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Launch Safety, Toxicity, and Environmental Effects of the High Performance Oxidizer ClF$_5$

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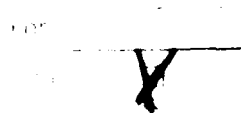94-34482

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13 ABSTRACT (Maximum 200 words)

An assessment is presented for the human toxicity, environmental, and ecological consequences resulting from accidental releases of ClF$_5$ liquid propellant. Various accident scenarios are considered involving instantaneous releases of 2000 kg of propellant. Plume dispersion profiles were calculated using the AFTOX code for typical climate conditions at Vandenberg Air Force Base (VAFB). For a ground-based cold spill or combustion, the area exceeding long-term human exposure levels is less than 1 km^2, and the exposure time is well under an hour (typically several minutes). The area exceeding short-term exposure levels is probably less than 0.1 km^2. The toxic hazard is is likely to be less important than the combustion and fire hazard to on-site personnel. Plant life damage would be limited to temporary leaf burns and some defoliation within 300 meters of the spill site. Sea life would be unaffected in the vicinity of VAFB. Further study should consider the complex interplay of aerosol dynamics and heterogeneous chemistry with propellant and by-products as well as ground deposition of propellant and by-products by gaseous (dry) and aerosol (wet) fallout.

The stratospheric impact of a post-launch explosion is small. Fluorine is not very destructive of the ozone due to the extreme stability of the sink molecule HF. The amount of chlorine compound resulting from a combustion of 2000 kg of ClF$_5$ is not large enough to have a significant effect on the stratosphere, even on a transient scale. Routine solid rocket motor firings present a far greater chlorine load on the atmosphere than does any credible ClF$_5$ accident scenario.

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1. Introduction

This report contains an assessment of the launch safety, human toxicity, and environmental impact associated with ClF_5 usage. ClF_5 is a high performance liquid oxidizer for use with N_2H_4 or monomethyl hydrazine fuels.[1-4] It had once been considered for use in Brilliant Pebbles, which was the original focus of this work. In this report, we examine the hazards resulting from a prelaunch propellant handling and loading accident and from a launch vehicle explosion at the launch site or in-flight.

ClF_5 is also likely to pose unique problems in transport, storage, transfer, and fueling to operational personnel and to the public at large. The operational use of ClF_5 may require review of personnel safety, industrial hygiene, and handling procedures, especially for transport on public highways. The reactivity of ClF_5 and incompatibility with materials makes it more hazardous than N_2O_4. These issues are outside the scope of this report. However, a library of relevant documents and reports has been assembled and a bibliography is available.[5] For the present case of liquid ClF_5, we consider three accident scenarios:

(1) prelaunch accidents such as during propellant handling and loading leading to an uncombusted cold propellant spill,

(2) a launch site explosion creating a plume of propellant combustion products settling over the immediate ground area,

(3) an in-flight explosion dispersing propellant combustion products into the troposphere and stratosphere depending on altitude.

The impact of these accidents are examined in terms of their environmental effects on:

(1) human toxicity,

(2) animal and plant toxicity, including land and sea life,

(3) atmospheric disturbance in terms of pollution (troposphere) and ozone depletion (stratosphere).

This report is organized as follows: Background information on ClF_5 is given in Sec. 2 consisting of material properties and known relevant chemistry (Sec. 2.1), and toxicity data and threshold exposure levels (Sec. 2.2). Accident scenarios are modeled in Sec. 3 for cases of ground-based cold and combusted propellant releases (Sec. 3.1) and post-launch

explosions in the troposphere and stratosphere (Sec. 3.2). Each assessment is supported by a simple worst case model and calculation. More realistic calculations for ClF_5 release and dispersion are then presented based on the AFTOX dispersion model for toxic chemical releases. Ground-based accidents are modeled for a range of weather conditions reported for the most probable sites of accidents at Vandenberg AFB. The environmental effects and mitigation are discussed in Sec. 4 and the summary and conclusions, along with suggested areas of future study, are given in Sec. 5. A glossary of terms is appended to this report.

2. Background

The natural abundance of fluorine is rather high, accounting for about 0.65% of the earth's crust. It exists mainly in mineral form, the two most common being fluorspar or fluorite (CaF_2) and villiaumite (NaF).

2.1. Chemistry

The kinetics of thermal decomposition of ClF_5 have been reported before,[6,7] as have the photochemistry of interhalogens Cl_xF_y other than ClF_5.[8] The chemistry of some reactive fluorine and interhalogen intermediates has been reported which may be pertinent to ClF_5 chemistry.[9-11] A mass spectrometric study of the combustion products for $N_2H_4 + ClF_5$ indicates that the major products are N_2 and HF with all other constituents formed in much lower yield.

Almost all scenarios involving a ClF_5 accident are expected to reduce the fluorine content into the form of HF due to sufficiently high levels of water vapor and other hydrogen-containing species for almost all relevant atmospheric conditions. Reaction will be accelerated in the event of an explosion due to the presence of hydrazine fuel and/or by pyrolysis of ClF_5 to form reactive F atoms, which would initiate reactions with H_2O. In the case of a cold spill, it is not certain how rapidly the oxidizer would reduce to HF, although it would be prudent to flood the area with a mist of aqueous base or lime to accelerate acidification and neutralization to fluorine salts (discussed later under accident mitigation). The proposed reaction for hydrolysis of ClF_5 by Darmer[12,13] is

$$\text{ClF}_5 + 2\text{H}_2\text{O} \longrightarrow \text{ClO}_2\text{F} + 4\text{HF} \tag{1}$$
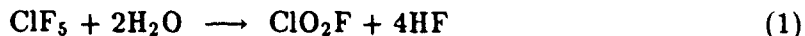
The reaction is overall very exothermic ($\Delta H = -98.8$ kcal/mol); however, two early studies indicate that the reaction proceeds slowly,[14,15] while another early study claims that ClF_5 reacts vigorously with water.[16]

