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Depletion of stratospheric ozone by chlorinated exhaust of ammonium perchlorate based composite solid propellant formulations: A review

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Abstract

The exhaust of a composite solid propellant (CSP) rocket can contain free radicals of NO, NO_2, H, OH, Cl, ClO, etc., formed directly or indirectly, in its combustion products. Hydrogen chloride (HCl) gas is one of the main combustion products of solid rocket boosters (SRBs) using Ammonium Perchlorate (AP) as oxidizer in its grain. The exhaust of the composite solid propellant (CSPs) rockets undergoes afterburning due to high temperatures encountered during the combustion of propellants and this afterburning facilitates extensive conversion of considerable volumes of HCl to free radicals of chlorine (Cl·**)** and molecular chlorine (Cl_2). The Cl· so discharged reacts instantaneously with nearby ozone molecules to start a catalytic destruction cycle as chlorine (Cl) is a known halogen accountable for the dissociation of ozone into oxygen. The continuous rise in the number of rocket launches per year poses a threat of intensified release of chlorinated compounds in the atmosphere which may results in substantial ozone layer depletion on shorter time scales. Though rocket exhaust usually comprises of numerous environmentally hazardous and ozone-depletion substances (ODS) depending on the ingredients used in the formulation of propellant grains, this study primarily focuses on the potential destruction of ozone caused by chlorinated compounds. This study presents a brief review of the interaction mechanism of chlorinated compounds of a rocket's exhaust with local environment and henceforth imposed effects on local and global ozone concentrations.

Keywords: solid propellant rocket exhaust, rocket plume, hydrogen chloride gas, ozone layer, local ozone depletion, ozone hole

1. Introduction

Ozone (O_3), discovered by *Christian Schönbein* in the 1830s, is a molecule consisting of three oxygen atoms [1]. It is a pungent- smelling bluish gas and is continuously created in the upper atmosphere when sun rays dissociate airborne water molecules. Free oxygen ions fuse with dioxygen molecules (O_2) to synthesize O_3 molecules. Absorption of solar energy by an O_3 molecule causes it to dissociate into an O_2 molecule and a free radical of oxygen (O·). This dissociation and fusion process, due to high energy radiation from the sun, occurs incessantly keeping a relatively constant amount of O_3 in the stratosphere [2]. Concentration of O_3 varies with the altitude and is highest in the stratosphere at an altitude of around 25-30km above earth's surface. Figure 1 represents the average ozone distribution and concentrations with respect to changes in altitude [3]. The part of the stratosphere where its concentration is approximately 91% of the total O_3 present in the earth's atmosphere is known as ozone layer and was discovered in 1913 [4]. Ozone layer is a very vital component of our atmosphere as it protects life on earth by absorbing 97-99% of medium-frequency ultraviolet (UV, 200-315nm wavelength) light emanating from the sun. Ozone sieves out the harmful UV-B (280-315nm wavelength) part of the radiation spectrum emitted by the sun which is identified as to have cell-destructive effects on living organisms and all life on the earth has accustomed itself to this sieved solar radiation [5].

In 1960s, mankind's potential contribution in the destruction of the ozone layer was suggested for the first time and in 1974 the danger of ozone depletion was first indicated. It was postulated that chlorofluorocarbons (CFCs) could deliver Cl to the stratosphere where catalytic destruction of ozone could take place. Such destruction of ozone due to catalytic effect of Cl atoms results in an adverse disturbance in the ozone balance thereby increasing the intensity of UV-B radiations reaching at earth's surface [6].

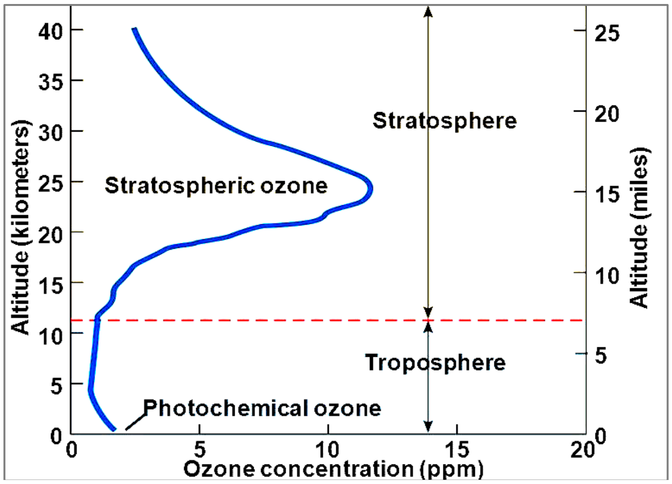


Fig 1: Ozone concentration in parts per million at different altitudes [3]

Chronic exposure of UV-B radiations to humans and/or animals increases the potential risk of skin cancer, damage to cornea and lens of the eyes and decreases the efficienc of the body's immune response to infectious agents [7-9].

