sources to the stratospheric chlorine burden.[8] Industrial halocarbon-derived chemicals, primarily CFCs, producing 300 kilotons per year, are a major contributor to stratospheric chlorine and are the principle source of anthropogenic chlorine. Natural sources, primarily methyl chloride (CH_3Cl) from the oceans and burning vegetation, were estimated to add an additional 75 kilotons of chlorine to the stratosphere. Volcanoes can inject HCl directly into the stratosphere, and when major volcanic activity occurs, such as the 1991 Mount Pinatubo eruption in the Philippines, it tends to

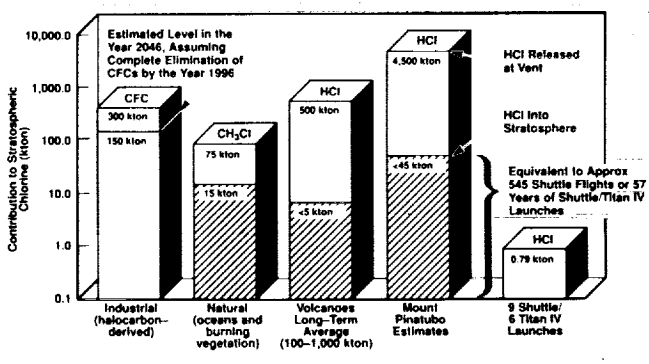

Fig. 8. Relative Annual Contributions to Stratospheric Chlorine

overshadow all other sources during the rather short period of time of volcanic activity. Volcanoes are very random and sporadic sources of chlorine, but it was estimated that on a long–term average, volcanoes could inject anywhere from 100 to 1,000 kilotons of chlorine in the form of HCl directly into the stratosphere on an annual basis.[9] The chlorine burden from SRBs producing HCl adds less than 1 kiloton of chlorine to the stratosphere per year based upon a flight rate of nine Space Shuttles and six Titan IV launches per year. It should also be noted from Fig. 8 that, if we are successful in eliminating all CFC production by 1996 as mandated by the Montreal Protocol, we will still be adding 150 kilotons of chlorine to the stratosphere some 50 years later as a result of the long life and huge reservoir of these chemicals.

It should be noted in Fig. 8 that more recent data (represented by the cross–hatched area) obtained from volcanic activity indicate that only a small fraction of the HCl emitted from a volcano ever reaches the stratosphere as hydrogen chloride gas.[10] Data obtained from Mount Pinatubo, along with detailed computer modeling studies, indicated that less than 1 percent of the HCl gas emitted from the vent of the volcano reached the stratosphere in that form; more than 99 percent of the HCl is rained out of the stratosphere by the huge quantities of steam and water contained in the volcanic cloud. The quantities of steam emitted from the volcano produce roughly 1,000 times as much water as HCl while the volcanic cloud rises and cools. Nevertheless, the Mount Pinatubo eruption in June 1991 is estimated to have released 4.5 million metric tons of HCl. Assuming only 1 percent of the HCl reached the stratosphere, it would still result in injecting 45 kilotons of chlorine into the stratosphere, which is equivalent to approximately 545 flights of the U.S. Space Shuttle.

More recent data obtained from measurements taken by stratospheric aircraft (represented by the cross–hatched area) have also indicated less methyl chloride in the stratosphere than was originally thought.[11] As shown in Fig. 8, more recent data would reduce the stratospheric loading of methyl chloride from oceans and biomass burning from 75 kilotons to approximately 15 kilotons per year. These more recent data would indicate that natural sources of chlorine are considerably lower than was originally believed. If chlorine contributions from CFCs are as high as predicted (300 kilotons per year), then these anthropogenic contributions to stratospheric chlorine would be the major source of chlorine in the stratosphere. In any event, the 0.79 kilotons per year of chlorine from rocket launches remains small compared to CFCs or natural sources of chlorine.

Figure 9 presents a Pareto chart of the stratospheric ozone–depleting chemistries and the portion that can be attributed to chemical rockets. As can be readily seen, rocket contribution to stratospheric ozone depletion is extremely small, representing approximately 0.03 percent of the ozone depletion from all other sources. Therefore, based upon the current state of knowledge, it certainly would not appear to be technically or financially responsible to spend large sums of money trying to reduce the contribution of chemical rockets to destruction of stratospheric ozone.

There have been several numbers published in the literature for the magnitude of stratospheric ozone depletion due to solid rockets over the past few years. These numbers are not inconsistent, but

