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EXPOSURE OF MARIGOLD (TAGETES) TO GASEOUS HYDROGEN CHLORIDE

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13. ABSTRACT

To ascertain the extent of environmental pollution problems attendant with Air Force missile operations, mature flowering marigold plants were exposed to one of the known exhaust products, hydrogen chloride. All plants died after 5 min exposure to 2071 ppm, the highest concentration used. At 95 ppm no effect was noted. Seeds obtained from the exposed plants did not appear to be affected by the HCl treatment.

Key Words:
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NOTICES

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FOREWORD

This study was conducted by members of the Chemical Hazards Branch, Toxic Hazards Division, Aerospace Medical Research Laboratory, Wright-Patterson AFB, Ohio, under Project 6302, "Toxic Hazards of Propellants and Materials, Task 630204, "Environmental Pollution Aspects of Propellants and Materials." The study was initiated in November 1970 and completed in June 1971. The authors gratefully acknowledge L. DiPasquale, M. Schneider, and D. Wohlslagel, Toxic Hazards Research Unit, Syste-Med Corporation, Dayton, Ohio, for conducting the plant exposures.

This technical report has been reviewed and is approved.

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SECTION I

INTRODUCTION

The use of various solid boosters has raised the question of the possible environmental pollution caused by the exhaust and its effect upon plant growth. A major portion of the exhaust of solid rocket motors using perchlorate formulations is gaseous hydrogen chloride. A large percentage of HCl is present in the exhaust, released during a complete burn. Of practical and immediate importance is the first 10 seconds of a launch, when the exhaust products are near the earth's surface. During this initial 10-second burn, significant amounts of HCl are produced. In addition, studies have indicated the impact of micrometeorological profiles on exhaust cloud travel and the potential hazard implications of various operational conditions.

Hydrogen chloride, although involved as a product or by-product of many industrial processes, has not been included in the list of air pollutants of major concern (Brandt and Heck, 1968). In the review by Stahl (1969), the paucity of data on toxicity of gaseous HCl to humans is discussed, as well as the rather limited studies with plant species. Consideration of the problems associated with HCl has been given, in general, only in specific industrial applications, although plant injury by this compound has been known for over a century (cited by Heck et al., 1970) However, the literature indicates that hydrochloric acid is a definite phytotoxicant, emissions of HCl having been responsible for plant damage in several instances (cited in Stahl, 1969). Haselhoff and Lindau (1903) showed that the effects of HCl on plants resulted from direct contact of the gas with the exposed parts of the plants rather than from reactant products arising in the soil. In a more recent study by Shriner and Lacasse (1968), the distribution of chloride in the tissue of tomato plants following exposure to HCl indicated that the HCl exposed plants contained 300% more chloride than unexposed control plants. Among the exposed plants, the immature leaves showed the greatest increase in chloride; however, the middleaged leaves were most seriously affected and showed interveinal bronzing and bleaching after a 2-hour exposure to 5 ppm HCl. (This concentration is the industrial threshold limit value for human exposure adopted by the American Conference of Government Industrial Hygienists.) Necrosis resulted within 72 hours after the exposure.

A knowledge of biological variability suggests that susceptibility to HCl damage, as with any toxicant, varies not only from species to species but also with specific strains (varieties). Stahl (1969) presents a summary of the available data that indicates this difference in response; however, rigidly controlled experiments to ascertain both quantitative data on response differences and mechanism of resistance are extremely limited. Brandt and Heck (1968) review a study wherein differential response of the guard cells to ozone was genetically determined and was responsible for the difference in susceptibility in two varieties of onion. Exposure of 12 coniferous and broadleafed trees to HCl (43 ppm for 4 hours) showed the conifers to be more resistant (Means and Lacasse, 1968). Table I shows the relative differences in HCl susceptibility of various plant species.

TABLE I[1]

SENSITIVITY OF SELECTED PLANTS TO HYDROGEN CHLORIDE

	<u>Sensitive</u>	
Beet, Sugar	Larch	Tomato
Cherry	Maple	Viburnum
	<u>Intermediate</u>	
Begonia	Rose	Spruce
	Rosebud	
	<u>Resistant</u>	
Beech	Maple	Pear
Birch	Oak	Spruce
Fir		

[1] Adapted from Heck et al., 1970

Additional factors that can influence the biological response to a potentially injurious substance include the environmental parameters of temperature, humidity, intensity, duration and wavelength of light, CO_2 concentration, and soil characteristics such as composition and type, microfloral content, moisture content, pH, and aeration. Thus the many interacting variables require that exposure conditions be rigidly controlled if definite dose response relationships are to be established and mechanisms of action are to be elucidated.