Stratospheric chemistry is too complex to treat in detail here.[17] Nor do we attempt to consider diffusion properties and how they vary with changing atmospheric conditions. Instead, we can focus on a few important reactions to help us understand the effect of ClF_5 by-products on the atmosphere. We begin with the most fundamental catalytic cycle for ozone depletion

$$\text{X} + \text{O}_3 \longrightarrow \text{XO} + \text{O}_2 \tag{2a}$$

$$\text{XO} + \text{O} \longrightarrow \text{X} + \text{O}_2 \tag{2b}$$

$$\text{O} + \text{O}_3 \longrightarrow 2\text{O}_2$$
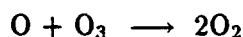
where X commonly refers to a halogen atom. The overall reaction is 94 kcal/mol exothermic, and each step is very exothermic and kinetically fast for halogen atoms (i.e., F, Cl, Br, I).[18,19] Many other cycles exist; however, what ultimately governs the ozone depletion effectiveness are the rates of production (sources) of reactive species X versus their decay and scavenging into unreactive species (sinks).[17] It is instructive to compare important reactions involving fluorine versus chlorine molecules.

The combustion of ClF_5 with hydrazine fuel or the pyrolysis of ClF_5 in the presence of H_2O will lead to reduction to the extremely stable molecule HF [reaction (1)]. The principal sources of reactive halogen atoms from halogenated molecules are photodissociation, reaction with OH, and reaction with O atoms. We show below that compared to HCl, HF is a significantly poorer source of halogen atoms.

The photodissociative absorption onset for HF lies much further in the UV than for HCl

$$\text{HF} + \text{h}\nu \longrightarrow \text{H} + \text{F} \qquad \lambda_{min} = 160 \text{ nm} \tag{3a}$$

$$\text{HCl} + \text{h}\nu \longrightarrow \text{H} + \text{Cl} \qquad \lambda_{min} = 200 \text{ nm} \tag{3b}$$

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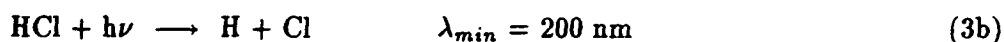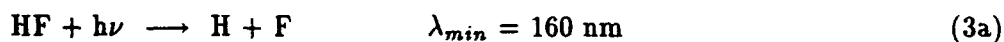
The spectral radiance of the sun, which behaves much like a blackbody radiator, falls off rapidly at short wavelengths. The radiance at 160 nm is a little more than an order of magnitude less intense than the radiance at 200 nm. Furthermore, short-wavelength radiation is attenuated to a much greater extent in the atmosphere than is long-wavelength radiation due to absorption by O_2 [log σ(cm^2) is –17.4 (160 nm) and –22.8 (200 nm)].[20,21] For example, an attenuation of a factor of e occurs at an altitude of 100 km for 160 nm radiation and at an altitude of about 50 km for 200 nm. The radiation flux in the stratosphere (10–50 km) at 160 nm is lower than at 200 nm by two to several orders of magnitude depending on sun angle and other factors.[21] These conditions preclude photolysis of HF as an important source of F atoms.[22]

The reaction of HF with OH is very endothermic and not a viable source of F atoms. By contrast, the reaction of HCl with OH is very reactive and a major source of Cl atoms as shown below.

$$HF + OH \longrightarrow F + H_2O \qquad \Delta H = 17.0 \text{ kcal/mol} \qquad (4a)$$

$$HCl + OH \longrightarrow Cl + H_2O \qquad \Delta H = -16.0 \text{ kcal/mol} \qquad (4b)$$

Finally, we consider the reaction of HF with O atoms as a source of F atoms. Above 20 km, the O atom density exceeds the OH radical density.[23] However, reaction of ground state $O(^3P)$ with HF(Cl) to form F(Cl) + OH is thermoneutral for HCl, but 34 kcal/mol endothermic for HF. The reaction of singlet $O(^1D)$ with HF, however, is rapid, but the density of $O(^1D)$ is not sufficiently high for F atom production to play a major role in ozone depletion. The catalytic role of F atoms is also limited because of the strong tendency to be reduced again to the stable HF molecule.

We now evaluate the efficiency of the catalytic cycle given by reactions (2). The reaction of F and FO is very exothermic with O_3 and O, but is also very exothermic with hydrogenated molecules (e.g., H_2, H_2O, CH_4, etc.) to form stable HF.[23] Reaction (2a) proceeds efficiently because O_3 is in higher abundance in the stratosphere than the other molecules mentioned. However, reaction (2b) is rate limiting because the O atom density is about four orders of magnitude less abundant than hydrogenated molecules.[24] A more rigorous model would include reaction rates; however, these are not all known for FO

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reactions. Nonetheless, it can be concluded based on these and other[23-26] arguments that relative to the case for chlorine, the efficiency of removing O atoms by a fluorine cycle is very low. Rather, F and FO are efficiently converted to the stable sink molecule HF.

The role of fluorine and chlorine chemistry in the atmosphere is discussed further in Sec. 3.2 with regard to actual quantities released, their global and transient effects, and the hazard relative to other launch vehicle effluent quantities.

2.2. Toxicity

The most acute symptomatic effects are due to inhalation or ingestion.[12,13,27,28] Exposure in air leads to respiratory distress. In dogs and monkeys, the typical progression of response is irritation, salivation, sneezing, nausea, and unconsciousness.[12,13] Corneal opacity is a common occurrence. LC_{50} values for 60 min exposures are 57 ppm for mice and 173 ppm for monkeys. The LC_{50} (60 min) value of 173 ppm for monkeys should be compared to the same value for other fluorinated compounds: 26 ppm (OF_2), 230 ppm (ClF_3), and 1774 ppm (HF). F_2 has not been tested with monkeys; however, the LC_{50} (60 min) value for mice of 150 ppm (233 mg/m^3)[29] is similar to the ClF_5 value of 57 ppm on a fluorine atom equivalent basis. The pathology indicates damage to the lungs and respiratory passages with accumulation of mucus, other fluids, and, in some cases, blood.[12,13] We speculate that the enhanced toxicity of ClF_5 relative to HF on a fluorine atom equivalent basis may be due to the aggravated effect of the heat of reaction from reaction (1) in the exposed animal.