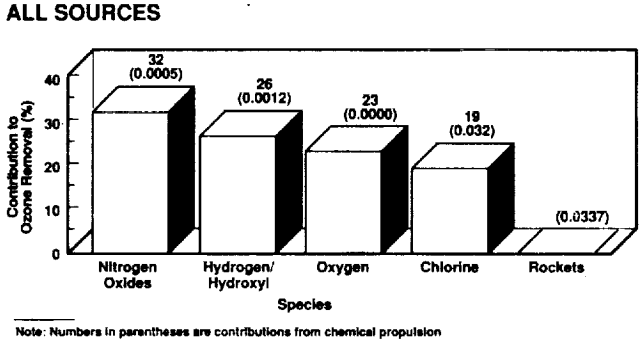

Fig. 9. Chemical Removal of Stratospheric Ozone

represent different sets of conditions as shown in Fig. 10.[12] Based on a two–dimensional (2–D) atmospheric computer model calculating local ozone depletion at a 40–kilometer altitude in the region (1,000 km by 1,000 km) above the launch site, long–term steady–state stratospheric ozone depletion approaching 0.25 percent would be calculated. This same analysis through the entire regional ozone column over the launch site reduces the ozone loss to less than 0.1 percent, which is further reduced to approximately 0.006 percent on a global scale. The global ozone depletion numbers presented in Fig. 9 are based upon first order approximations that are roughly five times more conservative than the 2–D models would predict, resulting in the 0.03 percent number shown. Since global stratospheric ozone depletion calculations based on these more sophisticated 2–D models (0.006 percent) have underpredicted ozone losses by a factor of two over the past few years, it is most probable that ozone depletion from rocket launches would not exceed a steady–state reduction of more than 0.012 percent based on the assumed yearly flight rate of nine Space Shuttles and six Titan IV vehicles.

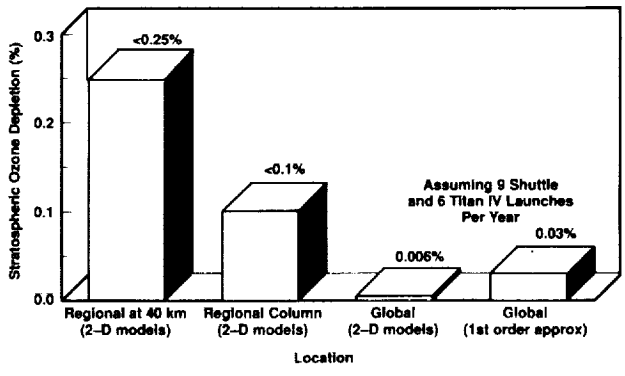

Fig. 10. Stratospheric Ozone Impact Due to Solid Rocket Motor Exhaust

There have been news media reports linking the ozone reduction in the stratosphere to rocket launches, and solid rocket motors in particular. It is clear that 0.006 to 0.012 percent reductions cannot be measured, especially when the natural annual variations in the northern hemisphere have varied over 20 percent, as shown in Fig. 11. Figure 11 covers a 33–year period from 1957 to 1991.[13]

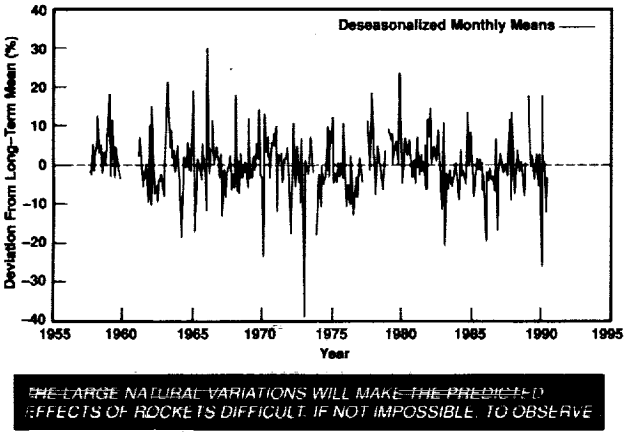

Fig. 11. Large Natural Variations in Stratospheric Ozone

Some people have been concerned that rockets may be creating an ozone hole directly over the launch site areas. As shown in Fig. 12, a typical Space Shuttle trajectory is not even close to being vertical, and, in fact, by the time the SRBs burn out near the top of the stratosphere, the Space Shuttle has as much down–range as vertical altitude.

