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THE PHYTOTOXICITY OF DESIGNATED POLLUTANTS ON PLANT SPECIES

THIRD ANNUAL REPORT

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NOTICES

TECHNICAL REVIEW AND APPROVAL

AFAMRL-TR-83-96

This report has been reviewed by the Office of Public Affairs (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

FOR THE COMMANDER

BRUCE O. STUART, PhD
Director Toxic Hazards Division
Air Force Aerospace Medical Research Laboratory

SECURITY CLASSIFICATION OF THIS PAGE

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A ground cloud is formed as the space shuttle rocket lifts off. The phytotoxicity of products released from this cloud was studied. Aluminum oxide dust and droplets of hydrogen chloride (HCl) were found on leaves of plants at the Kennedy Space Center following launch. The non-toxic nature of aluminum oxide was confirmed in laboratory tests. HCl droplets fell from the cloud as a mist and caused foliar spotting on plants at the Center. Similar necrotic lesions were produced on most species tested with HCl mist applied in glasshouse studies. Less injury occurred following evening exposures than morning or mid-day exposures. Acidity of the mist was more important than the length of exposure. Leaves were the most likely part of the plant to be injured with lower surfaces being more sensitive to damage than upper surfaces. Small depressions formed on lemons exposed to 1% HCl mist, but ripe tomatoes remained undamaged by the same exposure regime. Zinnia flowers were sensitive to injury, but radish roots were not reduced when plant tops were exposed to the mist. Biomass of other plants were reduced only slightly by single mist exposures. Marigold plants were exposed to HCl mist during different periods of flower development. Only seeds collected from those flowers exposed during pollin-

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Block 18 continued

Missile exhaust products	Phytotoxicity	Space shuttle
Plant injury	Scanning microscopy	X-ray microprobe

Block 19 continued

ation had reduced germination rates. If leaves were rinsed with tap water up to ten minutes after mist exposure , subsequent injury was greatly reduced. Pretreatment rinses, however, were not effective. In summary, plants are sensitive to HCl mists but the acid concentration must be high to cause serious visible injury. Although such concentrations are present in mist deposited from a launch ground cloud, actual numbers of plants exposed would depend on climatic conditions. Detecting foliar aluminum deposits may provide evidence that the ground cloud passed over certain vegetation.

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PREFACE

This report covers work performed by members of the Statewide Air Pollution Research Center at the University of California, Riverside, during the period from September 1, 1982 to August 31, 1983. The project was funded by United States Air Force Contract F-33615-80C-0512 administered by the University of California, Irvine. The author acknowledges the cooperation of Lt. Col. M. G. MacNaughton, Toxic Hazards Division, Air Force Aerospace Medical Research Laboratory, Wright-Patterson Air Force Base, Ohio. The comments of Drs. T. T. Crocker, H. Hodge, and J. D. McEwen of the Scientific Advisory Board have been useful. We also appreciate the advice and suggestions of Lt. Col. R. C. Wooten (SD/DEV), Lt. Col. J. E. Milligan (OEHL/ECE), and Dr. H. M. Stirts (SAC/DEVQ), and the help of Capt. E. A. Ayers (SD/DEV). We acknowledge the technical assistance and expertise of L. J. Ross and E. C. Smith and of University of California students, M. E. Williams, M. S. Pilgram, G. Villagomez, S. A. Flores, and J. C. Bonetti, who aided during portions of the project.

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SUMMARY

Investigations during the third contract year concerned the effects on vegetation of materials which could precipitate from the ground cloud formed after a shuttle launch. On combustion, solid rocket fuel in the shuttle boosters create large quantities of aluminum oxide dust and hydrogen chloride gas. The gas combines with atmospheric, rocket-generated, and fire-control water to form hydrochloric acid (HCl). Injury has been seen on plants impacted with HCl mist falling from the ground cloud after most shuttle launches at the Kennedy Space Center in Florida. Mist droplets collected several miles from the launch pad indicate solutions as concentrated as pH 0.5. Aluminum oxide dust is also distributed beneath the path of the ground.

Our investigations characterized plant injury created with HCl mist under controlled conditions. The mist typically formed bifacial necrotic lesions which were fully developed 24-48 hours after exposure. With concentrated solutions, lesions were first visible 10 minutes after droplets contacted the leaf surfaces. When different plant species were tested, some differences in sensitivity to the acidic mist were revealed. Some plants and plant parts were studied in more detail. Less injury resulted if only the upper leaf surface was exposed to mist than if the lower or both surfaces received the HCl treatment. Zinnia flowers exposed when mature and blooming were injured and showed striking color fading and petal edge necrosis. Marigold plants were exposed at different stages of flower development. Subsequent tests showed that only acid exposure during pollination lowered the germination rate of mature seeds.

Plant injury was chiefly a function of acid concentration, but amount of solution, time of day, and plant age also influenced amount of foliar necrosis. Plant yield in terms of biomass, flower numbers, and flower weights were relatively unchanged by single exposures to HCl mist.

Necrotic injury induced by HCl mist was reduced when plants were exposed in the early evening rather than at dawn or noon. Plant injury was even more effectively reduced by rinsing the plant with tap water up to 10 minutes after mist applications. This may be an effective strategy for reducing injury in specific high-cost crops likely to be impacted by HCl mists.

INTRODUCTION

This research was a continuation of Air Force-sponsored research funded under Contract F-33615-80C-0512. The effects of Air Force-related pollutants on terrestrial plants were studied. Most research has been concerned with the planned launches of the Air Force version of the space shuttle system, scheduled to commence operations from Vandenberg Air Force Base in October 1985.

The space shuttle is assisted on lift-off by two booster rockets. These engines burn solid fuel to produce tremendous lift releasing ca 60 tons of hydrogen chloride gas (HCl), ca 87 tons of 0.01-60 μm diameter aluminum oxide particles, and lesser amounts of other materials (Table 1) (Pellett et al., 1983; Nadler, 1976). A portion of the exhaust follows the rocket into the upper layers of the atmosphere, but 50-80% of these materials are initially trapped within a ground cloud which stabilizes below ca 1000 m.

Granett and Taylor (1977, 1978) reported that aluminum oxide alone did not cause plant injury. Similarly, response of plants exposed to aluminum oxide and HCl gas at ambient or elevated humidity levels was not influenced by the particles. Other studies by Granett and Taylor (1976, 1977, 1978, 1981) showed that at sufficiently high concentrations, HCl gas could seriously injure plants, that injury was influenced by gas concentrations, exposure durations, and environmental conditions, and that plant species, age, and general health also influenced sensitivity and amount of injury.

Environmental studies conducted at Kennedy Space Center after the first operational shuttle launches have shown that ground cloud gases and perhaps dust react with rocket-generated, fire control, and ambient water to create a hydrochloric acid aerosol (Knott, 1981; Bowie, 1981; Pellett et al., 1983). Ground clouds drifting with prevailing winds precipitated aluminum oxide dust and HCl mist. Vegetation very close to the launch site was rapidly and predictably killed by HCl gases, but beyond this area plant injury was characterized by necrotic and chlorotic leaf spots (Knott, 1981). Particles of aluminum oxide were found on the ground and on plants, but were not related to injury. Not all plants under the observed cloud path were injured.

Studies conducted during this period were undertaken to better characterize and define the response of commercial crops exposed to acidic mist under controlled conditions. The investigations were designed to develop an understanding of both the nature of injury and to predict possibly important influences that could be related to field exposures.

TABLE 1
THEORETICAL EXHAUST PRODUCTS OF SOLID ROCKET FUEL

Product species		Product weight (Grams per 100 g consumed propellant)
Hydrogen chloride	(HCl)	20.90
Chlorine gas	(Cl_2)	0.06
Carbon monoxide	(CO)	24.37
Nitrogen gas	(N_2)	8.50
Water vapor	(H_2O)	10.39
Hydrogen gas	(H_2)	2.11
Carbon dioxide	(CO_2)	4.32
Hydroxyl radicals	(OH & H)	0.02
Solid Particles		
Aluminum oxide	(Al_2O_3)	28.34
Aluminum chloride	($AlCl_3$)	0.02
Iron chloride	($FeCl_2$)	0.97

MATERIALS AND METHODS

EXPOSURE EQUIPMENT

Mist Chambers

During these studies, most plant exposures took place in a 1.0 x 0.75 x 0.9 m Lexane plastic chamber equipped with a sealable front door (Figure 1). A 0.3 rpm motor and gear train beneath the chamber's wooden base turned a 24-inch diameter plywood table to facilitate even distribution of mist on plants. The chamber could be drained of accumulated fluids and rinse water through a hole in the base.

In a few experiments plants were exposed in a standard continuous-stirred tank reactor (CSTR) (Heck et al., 1978) constructed of wooden supports and base completely covered with 5-mil Tedlar film. This chamber was 1.37 m high with a 1.37 m diameter. Four paddles, mounted on the interior upper surface, rotated at 120 rpm to provide necessary air stirring when desired. An exhaust system could evacuate the chamber of mist and gases after the exposure. The floor of the chamber had a single drainage hole.

Mist Generation Equipment

Acid solutions in a 60 mℓ plastic syringe were forced through a tube at a constant rate using a Sage model 35 syringe pump. The tube directed solutions into a Mini Ulva (Micron Corp, Houston, TX) spinning disk device which created a fine mist consisting of droplets in the 20-40 μ range (Figure 2a). The Mini Ulva motor was powered by batteries or a variable voltage power supply.

An alternate method for applying acidic mist to plants was with a plastic spray bottle held 6-8 inches from the leaf surface (Figure 2b).

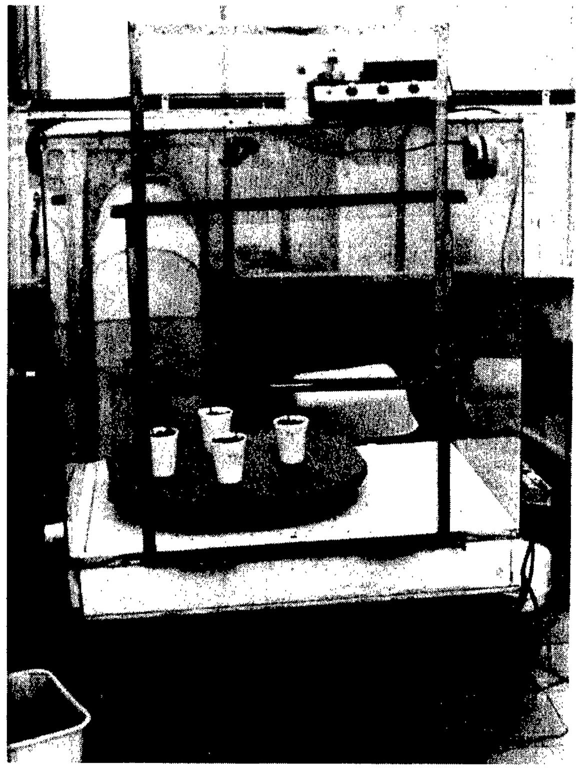


Figure 1. Mist exposure chamber. Plants are exposed to HCl mist in a chamber with rotating plywood platform.

Figure 2. Mist generators. 2a. (left) Mini Ulva spinning disk applicator used for fine mist production. 2b. (right) Plastic spray bottle used to apply mist-spray to individual plant leaves.

Spraying continued until leaves dripped. Amounts of solution reaching the leaf were comparable to the spinning disk applicator, but droplets were larger with the spray bottle. This method was used while developing the disk applicator technique or when specific leaf surfaces were to be sprayed.

Acidic Mist

Acidic mist solutions were prepared using distilled water and 12 M reagent grade HCl. Solutions were usually prepared on a percent (v/v) basis and then measured using an Orion model 901 ion analyzer-pH meter (Table 2). The analyzer was calibrated with standard prepared buffers, usually of pH 2.0 and 4.0. In some trials, mist of simulated acidic rain was compared with HCl mist using the same system. Simulated rain mist was prepared with nitric and sulfuric acids mixed at the 2.5:1 ratio found in the Los Angeles area (Waldman, 1982). No attempt was made to adjust the ionic balance of this material.