The effect of ClF_5 on microorganisms, fish, and plants has also been reported.[27] As a group, interhalogens, including ClF_5, have damaging effects on plants for 10–30 ppm exposures of less than an hour, and are lethal to fish and microorganisms at concentrations of 10–25 mg(F)/l.[30] Though not explicitly stated, we assume that the ClF_5 is converted mostly to HF within the timescale for expression of toxic effects. Again, heat of reaction from ClF_5 decomposition to HF may further aggravate the exposed organism.

A recommended ClF_5 threshold level value (TLV) of 2.5 mg(F)/m^3 (0.4 ppm) TWA has been adopted by OSHA, ACGIH, and NIOSH.[31] As mentioned earlier, ClF_5 undergoes a violent reaction in water by a postulated reaction [Eq. (1)] that yields four equivalents of HF. In the atmosphere ClF_5 most likely hydrolyzes quickly; hence, toxic and environmental impact should consider the importance of HF. The ACGIH TLV for HF is 2 mg/m^3 (3

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ppm).[29] We note that these standards indicate that HF is slightly less toxic than ClF_5 on a fluorine equivalent basis, which is counter to the LC_{50} toxicity results summarized above. In our modeling calculations we consider the limiting cases of pure ClF_5 and pure HF releases.

3. Accident Scenarios

In our original assessment, we used Brilliant Pebbles (BPs) as an example and considered 100 BPs per launch, each containing 20 kg of ClF_5. These values were chosen to overstate the expected mass of propellant payload per launch. A likely future use of ClF_5 is as a bipropellant for long duration satellite operation. A launch mass of 2000 kg should represent a conservative upper limit for most situations.

3.1. Ground-based accident

The potential ground-based accidents considered here include a cold ClF_5 spill due to propellant handling and loading that hydrolyzes to HF, and a launch pad explosion that would rapidly release HF as a combustion product of ClF_5 and MMH. These events involve a complex series of processes[32,33] that we summarize: (1) The rate of hydrolysis to HF will differ by gas-phase and aerosol mechanisms, neither of which are known. (2) The aerosol growth (condensation) and evaporation rates are sensitive to the ClF_5 sticking coefficient (unknown), gas-phase density and liquid-phase concentration (which should be in equilibrium), and the heterogeneous chemistry that takes place in the aerosol. (3) The size of the aerosol affects the deposition rate on the ground as the plume disperses. The wet (aerosol) and dry (gas-phase) ClF_5 deposition rates are unknown. Reasonable estimates of unknown quantities can be made, but still the modeling of all processes is a major undertaking. Martin and Brady of the Propulsion and Environmental Sciences Section of the Mechanics and Materials Technology Center are developing computer models for dealing with the complexities of toxic spills.[33]

In this work we will adopt a plume dispersion model that assumes gaseous products. Because TLVs are reported as airborne concentrations, it makes sense to calculate levels without including losses due to deposition or rainout. The calculated levels will therefore be overstated and hence represent a worst case situation. Rainout becomes important as

the aerosols grow to sizes that are strongly affected by gravity (about 100 μ). However, hydrolysis of ClF_5 by water vapor will produce cloud-size aerosol particles (typically < 10μ) that disperse like gas-phase molecules. A slow but steady adhesion to the ground as the cloud disperses will occur (i.e., deposition); however, we defer this analysis for future study. A treatment of aerosol formation, heterogenous chemistry, and deposition has been presented by Martin and Brady for an NO_2 spill, which may be applicable to ClF_5 spills.[33] However, the plume dispersion was treated as a dynamic steady state, whereas the focus in this report is on time-dependent exposure levels for instantaneous releases.

3.1.1. Homogeneous hemispheric model (HHM)

A simple calculation is presented for an instantaneous ground-based release that disperses homogeneously and uniformly into a hemisphere centered at the spill site. This model assumes no wind, eddy currents, or vertical convection forces to disperse the plume. No dynamics are included; we are simply interested in how large a volume the release must expand to in order to fall below some threshold exposure level. The HHM overstates the severity of the toxic exposure because it ignores the climatic forces that help to disperse and dilute the toxic concentration. Hence, the HHM results should represent an upper bound to the actual severity of a toxic release. We compare these results to more sophisticated atmospheric dispersal model calculations (e.g., AFTOX) shortly.

The HHM model assumes that a release from a fixed point expands into a volume of $0.67\pi r^3$. A 2000 kg release of ClF_5 corresponds to 1456 kg of fluorine. For a TLV of 2.5 mg(F)/m^3, one calculates a volume of radius 725 m, corresponding to an infected ground-based area of 1.65 km^2. For ClF_5 decomposition to HF, we use the TLV of 2 mg(F)/m^3 to obtain a radius of 780 m. The radius corresponding to the ClF_5 LC_{50} (60 min) value of 173 ppm for monkeys is 100 m. The HHM results are summarized in Table I.

3.1.2. Air Force Toxic Release Model (AFTOX)

The toxic chemical release code AFTOX is used by the Air Force for disaster and emergency preparedness at many sites, including Vandenberg AFB. Typical input data parameters are given in Table II, and calculated results relevant to this study are presented in Figs. 1-3 and Table I. AFTOX assumes that gaseous chemicals are carried at wind

velocities and that the moving chemical volume spreads out as a Gaussian distribution. The rate of spread or dispersion depends on an atmospheric stability factor determined from wind speed, temperature, sun elevation (computed from location, date, and time), cloud cover and type, and roughness of ground terrain. The model does not allow for changes in wind speed and direction, nor does it treat vertical dispersion by convection from actual thermal gradient information. Vertical dispersion is accounted for solely by the atmospheric stability factor.[34]

More sophisticated models exist. WADOCT was developed to allow for a spatially nonuniform wind field and buoyancy due to a vertical temperature gradient. Otherwise the diffusion part of the model is based on the AFTOX model. The AFTOX and WADOCT codes were evaluated by comparing the model calculations to measured release profiles for terrain of varying complexity. The two models gave similar results and were in good agreement with observation for fairly uniform conditions of terrain and wind field. Both models falter for complex conditions. It was concluded that WADOCT does a little better, but not sufficiently better to justify the additional computational complexity and necessity of knowing the wind field to great detail.[35] We dismissed other more rigorous dispersion models because the required input data were too detailed to be known with sufficient precision and because actual conditions are too variable to validate the results of any single calculation.