UV-B radiation is understood to adversely affect plant's growth rates, to disturb the balance of terrestrial and aquatic ecosystems, to accelerate the photo degradation rates of various synthetic polymers, biopolymers and other materials and can cause damages ranging from material discoloration to substantial loss of mechanical strength and structural integrity [10, 11].

Ozone depletion is generally described by two different but correlated phenomena i.e. a decline in the total quantity of ozone in earth's stratosphere at a steady rate of about 4% per decade and a seasonal local decrease in the concentrations of stratospheric ozone over Earth's Glacial Regions [12]. The second phenomenon is recognized as the *ozone hole* and is geologically defined as an area where the columnar density of ozone has fallen below a baseline value of 220 Dobson Units (DU) [13-15].

Numerous man-made chemicals are identified to be liable for the creation of the ozone hole [16-19]. These harmful chemicals reach the stratosphere either by moving up slowly from the lower atmosphere or by being discharged directly into the stratosphere by aircrafts having high service ceilings and space vehicles [20]. All such potentially harmful chemicals, halogens like chlorine, bromine etc., are stable in lower atmosphere. The stability of such chemicals allows them to diffuse to a broader area and gradually rise up to stratosphere where they are dissociated into free radicals by the action of solar radiations. Free radicals of chlorine and bromine are formed due to this dissociation phenomenon and participate in destructive chain reactions of breaking down O_3 molecules [21, 22].

Concerns have been expressed around the world by researchers as well as environmentalists about the emission of chlorinated compounds by the exhaust of the space shuttles and other rockets, which travel through ozone layer [23, 24]. NASA's Space Shuttle and Titan IV rockets and European Space Agency's (ESA's) Ariane-5 rockets are identified to release relatively massive amounts of chlorinated compounds into the stratosphere on each launch [25-27]. Worldwide attention has been focused on the deterioration of ozone caused by chlorine compounds released by conventional AP-based composite solid propellant (APCP) rockets. The present study summarizes the generation mechanisms of Cl· in the exhaust of CSP rockets and the interaction mechanisms between Cl· and O_3 molecules leading to local and/or global depletion of ozone layer.

2. Chlorinated Exhaust of Ap-Based Propellants

Solid rocket motors (SRMs) are frequently used in on-demand launch systems, boosters-assisted launch systems and small-lift launch systems. Hydrocarbon-based solid fuels/binders in combination with solid oxidizer i.e. AP are being widely used all over the globe in the formulation of CSP grains [28]. The vast information available about APCPs combustion mechanism and their superior ballistic performance has favored the heightened use of AP as oxidizer in the field of solid propellant rockets over the last decades. A conventional APCP has excellent performance characteristics, good thermal stability, as well as low friction and shock sensitivity. The most perceptible and inevitable shortcoming concerned with the use of AP as an oxidizer is its chlorinated exhaust products [29]. During the firing of large size boosters of launch vehicles such as Space Shuttle Boosters (SRBs) (containing around 503 tons of propellant), each of its SRB produces on an average of 100 tons of HCl gas during its flight. The European space launcher Ariane-5 and the Vega launcher contain 476 and 122 tons of APCP each, which upon combustion produces an equivalence of 270 and 71 tons of concentrated hydrochloric acid respectively during the initial 120 seconds of flight [30].

The decomposition of AP releases significant amounts of free oxygen which facilitates the self-sustaining combustion of the hydrocarbon fuel/binder in the combustion chamber of the rocket motor [31]. But along with oxygen, HCl gas is also produced as an inexorable decomposition product. The decomposition reaction of AP, stated below, indicates the process of production of HCl gas in considerable quantities [32].

$$2NH_4ClO_4 \rightarrow N_2 + 3H_2O + 2HCl + 5/2O_2 \qquad (1)$$

Studies have suggested that as the exhaust gases leave the SRM, afterburning of these gases take place in the exhaust plume. Afterburning enables the reaction of surplus hydrogen and carbon monoxide with ambient oxygen, leading to an elevation-dependent conversion of HCl into a blend of inorganic chlorine compounds [33]. Such mixture of inorganic chlorine compounds includes, largely, HCl, atomic and molecular chlorine (Cl·, Cl_2), chlorine oxides (ClO·, Cl_2O_2, OClO, and ClOO), hypochlorous acid (HOCl), and chlorine nitrate ($ClONO_2$) [34]. These compounds are released directly in the stratosphere where they can exist for a timespan ranging from a few seconds to several months depending on the altitude, atmospheric conditions and time of day, and participate into the catalytic ozone depletion progressions [35].