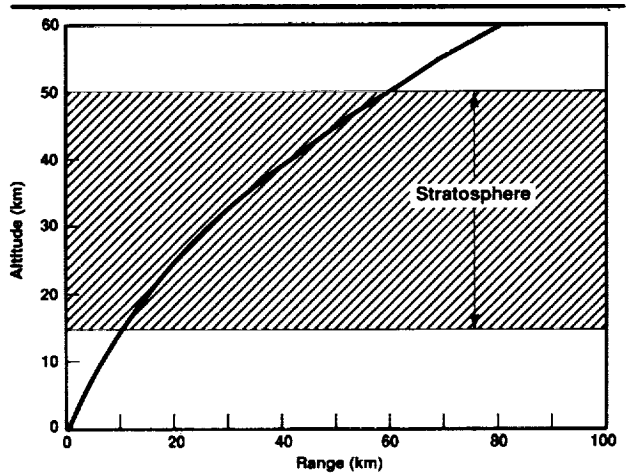

Fig. 12. Typical Space Shuttle Trajectory

Atmospheric scientists (Karol, Ozolin, and Rozanov[14]) from the Main Geophysical Observatory in Russia have examined the impact of rocket launches on local stratospheric ozone above the launch site. These Russian scientists concluded that 50 launches per year of either the U.S. Space Shuttle or Russian Energia would not significantly impact local or global ozone depletion in the stratosphere. Scaling the Russian data to an equivalent launch model consisting of nine Space Shuttles and six Titan IV launches per year results in good agreement with NASA's projection of 0.0065 percent global ozone depletion. Similar analysis conducted by the European Space Agency for the Ariane V,[3] when scaled to the same equivalent launch model, produced comparable results. The Russian scientists conducted time–dependent analytical calculations of local ozone depletion in the rocket plume as it mixes with the ambient air as the vehicle flies through the stratosphere. Calculations were conducted for both the U.S. Space Shuttle (S) and the Russian Energia (E) vehicle, as shown in Fig. 13. Figure 13 presents results at 40– and 16–kilometer altitudes for both vehicles up to one day after launch.[2] Ozone destruction in the near field of the rocket plume can be very severe (>90 percent) within just a few minutes after the launch vehicle enters the stratosphere; however, the ozone concentration is totally restored to background levels from natural mixing of the plume with surrounding air in this very localized area within a few hours after launch. It is also interesting to note that the magnitude of local ozone destruction is basically the same for the U.S. Space Shuttle with its SRBs and the all–liquid Russian Energia vehicle that does not produce any chlorine–containing compounds in the exhaust. The only difference noted between the two vehicles is that the non–chlorine Energia destroys ozone more quickly, but recovers faster, than the Space Shuttle; this recovery time difference is attributed to the HCl, as shown in Fig. 13.

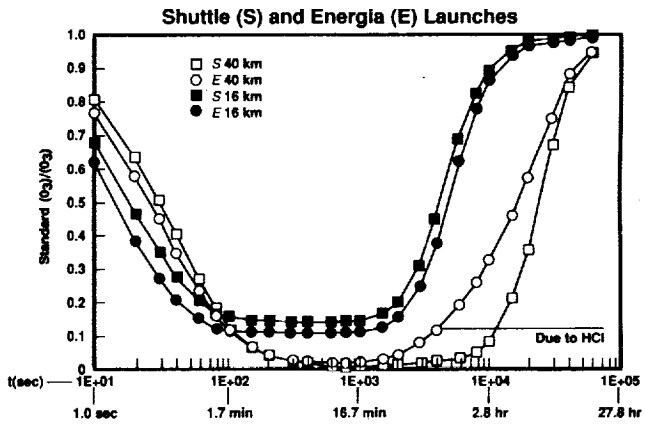

Fig. 13. Shuttle and Energia Impact on Local Ozone

The Russian atmospheric scientists Karol et al.[14] analyzed two sets of conditions to determine the local impact of NO_x and chlorine production from the Space Shuttle vehicle. Figure 14 presents the impact on local column ozone changes comparing the baseline calculations shown in Fig. 13 (Scenario A) assuming HCl and NO_x are the primary ozone–depleting chemistries in the plume with a second scenario (Scenario B) with decreased NO_x production and all chlorine from the SRBs in the form of chlorine gas (Cl_2) rather than HCl. As shown in Fig. 14, total column ozone destruction at any given time is less than 8 percent and is restored to normal background levels within a few hours after launch. The production of Cl_2 rather than HCl results in slightly more ozone destruction, but does not significantly affect the recovery time.

Computer modeling work conducted by Denison et al. at TRW[15] suggests that HCl from solid rocket plumes may be quickly converted to Cl_2 at high altitudes from afterburning. The TRW paper describes model calculations examining the local effects of solid rocket exhaust on stratospheric ozone at different altitudes. The afterburning calculations suggest that a significant fraction of the

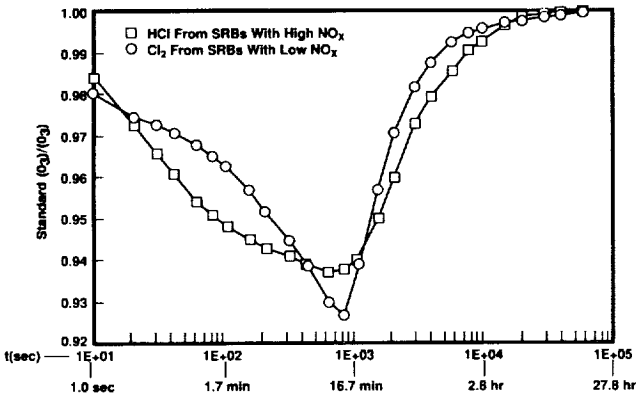

Fig. 14. Local Column Ozone Changes From Shuttle Launch

HCl is converted to Cl_2 in the hot plume—about 20 percent at an 18–kilometer altitude and as much as 80 percent at 30 kilometers. Ozone depletion is extensive during the first few minutes following a launch, but quickly recovers (within about one–half hour) to near background levels. It was found that the rate of plume dispersion has a very significant effect on local ozone loss. The differences in plume dispersion rates explains, at least in part, the differences between the Karol results[14] and the TRW results.[15] Both studies indicated local total column ozone depletion less than 10 percent; the major differences noted were in the time it took for recovery. The TRW results predicted much more rapid loss and recovery within seconds to minutes while the Karol results indicate somewhat similar impacts with total recovery occurring over a much longer period of time, i.e., a few hours.