We use the AFTOX code to model dispersion based on worst case wind conditions obtained from VAFB weather stations at SLC 4 (Titan complex), SLC 3 (Atlas complex), and the hypergolic service and storage facility (HSSF). Our calculations are based on a noontime release for July 8, 1992, and ambient conditions of 25°C, 25% high altitude cloud cover, and a dry ground. A roughness parameter of 50 is typically used by VAFB modelers and is defined by AFTOX as "parkland, bushes, and numerous large obstacles" (cf. Table II).

We consider here releases of ClF_5 (cold spill, hydrolyzed, or combusted) that disperse as molecular gases or small aerosols that are unaffected by gravity. AFTOX calculations are presented in Figs. 1–3 and summarized in Table I. The input parameters are from Table II unless otherwise noted. Averaged seasonal wind pattern data from various sites at VAFB are given in Table III.

Figure 1 shows ground-level concentration as a function of time for various distances

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downwind of an instantaneous 2000 kg release. The results are given for the wind vector centerline and, therefore, represent the most adverse conditions. Results for 0.5 m/s (1 knot) and 2.0 m/s (4 knots) are given in Fig. 1. These speeds are less than typical conditions and, therefore, the results are conservative estimates of the toxic exposure hazard. The plots show that concentration builds and then decays as the expanding plume moves through an area. For increasing distances downstream, the peak concentration decreases, but the exposure time increases due to greater dispersion at longer times. Similar trends are observed as a function of altitude; Figure 2 shows concentrations that are lower, but extend to higher altitude as one probes further downwind of a release.

The risk of exposure to a propellant release depends in large part on the rate of dispersion and dissipation. The dispersion width is a function of atmospheric stability factors mentioned above. We investigated the sensitivity of each of these parameters and only observed significant dependences of dispersion rate on wind speed (due to standard deviation of wind direction), terrain roughness, and whether the release was daytime or nighttime (the latter gives less dispersion). Calculating for a relatively smooth terrain (AFTOX roughness parameter of 10 defined as low crops and occasional large obstacles) gives the results shown by dashed curves in Figs. 1 and 2. These conditions give about twice the peak concentrations, but noticeably narrower dispersion widths and exposure times relative to the terrain conditions assumed for VAFB in Fig. 1. These results, however, are similar enough that uncertainty about actual terrain or variation in terrain would not have great impact on the interpretation of the AFTOX calculations in assessing risk at VAFB.

Toxic level values are indicated in Fig. 1 for ClF_5 and HF (hydrolysis product of ClF_5). These TLVs are for continuous exposure (time-weighted-average, TWA); the short-term TLV is expected to be about a factor of ten greater, but for this discussion we will use the conservative TWA value. There is negligible hazard for ClF_5 or HF beyond 1000 meters on the wind-vector centerline.

To evaluate the angular dependence of the toxic hazard and define toxic corridors, we have plotted in Fig. 3 the total ground-level areas for which the stated TLVs were exceeded during some period of the dispersion. Also shown are the exposed areas calculated for the HHM model assuming no wind. All results are summarized in Table I. The characteristic dispersion angle or toxic corrider width is defined as the angle from the origin to the points marking the maximum spatial width of the dispersion. The dispersion angle is actually

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larger at shorter distances and smaller at larger distances. Inputting a smoother surface terrain parameter narrows and lengthens the toxic corridor, but the difference, shown in Fig. 3, is not very significant. Wind speed does not markedly change the shape of the exposed area, but rather changes the exposure time. The exposure time is inversely proportional (and roughly linear) with wind speed; hence, the time-averaged exposure hazard is diminished for increasing wind speed.

3.2. Post-launch accident

A post-launch explosion in the troposphere or stratosphere may induce adverse chemistry between the atmosphere and the combusted ClF_5 fuel. The principal combustion product is HF with minor amounts of ClO_2F, and other fluorine and chlorine oxides [reaction (1)]. HF is a highly stable molecule that is unlikely to react further in the troposphere. The reaction of HF with OH [reaction (4a)] is very endothermic and reacts at a negligible rate.[19,23] HF is water soluble and is, therefore, most likely to rainout. The reaction of ClO_2F is not well known, so for simplicity we assume they dissociate to the reactive species FO and ClO. These species are important O atom scavengers and participate in catalytic ozone depletion cycles (Sec. 2.1) in the stratosphere. Given the presence of H_2O and nitrogen oxides in the troposphere, it is likely that FO will reduce to the stable molecule HF and eventually rainout without any significant consequences. The fate of ClO would probably be similar.

A greater concern is propellant release in the stratosphere. Fluorine atoms lead to catalytic decomposition of O_3 at rates similar to chlorine atoms.[18] What sets these two elements apart, however, is the effective number of catalytic cycles each atom can undergo before being scavenged or tied up in a sink molecule. In this regard chlorine has an ozone destruction effectiveness substantially greater than fluorine owing to the extreme stability of the molecule HF (cf., Sec. 2.1). The photolysis of HF

$$HF + h\nu \longrightarrow H + F \qquad \sigma \sim 1.5 \times 10^{-22} \text{ cm}^2 \text{ at } 161.3 \text{ nm } [36] \tag{5}$$
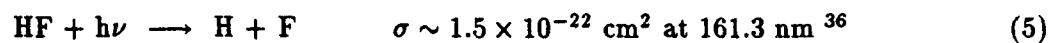
is unimportant below 80 km and, therefore, not a viable source of F atoms.[23] Likewise, reaction with OH [reaction (4a)] is endothermic and very slow, unlike for the case with HCl, which is readily attacked by OH. The most likely source of F atoms is reaction with

singlet oxygen

$$HF + O(^1D) \longrightarrow F + OH \qquad k_{298} \sim 1 \times 10^{-10} \ cm^3 molecule^{-1}s^{-1} \ [23] \qquad (6)$$

A less likely, but possible contribution to F atoms is reaction with vibrationally excited $OH(v \geq 2)$.[23] JPL conducted an assessment of F_2 atmospheric injections of approximately twice the fluorine weight considered here and determined that no adverse effects occured other than a very local and transient ozone depletion that dissipated quickly.