Aluminum Oxide Applications and Generation

Aluminum oxide particles with mean diameters of 40 µm or less were applied in massive amounts using a homemade device consisting of a 50 µm stainless steel mesh screen (Microdur Wire Cloth) secured over an 8.5 cm diameter canning jar ring (Figure 3). Particles were forced through the taut screen with a test tube brush.

TABLE 2
CHARACTERISTICS OF HCl MIST SOLUTIONS

Prepared concentration		Measured
ppm	%	pH
0	0	4.91
8	0.001	3.56
16	0.002	3.28
31	0.003	3.00
62	0.006	2.70
125	0.012	2.41
250	0.025	2.14
500	0.050	1.76
1000	0.125	1.56
2500	0.250	1.28
5000	0.500	1.01
1000	1.000	0.75

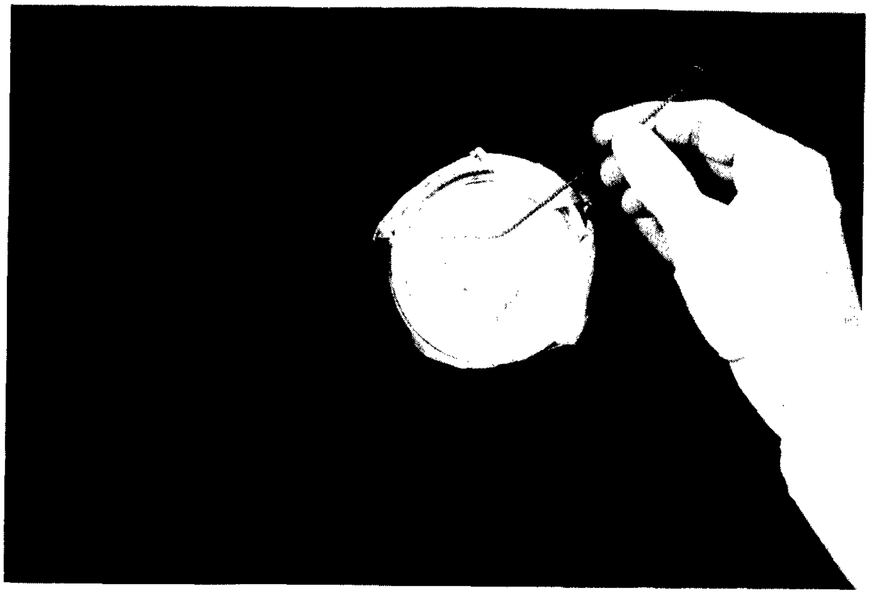


Figure 3. Aluminum oxide dust applicator.

For some tests, aluminum oxide particles and HCl gas were generated simultaneously by burning 50-1600 mg pieces of solid rocket fuel in a closed exposure chamber. Fuel was ignited by electrically heating a model rocket starter which was described in an earlier report (see Figure 1 and related text, Granett and Taylor, 1978). For current tests, aluminum oxide and not HCl gas was of primary concern.

PLANT PRODUCTION AND EXPERIMENTAL MEASUREMENTS

Glasshouse Facilities

Experiments and plant production took place in a 6 x 30 m glasshouse equipped with steam heat, evaporative coolers, and charcoal-filtered air. Temperatures in the glasshouse ranged from 58-68^{o} F at night to 70-95^{o} F during the day. Relative humidity ranged from 20 to 70% depending on the season of the year.

Plant Growth

Plants in most experiments were grown from seed in prepared glasshouse soil (Table 3). Plant species were chosen to include two monocots and six dicots representing field, vegetable, and garden crops (Table 4). Plants were watered regularly and fertilized as needed with a liquid nutrient solution described by Hoagland and Arnon (1950) (Table 5).

TABLE 3
COMPOSITION OF GLASSHOUSE SOIL MIX

Components	Amounts	
Soil (Oakley sand)	0.40 m^3	(14 ft^3)
Canadian peat moss	0.20 m^3	(7 ft^3)
Redwood shavings or fir bark	0.20 m^3	(7 ft^3)
Single super phosphate [$Ca(H_2PO_4)_2$]	1.13 kg	(2.5 lbs)
Potassium nitrate [KNO_3]	0.11 kg	(4 oz)
Potassium sulfate [K_2SO_4]	0.11 kg	(4 oz)
Dolomite limestone	1.70 kg	(3.75 lbs)
Oyster shell lime	0.68 kg	(1.5 lb)
Micronutrients		
Cu	30 ppm (dry basis)	
Zn	10 ppm (dry basis)	
Mn	15 ppm (dry basis)	
Fe	15 ppm (dry basis)	

TABLE 4
PLANT SPECIES USED IN MIST TESTS

Species	Name	Variety
Barley	*Hordeum vulgare* L.	CM67
Bean	*Phaseolus vulgaris* L.	Pinto
Citrus	*Citrus limon* (L.)	Lupe Lemon
Lettuce	*Lactuca sativa* L.	Black-seeded Simpson
Marigold	*Tagetes patula* L.	Goldie
Radish	*Raphanus sativus* L.	Cherry Belle
Sorghum	*Sorghum sudanensis* (Piper) Stapf.	Piper
Tomato	*Lycopersicon esculentum* Var. *cerasiforme* (Dan) A. Gray	Tiny Tim
Zinnia	*Zinnia elegans* Jacq.	Scarlet Queen

TABLE 5
NUTRIENT SOLUTION FOR PLANTS

Material	Amount
K_2HPO_4	1.37 g
KH_2PO_4	2.04 g
KNO_3	10.10 g
$Ca(NO_3)_2$	23.60 g
$MgSO_4$	9.86 g
Iron chelate	1.00 g
Micronutrients	19 mℓ
Water to make	10 gal

Environmental and pH Measurements

Glasshouse temperatures and relative humidity were recorded on a Weather Measure recording hydrograph. Individual chamber temperatures were measured with a standard laboratory mercury thermometer or with a thermocouple. Thermocouples or a sling- or motor driven-psychrometer were used to measure relative humidity. Light was measured in μ-einsteins cm^{-2} sec^{-1} units of photosynthetically active radiation (PAR) using a Lambda model LI-185 radiation sensor. Some pH measurements were made on plant surfaces or during mist generation, using Hydrion paper of pH 0-1.5 and 0-3.

Plant Injury

Leaf injury was the major plant response after exposure to acidic mist. Counting the number of leaves injured of total exposed provided a percent-leaves-injured rating. Since a leaf would be counted injured even with minimal injury, an estimate of leaf area injured was also used. The estimate was based on a pretransformed scale from 1 to 12, with 1 being no injury and 12 meaning 100% necrosis (Table 6) (Granett, 1982). Accuracy of the estimate was verified by placing a clear plastic 1 x 1 cm grid over the leaf. Number of grid intersections over injured tissue was compared to total number of intersections (Gumpertz et al., 1982).

Plant Harvest

Plants were usually graded for injury 24-48 hours postexposure. In addition, plants were sometimes harvested one or more weeks later at which time leaf injury could be reevaluated and part weights and leaf area could be recorded. An Arbor model 3006 electronic balance and a Lambda model 3000 portable area meter were used. In some experiments plant height, leaf, flower, bud, and pod numbers were recorded.

TABLE 6
ESTIMATING FOLIAR INJURY ON HCl-MISTED PLANTS

Scale	Area of leaf injury (%)
1	0 (no visible injury)
2	0-3
3	3-6
4	6-12
5	12-25
6	25-50
7	50-75
8	75-87
9	87-94
10	94-97
11	97-100
12	100 (death of leaf)

EXPOSURE METHODS

Mist Distribution Calibration

Mist distribution within the chamber was calibrated by distributing weighed filter paper discs in open glass petri plates on the chamber base. Paper was reweighed after mist generation and statistical techniques identified chamber areas receiving equal deposition.

Typical Exposure

In a typical acidic mist exposure, uniform-sized plants were selected from a larger population of the same age and placed on the platform in the chamber. After the door was sealed, power was applied to the syringe pump, platform-rotating motor, and spinning-disk applicator. Most exposures lasted three minutes or one complete platform revolution. Power was switched off and the plants were removed from the glasshouse to an area with subdued light and cooler temperatures where leaves were allowed to dry several hours before being returned to the glasshouse benches. Grading of leaf injury usually took place within 48 hours of exposure.

CALIBRATION

Chamber and Generator

Generator output and mist distribution in the chamber was determined by adding red dye to the mist solution and recording distribution patterns on paper. The donut-shaped pattern varied with the amount of liquid and the speed (controlled by motor voltage) of the generator disk. Largest area of coverage with smallest droplets resulted when spinning disk applicator was driven with 12 volts and 45 mℓ of solution was injected at 15 mℓ min^{-1}. Droplet sizes, determined by measuring dried dye spots ranged from 10 to 1000 µm and compared satisfactorily with HCl droplets reported for the space shuttle mists (Bowie, 1981; Knott, 1981).

Even coverage provided by the rotating platform within a ca 20-cm wide band was verified by weighing mist-exposed filter paper disks (Table 7). Positions 1-14 on the perimeter edge had statistically equal coverage (Figure 4). The rate of deposition in this area, about 0.002 mℓ cm^{-2} min^{-1}, was considered satisfactory for our work.

TABLE 7
DISTRIBUTION OF MIST DEPOSITION AT POSITIONS ON ROTATING CHAMBER PLATFORM

Chamber position[1]	Mass deposited (mg)
1	203 ± 45[2] h[3]
2	157 ± 55 h
3	207 ± 15 h
4	240 ± 63 h
5	157 ± 21 h
6	213 ± 32 h
7	280 ± 55 gh
8	227 ± 45 h
9	367 ± 105 gh
10	647 ± 155 cdef
11	690 ± 138 bcde
12	530 ± 77 defg
13	443 ± 114 efg
14	403 ± 63 fgh
15	877 ± 225 abc
16	740 ± 100 abcd
17	880 ± 109 abc
18	787 ± 152 abcd
19	857 ± 155 abc
20	960 ± 84 ab
21	1037 ± 192 a
22	1020 ± 187 a

[1]Positions 1-14 (see Figure 4) were on outside perimeter of 61 cm diameter rotating platform; positions 15-21 were in an inner ring; position 22 was at platform center

[2]Net mass of water in mg collected on 9-cm diameter filter paper disk, mean and standard deviation for three replicates

[3]Means followed by same letter(s) were not significantly different at $P < 0.05$ by Duncan's New Multiple Range Test (NMRT)

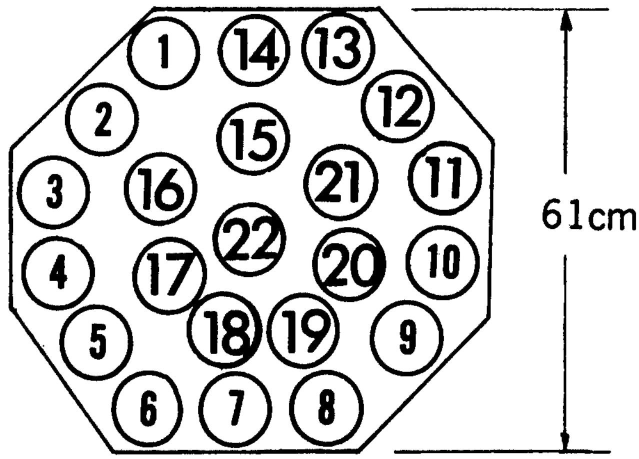


Figure 4. Distribution of Petri dishes on rotating platform.

HCl mist collected on filter paper disks at 14 different chamber positions varied with the total HCl solution entering the mist applicator (Table 8). Analysis of variance of the weight means indicated that collection in each position was not significantly different at $P < 0.05$ (Table 9). Actual deposition varied from 0.2 to 3.4 mℓ.

Plant Injury Symptom Development

Plants were exposed to 1% mist applied with spray bottles to observe injury. Leaves became wetted with large coalescing droplets in the 5 to 10 mm diameter range. After 10 minutes, the surface was coated with a thin liquid layer and first signs of injury appeared as 1 mm diameter brown specks. After 15 minutes, more specks were visible. The leaf was dry at 27 minutes after mist application, white 2- to 5-mm diameter spots appeared, and the leaf began to wilt. One hour after exposure, the entire leaf had wilted and areas of necrotic spots and specks covered much of the leaf surface. Lower HCl concentrations reduced the amount of wilt and area of necrotic tissue. Initial injury usually began 10 to 20 minutes after initial acidic mist application and was fully developed by 24 hours.