In the afterburning region and depending on the altitude, HCl is anticipated to be transformed to Cl· through reaction 2 stated as below:

$$HCl + OH\cdot \rightarrow Cl\cdot + H_2O \qquad (2)$$

It has been speculated that HCl predominantly adds to the worldwide chlorine burden leading to comprehensive ozone depletion whereas the extremely active Cl· can partake in immediate, local destruction of ozone. Most of the Cl· atoms combine in the cooler post-afterburning region of the exhaust plume leading to production of molecular chlorine [36-38]. The distinction between Cl_2 and Cl· is not substantial for daytime launches because rapid photolysis again liberates Cl·, following reaction 3 stated as below:

$$Cl_2 + light \rightarrow 2Cl\cdot \qquad (3)$$

Dissociation of these exhaust products is a naturally occurring phenomenon which takes place due to high temperatures encountered in the exhaust plumes. Water vapors present in the combustion products are also broken into hydrogen (H·) and hydroxyl (OH·) radicals where they react with HCl gas, emitted by APCPs and Cl· is released [39]. The interaction mechanism of HCl gas, H· and OH· radicals resulting in the generation of Cl· may be represented by reaction 4 and 5 stated as below:

$$OH\cdot + HCl \rightarrow Cl\cdot + H_2O \qquad (4)$$
$$H\cdot + HCl \rightarrow Cl\cdot + H_2 \qquad (5)$$

While all kinds of launch vehicle rocket engines discharge exhaust products that may potentially affect the environment, emissions from SRMs have experienced special scrutiny since due to their highly reactive exhaust products. With the introduction and utilization of large Al-AP based SRMs for the Space Shuttle, particular interest has been established in defining the instantaneous and long term impacts of the inorganic chlorine compounds released by rocket motor exhaust on the stratospheric ozone depletion.

2.1 Interaction Mechanism of Cl· and O_3 Molecules

The Cl· produced in the exhaust is understood to undergo chemical reactions producing chlorine monoxide (ClO·) which is also known to attack an O_3 molecule transforming it into two molecules of oxygen and in the process restoring Cl· again [40, 41]. The interaction of Cl· with the O_3 molecules can be represented by the below stated reactions 6 and 7:

$$Cl\cdot + O_3 \rightarrow ClO\cdot + O_2 \quad (6)$$
$$O\cdot + ClO\cdot \rightarrow Cl\cdot + O_2 \quad (7)$$

Since the ozone depletion effect due to Cl· is recurring and catalytic, a few of Cl· react with a much great number of O_3 molecules. A single Cl· left intact after such reactions may participate in around 100,000 similar reactions before ultimately being dropped out of the stratosphere into the troposphere [42].

These aforementioned reaction cycles will continue to deplete ozone layer until Cl· and ClO· react with hydrogen-containing molecules e.g. methane or atomic hydrogen and result in regeneration of HCl by following reactions 8, 9 or 10 [43, 44].

$$Cl\cdot + H_2 \rightarrow HCl + H\cdot \quad (8)$$
$$Cl\cdot + H\cdot \rightarrow HCl \quad (9)$$
$$Cl\cdot + CH_4 \rightarrow HCl + CH_3 \quad (10)$$

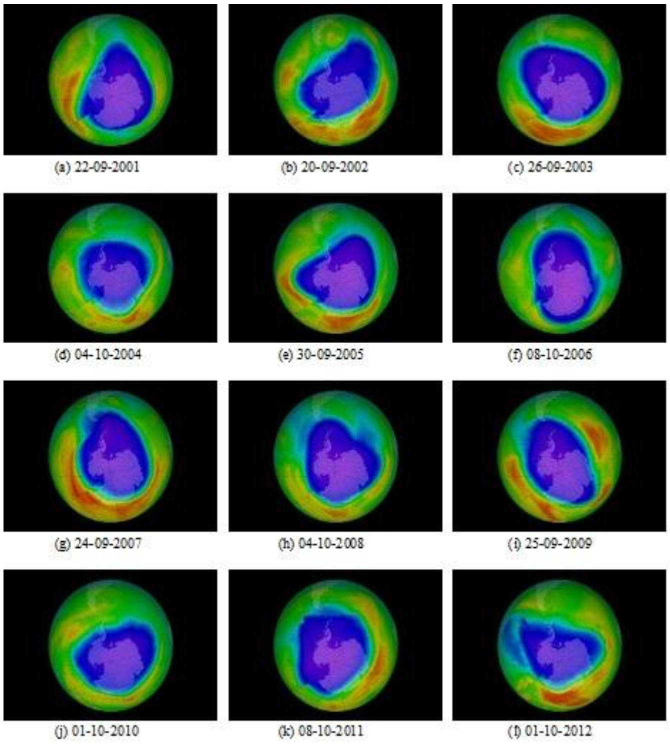
In the normal stratosphere, Cl· and ClO· are typically transformed to HCl in a few days, with HCl returning slowly to active form. The HCl discharged into the stratosphere ultimately returns to the troposphere and rains out, with an average characteristic time of a few years. An incessant destruction of ozone layer is likely to occur with no net loss of such interminable Cl· which is again available to restart the destruction cycles [45, 46].