Plume modeling work reported by Dr. R. B. Cohen of the Aerospace Corporation[16] has also indicated that high temperature afterburning reactions may rapidly convert the HCl to active Cl_2 and Cl in the plume in the stratosphere. More recent work done by German atmospheric research scientist, Dr. B. C. Kruger from the Institute for Geophysics and Meteorology at the University of Köln,[17] has examined the influence of chlorine production from solid–fuel rockets on local ozone depletion in the plume. Dr. Kruger's paper is a model study of the impact of the chlorine emissions from the Space Shuttle SRBs at various altitudes as a function of distance from the center of the plume as the plume evolves over time. Chlorine emissions were considered both in the form of HCl and Cl_2. The cases run were 100 percent HCl, 95 percent HCl and 5 percent Cl_2, and 50 percent HCl and 50 percent Cl_2. For the case of 100 percent HCl, Kruger predicts that ozone destruction will begin between 5 and 10 minutes after launch as the HCl reacts and begins to release its chlorine. The maximum depletion at 35 kilometers is about two percent at the center of the plume and lasts for more than 24 hours. At lower altitudes, the ozone depletion is much less—about 0.19 percent at 28.5 kilometers, and about 0.26 percent at 31.9 kilometers in altitude. Maximum column ozone depletion values given by Kruger are related to what an instrument with a given field of view (FOV) in orbit would see. In the case of 100 percent HCl, for a true vertical trajectory, the maximum column ozone decrease seen for a 1,664–km^2 (41 km x 41 km) FOV instrument like the NASA total ozone mapping spectrometer (TOMS) instrument would be about 0.5 percent. For the case of 50 percent chlorine and 50 percent HCl, the ozone is virtually depleted at high altitudes within 10 minutes of the launch. Maximum column ozone depletion which would be observed by an instrument with a 1,664–km^2 FOV is about 3 percent over the entire FOV. The predicted column values are somewhat lower than those calculated by Karol[14] and predict that the TOMS instrument would not have sufficient resolution to observe the impact on the local stratospheric ozone column from a Space Shuttle launch.

Thermochemical equilibrium calculations for Space Shuttle SRB propellant indicate HCl will be produced rather than Cl_2. Experimental sampling of solid rocket combustion gases at ground level has indicated that HCl is the major combustion product at a ratio of approximately 10:1 over Cl_2. There have not been any plume chemistry measurements made at stratospheric altitudes. There are very limited experimental data for determining the effects of rocket plumes on stratospheric ozone depletion; however, what data are available tend to support Russian scientific analysis. Ozone reductions greater than 40 percent were measured in the exhaust trail of a Titan III SRB at an altitude of 18 kilometers approximately 13 minutes after launch.[18] Considerable NO_x formation was also detected in the plume and the ozone depletion was attributed to NO_x at that time; chlorine measurements were not made. NASA has made several measurements of total column ozone concentration directly over Kennedy Space Center (KSC) after eight different Space Shuttle launches with the TOMS aboard the NIMBUS–7 satellite.[19] No evidence of ozone depletion was ever detected; however, the measurements that were taken were generally obtained several hours after launch. These data appear to be consistent with the Russian scientific calculations[14] and the Kruger analysis[17] which would predict that normal background levels of ozone are restored within a few hours of the launch and the ozone loss at any given time would be below the threshold of detectability within the FOV of the TOMS instrument.

Most of the local and global ozone depletion calculations to date have considered homogeneous gas phase chemical reactions only. Recent studies of the Antarctic ozone hole have identified the importance of heterogeneous chemistries on ice crystals in the polar stratospheric clouds. Decreases in mid–latitude ozone levels have also been attributed to catalytic activity on the surface of finely divided particulate matter injected directly into the stratosphere from volcanic eruptions. The question arises, "Can finely divided aluminum oxide (Al_2O_3) from SRBs, soot from liquid oxygen and hydrocarbon boosters, and ice contrails from all rockets also provide catalytic surfaces for ozone–destroying chemistries?"

There have been few published calculations for the potential impact of rockets in this area. The limited heterogeneous modeling of solid rocket plumes by several researchers has indicated that the effects on local plume chemistry are minor, and, therefore, the influence on local ozone depletion, if any, appears to be small.[15,17,20,21] The impact on global ozone depletion from rocket–produced aerosols is even less significant, i.e., could be responsible for about 1/1,000th of the current ozone depletion associated

with the unperturbed background heterogeneous chemistry in the absence of volcanic aerosols.[22]

Analysis of data from volcanoes can provide good qualitative insight as to the potential magnitude of particulate matter from solid rockets. Figure 15 shows the estimated total integrated surface area of finely divided particulate matter injected into the stratosphere by the El Chichon volcanic eruption in Mexico in 1982.[23] This figure also compares the natural background levels of stratospheric aerosols to the total quantities of aluminum oxide deposited by nine Space Shuttle and six Titan IV launches if all of the Al_2O_3 were deposited in the same region as the El Chichon cloud. The rocket contribution does not include any ice or soot particles from the launch vehicles.

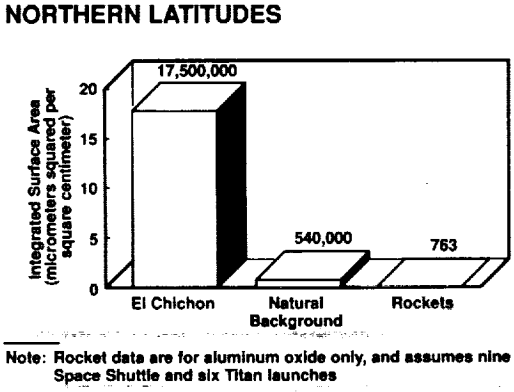

Fig. 15. Stratospheric Surface Area Available for Heterogeneous Chemistry

Figure 16 shows the maximum estimated ozone depletion in the region of the El Chichon–induced stratospheric cloud as compared to the estimated ozone depletion from natural aerosols and rockets producing Al_2O_3.[23,24] As can be seen from the figure, the ozone destruction within the cloud of El Chichon could be as high as 17 percent, as compared to the SRB contribution of less than 0.0007 percent on the same basis.