It may be more important to consider the effect on the stratosphere of the chlorine content from ClF_5 decomposition. The reactivity of the presumed by-product ClO_2F is not well known, although it is considered to decompose on metals. We will assume that free chlorine can form. The chlorine weight of 2000 kg ClF_5 is 544 kg. Transient stratospheric effects due to the local chlorine load can be assessed by comparing to the chlorine load resulting from routine solid rocket motor launches. The Minuteman first-stage has a SRM propellant weight of about 22,000 kg consisting of nearly 20% by weight chlorine (as ammonium perchlorate oxizider).[37] The Titan IV and Shuttle exhaust about 44,000 kg and 72,000 kg of chlorine in the stratosphere alone. Finally, we contrast the 544 kg chlorine burden of a hypothetical BP accident to the $\sim 10^9$ kg annual contribution to stratospheric chlorine from industrial, volcanic, and natural sources.[38] Studies on Space Shuttle and Titan SRM releases reach the conclusion that global ozone depletion is negligible, but a significant transient local hole forms that may persist for many hours.[39-41]

4. Toxicity and Environmental Impact

Based on the plume dispersion calculations for a ClF_5 spill and potential combustion or hydrolysis, we can make a risk assessment in terms of toxicity toward humans, plant life, and sea life for ground-based accidents, and in terms of environmental impact on the atmosphere for post-launch accidents.

4.1. Human toxicity

As summarized in Table I and plotted in Fig. 3, the total area that exceeds the

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TWA value is less than 1 km^2 and maximum exposure times are well under an hour and typically just a few minutes. The area exceeding STELs for ClF$_5$ (estimated to be about ten times greater than the TWA value) should be less than 0.1 km^2. The exposed areas lie well within the perimeter of VAFB and do not overlap with populated areas. Launch pad operations allow anticipation of an accident, and certainly the immediate area will be cleared of personnel during launch. Accidents at storage facility may strike randomly; however, the toxic hazard is likely to be less important than the combustion and fire hazard to on-site personnel. It is concluded that the instantaneous release at VAFB of 2000 kg of ClF$_5$ as a cold spill or as combustion or hydrolysis by-products poses a minor toxic hazard.

A point that needs further study is whether ground water contributes to the community water supply, creating a potential of contamination by seepage of wate- soluble ClF$_5$ by-products such as HF. This potential problem can be mitigated to some extent by neutralizing the HF using lime to form the water-insoluble salt CaF$_2$ (see Sec. 4.5). Alternatively, the natural calcium content of the ground soil may be sufficient to achieve neutralization.

4.2 Plant life

The foliage at VAFB consists of natural and wild plant life and ground cover. No commercial crops are near to potential exposure areas. This is in contrast to KSC where several citrus groves lie in the surrounding areas. Two NASA studies evaluated the short term acute effects from fluorine propellant accidents.[42,43] Damaging effects can occur to plants for 10–30 ppm exposures of less than 1 hr ($\sim$ 200 mg/m^3). For the 2000 kg ClF$_5$ spill scenario at VAFB, damaging exposure levels are reached only within 300 meters of the spill site and dissipate rapidly (about 2 min for 2 m/s wind and about 8 min for 0.5 m/s wind, cf. Fig. 1). Some plant damage, limited to temporary leaf scorching and some defoliation, may be expected within an immediate area of considerably less than 0.1 km^2. The conclusion is that a toxic spill and dispersion will have insignificant adverse affect on plant life.

4.3. Sea life

There are no significant lakes on the VAFB complex, and the ocean is protected by an off-shore breeze. The only possibility for dispersion over the ocean is during winter nights due to a mild northeasterly wind. Still, only a small fraction of the spill would reach the distant ocean, and most would dissipate upward into the atmosphere. Even if we assume that the entire propellant is dissolved in the ocean, the affected volume is small. The lethal level for fish and microorganisms is about 10–25 mg(F)/l (Sec. 2.2). 2000 kg of ClF$_5$ (1456 kg weight F) at 10 mg(F)/l would occupy a volume of 1.5×10^8 l. If we assume a penetrating depth of 15 meters in the ocean, then the maximum infected area is only 100 m × 100 m. A realistic calculation places the hazard to sea life as negligible.

4.4. Atmosphere

The extreme stability of HF makes it unreactive in the troposphere where it eventually will rain out. HF is also very unreactive in the stratosphere. The photodissociation threshold for HF is at too short a wavelength to be important below 80 km. Because of the strong HF fluorine sink, the chlorine content in ClF$_5$ poses a much greater stratospheric hazard than the more abundant fluorine content. However, the chlorine weight load on the atmosphere (about 1000 lb) is significantly less then that of typical SRM firings, such as a Minuteman first stage (10,000 lb chlorine release) or a Titan or Shuttle (more than 100,000 lb chlorine in the stratosphere alone). The atmospheric consequence of a 2000 kg ClF$_5$ explosion in the troposphere or stratosphere is negligible by comparison.

4.5. Spill mitigation

As benign as these scenarios play out, there are established procedures for mitigating gaseous acid spills that would further reduce any toxic or adverse effects. JPL has found that a 2% NaOH solution as a water fog spray can effectively scrub fluorine (> 99% neutralization) to form a soluble NaF. Pure water sprays do not extract gaseous fluorine compounds as effectively. A rapid disbursement system is now in place at the JPL Edwards Test Station to mitigate sudden fluorine releases.[44] When aqueous scrubbers are used, catch basins should be installed to collect the neutralized NaF solution. The aqueous solution can

then be treated with $Ca(OH)_2$ to form the insoluble salt CaF_2, which precipitates out of solution for easy disposal. The use of a $Ca(OH)_2$ aqueous fog spray for neutralization is not recommended because the insoluble CaF_2 would fall out over a large area, thus complicating cleanup.