2.2 Imposed Local and Regional Effects

Rockets are the only direct anthropogenic emission sources into the upper atmosphere. Emissions from launch vehicles considerably affect the atmosphere along the launch trajectory at an estimated range of around 10km [47]. Combustion products like chlorine compounds, alumina, NO_x, and reactive radicals momentarily change the atmospheric compositions along the vehicle's flight path [48, 49]. The substances released by rocket exhausts are primarily restricted to a minor volume of atmosphere, a few hundred meters in width and covering the length of the flight path. This affected volume disperses from the neighborhood of the launch site due to winds and is simultaneously mixed with the contiguous air. This scattering increases the contaminated volume while the concentrations of pollutants decline. The subsequent degree at which chlorine compounds disperse is also dependent on season as summer atmosphere is observed to be less dispersive than the winter [50]. Rocket launches are mentioned to have a noteworthy local effect on the stratosphere up to 2 hours after launch by substantial dissociation of ozone within the expanding exhaust plume. A moderate ozone hole is likely to be observed within this plume whose size may increase during this period [51]. Ozone concentrations recover to adequate levels with the passage of time and proximal ozone fills back into the hole by diffusive processes. The extent of such local ozone hole depends on the amount of emission and the size of the launch vehicle [52, 53]. Dependence of abovementioned interaction mechanisms on local meteorological conditions at the time of launch makes it challenging to precisely reckon the local and/or regional detrimental effects than global effects. It should be kept in understanding that plume dissipation rate extensively governs the intensity of these chemical reactions and reaction chain lengths and is one of the many crucial factors in calculating the effects of chlorine compounds on ozone layer depletion.

2.3 Global Effects on Ozone Depletion

In addition to local effects, emissions from rockets also have long-lasting or global influences on stratospheric ozone. These potential global influences are governed by relatively long lifespans of Cl (primarily as HCl) in the stratosphere [54, 55]. Potential lasting effects comprise a worldwide reduction in stratospheric ozone, an increase in the Cl loading of the stratosphere and an upsurge in the atmospheric particulate burden [56, 57]. Utilizing ground-based and satellite measurement techniques, it has been observed by scientists that the thinning of ozone layer occurs over the South Pole. Figure 2 represents a series of images which shows the maximum recorded size and shape of ozone hole on any given day during a year over the last 15 years. Dark Blue and Purple color represents the extent of ozone hole in these series of images [58, 59]. NASA's *Total Ozone Mapping Spectrometer (TOMS)* instruments had made measurements and observations from 2001-2003 followed by the Royal Netherlands Meteorological Institute (KNMI) *Ozone Monitoring Instrument* (OMI) from 2004-present. Figure 3 depicts the maximum daily ozone whole area (in Million km^2) and minimum daily ozone whole concentration (in Dobson Units) during any given year over a span of last 15 years.



(a) 22-09-2001 (b) 20-09-2002 (c) 26-09-2003

(d) 04-10-2004 (e) 30-09-2005 (f) 08-10-2006

(g) 24-09-2007 (h) 04-10-2008 (i) 25-09-2009

(j) 01-10-2010 (k) 08-10-2011 (l) 01-10-2012

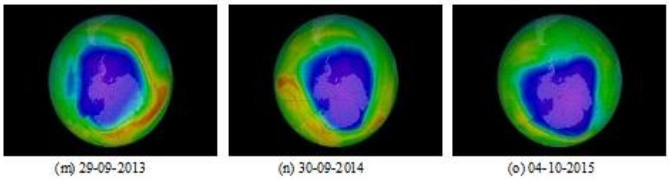

(m) 29-09-2013 (n) 30-09-2014 (o) 04-10-2015

Fig 2: Maximum recorded size and shape of ozone hole on a given day during a year [59]

Figure 4, on the other hand, depicts the mean ozone hole area (from 07 September through 13 October each year) and mean ozone hole concentration (from 21 September through 16 October each year) over the span of last 15 years.