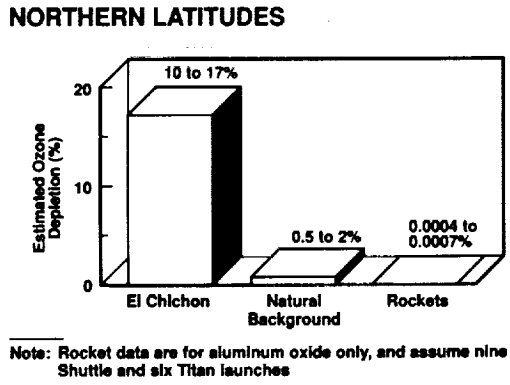

Fig. 16. Estimated Effects of Heterogeneous Chemistry on Stratospheric Ozone

The 1991 eruption of Mount Pinatubo in the Philippines was far more powerful than El Chichon. Atmospheric scientists believe that the aerosols from this volcano were probably responsible for the intensification of global ozone thinning noted since the eruption of Mount Pinatubo.[5]

ACID RAIN

Since SRBs produce hydrochloric acid in the exhaust plume, there has been considerable concern over the impact that this acid rain may have on the global environment, as well as local launch sites. All rockets produce some acid rain as a result of the formation of NO_x in the near field of the plume from afterburning that forms nitric acid in the presence of water. The studies presented here only consider HCl from solid rockets as a source of acid rain.

Figure 17 depicts the annual U.S. contribution to the global acid rain problem from various anthropogenic sources, including solid rockets.[25,26,27] As can be seen from the figure, other energy conversion processes such as heating and power production (33,000 kilotons), transportation (9,100 kilotons), and industrial processes (6,100 kilotons) clearly overshadow the acid production (3 kilotons) from solid rocket launches. Most of the acid produced from these industrial activities is in the form of sulfuric acid, with significant quantities of nitric and hydrochloric acid also produced. Without considering other countries in the world, rockets are responsible for less than 0.006 percent of acid rain produced by U.S. industries alone.

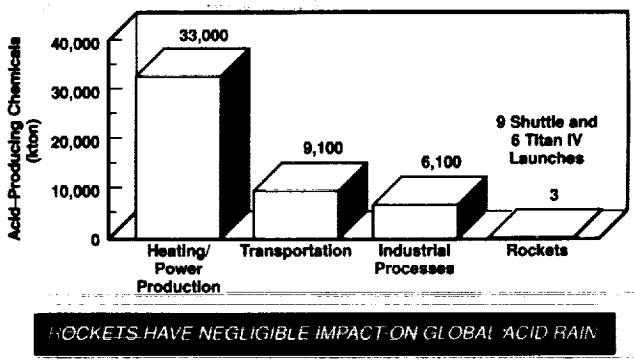

Fig. 17. Annual Contribution to Acid Rain (Continental U.S. Data)

Figure 18 reflects sources of hydrochloric acid other than rockets.[9] As can be seen in Fig. 18, natural sources of HCl from the oceans (330,000 kilotons), volcanoes (5,000 kilotons), and coal burning processes (1,980 kilotons) make solid rockets (3 kilotons) an insignificant contributor to global atmospheric HCl releases. It is estimated that launching nine Space Shuttles and six Titan IVs each year would deposit the same amount of HCl into the troposphere as is produced by the Atlantic ocean each year just east of the KSC launch site in an area of the ocean represented by a square less than 30 miles on each side. On a global scale, HCl produced by rocket launches is less than 0.001 percent of the total HCl production from the ocean alone and only 0.15 percent of anthropogenic sources, primarily coal burning power plants in the United States.

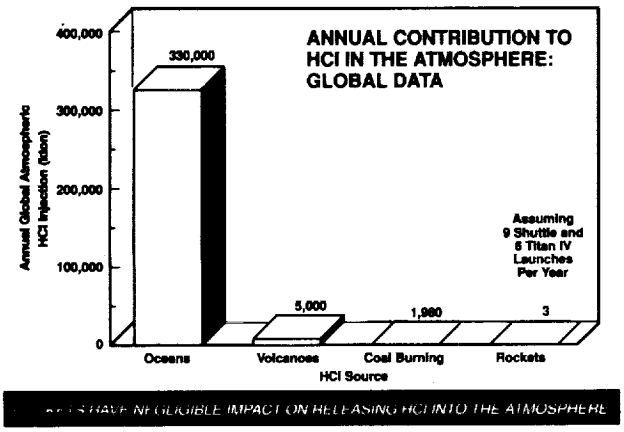

Fig. 18. Global HCl Releases

On a local scale, acid rain from SRBs is more significant and does have near–field acidification effects in the vicinity of the launch site.[28] These effects are limited to a very localized area within less than one–half mile from the launch pad directly in line with the SRB flame trenches, as shown in Fig. 19. Some plant and small fish (minnows) mortalities occur in the lagoon area just north of the launch pad, less than 0.1 square mile of area (which is much smaller than the launch pad itself). Catch basins for the sound suppression water is neutralized after each launch and the pre– and post–launch environmental conditions are documented on each Space Shuttle launch.