Attempts to construct specific concentration-time relationships have met with limited success. One relationship determined by O'Gara (cited by Brandt and Heck, 1968) for SO_2 damage is:

$$c = b\left(\frac{1}{t}\right) + a$$

where c is concentration, t is time, and a and b are constants dependent upon species and extent of injury. If c is plotted vs. 1/t, a at 1/t = 0 is the intercept and becomes the injury threshold. Extrapolation of this equation and others have not proven of great value, undoubtedly due to the complexity of interacting factors.

Since some large solid booster exhausts are known to contain high levels of hydrogen chloride, damage to native plant communities, economically important agricultural species, and ornamental species could result in the vicinity of a firing pad if the ground level HCl concentration becomes high. Ground level HCl concentrations have not been obtained from actual firings, but various levels have been postulated from the known characteristics of the booster. Although a large amount of HCl is present in the exhaust during the total burn, only low concentrations for short time periods are expected on the ground. These low concentrations are anticipated during favorable weather situations; however, higher levels could be expected under certain meteorological conditions. For example, a toxic cloud caught in an inversion could mix to the ground when the inversion is destroyed by warm, unstable air. An additional problem, scavenging, can occur in the presence of rain, fog, or mist when practically all of the HCl gas is absorbed by the liquid droplets. The possible result is a downwind acid rain or mist.

The present study was undertaken to determine the sensitivity of a representative horticultural species, Tagetes (marigold), to various levels of hydrogen chloride during short term (5-minute) exposure periods. Interest was directed to both visually observable damage (wilting, necrosis, death) and secondary effects on seeds obtained from exposed plants.

SECTION II

METHODS

Mature flowering marigold plants were obtained from seeds germinated in a controlled environment room. Except for a short period when the plants were kept in a greenhouse, growth and maturation occurred under the following conditions: RH of 60% to 70%; 8- to 9-hour photo pheriod at 1000 footcandles, 67 F dark (night) temperature and 73 F light temperature. The plants (83 days old) were exposed to one of three concentrations of hydrogen chloride. Twenty-four individual plants were exposed for 5 minutes to the following average HCl levels: 2071, 300, and 95 parts per million (ppm). Suitable controls receiving no HCl treatment were included. The plants were observed during, immediately after, and 24 hours postexposure and all visible damage was recorded for each test plant.

The exposures were accomplished in a Rochester chamber (figure 1) which has a volume of approximately 100 cubic feet. Airflow through the chamber was 10 cfm of predried air at 70 to 72 F. Gaseous HCl (Matheson, Technical grade, 99.0% min purity) was metered into the airstream to obtain the desired nominal concentration in the chamber. The chloride concentration was monitored throughout the 5-minute exposure period and the ppm level was determined at 30-second intervals. The hydrogen chloride level was measured by analyzing an aqueous sample of the chamber atmosphere with an Orion chloride electrode. The resulting reading in millivolts was converted to moles/liter, which was corrected by the appropriate dilution factor to yield chamber concentration in ppm. Some difficulty was experienced in maintaining a uniform concentration during the short exposure period. The observed concentrations for the three exposures are shown in Table II.

TABLE II

HCL CONCENTRATION DURING THREE EXPOSURES

	concentration ppm		
Time, sec	95[1]	300[1]	2071[1]
0	88	490	1466
30	88	473	1567
60	88	441	1713
90	88	375	1795
120	88	310	2040
150	96	237	2285
180	96	204	2366
210	100	204	2366
240	108	204	2366
270	100	180	2366
300	100	180	2448

[1]Average concentration

For germination studies, seeds were obtained from control and exposed plants. The first experiment occurred 57 days postexposure with 180 seeds from each treatment and the second experiment was conducted 125 days postexposure with 60 seeds from each treatment. Germination was accomplished in the laboratory in specially designed chambers using BR-8 for the support substrate as described by Lind (1971).