5. Summary and Conclusions

We have considered the environmental and ecological consequences for various accident scenarios involving release of ClF_5 liquid propellant. Ground-based releases were modeled for fueling accidents and a launch-pad explosion involving a quantity of 2000 kg of propellant. Ground-level exposure profiles were calculated using the AFTOX dispersion code for typical wind and climate patterns at various sites at VAFB. These results show that for instantaneous releases, only small unpopulated areas within the VAFB perimeter exceed TLV exposures and that the exposure times are very short (much less than an hour). The probability of long-term chronic effects to humans, plant life and sea life is virtually nil. Short-term acute effects to humans are unlikely for a launch-pad accident since the area will normally be cleared for lift-off. In any case, the fire hazard due to the explosion probably outweighs the toxic hazard. An accident during a manned fueling operation is the most likely scenario for human casualty; however, safety procedures and mitigation should minimize this risk. The quantity of propellant involved is small relative to many other manned-propellant operations in the space program.

The consequences of a post-launch propellant accident on the atmosphere are minor due to the small quantity of propellant and the inertness of HF. The ozone destruction efficiency of fluorides is considerably less than that of chlorides. The chlorine load on the atmosphere due to a 2000 kg ClF_5 accidental release is about 10% that of a Minuteman SRM first stage and about 1% that of a Titan or Shuttle launch.

The quantity of propellant involved in the accident scenarios presented here is determined by the estimated single launch-vehicle payload weight. There are two scenarios not considered here that could give rise to greater quantities of propellant dispersion. First, an accident at a propellant storage facility could involve greater quantities. Second, the total number of launched BPs will be much greater than the 100 assumed for a single launch

vehicle. The controlled deorbit of the entire fleet of BPs at the end of their mission lifetime could provide a sizable halogen load on the atmosphere. Rough estimates, however, indicate that the problem will be minor because the total chlorine weight is probably no greater than a moderate-sized SRM firing and the debris will be spread across a large surface area of the earth.

This report made use of a Gaussian dispersion model to calculate time-dependent exposure levels for instantaneous releases assuming in most cases gas-phase hydrolysis of ClF_5 to HF. As discussed earlier, a more complex series of events occurs involving the interplay of aerosol formation, ClF_5 uptake, heterogeneous chemistry, evaporation, and deposition. Sophisticated new computer models are currently being developed and integrated that could deal with these issues in greater detail. The program SURFACE CHEMKIN holds great promise for handling aerosol heterogeneous chemistry.[33] It may be useful to re-examine some of the scenarios described in this report as these new computational capabilities are brought online.

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GLOSSARY

ACGIH – American Conference of Governmental Industrial Hygienists

AFTOX – Air Force toxic chemical release program

AP – Ammonium perchlorate

BP – Brilliant pebble

bp – Boiling point

CFC – Chlorofluorocarbon

DS – Drop stage

ΔH – Enthalpy or heat of reaction

decomp – Decomposition

HHM – Homogeneous hemispheric model

HSSF – Hypergolic service and storage facility

HTPB – Hydroxy-terminated polybutadiene

IV – Interceptor vehicle

JPL – Jet Propulsion Laboratory

KKV – Kinetic kill vehicle

KSC – Kennedy Space Center

LC_{50} – Lethal concentration for half the sample population

mp – Melting point

NIOSH – National Institute for Occupational Safety and Health

OSHA – Occupational Safety and Health Administration

SLC – Satellite launch complex

SRM – Solid rocket motor

$STEL_x$ – Short-term exposure level for x minutes

subl   –   Sublime

TLV   –   Threshold level value

TWA   –   Time-weighted average

UV   –   Ultraviolet

VAFB   –   Vandenberg Air Force Base

WADOCT   –   Wind and diffusion over complex terrain

TABLE I. Dispersion Properties for a Ground-Based ClF_5 Release.

Accident	HHM[a]				AFTOX[b]			
	width[c] (deg)	dist (m)	area (km^2)	time[d] (min)	width[c] (deg)	dist (m)	area (km^2)	time[e] (min)
ClF_5 cold spill	360	450	0.64	∞	53	1150	0.80	5
ClF_5 combustion or hydrolysis	360	480	0.80	∞	53	1200	0.90	5

[a] Homogeneous hemispheric model for dispersion. [b] Air Force toxic chemical release program. [c] The characteristic toxic corridor width is defined as the angle from the origin to the points marking the maximum spatial width of the dispersion. [d] Assumes no wind. [e] Maximum time that any area exceeds TLV for 2 m/s wind speed. Maximum time is 20 min for ClF_5 for a 0.5 m/s wind speed.