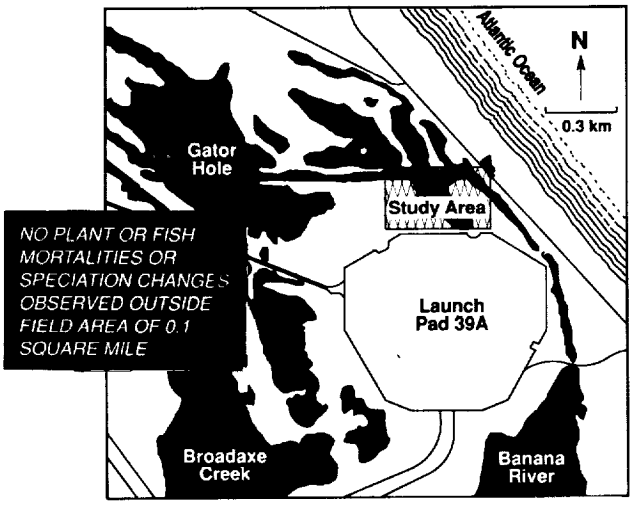

Fig. 19. Acid Rain: Near–Field Deposition Area

TOXICITY

Hydrochloric acid is the most toxic substance associated with cured solid propellants and it is only produced by combustion. Storable liquid bipropellants consisting of nitrogen tetroxide (N_2O_4) and hydrazine compounds are far more toxic, but have been safely and routinely handled at various launch sites for decades. As shown in Table II, even in very minute concentrations, these liquid bipropellants can be a significant health hazard while HCl in minute quantities is only considered a corrosive or irritant.[29]

- **Liquid rocket components—nitrogen tetroxide (N_2O_4), dimethylhydrazine, and hydrazine—are highly toxic, and handling is a local concern**
- **HCl is the most toxic of the common solid rocket exhaust species**

	Lethal Concentration, 50% (inhalation, rats)	Additional Concerns at Very Low Concentration Levels
N_2O_4	88 ppm/4 hr	Pulmonary edema
Dimethylhydrazine	242 ppm/4 hr	Suspected carcinogen
Hydrazine	570 ppm/4 hr	Suspected carcinogen
HCl	3,124 ppm/1 hr	Corrosive/irritant

Table II. Propellant and Exhaust Toxicity

Considerable concern has been raised relative to the toxicity and corrosiveness of the SRB ground cloud as it drifts away from the launch site. Figure 20 represents one of the rare Space Shuttle launch plume conditions that drifted inland rather than out over the ocean after the launch.[30] Bionetics Corporation has periodically monitored HCl concentrations for NASA and routinely conducts model calculations on HCl concentration in the far field of the Space Shuttle plume, as shown in Fig. 20. It should be noted that the maximum HCl concentration in the ground cloud of 0.9 parts per million is well below the American Conference of Governmental Industrial Hygienists' recommended threshold limit value (TLV) of 5 parts per million for long–term continuous exposure (8 hours per day—40 hours per week). HCl concentrations measured in the path of the Titan III SRB ground cloud as it drifted several kilometers from the launch site at Vandenberg AFB have also been well below the 5 ppm threshold limit values, i.e., 0.005 ppm to 0.5 ppm. Aircraft fly–throughs of the stabilized exhaust plumes of the Titan III and Space Shuttle at 1 to 2 kilometers above ground level have measured HCl concentrations at the TLV of 5 ppm for 10 to 60 minutes after launch.[31]

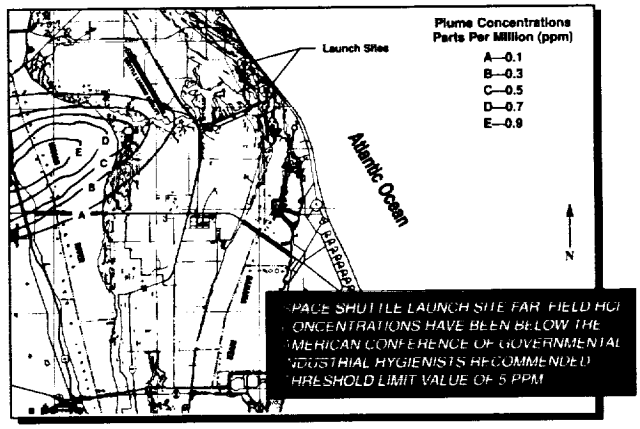

Fig. 20. Toxicity of Shuttle Exhaust Plume

There have been some published studies that have suggested an association of aluminum compounds with Alzheimer's disease. Solid rockets consume less than 0.01 percent of the 69 billion pounds of aluminum metal produced in the U.S. each year, and approximately 8 percent of the earth's crust consists of aluminum compounds, such as oxides, silicates, etc. Furthermore, many pharmaceuticals, food additives, and health care products (deodorants, for instance) contain aluminum compounds. To prevent people from throwing away their aluminum cookware and stop drinking from aluminum beverage cans, the U.S. Food and Drug Administration (FDA), the Alzheimer's Disease and Related Disorders Association, and the U.S. Environmental Protection Agency (EPA) released statements in 1989 that there was no evidence to support the hypothesis that aluminum contributed to Alzheimer's disease.