Measurement of Plant Injury

Several methods were tested for estimating foliar injury. Percent injury was adequate if enough leaves were present on the plant. On pinto bean, primary leaves were often most sensitive so only those were evaluated and percent numbers was unsatisfactory. A pretransformed 1 to 12 scale of leaf area injured used in other pollution work (Granett, 1982) proved helpful (Table 6).

TABLE 8
DISTRIBUTION OF HCl MIST WITH INCREASING MIST GENERATION

Chamber position	Amount of HCl entering applicator (mℓ) 10	20	30	40	50
1	20[1]	110	190	320	430
2	30	110	200	320	450
3	30	150	270	420	630
4	30	170	320	400	680
5	50	150	270	350	590
6	60	160	310	460	660
7	40	170	340	560	740
8	60	160	310	530	700
9	40	140	290	490	690
10	30	350	260	500	600
11	40	160	290	580	670
12	40	190	350	550	810
13	60	190	320	570	730
14	60	170	320	500	720
Mean weight:	42 ± 14	170 ± 57	289 ± 48	468 ± 92	650 ± 106
Mean deposition:	0.2 ± 0.1[2]	0.9 ± 0.3	1.5 ± 0.2	2.4 ± 0.5	3.4 ± 0.6

[1]Weight of mist collected on filter paper in mg, mean of three replicates
[2]Volume of HCl deposited in μℓ cm^{-2} min^{-1}, mean of 14 positions

TABLE 9
TWO-WAY ANALYSIS OF VARIANCE FOR HCl WEIGHTS IN DIFFERENT CHAMBER POSITIONS

Source of variation	Degrees of freedom	Mean sum of square	F-value	Significance[1]
Position (P)	13	0.0419	1.55	NS
Amount HCl (A)	4	2.4862	92.12	**
P x A interaction	52	0.0060	0.24	NS
Error	140	0.0270		
Total	209			

[1]** = significant F-value at $P < 0.01$, NS = not significant

The efficiency of the 1 to 12 injury scale was tested by exposing bean plants to one of 12 acidic mists. Treated leaves were first scored 2 hours after misting (Table 10). Injury similarly recorded 19, 24, 48, and 168 hours after treatment showed that more dilute acid treatments produced detectable injury with time. Injury estimates were compared to measurements made using the overlay grid 7 days after treatments. At this time, leaf area and plant weights were recorded (Table 11). Statistical comparisons of means indicated that only the visible estimates of injury significantly separated treatments. The strongest acidic mist, 1.0% HCl, caused most severe injury with more dilute treatments injuring plants less.

The first six treatments caused no significant injury. Acidic mists of 0.025% HCl through 0.25% HCl caused minimal amounts of injury that were not significantly different. Mists of 0.5% and 1.0% HCl caused severe injury. These last two treatments also reduced average leaf area and plant dry weight. Grid assessment of injury was analyzed after making arc-sin transformations. The grid method indicated that visible estimates of area reliably quantitated injury.

PHYTOTOXICITY OF ALUMINUM OXIDE DUST

This study tested the phytotoxicity of massive amounts of aluminum oxide dust on zinnia plant seedlings. Seedlings were 4 or 5 weeks of age when dusted on the two or four existing leafsets, respectively. Aluminum oxide dust, at ca 265 ± 42 $\mu g\ cm^{-2}$, was visible as a faint white coating on leaves of treated plants.

TABLE 10
INJURY ESTIMATES ON BEAN LEAVES EXPOSED TO HCl MIST

HCl conc. (%)	Time after exposure (hours) 2	19	24	48	168
0	1	1	1	1	1
0.001	1	1	1	1	1
0.002	1	1	1	1	1
0.003	1	1	1.3	1.4	1.5
0.006	1	1.4	1.8	1.9	1.8
0.012	1	1.9	2.0	2.2	2.1
0.025	2.7	3.1	2.6	3.3	3.7
0.050	3.4	3.9	3.9	3.9	4.0
0.125	3.8	4.4	4.3	4.3	4.2
0.250	3.9	5.4	5.1	5.1	4.9
0.500	5.7	7.3	7.0	6.9	6.9
1.000	8.1	10.2	9.9	9.9	10.2

TABLE 11
COMPARISON OF MEASUREMENTS FOR PINTO BEANS EXPOSED TO HCl MIST

Treat- ment (%)	Leaf injury: Visible estimate (1-12)	Leaf injury: Grid (%)	Leaf area (cm^2)	Dry weight: Leaf (g)	Dry weight: Plant (g)
0	1.0[1] f[2]	0 d	37.7[3]	0.3	1.1
0.001	1.0 f	0 d	33.3	0.3	0.8
0.002	1.2 f	0.2 d	32.9	0.3	0.9
0.003	1.5 ef	0.5 d	32.1	0.3	0.9
0.006	1.8 ef	1.0 d	32.4	0.3	0.9
0.012	2.1 e	1.4 d	33.2	0.3	0.9
0.025	3.7 d	8.2 c	32.4	0.3	1.0
0.050	4.0 d	11.6 c	30.2	0.2	0.8
0.125	4.2 cd	12.2 c	30.6	0.2	0.8
0.250	4.9 c	20.3 c	34.1	0.3	0.9
0.500	6.9 b	51.6 b	27.4	0.3	0.8
1.000	10.2 a	95.7 a	16.2	0.2	0.5

[1]Each data point is mean of five plants

[2]Means in columns followed by the same letter(s) were not significantly different at $P < 0.05$

[3]Means followed by no letters were not significantly different from means in same column by Duncan's NMRT

Leaf burn, noted during the first two weeks after treatment on 30% of the treated leaves of younger plants, could not be definitely assigned to aluminum oxide dust (Figure 5a). However, an increase in leaf damage beginning at about 8 weeks after applications was judged to be due chiefly to senescence since undusted control plants were similarly affected (Figure 5b). By this time, aluminum oxide was no longer visible on leaf surfaces due to plant growth, leaf drop and/or leaf washing or movement. Weekly height measurements revealed that plants treated with aluminum oxide dust were never significantly shorter than untreated controls (Figure 6). Plants were harvested when 17 weeks old and heights, bud and flower numbers, and weights were recorded (Table 12). No inhibitory effects could be linked to aluminum toxicity.

These results corroborate earlier findings that Al_2O_3 dust, even in massive amounts, fails to visibly injure bean plants, nor does the dust significantly reduce plant height, flower or bud numbers, or plant top weight.

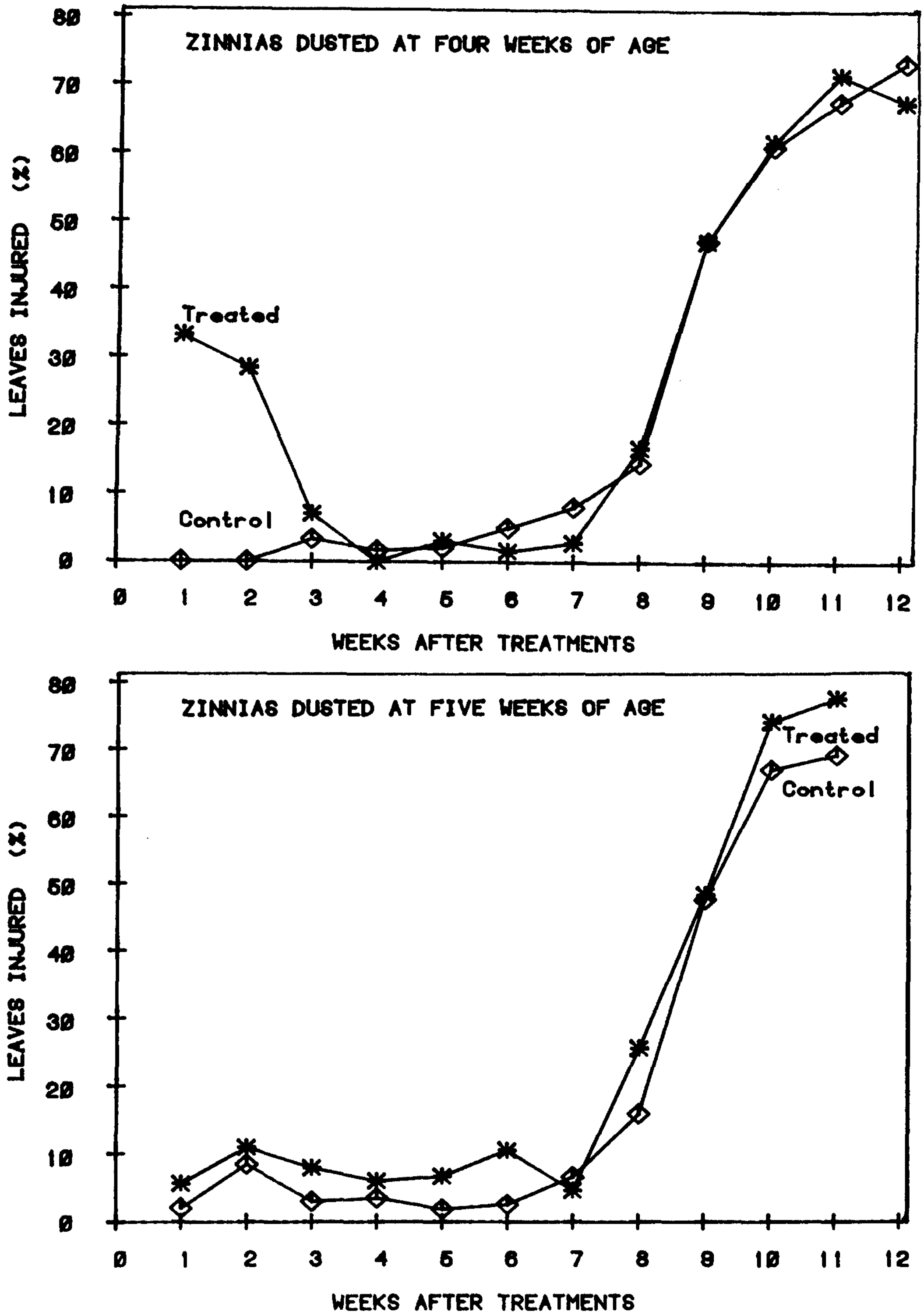


Figure 5. Injury on zinnia plants treated with aluminum oxide dust. Injury was percent number of leaves with any injury. Treated plants (represented by stars) were dusted with massive amounts of aluminum oxide powder whereas controls (represented by diamonds) were not so treated. 5a. (above) Zinnia plants four weeks old when exposed. 5b. (below) Zinnia plants five weeks old when exposed.