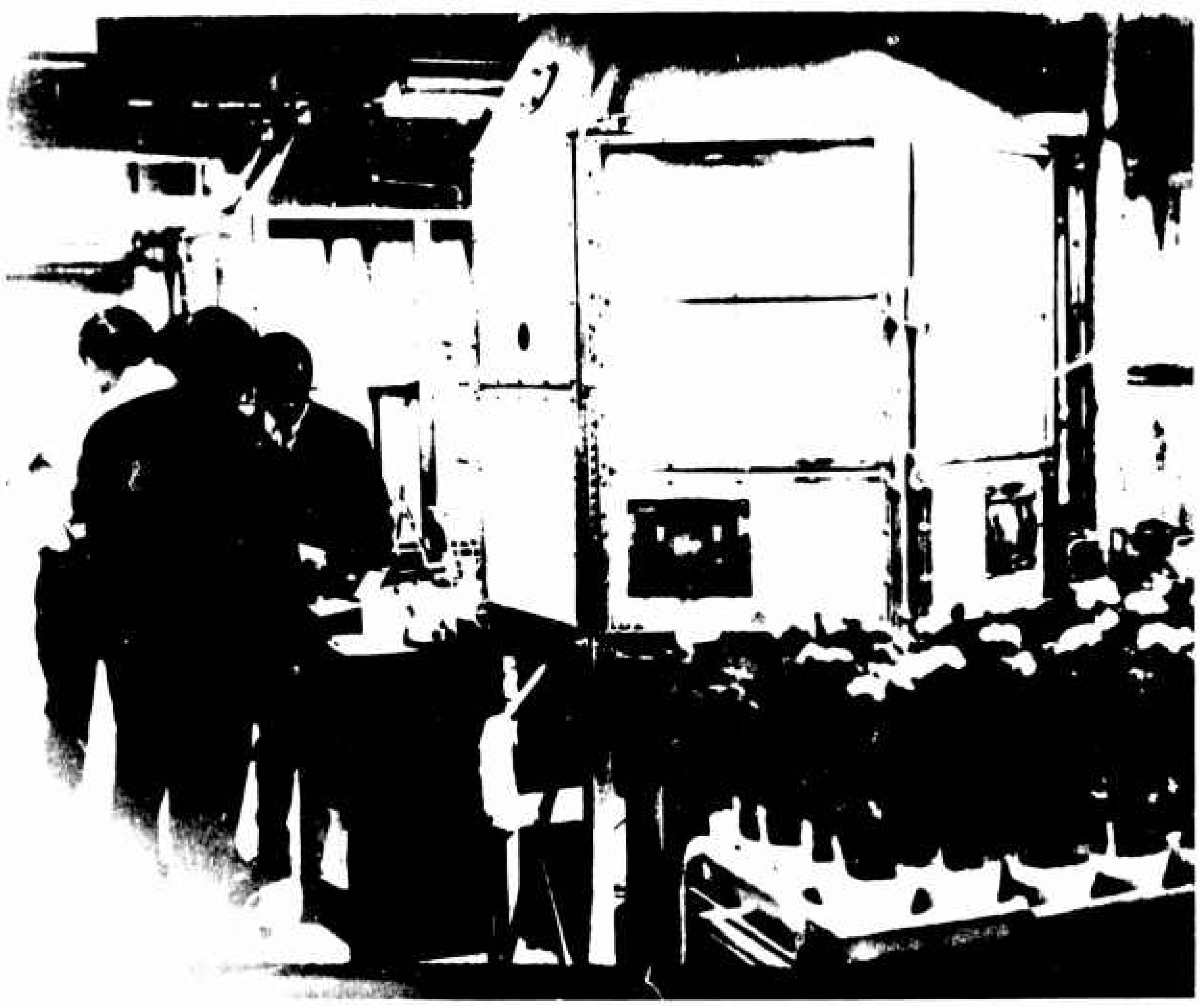

Figure 1. Rochester Exposure Chamber

SECTION III

RESULTS AND DISCUSSION

Plants were observed during, immediately after, and 24 hours postexposure. In general, the 95 ppm group showed little or no visible damage due to the hydrogen chloride treatment (figure 2). A slight amount of leaf wilting was noted at 15 minutes postexposure; and at 24 hours, three individual plants displayed slightly bleached, chlorotic leaves.

Among plants treated for 5 minutes with an average HCl concentration of 300 ppm the effects were more severe although plant death did not result. Observations immediately following the exposure showed that many plants developed both a loss of leaf turgor and bleached spots on the leaves. After 24 hours, 42% of the plants showed a stem constriction below the floral head. All plants displayed a loss of leaf turgor and bleached spots on the margin and interveinal portions of the leaves (figure 3).