GLOBAL WARMING

It has been postulated by several scientists that production of certain gases, such as carbon dioxide (CO_2), from the continued burning of fossil fuels could eventually cause more of the sun's energy to be trapped in the earth's atmosphere, resulting in global warming or a greenhouse–type effect. As shown in Fig. 21, the amount of CO_2 produced from chemical rockets is extremely minute, representing less than 0.00004 percent of anthropogenic sources of CO_2.[27,32]

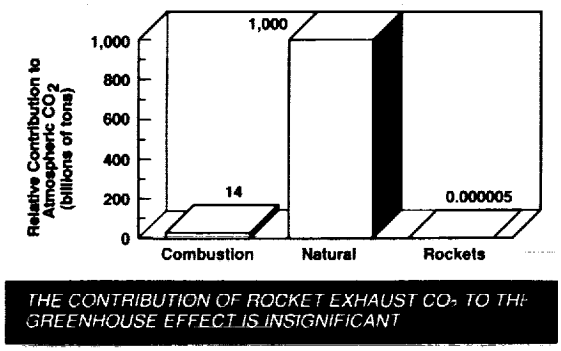

Fig. 21. Greenhouse Effect Gases

It has also been suggested that particles from rocket launches could also contribute to global warming conditions or possibly global cooling. As indicated earlier, aluminum oxide deposited into the stratosphere by SRBs is so small that it would take nearly 300,000 Space Shuttle launches to equal a volcano the size of El Chichon.

CONCLUSIONS

Based upon our current state of understanding of the earth's atmosphere, the following conclusions can be drawn relative to the impact of chemical rocket launches:

1. The environmental impact of chemical rocket propulsion is extremely small, i.e., annual global stratospheric ozone depletion and tropospheric acid rain contributions are estimated to be less than 0.01 percent.
2. There is no significant difference in local stratospheric ozone depletion from the U.S. Space Shuttle with its solid rocket boosters and the all–liquid Russian Energia launch vehicle, and the impact is small even at launch rates as high as 50 flights per year of either vehicle.
3. Contrary to manmade CFCs, chemicals released from rockets are not foreign to the environment, but represent an extremely small fraction of large natural reservoirs of these materials in the atmosphere.
4. As a potential source of chlorine in the stratosphere, all rocket launches combined produce less than 0.25 percent of the chlorine introduced by CFCs on an annual basis. Enactment of the ban on the production of CFCs by 1996 will eliminate 99.75 percent of the current anthropogenic sources of new chlorine that could eventually find its way to the stratosphere.
5. The impact on the potential for global warming due to CO_2 from chemical rockets is minuscule (less than 0.00004 percent).
6. Local launch site area acidification is minor and manageable.
7. There is no rocket system that is totally "clean," and the environmental improvements available appear to be very limited. The amount of energy released to place objects into earth orbit will cause some minor damage to the earth's atmosphere independent of rocket chemistry.
8. The benefits of obtaining global weather and environmental data from satellites and space laboratories in earth orbit far outweigh the minor environmental impacts of placing these assets into space.

RECOMMENDATIONS

Recommendations for further work are primarily focused on improved atmospheric computer modeling, environmental data gathering, and establishing reasonable environmental criteria for future launch systems. These following recommendations are summarized:

1. More measured data need to be obtained to verify the minimal impacts that are being projected.
2. Atmospheric computer modeling, which includes both homogeneous and heterogeneous chemistry, needs to reflect actual measured conditions for improving confidence in future projections and assessing effectiveness of potential mitigating strategies. These models need to include afterburning, equilibrium and non–equilibrium plume chemistry and combined exhaust gas chemistry from mixed propulsion launch vehicles.
3. "Clean" solid propellant work should be renamed "alternative propellants" and continued on a laboratory scale until more atmospheric experimental data are available to verify the minimal environmental impact conclusions that have been drawn to date.

4. New launch system development should include criteria for assessment of the environmental impacts along with safety, performance, reliability, and cost requirements.

5. A detailed environmental–cost–benefit–risk analysis should be conducted for any new launch system, and any potential environmental benefits that are identified should be adequately demonstrated and verified prior to incorporation into the launch vehicle.

Based upon the environmental impact studies conducted to date, there is no reason to modify any launch vehicles or change any propellant chemistry at this time.

REFERENCES

1. American Institute of Aeronautics and Astronautics Report, *Atmospheric Effects of Chemical Rocket Propulsion* (1 October 1991).

2. R. S. Harwood, C. H. Jackman, I. L. Karol, L. X. Qiu, M. J. Prather, and J. A. Pyle, World Meteorological Organization Ozone Report No. 25, *Scientific Assessment of Ozone Depletion,* 1991, Chapter 10: "Predicted Rocket and Shuttle Effects on Stratospheric Ozone," Sponsored by the World Meteorological Organization and the United Nations Environment Program, National Aeronautics and Space Administration, National Oceanic and Atmospheric Administration, and the United Kingdom Department of Environment (Spring 1992).

3. A. E. Jones, S. Bekki, and J. A. Pyle, "Modelling Assessment of the Atmospheric Impact of Exhaust Products (chlorine, H_2O, Al_2O_3) From Ariane 5 Rocket Launches," Report to the European Space Agency, University of Cambridge, United Kingdom (June 1993).

4. M. McElroy and R. Salawitch, "Changing Composition of the Global Stratosphere," *Science*, 243, 763 (1989).

5. P. S. Zurer, "Ozone Depletion's Recurring Surprises Challenge Atmospheric Scientists," *Chemical and Engineering News* (24 May 1993).