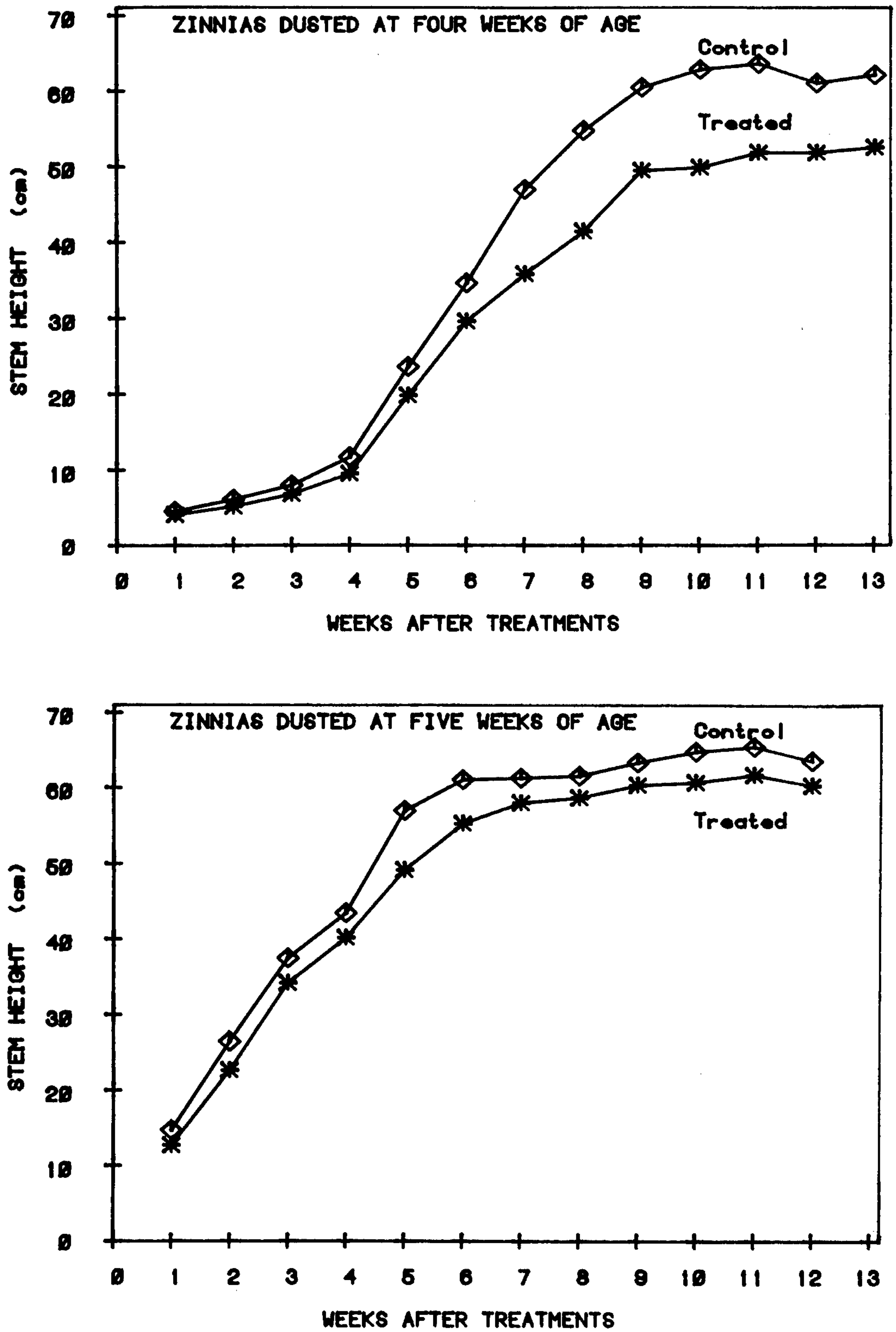


Figure 6. Heights of zinnia plants after aluminum oxide dust treatments. 6a. (above) Zinnia plants treated when four weeks old. 6b. (below) Zinnia plants treated when five weeks old.

TABLE 12
HARVEST OF 17-WEEK-OLD ALUMINUM OXIDE DUSTED ZINNIA PLANTS

Measurement	Age treated (wk)	Treated	Control	Significance t-test
Number buds and flowers	4	6.9 ± 2.7[1]	6.7 ± 2.0	0.19[2]
	5	10.8 ± 3.1	9.0 ± 3.2	1.28
Flowers, dry weight (g)	4	4.2 ± 1.7	5.0 ± 1.7	1.00
	5	6.6 ± 0.5	6.5 ± 1.4	0.31
Above-ground dry weight (g)	4	3.5 ± 1.5	4.9 ± 1.2	1.01
	5	5.4 ± 1.1	4.9 ± 1.2	1.01
Roots, fresh weight (g)	4	8.2 ± 1.9	7.5 ± 3.1	0.68
	5	10.8 ± 3.9	7.9 ± 3.3	1.81
Roots, dry weight (g)	4	0.6 ± 0.2	0.8 ± 0.2	1.63
	5	1.1 ± 0.3	0.8 ± 0.2	2.46*
Final height (cm)	4	52.5 ± 12.3	62.1 ± 13.4	1.67
	5	60.4 ± 11.1	63.7 ± 9.7	0.72
Injury and sensescence (1-12)	4	6.3 ± 3.7	7.7 ± 3.4	0.86
	5	8.7 ± 2.8	7.1 ± 2.6	1.30

[1]Mean and standard deviation of measurement

[2]t-value comparing treated and control values; significant (*) at $P < 0.05$ if $t > 2.262$

PHYTOTOXICITY OF HYDROCHLORIC ACID MIST

DIFFERENTIAL SURFACE SENSITIVITY

To determine differential response of leaf surfaces to acidic mist, pinto bean primary leaves were individually treated with 0.5% HCl solution using a plastic spray bottle. Plants were positioned such that the desired side of the leaves was exposed. Leaf injury was assessed on both surfaces one and two days after exposure, and plants were harvested after seven days. Lower surface injury initially appeared as browning of veins with watery intercostal areas, whereas upper surface damage was white to brown spotting. Ratings of visual injury for the two primary leaves using the 1 to 12 scale were averaged for five plants for each treatment at the three times (Table 13). Early injury was difficult to assess since tissue partially recovered from initial water-soak stress.

TABLE 13
VISIBLE INJURY ON PINTO BEAN LEAVES DIFFERENTIALLY MISTED WITH HCl

Time of assay after treatment	Surface exposed	Surface assayed: Upper	Surface assayed: Lower
1 Day	Top	5.2 ± 1.1[1] a[2]	5.0 ± 1.0 a
	Bottom	9.5 ± 0.6 b	7.2 ± 0.4 b
	Both	9.7 ± 1.5 c	11.1 ± 1.2 c
2 Days	Top	5.3 ± 1.0 a	5.3 ± 1.0 a
	Bottom	7.3 ± 0.6 b	7.3 ± 0.6 b
	Both	9.1 ± 1.5 c	9.4 ± 1.7 c
7 Days	Top	5.1 ± 1.5	5.1 ± 0.8
	Bottom	7.1 ± 0.7	7.1 ± 0.7
	Both	9.1 ± 1.5	9.1 ± 1.5

[1]Estimates of area injured (1 to 12), mean of five plants

[2]Means followed by same letter(s) were not significantly different by Duncan's NMRT at $P < 0.05$; three means considered at a time

In no case, however, was top surface injury any greater than lower surface injury for the same treatment. Transient symptoms had disappeared after seven days and amount of bifacial necrosis was equal on both sides of the same leaf. Exposure of lower surfaces caused significantly more injury ($P < 0.05$) than upper surface exposures. Injury was greatest when both surfaces were exposed to acidic mist.

Leaf injury assessed at harvest by counting intersections on an overlay grid provided the same results of significant treatment differences as the visual estimates (Table 14). Leaf area and dry weight differences among the treatments were not significant (Table 14).

In summary, upper surfaces of bean leaves exposed to HCl mist had significantly less visible injury than leaves exposed to acidic mist on the lower surface or on both surfaces. This may be related to the fact that almost all stomata are located on the lower surface of bean leaves and may afford a point of entry for the acid. Mist treatments did not alter phytomass seven days after applications.

TABLE 14

RESPONSE OF BEANS SEVEN DAYS AFTER DIFFERENTIAL APPLICATIONS OF HCl MIST

Response measured	Leaf surface exposed to mist		
	Upper	Lower	Both
Visible injury (1-12)	5.1 ± 0.8[1] a[2]	7.1 ± 0.8 b	9.1 ± 1.5 c
Grid injury (%)	38.1 ± 9.4 a	56.6 ± 10.9 b	74.1 ± 12.2 a
Leaf dry weight (g)	21.2 ± 4.7 a	20.6 ± 3.9 a	27.2 ± 3.8 a
Plant dry weight (g)	7.4 ± 12.9 a	58.0 ± 20.0 a	73.6 ± 24.4 a
Leaf area (cm^2)	27.0 ± 6.0 a	20.4 ± 7.2 a	19.5 ± 6.1 a

[1] Response is given in terms listed, mean and standard deviation of five plants

[2] Means for same response followed by the same letter were not significantly different at $P < 0.05$ by Duncan's NMRT

DOSE RESPONSE OF PLANTS TO MIST

The influence of mist dose on bean and zinnia plant response was investigated using a two-way factorial design in which three HCl concentrations (0.5, 0.025, and 0.012%) were applied at one of three total amounts (20, 50, and 100 mℓ) generated at 10 mℓ HCl per minute. Leaf injury assessments and above-ground dry weights were recorded one week after treatments.

Bean

The three trifoliate bean leaves showing greatest injury were visually rated (Table 15) and the percent injured leaves per plant was recorded. Injury and weight means were compared separately for concentration and amount HCl-applied using two-way analyses of variance (Table 16). Differences were noted for leaf injury due to HCl concentration but not due to amount supplied. No significant differences existed among treatments when weights were considered.

Zinnia

Injury was recorded on zinnia by estimating area damaged on the three most affected leafsets (Table 15) and by calculating the percent leaves injured. Analyses of injury and weight measurements revealed that HCl concentration was a significant factor at $P < 0.05$ (Table 17). The most acidic mist caused significantly more injury and weight loss than did the other two concentrations. Zinnia plants responded differently from beans since the amount of acid supplied as mist was an important factor in causing leaf injury. One hundred mℓ caused the most injury at any HCl concentration tested, just as 0.5% HCl was most injurious regardless of amount. The 100 mℓ mist treatment caused greater biomass reduction (at $P < 0.05$) than other amounts.

TABLE 15
INJURY ON PINTO BEAN AND ZINNIA LEAVES EXPOSED TO HCl MISTS

Amount applied mℓ	HCl concentration (%)					
	0.012 (pH 2.5)		0.025 (pH 1.9)		0.5 (pH 1.1)	
	Bean	Zinnia	Bean	Zinnia	Bean	Zinnia
20	3.0 ± 1.7[1]	2.0 ± 0.2	3.5 ± 1.8	1.9 ± 0.3	4.2 ± 1.3	4.9 ± 0.2
50	2.4 ± 0.6	2.1 ± 0.4	4.8 ± 1.8	2.4 ± 0.2	3.9 ± 0.4	6.2 ± 0.6
100	2.1 ± 0.1	2.5 ± 0.4	2.9 ± 1.8	2.9 ± 0.2	5.9 ± 1.2	7.1 ± 0.4

[1]Visible injury rating on 1 to 12 scale, mean and standard deviation of five plants (injury rated and averaged on three leaves per plant for beans and 15 ± 3 leaves per plant for zinnias)

TABLE 16
SUMMARIES OF ANALYSES ON PINTO BEANS HARVESTED AFTER HCl MIST TREATMENT

Variable	HCl concentration (%)			Amount supplied (mℓ)		
	0.012	0.025	0.50	20	50	100
Visible injury rating (1-12 scale)	2.5[1]b[2]	4.4 a	4.6 a	3.6 x	3.7 x	4.3 x
Leaves injured per plant (%)	51.8 b	45.7 b	63.9 a	52.4 x	56.0 x	53.1 x
Fresh weight (g)	41.2 a	38.7 a	39.7 a	39.5 x	39.6 x	40.4 x
Dry weight (g)	7.7 a	7.2 a	7.4 a	7.3 x	7.3 x	7.7 x

[1]Values are average injury or weight per plant, mean of 15 plants

[2]Means followed by same letter(s) were not significantly different at $P < 0.05$ by Duncan's NMRT, three means compared at a time

TABLE 17
SUMMARIES OF ANALYSES ON DATA FOR ZINNIA PLANTS MISTED WITH HCl

Variable	pH of HCl solution			Amount supplied (mℓ)		
	2.5	1.9	1.1	20	50	100
Visible injury rating (1-12 scale)	2.2[1]b[2]	2.4 b	6.1 a	2.9 z	3.6 y	4.2 x
Leaves injured per plant (%)	29.4 b	29.2 b	54.6 a	29.6 y	38.5 x	48.2 x
Fresh weight (g)	20.7 a	21.6 a	15.8 b	20.9 x	19.1 xy	18.2 y
Dry weight (g)	2.5 a	2.6 a	2.0 b	2.5 x	2.3 x	2.2 y

[1,2]Same notes as for Table 16

Dose could be described as deposition times concentration. At a deposition rate of 0.2 $\mu\ell$ cm^2 min^{-1}, the 20, 50, and 100 mℓ applications were 0.4, 1.0, and 2.0 $\mu\ell$ cm^2, respectively. The concentrations could be expressed as 120, 250, and 5000 ppm HCl rather than 0.012, 0.025, or 0.500%. A ppm-$\mu\ell$ cm^2 product thus could denote nine treatments ranging from 48 to 10,000. Using this unit, linear regressions could be calculated (Table 18) but were significant only for correlating zinnia injury and weight.