TABLE II. Input Parameters for AFTOX Calculations.

```
    USAF TOXIC CHEMICAL DISPERSION MODEL --- AFTOX
VANDENBERG AFB CA
DATE: 07-08 1992
TIME: 1200 LST

INSTANTANEOUS RELEASE

CHLORINE PENTAFLUORIDE
 TIME WEIGHTED AVERAGE(TWA) IS NOT AVAILABLE
 SHORT TERM EXPOSURE LIMIT(STEL) IS .3 PPM
TEMPERATURE - 25 C
WIND DIRECTION - 0
WIND SPEED - 2 M/S
SUN ELEVATION ANGLE IS 77 DEGREES
CLOUD COVER IS 2 EIGHTHS
CLOUD TYPE IS HIGH (Ci, Cc, Cs)
GROUND IS DRY
THERE IS NO INVERSION
ATMOSPHERIC STABILITY PARAMETER IS .5
SPILL SITE ROUGHNESS LENGTH IS 50 CM

THIS IS A GAS RELEASE
HEIGHT OF LEAK ABOVE GROUND IS 10 M
SPILL IS AT GROUND LEVEL
TOTAL AMOUNT SPILLED IS 2000 KG
CONCENTRATION AVERAGING TIME IS 1 MIN
ELAPSED TIME SINCE START OF SPILL IS 10 MIN
HEIGHT OF INTEREST IS 2 M

-----------------------------------------------------
THE MAXIMUM DISTANCE FOR 1 MG/M3 IS 1.44 KM
 10 MG/M3 IS TOO HIGH
-----------------------------------------------------
THE MAXIMUM DISTANCE FOR .1 MG/M3 IS 1.92 KM
THE MAXIMUM DISTANCE FOR .5 MG/M3 IS 1.59 KM
THE MAXIMUM DISTANCE FOR 2.5 MG/M3 IS 1.23 KM
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TABLE III. Averaged Seasonal Wind Patterns at Various Sites at Vandenberg AFB.

Time Period		SLC-3[a]	SLC-4	HSSF[b]
Apr.–Sept.	day	7 knots (320°)[c]	7 knots (300°)	5 knots (320°)
	night	6 knots (360°)	6 knots (340°)	6 knots (340°)
Oct.– Mar.	day	10 knots (320°)	10 knots (320°)	7 knots (330°)
	night	4 knots (030°)	4 knots (030°)	3 knots (060°)