6. P. S. Zurer, "Looming Ban on Production of CFCs, Halons Spurs Switch to Substitutes," *Chemical and Engineering News* (15 November 1993).

7. M. K. W. Ko, N. D. Sze, and M. J. Prather, "Better Protection of the Ozone Layer," *Nature*, 367, 505 (10 February 1994).

8. R. Cicerone, "Halogens in the Atmosphere," *Rev. Geophys. Space Phys.* 19, 732 (1981).

9. R. Symonds, W. Rose, and M. Reed, "Contributions of Cl– and F–Bearing Gases to the Atmosphere by Volcanoes," *Nature* 334, 415 (1988).

10. A. Tabazadeh and R. P. Turco, "Stratospheric Chlorine Injection by Volcanic Eruptions: HCl Scavenging and Implications for Ozone," *Science*, Vol. 260, p. 1,085 (21 May 1993).

11. G. Taubes, "The Ozone Backlash," *Science*, 260, p. 1,582 (11 June 1993).

12. M. Prather, M. M. Garcia, A. R. Douglass, C. H. Jackman, M. Ko, and N. D. Sze, "The Space Shuttle's Impact on the Stratosphere," *J. Geophys. Res.* 95 (D11), 18583 (1990).

13. G. G. Bjarnason, O. E. Rognvaldsson, T. I. Sigfusson, T. Jakobsson, and B. Thorkelsson, *Analysis of Total Ozone Data From Reykjavik for the Period 1957–1991*, Science Institute, University of Iceland, Report RH92–3 (April 1992).

14. I. L. Karol, Y.E. Ozolin, and E. Y. Rozanov, "Effect of Space Rocket Launches on Ozone and Other Atmospheric Gases," Presented at the European Geophysical Association Conference, Wiesbaden, Germany (1991).

15. M. R. Denison, J. J. Lamb, W. D. Bjorndahl, E. Y. Wong, and P. D. Lohn, "Solid Rocket Exhaust in the Stratosphere: Plume Diffusion and Chemical Reactions," AIAA Paper No. 92–3399, AIAA 28th Joint Propulsion Conference, Nashville, Tennessee (July 1992).

16. R. B. Cohen, "Learning About Potential Effects of Solid Propellants Exhaust on the Stratosphere," Presented at the Air Force Phillips Laboratory Solid Propellant Environmental Issues Technical Interchange Meeting and Conference, Ogden, Utah (24–25 March 1994).

17. B. C. Kruger, "Ozone Depletion in the Plume of a Solid–Fueled Rocket," To Be Published in the *Annales Geophysicae* (Summer 1994).

18. R. B. Stewart and R. I. Gomberg, "The Production of Nitric Oxide in the Troposphere as a Result of Solid–Rocket Motor Afterburning," NASA TN D–8137 (1976).

19. R. McPeters, M. Prather, and S. Doiron, Reply to Comment on "The Space Shuttle's Impact on the Stratosphere," by M. J. Prather, et al., *Journal of Geophysical Research*, 96 (D9), 17379 (1991).

20. M. Y. Danilin, "Local Stratospheric Effects of Solid–Fueled Rocket Emissions," *Annales Geophysicae*, 11, 828–836 (1993).

21. G. F. Carrier, F. E. Fendell, and R. S. Dahbura, "Chlorine Production by Particle–Catalyzed Reaction Between Rocket Exhaust and Ambient Stratospheric Reservoir Species," AIAA Paper No. 92–3505, AIAA 28th Joint Propulsion Conference, Nashville, Tennessee (July 1992).

22. C. H. Jackman, "The Impact of Emissions from Space Transport Systems on the State of the Atmosphere," International Scientific Colloquium on the Impact of Emissions from Aircraft and Spacecraft Upon the Atmosphere, Cologne, Germany (18–20 April 1994).

23. D. J. Hofmann and S. Solomon, "Ozone Destruction Through Heterogeneous Chemistry Following the Eruption of El Chichon," *J. Geophys. Res.* 94 (D4), 5029 (1989).

24. G. P. Brasseur, C. Granier, and S. Walters, "Future Changes in Stratospheric Ozone and the Role of Heterogeneous Chemistry," *Nature* 348, 626 (1990).

25. National Acid Precipitation Assessment Program, *Interim Assessment: The Causes and Effects of Acidic Deposition,* Government Printing Office, Washington, D.C. (1987).

26. S. E. Schwartz, "Acid Deposition: Unraveling a Regional Phenomenon," *Science* 243, 753 (1989).

27. E. Robinson and R. C. Robbins, *Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants*, Stanford Research Institute, Report SRI Project PR–6755 (February 1968), Supplemental Report (June 1969).

28. Bionetics Corporation, "STS–32 Launch Effects Summary Report," Contract No. NAS10–11624, BIO–EN4–007 (March 1990).

29. N. L. Sax and R. Lewis, Jr., *Dangerous Properties of Industrial Materials*, 7th Edition, Van Nostrand Reinhold, New York (1989).

30. Bionetics Corporation, *STS–5 Launch Effects Summary Report*, Kennedy Space Center, Florida, KSC–STS–Effects–STS 5 (July 1983).

31. B. Lundblad, Aerospace Corporation presentation "Environmental Characteristics and Potential Impacts of Solid Rocket Motor Exhaust Ground Clouds" (May 1994).

32. H. Schneider, "The Greenhouse Effect: Science and Policy," *Science*, 243, 771 (1989).