Although bean and zinnia plants both responded to HCl mist with necrotic foliar injury, response to dose differed. Rapidly expanding zinnia leaves may have been more susceptible to weight reduction than pinto beans. In general, amount of acid did not seem as critical with either species as the concentration of the acid used to produce the mist.

PLANT SPECIES SENSITIVITY

Barley, bean, citrus, marigold, nasturtium, radish, tomato, and zinnia were exposed to HCl mist generated for three minutes at 15 mℓ per minute. HCl content of the mist ranged from 0 to 1% in 12 treatments. Solutions were prepared as a two-fold dilution series (Table 9). Plants were all two to four week-old seedlings, except citrus for which leaves were collected from mature lemon trees.

Plants were inspected for injury 24 to 48 hours after mist treatments. One week later, leaf area injured was estimated and biomass was determined by weighing plant parts.

TABLE 18
DOSE-RESPONSE OF PLANTS TO HCl MIST TREATMENTS

Dose (ppm μℓ cm^{-1})	Bean		Zinnia	
	Injury	Dry weight (g)	Injury	Dry weight (g)
48	3.0[1]bcd[2]	7.6	2.0 ef	2.4 a
100	3.5 abcd	7.0	1.9 f	2.6 ab
120	2.4 cd	7.5	2.1 ef	2.5 ab
240	2.1 d	8.0	2.5 de	2.5 ab
250	4.8 abc	7.1	2.4 def	2.5 ab
500	4.9 ab	7.5	2.9 d	2.5 ab
2,000	3.9 abcd	7.2	6.2 b	2.0 bc
5,000	3.9 abcd	7.2	6.2 b	2.0 bc
10,000	5.9 a	7.4	7.1 a	1.7 c
Linear correlation (r)	0.639	0.132	0.862	0.912

[1]Injury or dry weight values were means of five plants

[2]Means in columns followed by the same letter(s) were not significantly different at $P < 0.05$ by Duncan's NMRT

Barley

Barley seedlings of variety CM 67 were four weeks old when exposed to acidic mist. The data were summarized (Table 19). Initial injury, consisting of elongated water spots and orange colored chlorosis, was found in plants exposed to concentrations as dilute as 0.006% HCl (pH 2.7). Those plants exposed to HCl mists of 0.1% (pH 1.5) or stronger had significantly more injured leaves at $P < 0.05$ than after exposure to lower concentrations.

Bifacial necrosis had developed on exposed leaves seven days after treatment. Injury assessments made at this time were significantly greater for 0.1, 0.25, 0.5 and 1% HCl than for less concentrated acidic treatments. No significant differences (at $P < 0.05$) were found in the fresh or dry weights of the treated plants compared to controls. Fewer flowers appeared on those barley plants exposed to the more concentrated treatments of 0.1, 0.25, 0.5 and 1%. It is possible that flowering was delayed.

Pinto Bean

Pinto bean plants, grown from seed in 10-cm diameter plastic pots, were thinned to one seedling per pot one week after sowing. Only plants with fully expanded primary leaves (12-14 days old) were exposed to HCl mist.

TABLE 19
RESPONSE OF BARLEY PLANTS TO HCl MIST

Treatment % HCl	After 2-4 hrs: Leaves injured (%)	After 7 days: Estimated area injured[3]	After 7 days: Leaves injured (%)	After 7 days: Plant top biomass Fresh (g)	After 7 days: Plant top biomass Dry (mg)	Plants with flowers (%)
0	7 ± 8[1]ef[2]	2.5 ± 1.3 de	29 ± 11 e	3.1 ± 0.8 a	459 ± 94 ab	67.5
0.001	6 ± 8 ef	2.3 ± 0.7 de	29 ± 7 e	2.2 ± 0.9 b	327 ± 122 e	67.5
0.002	0 f	3.5 ± 1.9 d	25 ± 9 e	2.6 ± 0.5 ab	427 ± 89 ab	67.5
0.003	10 ± 14 ef	2.1 ± 1.0 e	29 ± 13 e	2.9 ± 1.0 ab	499 ± 145 ab	67.5
0.006	28 ± 16 bcd	2.5 ± 0.9 de	38 ± 20 de	2.7 ± 1.3 ab	465 ± 200 ab	67.5
0.012	16 ± 16 de	2.6 ± 0.8 de	35 ± 9 de	2.4 ± 0.8 ab	404 ± 126 abc	67.5
0.025	27 ± 17 cd	3.5 ± 1.4 d	43 ± 12 cd	2.6 ± 0.6 ab	453 ± 126 abc	67.5
0.050	26 ± 10 d	3.6 ± 1.0 d	53 ± 13 c	2.8 ± 1.0 ab	529 ± 152 a	67.5
0.100	50 ± 20 a	4.9 ± 1.2 c	66 ± 10 b	2.1 ± 0.5 b	363 ± 110 bc	30.0
0.250	50 ± 18 a	5.1 ± 1.6 bc	67 ± 21 b	2.5 ± 0.8 ab	426 ± 118 abc	40.0
0.500	42 ± 22 ab	6.9 ± 1.5 a	80 ± 15 a	2.4 ± 0.7 ab	425 ± 141 abc	60.0
1.000	41 ± 18 abc	6.2 ± 1.7 ab	78 ± 13 ab	2.6 ± 0.5 ab	468 ± 110 ab	40.0

[1]Mean and standard deviation of 10 plants

[2]Means in response-columns followed by the same letter(s) were not significantly different by Duncan's NMRT at $P < 0.05$

[3]Percent leaf area injured estimated using pretransformed 1-12 scale

Injury development on beans consisted of lesions first visible after 10 minutes and fully developed after 48 hours. The detailed results are described in a previous section (see Table 11). Threshold for visible injury was near 0.01% HCl (pH 2.4) with more concentrated solutions causing significant leaf injury. Highest concentrations decreased subsequent leaf size and reduced plant weight.

Citrus

Samples were removed from 15-year-old producing Lupe lemon trees in an University orchard. Flower buds, flowers, green fruit, yellow fruit, and mature leaves were collected the morning of treatments. Twigs with flowers and buds or with leaves were placed into flasks of distilled water and were treated with 50 mℓ HCl mist. Five replicates of each plant part were sprayed.

Leaves were observed 1, 2, 5, and 7 days after exposures (Table 20) and numbers of twigs having any injured leaves were noted. These numbers increased as symptoms developed over the seven days. Small brown lesions enlarged and bleached white with necrosis. By the seventh day, leaves exposed to 0.1, 0.5,

TABLE 20
CITRUS INJURY FOLLOWING EXPOSURE TO HCl MIST

Time of assay (days after treatment)	HCl concentration (%)						
	0	0.002	0.006	0.025	0.100	0.500	1.000
1	0[1]	0	0	0	0	1	2
2	0	0	0	0	1	4	4
5	0	0	0	0	2	4	4
7	2	2	1	1	5	5	4

[1]Number twigs (with three leaves each) with any injury, average of five twigs

and 1% HCl mist had significant amounts of injury compared to the controls (Table 21).

Injury was also assessed on the seventh day by calculating percent leaves injured and by estimating leaf area injured (Table 21). The three highest concentrations produced significantly greater injury than the more dilute treatments. Threshold for foliar injury was 0.1% HCl mist.

Flower buds were observed every 15 minutes for two hours after treatments and daily thereafter. Only 0.5 and 1.0% mists, the most concentrated acid tested, produced any observable damage. Colorless surface depressions were noted after 24 hours. After one week, injury was found only on buds treated with 1% spray and consisted of white or brown depressions. A Chi-square test of number of injured buds showed that damage, even at the high HCl concentrations, was not significant ($\chi^2 = 2.84$) at $P < 0.05$.

Depressions were first noted about an hour after exposures on flower petals sprayed with 0.5 or 1% HCl. These became small brown burn areas. A Chi square test on uninjured flowers revealed that the acidic mists significantly affected this plant part where $\chi^2 = 21.88$ was significant at $P < 0.001$.

Fruit marked to identify sprayed surfaces were supported on beakers during mist treatments. Observations made immediately after exposure and at 15, 30, and 60 minutes later revealed that 37% of the yellow fruit had dry surfaces after 30 minutes and all were dry 60 minutes after exposure. Visible injury noted after 20 hours (overnight) was found only on fruit exposed to 0.5 or 1% HCl sprays and appeared as brown spots. Spots were larger with the 1% HCl treatment. After three days many depressions turned white in color and covered the exposed surfaces of fruit treated with 0.5 or 1% HCl. Treated fruit was significantly

TABLE 21
INJURY ON CITRUS LEAVES EXPOSED TO HCl MIST

Treatment (% HCl)	Injury: No. leaves (%)	Injury: Estimated leaf area
0	13[1]b[2]	1.1 cd
0.002	13 b	1.1 cd
0.006	7 b	1.1 d
0.025	13 b	1.1 cd
0.100	73 a	1.7 bc
0.500	86 a	2.9 a
1.000	86 a	2.3 ab

[1]Mean percent leaves injured, average of 15 leaves

[2]Treatment means in columns followed by the same letter(s) were not significantly different at $P < 0.05$ by Duncan's NMRT

[3]Mean leaf area injured on 1 to 12 scale, average of 15 leaves

more damaged than untreated fruit ($\chi^2 = 34.99$) at $P < 0.05$. Very small white depressions were found on three of five fruit treated with 0.1% HCl; too few were found for this concentration to be considered significantly injurious ($P < 0.05$).

After 30 minutes, 51% of the treated green fruit were dry and all five fruit sprayed with 1% HCl were beginning to show spots. One hour after treatment, spotting was seen on fruit sprayed with 0.5% HCl. Brown spots were noted the next day (20 hours) and these turned white after two or three days. Damage produced by 0.5 or 1% HCl mists was significant ($\chi^2 = 34.99$) at $P < 0.05$.

All fruit was placed into plastic bags and stored in a cold room at ca 50°C. Injury did not visibly increase with time nor was any decay evident on any fruit after six weeks. The HCl mist did not favor or reduce the growth of organisms.

Nasturtium

Nasturtium plants were five weeks old and in a vegetative growth stage when exposed to HCl mist. Ten plants were treated for each mist concentration. Injury, visible as necrotic foliar lesions, was noted with concentrations of 0.05% HCl when measured 5 to 18 hours after treatments.

Plants were harvested one week after acidic mistings; leaf area injured per plant was estimated and above-ground biomass was calculated (Table 22). Amount of visible leaf injury increased during the seven days following treatment, particularly on those plants exposed to weaker acidic concentrations whereas the stronger HCl solutions had caused immediate and maximum damage. Threshold for visible foliar injury on nasturtiums was determined to be 0.012% HCl.

Fresh and dry weights of above-ground parts of exposed nasturtium did not clearly differentiate the effects of the acid treatments (Table 22). No clear trends were found; the lightest plant biomass did not always correspond to the strongest acid treatment.