[a] Satellite launch complex three. [b] Hypergolic service and storage facility. [c] 1 knot = 0.51 m/s; wind direction refers to upwind due north.

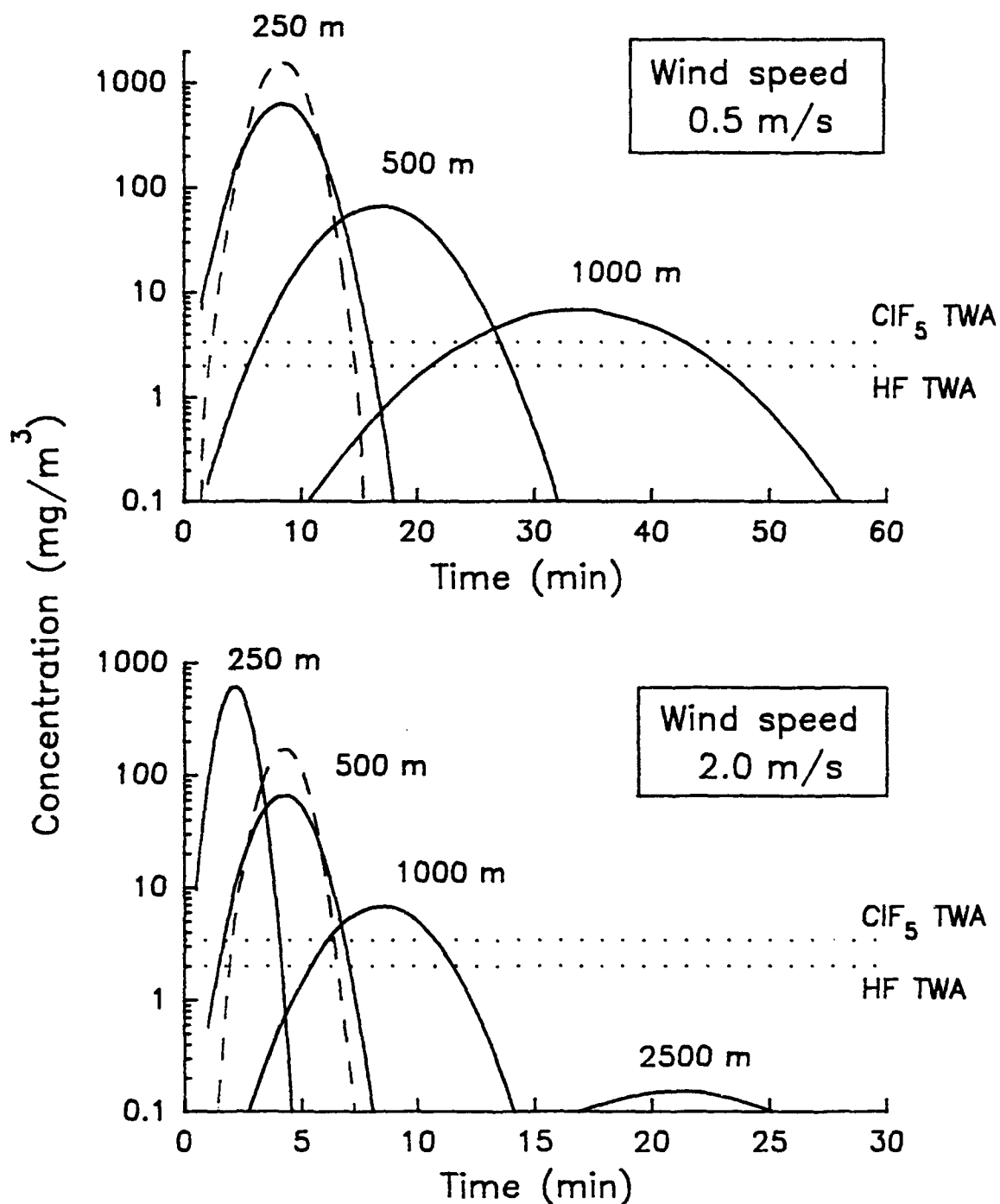# CIF$_5$ Release and Dispersion along Wind Vector Centerline (VAFB Site)

Fig. 1. Concentration as a function of time at various distances along the downwind centerline. Results are for a 2000 kg propellant release. Input parameters given in Table II unless otherwise noted. (—) course terrain, roughness parameter of 50; (– – –) smooth terrain, roughness parameter of 10.
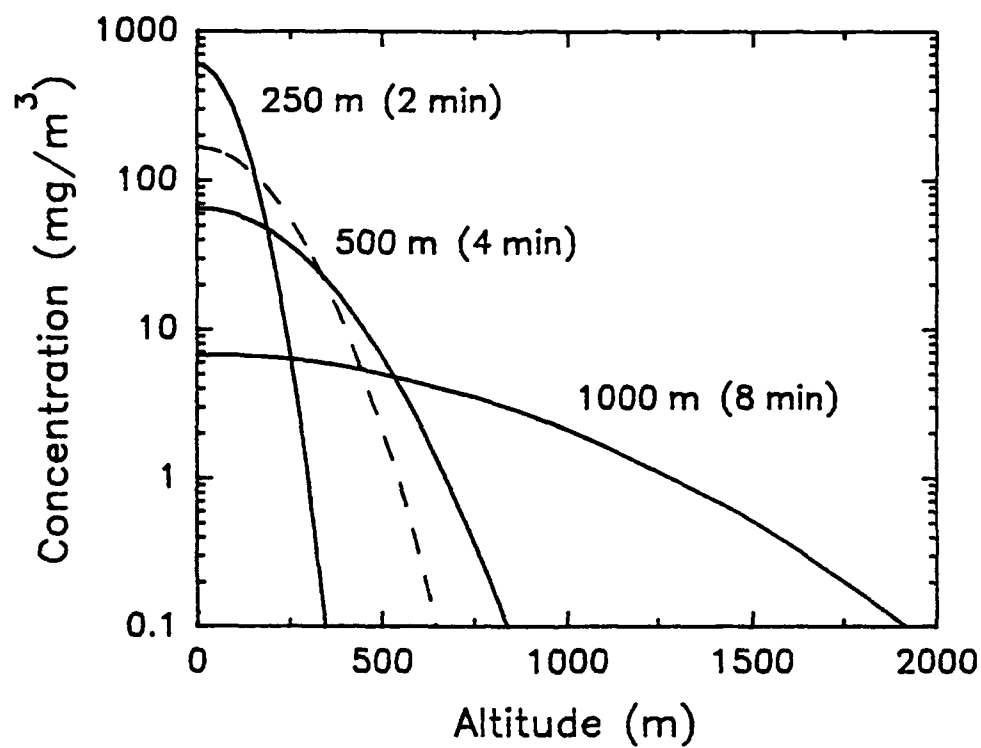
Fig. 2.   Concentration as a function of altitude for various distances along the downwind
          centerline. Data calculated for times corresponding to peak concentrations at
          each site. Wind speed was 2.0 m/s and roughness parameter was either 50 (—)
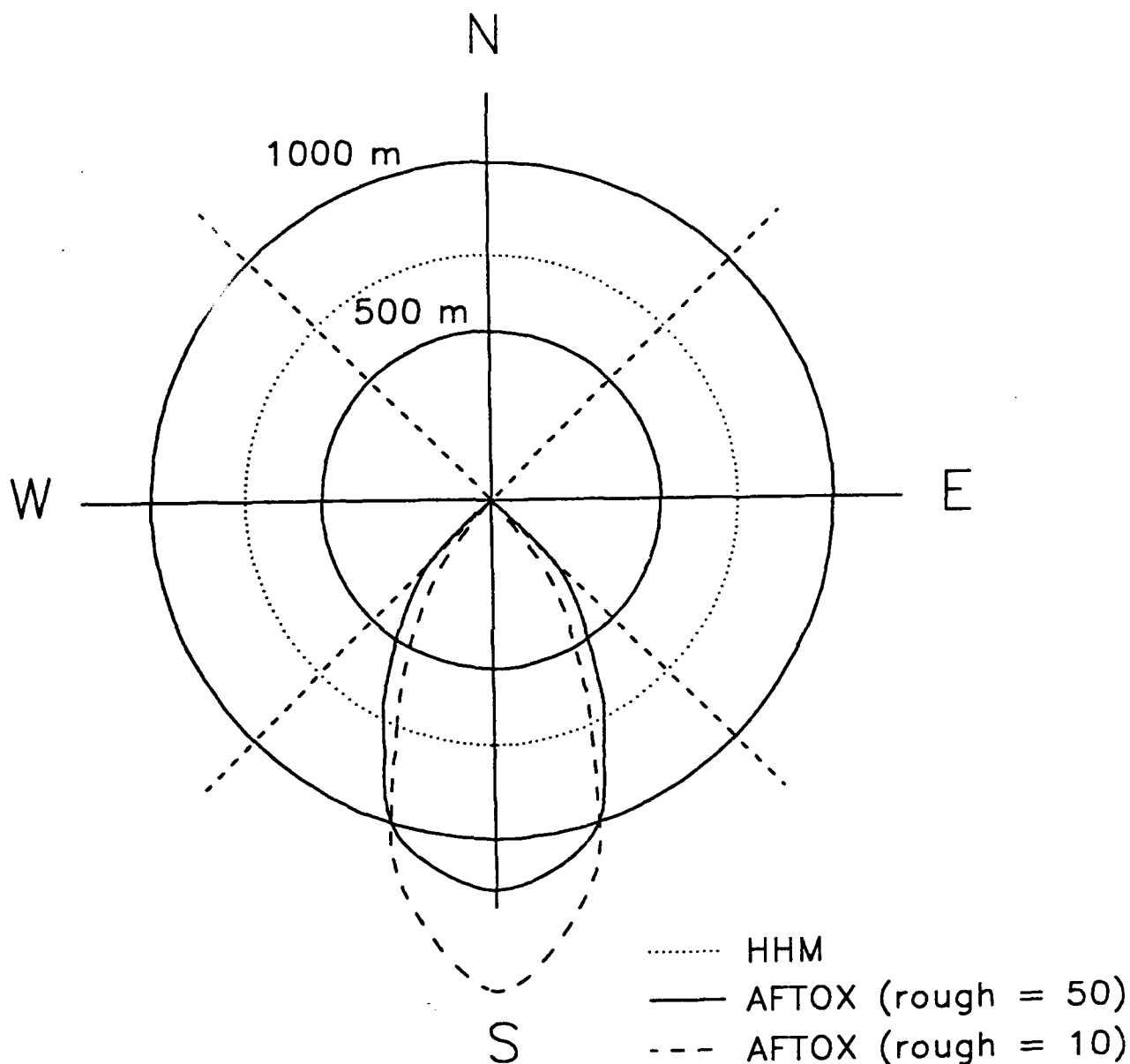   or 10 (– – –). All other input parameters are from Table II.

Fig. 3.   Dispersion maps showing area over which ground-level concentrations exceeded stated exposure levels. AFTOX results were calculated for a ClF$_5$ release and a TWA TLV of 2.5 g(F)/m^3. Calculations assume a northerly (i.e., 0°) 2.0 m/s wind field and a roughness parameter of either 50 (—) or 10 (– – –). See Table II for other input parameters. HHM results, which assume no wind, are also given.

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