Plants exposed to 2071 ppm HCl were severely damaged by the exposure. Wilting was evident during the 5-minute treatment period and severe marginal and interveinal leaf burn was observed following the exposure. After 24 hours, the stem below the floral head became constricted and stem collapse occurred. Complete wilting of all leaves characterized the plants in this test group. Leaf necrosis and necrosis of the upper portion of the stem developed. All 24 plants exposed to an average concentration of 2071 ppm HCl for the 5-minute period died (see figure 4). A summary of the visible effects caused by each treatment is presented in Table III. Comparison of all exposures is shown on figure 5.

TABLE III

EXPOSURE OF MATURE FLOWERING MARIGOLD PLANTS TO HYDROGEN CHLORIDE FOR 5 MINUTES

Treatment	Effects
2071 ppm or 10,355 ppm-min	Severe wilting, marginal and interveinal leaf necrosis, stem collapse, death
300 ppm or 1500 ppm-min	Wilting, bleached leaf spots, recovery
95 ppm or 475 ppm-min	No visible damage
Control	Normal Appearance

Figure 2. Plant After Exposure to 95 ppm HCl

Figure 3. Plant After Exposure to 300 ppm HCl

Figure 4. Plant After Exposure to 2071 ppm HCl

Figure 5. Comparison of Plants After Various HCl Exposures

The results of the seed germination studies are rather equivocal due to the reduced germination rates of the control seeds. This may have been influenced by the erratic temperature variations in the controlled environment room and the laboratory that occurred during the experimental periods. The data shown in table IV, while definitely not conclusive, are suggestive that seed germination may not be affected by HCl exposure at the levels tested. In the 5-day germination experiment, the seeds from the 95 and 2071 ppm exposures gave a higher rate than the controls, the 300-ppm exposure seeds showing an inconsistent rate. The 95-ppm exposure seeds from the 14-day study showed a significantly higher germination rate than the controls. The variation in similar groups (ranging from equal to 2.7x) from the two germination studies would certainly indicate inadequate control of germination conditions. The low numbers of seeds used in these experiments (120 and 60) could also contribute to this variability. It is mandatory that these exposures be repeated with a sufficient number of plants to provide a statistically significant and representative number of seeds.

TABLE IV

GERMINATION OF SEEDS FROM HCL EXPOSED MARIGOLDS

HCl conc, ppm	Exp. 1 - 5-day Germination, %	Exp. 2 - 14-day Germination %
Control	8.3	15.0
95	15.0	40.0
300	5.0	5.0
2071	13.9	8.3

Additionally, seed treatment immediately after the exposure, during storage, and during actual germination must be rigidly standardized.

Exposure of marigold plants to various levels of HCl resulted in a gradation of effects upon the plants. Visible plant damage increased as the concentration of HCl increased. For this species and variety, the no-effect level appears to be about 100 ppm HCl for 5-minutes duration. However, the actual effect upon a plant caused by this HCl level could vary depending upon the relative humidity surrounding the exposed leaves. Hydrogen chloride is readily converted to hydrochloric acid in the presence of water and a 100 ppm hydrochloric acid mist may cause more damage to the plant tissue than the same level of gaseous hydrogen chloride. The exposure to 2071 ppm HCl resulted in the death of all individuals in this test group. However, the plants treated with the intermediate 300-ppm level recovered from any damage and continued to produce normal flowers.

In general the plant damage caused by HCl exposure was due to acid burns causing a loss of leaf turgor and bleaching of leaf tissues. The visible damage was mostly confined to the leaves although collapse of the stem immediately below the floral head was common in the high level exposure group.

The results of this study indicate that HCl is a phytotoxicant which could cause local plant damage in the vicinity of launch facilities. The actual damage sustained by the plants after a firing would depend upon the HCl level experienced on the ground, the duration of the exposure, the meteorological conditions during the exposure, and the plant species exposed. No-effect levels should be determined for the economically important species grown in the vicinity of launch sites. More importantly, the dominant species of native plant communities which may be exposed to HCl pollution should be studied under variations of light, temperature and relative humidity to determine no-effect levels. The concentrations must be determined for specific injury indices, i.e., visible topical damage to ornamental and vegetable crops and systemic effects influencing seed germination and crop yield. Studies should also include acute exposure conditions as well as chronic (repeated) exposures. Such programs will insure that Air Force operations will be in compliance with all federal, state, and local pollution directives as is required by AFR 161-22.

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