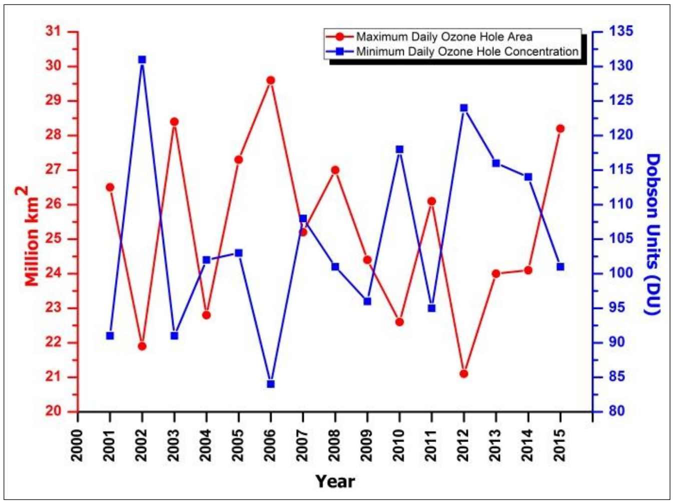


Fig 3: Maximum daily ozone whole area and minimum daily ozone hole concentration

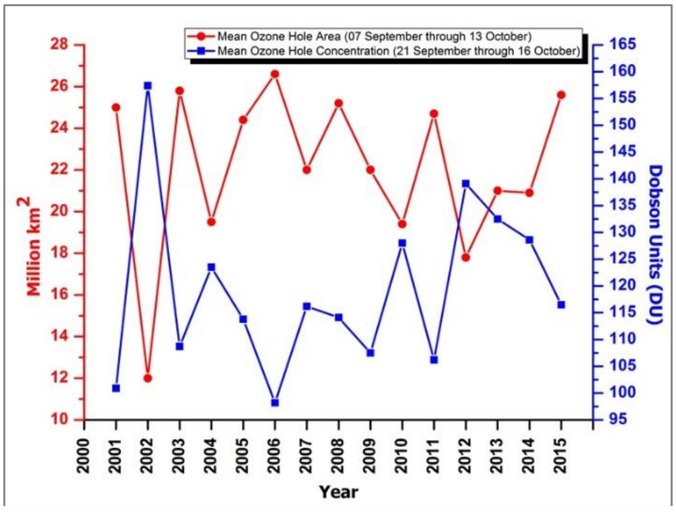


Fig 4: Mean ozone whole area and ozone whole concentration

Modeling efforts of various researchers have established that global implications on stratospheric ozone appear to be inconsequential at present-day launch rates but are however existent and prolonged. The degree of global ozone depletion is bound to increase as the occurrence of rocket launches using solid propellants will escalate in near future.

3. Conclusion

In the last 15 years, the minimum daily ozone hole concentration has fluctuated between a highest value of 131 DU in 2002 and a least value of 84 DU in 2006. Since 2012, a significant decline of 23 DU in the ozone whole concentration has been observed. The maximum mean ozone whole area of 26.6 Million km^2 was recorded in the year of 2006. After 2006, in the span of last 9 years, the maximum mean ozone whole area of 25.4 Million km^2 has been recorded in 2015. The local effects of rocket exhausts has not yet been studied extensively but the studies that has been undertaken noticeably indicate that rocket exhausts can lead to severe ozone loss over a restricted volume within a few kilometers of the plume axis. Within a few kilometers of the exhaust trail of rockets, local ozone may get reduced by as much as 80 percent at some heights for up to 3 hours. Even with severe reductions taking place, the reduction in columnar ozone is possibly less than 10 percent over an area of few square kilometers. After considerable time, the effluents of a certain launch are spread over an adequately large portion of the atmosphere and are diluted to the extent where they contribute negligible to any ozone reduction. But no matter how small the effects may be, there is a need to equip the rocket motors with HCl scavenging systems or to completely replace HCl producing propellants with eco-friendly or clean-burning propellants which doesn't contain chlorine in their molecular structure. Though the ozone depletion presently caused by rocket launches are of lesser magnitudes than that of caused by automobiles, possible substantial increments in rocket launches per year in the near future can result in extensive global impacts on the ozone layer.

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