Radish

The Cherry Belle variety of radish was exposed to HCl acidic mist when 5.5 weeks old. The seedlings had begun to develop fleshy roots. As with the nasturtium plants, injury was assessed one and seven days after treatments. Biomasses

TABLE 22
EFFECT OF HCl MIST ON NASTURTIUM PLANTS

Treatment (% HCl)	Injury: 1 day No. leaves (%)	Injury: 7 days No. leaves (%)	Injury: 7 days Leaf area rating[3]	Weight[4] (g) Fresh	Weight[4] (g) Dry
0	0.0 ± 0.0[1] d[2]	0.7 ± 2.2 d	1.0 ± 0.1 d	4.58 ± 1.31 ab	0.60 ± 0.20 ab
0.002	0.0 ± 0.0 d	0.9 ± 2.9 d	1.0 ± 0.1 d	4.39 ± 1.00 ab	0.56 ± 0.17 ab
0.003	2.8 ± 6.0 d	4.6 ± 6.2 d	1.2 ± 0.3 d	4.06 ± 1.11 abc	0.53 ± 0.16 b
0.006	2.0 ± 6.3 d	6.7 ± 3.6 d	1.2 ± 0.1 d	4.96 ± 0.85 a	0.72 ± 0.14 a
0.012	7.2 ± 10.4 d	20.6 ± 11.4 c	1.6 ± 0.3 c	4.15 ± 1.00 abc	0.59 ± 0.17 ab
0.025	0.0 ± 0.0 d	18.6 ± 12.2 c	1.6 ± 0.4 c	3.57 ± 0.46 bc	0.52 ± 0.12 b
0.050	50.1 ± 24.4 c	37.7 ± 23.1 b	1.9 ± 0.3 bc	3.89 ± 1.17 bc	0.53 ± 0.15 b
0.100	57.7 ± 24.8 c	46.0 ± 16.9 b	2.1 ± 0.4 b	2.44 ± 1.13 d	0.34 ± 0.22 c
0.250	70.9 ± 10.0 b	64.2 ± 9.0 a	2.1 ± 0.1 b	3.84 ± 1.01 bc	0.57 ± 0.18 ab
0.500	79.8 ± 19.8 ab	65.4 ± 12.1 a	2.8 ± 0.7 a	4.56 ± 0.99 ab	0.57 ± 0.13 ab
1.000	90.0 ± 11.1 a	62.5 ± 7.8 a	2.8 ± 0.7 c	3.26 ± 0.66 cd	0.33 ± 0.84 c

[1]Percent injured leaves of total exposed, mean and standard deviation of 10 plants. Average total number of leaves assayed per plant was 8.6 on day 1 and 11.9 on day 7

[2]Means in columns for species followed by the same letter(s) were not significantly different by Duncan's NMRT at $P < 0.05$

[3]Rating was on a scale where 1 was 0% area injured and 12 was 100%

[4]Biomass in g of above-ground parts of nasturtium plants 7 days after exposure to mist, mean and standard deviation of 10 plants

of top and roots were measured after the seven-day harvest. Initial response of radish plants to the mist, typically necrotic lesions, was seen on leaves of individuals exposed to between 0.012 and 0.025% HCl (Table 23). More injury developed during the next week. A significant difference existed between numbers of leaves injured on plants treated with 0.002% HCl and plants treated with 0% HCl. When estimated as injured leaf area, the threshold was closer to 0.05% HCl, possibly because radish plants had only a few leaves present.

Fresh weights of above-ground parts of exposed radish were significantly lighter (at $P < 0.05$) for plants treated with 0.5 or 1.0% HCl than for all other treatments (Table 24). Plants exposed to 1.0% HCl had significantly heavier ($P < 0.05$) roots than control plants, but no other clear trends were observed in the data. Likewise, the radish dry weights were not statistically different among the 12 treatments for either above-ground parts or roots. Thus, plant biomass was not a useful criterion for judging acidic effects on these plants because weights did not significantly or systematically correlate with acid concentration increases.

TABLE 23
INJURY ON RADISH LEAVES ONE AND SEVEN DAYS AFTER HCl MIST TREATMENTS

Treatment (% HCl)	1 day	7 days	
	No. leaves	No. leaves (%)	Leaf area rating
0	0.0 ± 0.0[1]e[2]	15.5 ± 11.6 ef	1.2 ± 0.2 f
0.001	0.0 ± 0.0 e	6.5 ± 10.6 f	1.1 ± 0.1 f
0.002	0.0 ± 0.0 e	35.5 ± 32.9 d	1.6 ± 0.6 f
0.003	0.0 ± 0.0 e	24.4 ± 14.7 def	1.5 ± 0.3 f
0.006	12.5 ± 21.8 de	17.3 ± 20.8 def	1.6 ± 0.8 f
0.012	24.2 ± 12.0 d	29.6 ± 28.3 de	1.7 ± 0.6 f
0.025	43.0 ± 31.8 c	54.7 ± 27.2 c	2.2 ± 0.6 ef
0.050	52.0 ± 37.7 c	76.3 ± 28.0 b	3.0 ± 1.1 de
0.100	79.3 ± 17.0 b	86.7 ± 16.3 ab	3.6 ± 2.3 d
0.250	91.8 ± 10.7 ab	90.3 ± 10.2 ab	5.2 ± 1.7 e
0.500	94.0 ± 9.7 ab	91.5 ± 11.4 ab	6.6 ± 2.1 b
1.000	100.0 ± 0.0 a	100.0 ± 0.0 a	8.8 ± 2.1 a

[1-3]Same notes as for Table 22 except 4.9 average number of leaves per plant on day 1 and 5.1 on day 7

TABLE 24
BIOMASS OF RADISH PLANTS ONE WEEK AFTER EXPOSURE TO HCl-MIST SPRAY

Treatment (% HCl)	Fresh weight (g) Tops	Fresh weight (g) Roots	Dry weight (g) Tops	Dry weight (g) Roots
0	2.55 ± 0.49[1] cd[2]	5.24 ± 1.41 a	0.17 ± 0.04[2]	0.29 ± 0.09
0.001	2.65 ± 0.64 bcd	4.36 ± 1.56 abc	0.23 ± 0.05	0.26 ± 0.07
0.002	2.92 ± 0.58 abc	5.19 ± 1.50 a	0.22 ± 0.05	0.29 ± 0.08
0.003	2.73 ± 0.34 abcd	5.53 ± 1.60 a	0.24 ± 0.04	0.29 ± 0.04
0.006	2.60 ± 0.35 abcd	5.14 ± 1.01 a	0.21 ± 0.04	0.29 ± 0.04
0.012	3.12 ± 0.77 a	4.83 ± 2.58 ab	0.24 ± 0.08	0.27 ± 0.14
0.025	3.09 ± 0.42 ab	5.08 ± 2.00 ab	0.26 ± 0.03	0.32 ± 0.10
0.05	2.51 ± 0.41 cd	5.44 ± 2.05 a	0.24 ± 0.04	0.34 ± 0.10
0.10	2.50 ± 0.27 cd	5.00 ± 1.67 ab	0.22 ± 0.03	0.32 ± 0.10
0.25	2.33 ± 0.31 d	4.40 ± 1.70 ab	0.22 ± 0.06	0.26 ± 0.10
0.50	1.73 ± 0.31 e	3.44 ± 0.94 bc	0.21 ± 0.03	0.26 ± 0.06
1.00	1.30 ± 0.47 f	3.15 ± 0.99 c	0.21 ± 0.04	0.23 ± 0.06

[1]Biomass in g of above-ground parts (tops) or roots of radish plants seven days after exposure to HCl mist, mean and standard deviation of 10 plants

[2]Means followed by same or no letter(s) indicates that there were no significant differences between means in a column at $P < 0.05$

Tomato

Tomato plants of the cultivar Tiny Tim were exposed to HCl mists when 73 days old. Plants had ca 6 fully expanded leafsets and were 16-25 cm high with flowers present and fruit developing. Eight plants were exposed to each HCl mist treatment.

The three leaves with greatest damage were graded one day after exposure by estimating leaf area injured. Significant injury occurred after exposure to 0.1, 0.25, 0.50, or 1.00% HCl.

Plants were harvested one week after exposure to acidic mist. Buds, flowers, and fruit were counted (Table 25). Buds on plants exposed to 0.05% or stronger HCl mist had significantly more injury than appeared on buds from plants exposed to lower concentrations. Injured flowers were confined to plants exposed to 0.5 and 1% HCl. Fruit injury was negligible at all HCl concentrations.

Leaf and stem weights were recorded (Table 26). Neither fresh nor dry weights reflected any effect from the acidic mist. Leaf numbers per plant also had no relation to mist treatment.

TABLE 25

INJURY ON TOMATO LEAVES EXPOSED TO HCl MIST

HCl concentration (%)	Leaf injury		% Number injured		
	% Number	Estimated area	Buds	Flowers	Fruit
0	7.30[1]e[2]	2.00[3]d	3.73[4]e	0.00 b	1.17 a
0.001	10.15 de	2.04 d	5.00 de	4.81 b	0.40 a
0.002	18.82 cd	2.25 d	1.67 e	0.00 b	0.70 a
0.003	16.81 cde	2.04 d	0.00 e	0.00 b	0.00 a
0.006	6.70 e	2.25 d	5.34 de	0.96 b	0.00 a
0.012	14.16 de	2.00 d	0.40 e	0.00 b	0.00 a
0.025	26.61 c	2.00 d	0.55 e	0.00 b	1.43 a
0.050	37.80 b	2.04 d	15.61 cd	0.00 b	0.00 a
0.100	43.81 b	3.33 c	40.67 b	6.01 b	0.00 a
0.250	44.53 b	4.71 b	22.56 c	2.00 b	0.83 a
0.500	83.15 a	6.66 a	54.32 a	31.88 a	2.51 a
1.000	74.65 a	7.17 a	48.84 ab	39.06 a	1.83 a

[1]Means of percent leaves injured were average of ca 30 leaflets per plant on eight plants

[2]Means in each column followed by same letter(s) were not significantly different at $P < 0.05$ level by Duncan's NMRT

[3]Means for area estimates were average of three leafsets on eight plants (24 leaves)

[4]Average number of buds, flowers, or fruit per plant, mean of eight plants

TABLE 26

LEAF AND STEM FRESH WEIGHTS OF TOMATO PLANTS EXPOSED TO HCl MISTS

HCl concentration (%)	Leaf (g)	Stem (g)
0	16.77[1]bc[2]	15.56 a
0.001	18.58 ab	13.05 ab
0.002	17.60 abc	14.88 a
0.003	18.00 abc	13.82 ab
0.006	16.75 bc	13.86 ab
0.012	15.93 c	13.85 ab
0.025	18.39 ab	12.97 ab
0.050	19.48 a	13.44 ab
0.100	16.80 bc	14.84 a
0.250	16.93 bc	13.33 ab
0.500	16.50 bc	11.38 b
1.000	16.69 bc	14.52 a

[1]Fresh weight, mean of eight plants

[2]Same as note 2, Table 25

HCl mist can visibly injure tomato plant foliage at concentrations as low as 0.1% HCl. Buds exposed to the acid are injured significantly at concentrations of 0.05% and higher. Flowers were tolerant to higher doses and fruit appeared highly resistant to burn injury. Plant biomass was not altered by the treatments.

Zinnia

Zinnia seedlings of the variety Scarlet Queen were exposed to acidic mist. Injury measured by visual estimates registered a lower threshold concentration (0.025% HCl) than for percent leaf numbers (0.1%) (Table 27). Biomass reductions were noted only after treatments with concentrations of 0.5% HCl or higher.

Summary

Visible injury was noted on plants two days after exposure to threshold concentrations of HCl mist. In most cases, the injury consisted of bifacial necrotic burns. Barley leaves had elongated chlorotic lesions and barley flower production appeared reduced or delayed at certain elevated concentrations. Citrus leaves had bleached, white, necrotic spots and citrus buds, flowers, and fruit became spotted with sunken lesions after treatments. Tomato fruit showed no effects of the acid. Biomass of marigold and zinnia plants was reduced after very high acid exposure, possibly due to tissue and water loss, but radish tops or roots were not significantly reduced. A summary of these tests (Table 28) indicates that nasturtium and marigold are the most sensitive of species tested and citrus is most resistant to the acidic mist.

TABLE 27
ZINNIA RESPONSE TO HCl MIST

Treatment	Injury		Biomass[4] (g)	
(%) HCl	% numbers	Leaf area	Fresh	Dry
0.006	23.2[1]d[2]	1.5[3]d	9.2 a	1.2 a
0.025	47.4 d	2.3 c	8.1 b	1.1 a
0.100	63.5 c	4.2 b	8.7 ab	1.1 a
0.500	85.3 a	5.6 a	6.8 b	0.9 b
1.000	78.2 b	5.8 a	5.2 c	0.7 c

[1]Percent number of leaves injured per plant, mean of 60 plants

[2]Means in each column followed by the same letter(s) were not significantly different by Duncan's NMRT

[3]Leaf area injured was estimated on 1 to 12 scale, average of three most injured leaves

[4]Biomass measured as weight of plant tops one week after exposures, mean of 60 plants

TABLE 28
COMPARISON OF PLANT SENSITIVITIES TO HCl MIST EXPOSURES

Species	Injury threshold (% HCl)	Lowest concentration for reduced biomass[1] (% HCl)	Other notes
Barley	0.100	NE	Elongated, orange lesions Flower numbers reduced
Bean	0.100	0.5	
Citrus (mature leaves only)	0.500	NA	White lesions
Marigold	0.025	0.1	
Nasturtium	0.012	1.0	
Radish	0.050	0.5	
Tomato	0.100	NE	Bud numbers reduced at 0.05% Flowers injured at 0.5% No effect on fruit
Zinnia	0.025	0.5	

[1]HCl mist concentration necessary for exposures to cause significant reduction in biomass as measured by plant weight; NE means no effect, NA means not applicable

PLANT YIELD REDUCTION CAUSED BY HCl MIST

Marigold, zinnia, and pinto bean seedlings were exposed to single 50 mℓ applications of water or 0.5% HCl mist applied at different plant ages. Height was recorded weekly following exposures. Injury was estimated and yield was measured in terms of biomass, bud and flower production, and weight when marigolds were 19 weeks old, zinnia were 17 weeks old, and beans were 10 weeks old.

Marigold

The ratio of heights of HCl-treated vs water-exposed plants averaged 0.97 ± 0.04 (n = 64) and ranged from 0.82 to 1.08 indicating no real differences between treated and control plants (Table 29). This was true even though average plant size increased with age, reaching maximum height about 12 weeks after sowing (Table 30). Subsequent growth of plants treated when 4 weeks old was less than plants treated at older ages, with a trend for plants treated when older to have little or no height reduction. Harvest data were analyzed with three-way analyses of variance comprising 10 replicate plants, 5 ages, 2 treatments, and the age-treatment interaction (Table 31). Differences among plants due to age were significant at the $P < 0.05$ level when any of the variables were compared and were probably due to natural growth factors. Plants exposed at younger ages

TABLE 29

RATIO OF HEIGHTS OF MARIGOLDS MISTED WITH HCl AND WATER AT DIFFERENT AGES

Weeks after exposure	Age of plants at exposure (weeks) 4	6	7	8	10
0	103[1]	105	108	98	97
1	90	99	92	98	99
2	90	98	93	100	100
3	82	99	93	96	99
4	84	99	94	95	98
5	98	98	94	96	98
6	102	101	93	94	95
7	101	98	98	96	98
8	101	97	97	94	100
9	100	100	95	94	98
10	102	99	98	94	--
11	100	99	96	96	--
12	100	100	99	--	--
13	101	--[2]	--	--	--
14	99	--	--	--	--
15	103	--	--	--	--

[1]Height of treated/height of control plants x 100, average of 10 plants

[2]-- indicates plants were harvested

TABLE 30

AVERAGE HEIGHTS OF MARIGOLDS AFTER EXPOSURE TO MISTS

Treatment	Age at exposure (weeks) 4	6	7	8	10
HCl mist	12.17±4.52[1] d[2]	16.51±1.69 c	16.30±1.16 c	20.39±0.38 ab	19.03±0.39 b
H_2O mist	12.38±4.22 d	16.64±1.89 c	17.01±1.60 c	21.28±0.43 a	19.35±0.29 b
Number of measurements	16[3]	13	13	12	10

[1]Height of plant in cm, mean and standard deviation of 10-16 measurements made between exposure and harvest

[2]Means followed by the same letter(s) were not significantly different by Duncan's NMRT

[3]Number of times weekly measurements were made. Plants were harvested when 19 weeks old

TABLE 31
F-VALUES FOR HARVEST DATA FOR MARIGOLD AGE EXPERIMENT

Source of variation	Degrees of freedom	% Leaf[1] injury	Flowers (no.)	Buds (no.)	Fresh weight (g) Flower	Fresh weight (g) Plant[2]	Dry weight (g) Flower	Dry weight (g) Plant
Replicates	9	0.38	1.21	0.87	1.13	3.23*	1.18	1.67
Age (A)	4	96.65*[3]	38.60*	21.48*	47.67*	214.36*	34.92*	94.52*
Treatments (T)	1	116.73*	15.63*	0.65	7.48*	0.30	21.52*	0.31
A x T Interaction	4	20.73*	3.04*	0.28	3.25*	2.08	3.51*	1.65
Total	99							

[1]Leaf injury was percent number of leaves injured by treatment or senescent at harvest

[2]Plant weight included above-ground plant parts exclusive of flowers and buds

[3]* indicates significance at $P < 0.05$ or better

were more sensitive than those exposed at the older ages as evidenced by greater leaf injury or more reduction of flower and bud numbers. This generally held true for the oldest and youngest plants, but did not explain responses of plants of intermediate ages.

The acidic mist treatments significantly differed from the water control treatments in terms of percent leaf area injured, flower numbers, and flower dry weight. Treated plants also had more injury and fewer and lighter flowers than controls. Bud numbers and plant weights were not statistically affected by the treatment. Interactions of treatments and age showed that marigold yield losses were greater following exposure of younger plants than older plants (Table 32).

Zinnia

Zinnia plants were treated similarly to marigolds but were exposed to water or 0.5% HCl mist when 1, 2, 3, 4, and 5 weeks old and were harvested at 17 weeks of age.

Weekly height measurements were made. Height ratios averaged 0.78 ± 0.16 ($n = 65$), ranging from 0.39 to 1.04 (Table 33). Unlike corresponding marigold measurements, acid-treated zinnia plants were often shorter than control plants. The plants treated with HCl remained stunted for the first few weeks following exposure. Only for seedlings exposed when 1 or 2 weeks of age were harvest heights significantly greater for controls than treated plants (Table 34). Differences existed for the zinnias as they did for the marigolds, probably because the time span of the test was reduced from 6 weeks (4 to 10 weeks old when exposed) for marigolds to 4 weeks (1 to 5 weeks old) for the zinnia plants. In all harvest parameters checked, both age when exposed to mist and treatment (water or HCl) were significant at $P < 0.05$ (Table 35). In all cases

TABLE 32
MEANS AND SIGNIFICANT SEPARATIONS FOR AGE-TREATMENT INTERACTION FOR HCl-MISTED MARIGOLDS

Treatment	Age at exposure (weeks)	Injury	Flowers		
				Biomass (g)	
			Number	Fresh	Dry
HCl mist	4	81.4[1] v[2]	26.2 z	15.7 z	5.7 z
	6	50.0 x	27.9 z	15.7 z	5.5 z
	7	62.9 w	26.9 z	17.0 z	5.3 z
	8	53.1 x	39.2 x	23.2 x	5.8 z
	10	41.7 y	33.2 y	24.3 x	7.4 y
H_2O mist	4	89.5 v	26.1 z	14.7 z	6.1 z
	6	33.7 y	29.2 yz	15.6 z	5.4 z
	7	23.0 z	29.6 yz	20.0 y	5.8 z
	8	21.2 z	47.7 w	28.1 w	7.4 y
	10	24.4 z	37.7 x	25.6 wx	8.7 x

[1]Mean for variable, average of 10 replicate values

[2]Means in columns (by variable) followed by the same letter(s) were not significantly different at $P < 0.05$ by Duncan's NMRT

TABLE 33
RATIO OF HEIGHTS OF ZINNIA MISTED WITH HCl AND WATER AT DIFFERENT AGES THEN MEASURED WEEKLY

Weeks after exposure	Age of plants at exposure (weeks)				
	1	2	3	4	5
1	90[1]	70	96	76	81
2	98	60	85	61	83
3	65	59	74	61	85
4	53	49	77	67	85
5	55	45	81	70	88
6	45	44	90	77	94
7	39	42	85	76	93
8	39	60	95	80	92
9	69	85	104	92	96
10	86	84	97	89	90
11	80	83	101	90	92
12	80	86	100	92	--
13	81	87	99	--	--
14	81	87	--	--	--
15	81	--[2]	--	--	--

[1]Percent ratio height of treated/height of control plants x 100, average of 10 plants

[2]-- indicates plants were harvested

TABLE 34
HEIGHTS OF ZINNIA AFTER EXPOSURE TO HCl MIST

Treatment	Age at exposure (weeks) 1	2	3	4	5
Average height[1]					
HCl mist	40.2 ± 36.0[2]	35.5 ± 31.7	44.5 ± 28.0	38.1 ± 22.0	53.1 ± 12.2
H_2O mist	54.5 ± 42.8	47.7 ± 34.6	47.0 ± 26.7	46.5 ± 22.5	59.3 ± 11.5
	t = 0.99	t = 0.97	t = 0.23	t = 0.92	t = 1.23
Number of measurements	15[3]	14	13	12	11
Height at harvest					
HCl mist	79.4 ± 17.7 b[2]	73.8 ± 7.6 b	75.5 ± 11.7	65.3 ± 12.2	65.5 ± 6.6
H_2O mist	98.1 ± 14.0 a	84.4 ± 10.8 a	75.4 ± 15.5	71.2 ± 7.4	71.3 ± 10.9
	t = 2.62	t = 2.52	t = 0.02	t = 1.31	t = 1.44

[1]Height of plant in cm, mean and standard deviation of 11-15 measurements made weekly or at harvest

[2]Paired means followed by the same or no letters were not significantly different by Duncan's NMRT at $P < 0.05$. T-tests (t's) also compared two means

[3]Number of times weekly measurements were made. Plants were harvested when 17 weeks old

TABLE 35
F-VALUES FOR HARVEST DATA FOR ZINNIA AGE EXPERIMENT

Source of variation	Degrees of freedom	Injury % Leaf[1]	Injury Area[2]	Flowers (no.)	Fresh weight Flower	Fresh weight Plant[3]	Dry weight Flower	Dry weight Plant[3]
Replicates	9	1.24	0.87	1.22	1.99	0.54	0.61	0.52
Age (A)	4	17.52*[4]	17.62*	27.93*	15.41*	6.17*	12.00*	2.67*
Treatments (T)	1	6.40*	4.53*	5.76*	7.07*	16.13*	31.78*	20.54*
A x T Interaction	4	5.09*	5.71*	1.31	1.49	5.04*	5.11*	5.83*
Total	99							

[1]Leaf injury was percent number of leaves injured and/or senescent at harvest

[2]Area injured was estimate of injury on 1 to 12 scale

[3]Plant weight includes above-ground plant parts exclusive of flowers and buds

[4]* indicates significance at $P < 0.05$ or better

the controls treated with water mist were significantly larger, heavier, or more injured than the HCl-treated plants (Table 36). Leaf senescence of both treated and control plants was included in the estimation of injury at harvest since damaged leaves often fell from HCl-treated plants but old leaves remained on control plants longer and had become senescent by harvest. Plant injury decreased with age of plants at time of exposure (Table 37). Plants exposed when older had more flowers with greater weights than younger plants exposed when 1- or 2-weeks old.

Single exposures of zinnia plants to HCl mist injured the plants regardless of their ages at time of exposure (Table 38). The injury, however, could not be detected or distinguished from senescence at harvest 12 to 16 weeks after the exposure incident. Other parameters measured at harvest indicated that HCl-treated plants had a lower biomass and yield than control plants. Numbers and weights of flowers, and above-ground weight of treated plants were less than controls, but reductions were statistically significant only for plants exposed when 1 or 2 weeks of age, and not for plants exposed at 3 to 5 weeks of age. At several ages, older plants had enough injured foliage and above-ground growth to recover from injury received from the single acidic mist episode. In summary, growth of zinnia plants exposed at any age was likely to be delayed but not reduced by the acidic mist treatment.

Pinto Bean

Pinto bean seedlings were exposed to HCl mist 2, 3, or 4 weeks after seeds were sown. Necrotic spots occurred on many of the exposed leaves. The plants were harvested when flowers and seed pods began to develop at ca 10 weeks of age. Plants were graded for injury and above-ground plant parts were weighed (Table 39). Number, lengths, and weights of pods per plant were recorded.

TABLE 36
HARVEST DATA SUMMARIZED FOR TREATMENT EFFECTS ON ZINNIAS

	Injury		Flowers	Fresh weight (g)		Dry weight (g)	
Treatment	% Leaf[1]	Area[2]	(no.)	Flowers	Plant[3]	Flowers	Plant[3]
HCl mist	68.8[4]b[5]	7.5 b	7.50 b	25.2 b	26.0 b	6.0 b	6.0 b
H_2O mist	76.2 a	8.8 a	8.76 a	29.4 a	31.8 a	7.9 a	7.7 a

[1,2,3]Same as notes for Table 35

[4]Values are mean of 50 plants

[5]Means in same column followed by same letter were not significantly different at $P < 0.05$

TABLE 37
HARVEST DATA SUMMARIZED FOR AGE OF ZINNIAS WHEN EXPOSED

Age exposed (weeks)	Injury		Flowers (no.)	Fresh weight (g)		Dry weight (g)	
	% Leaf[1]	Area[2]		Flower	Plant[3]	Flower	Plant[3]
1	90[4] a[5]	12 a	4 d	20 c	22 c	5 c	6 a
2	74 b	10 b	6 c	21 c	25 bc	5 c	6 ab
3	66 bc	9 b	8 b	31 b	35 a	8 b	7 ab
4	60 c	7 c	9 b	27 b	29 ab	6 c	6 b
5	--[6]	--	13 a	37 a	34 a	10 a	7 a

[1,2,3]Same as notes for Table 35

[4]Mean for variable, average of 20 values (10 replicates x two treatments)

[5]Means in columns (by variable) followed by the same letter(s) were not significantly different at $P < 0.05$ by Duncan's NMRT

[6]Data recorded were not comparable

TABLE 38
MEANS AND SIGNIFICANT SEPARATIONS FOR AGE-TREATMENT INTERACTION FOR HCl-MISTED ZINNIAS

Treatment	Age at exposure (weeks)	Injury		Above-ground plant[3]	
		% Leaf[1]	Area[2]	Fresh weight (g)	Dry weight (g)
HCl mist	1	96[4] a[5]	12 a	15.4 c	4.2 c
	2	69 c	8 bc	17.9 c	4.2 c
	3	58 de	9 b	36.1 a	8.1 a
	4	52 e	7 c	27.0 b	5.5 bc
	5	--[6]	--	33.5 ab	7.7 a
H_2O mist	1	84 ab	12 a	27.7 b	7.9 a
	2	79 bcd	12 a	32.4 ab	8.2 a
	3	73 bc	8 bc	33.5 ab	7.4 a
	4	68 cd	8 bc	30.3 ab	6.5 ab
	5	--	--	35.1 a	8.3 a

[1-6]Same as notes for Table 37 except values were average of 10 values; separations were for all 9 or 10 means in a column

TABLE 39

VISIBLE LEAF INJURY AT HARVEST ON PINTO BEANS EXPOSED TO HCl MIST

Age when exposed to HCl mist (weeks)	Injury			
	% Leaves		Leaf area injured	
	Control	Treated	Control	Treated
4	0 ± 0[1]	46 ± 11	1.0 ± 0.0[2]	4.0 ± 0.6
3	2 ± 4	3 ± 4	1.1 ± 0.1	1.3 ± 0.4
2	2 ± 3	5 ± 6	1.2 ± 0.2	1.4 ± 0.4

[1]Percent leaves injured, mean and standard deviations of ten plants

[2]Leaf area injured was estimated using a 1 to 12 scale, mean and standard deviation of ten plants

Comparisons were made between harvest data for control and treated plants using t-tests (Table 40). Very few differences occurred, and those that did might be attributed more to plant variability than to HCl mist. Treated plants yielded more than the controls for number of pods per plant (4-week-old plants) and above-ground fresh weight (3-week-old plants). However, plants exposed to HCl when two weeks old had reduced bean pod fresh weight.

Each of the six variables was also analyzed using a split-plot design across different ages (Table 41). Date of planting was the most important source of variation. Seeds sown earlier developed significantly heavier and healthier-looking plants. Seasonal or environmental variations influenced final harvest data more than HCl treatment ('HCl concentration' had low F-values for all variables). The multiple range test indicated that pod values for the oldest plants did not always exceed that of younger plants. With pod numbers, for instance, date and HCl interaction was significant, however, it was the HCl-treated, 4-week-old plants that unexplainably had the largest number of pods. This experiment indicated that HCl mists were not a major factor in determining bean plant yield.

Summary

Marigold, zinnia, and pinto bean seedlings were tested for response and yield to HCl mist at different ages. The three species responded somewhat differently. All, however, were injured by the HCl mist treatments with younger plants generally being more sensitive than older. Weekly seedling heights of marigold and zinnia were not affected by the HCl treatment although exposure of zinnia at very young ages appeared to stunt the plant by harvest time. With marigold heights, age of the plant at time of treatment seemed to correlate with harvest height, probably due to weather or other environmental factors since differences between controls and HCl treatments did not exist. HCl mist had no

TABLE 40
YIELD OF BEANS EXPOSED TO HCl MISTS AT ONE OF THREE AGES

Variable	4 weeks old			3 weeks old			2 weeks old		
	Control		Treated	Control		Treated	Control		Treated
Pods/plant (#)	18.5±4.8[1]	**[2]	23.7±2.4	8.6±1.4	NS	8.4± 1.6	7.8±1.6	NS	6.8±1.0
Pod length (mm)	66.2±5.3	NS	61.9±6.5	93.3±7.1	NS	93.0±47.1	97.5±6.6	NS	94.4±7.5
Pod fresh wt. (g)	31.3±9.4	NS	33.4±5.3	34.1±4.3	NS	35.6± 7.4	31.6±4.2	NS	26.8±3.1
Pod dry wt. (g)	6.2±1.7	NS	7.2±1.2	7.6±1.1	NS	7.4± 1.6	5.2±0.1	NS	4.6±0.7
Top fresh wt. (g)	33.6±7.2	NS	38.5±3.3	21.5±3.0	*	25.8± 2.8	28.2±4.1	NS	27.4±3.8
Top dry wt. (g)	3.1±0.8	NS	3.4±1.3	4.0±0.5	NS	4.1± 0.5	4.7±1.0	NS	4.4±0.5

[1]Average data, mean and standard deviation of 10 plants

[2]NS = not significant at P < 0.02; ** = significant at P < 0.02; * = significant at P < 0.05 using t-tests

TABLE 41
F-VALUES FOR BEAN AGE-YIELD EXPERIMENT SPLIT-PLOT ANOVA
AND RANGE TEST FOR AGES

Source of variation	Variables					
	Pods				Plant top weight	
	Number	Length	Fresh weight	Dry weight	Fresh	Dry
Replicates (R)	1.24	1.30	1.99	2.58*	0.65	0.45
Date sown (D)	116.19**[1]	222.36***	9.06**	17.32***	36.23***	7.60**
HCl concentration (H)	2.37	1.69	0.01	0.03	3.02	0.00
D x H Interaction	5.06*	0.34	0.72	1.60	1.25	0.41
Date separation[2]	4-3-2	2-3-4	3-4-2	3-4-2	4-2-3	2-3-4

[1]*,**, and *** = significant F-values at P < 0.05, 0.01, and 0.001, respectively

[2]Separation of plants by ages (in weeks): Week numbers (when sown) underlined by same line were not significantly different by Duncan's NMRT at P < 0.05

effect on any of the marigold harvest variables except to reduce the number of flowers. Zinnia plants had significantly reduced values for harvest variables of HCl-exposed plants. Yield of bean plants did not appear at all affected by the exposures.

SENSITIVITY OF SEEDS

Sensitivity of marigold seeds to HCl mist was tested by exposing plants at stages during flower development. Flowers were allowed to continue growing following exposures. Mature seeds were collected and tested for germination.

Only one flower growth stage was sensitive (Table 42). Seeds which developed on plants exposed to HCl mist when flowers were mature, at the time pollen was transferred, had germination rates reduced nearly 56% compared to seeds from plants exposed to water mist at the same developmental stage.

Marigold seed development was thus not sensitive to acidic mist when flowers were immature or after fertilization had taken place. Developing seedlings from HCl-mist-treated plants had the same appearance in size and shape as seedlings of control seeds from plants treated with water.

DAMAGE TO INFLORESCENCES

Zinnia flowers can be large and spectacular. The impact of HCl mist on the visual appearance of petals was determined by exposing open flowers of Scarlet Queen zinnias to HCl mist at concentrations of 0.1, 0.5, or 1% or to tap water mist.

Petals, injured by all three acid concentrations, developed edge burn and fading color. Injury was more pronounced at 1% than 0.1%. Red petals had orange tips often with necrotic edges. Percent area injured or senesced was estimated on 21 flowers (three replicates of seven flowers each) for each treatment 48 hours after exposures. Injury on acid-treated flowers was significantly greater than the water-mist controls and each acid concentration differed significantly from the others. Thus, 0.5% HCl produced more injury than 0.1% and less injury than 1.0%.

Flowers can be injured by relatively short exposure to acidic mists. Such injury would certainly diminish the commercial value of cut flowers although the plant as a whole may not be seriously threatened.

COMPARISON OF ACIDIC RAIN AND HCl MIST PHYTOTOXICITY

BACKGROUND

Acidic rain is a phenomenon of increasing concern worldwide. First recognized in Scandinavia more than 20 years ago, it is precipitation which has entrained industrial air pollution. Rain and snow contain quantities of sulfuric

TABLE 42
GERMINATION OF MARGIOLD SEEDS TREATED WITH HCl MIST

Plant stage when exposed to mist	Plant age (days)	Mist		Significance	Reduction[3] (%)
		HCl	H_2O		
Flowers just opening, immature floral parts	90	10.5±10.9[1]	18.8±15.6	NS[2]	44.2
Flowers fully open, pollen not transferred	90	27.3±16.7	18.8± 9.6	NS	-
Flowers open, pollen transferred	90	15.0±10.6	33.8±11.1	*	55.6
Dry flowers, seeds mature	104	17.5± 9.2	21.4±12.8	NS	18.2
Mature seeds collected from flowers	107	10.9± 7.8	20.7± 9.0	NS	47.3
Seeds from a commercial package	-	26.9±10.5	31.8± 6.5	NS	15.4

[1]Percent germination, mean and standard deviation of seeds from five flowers

[2]Acid and water measurements significantly different (*) or not (NS) at $P < 0.05$ by non-parametric Mann-Whitney U tests

[3]Percent reduction in germination when seeds were exposed to HCl mist, $[1.0 - (HCl/H_2O)] \times 100\%$

and nitric acids sufficient to reduce the precipitation to pH 4.0 or lower. The consequences of acidic precipitation are not always easy to identify, but damage to materials and the acidification of low-buffered mountain lakes are examples of the environmental results. Controversy exists on the direct effects of acidic precipitation on vegetation. Acidic rain has been long recognized as a problem in the Northeast United States. Because most western soils are alkaline, concern about acidic precipitation in the West has been low. Recently acidic fogs have been reported in the Los Angeles area. Due to the different pollutants in western skies, the ratio of major ingredients in the acidic rains and fogs is close to 2.5 parts nitric and 1 part sulfuric acids, the reverse of eastern mixtures. A series of experiments was conducted to compare acidic rain mist with HCl mist.

PINTO BEAN EFFECTS

Pinto bean plants were treated with acidic rain (AR) or HCl mist episodes and plant responses to the treatments were compared. Groups of eight bean seedlings were first misted when two weeks old. Weekly mistings continued for five additional weeks. Mists of simulated AR solutions were created and dispersed in the same way as described for HCl using solutions ranging from pH 1.0 to 3.5 (Table 43). Foliar injury and plant heights were measured after the third and fifth mist episodes and again at harvest one week after final exposures. Harvest data included pod number, leaf area, and fresh and dry weights of leaves, stems, and pods. The variables were analyzed with one-way ANOVA tests.

After three treatments foliar injury was significantly greater on plants exposed to pH 1.0 and 1.5 mists than to other pH's or controls (Table 44). However, no differences were noted between heights of treated and control plants nor was HCl more injurious than AR at any given pH.

Plants grew little between the third and fifth treatments when the second measurements were made. Heights of treated and control plants were still not significantly different (Table 45). Injury results paralleled the findings of the first measurements: HCl was no more injurious than simulated AR mist. For either solution, injury was significantly greater on plants treated with pH 1.0 and 1.5 than with other pH's or controls.

Plants were harvested one week after the sixth mist treatment. Injury was greatest for plants treated with AR mist of pH 1.0 when estimated area damaged was considered (Table 46). Fewer injured leaves were found on plants exposed to HCl at pH 1.0 than at other pH's because senescent and badly damaged leaves had fallen off and new leaves were not badly damaged.

TABLE 43
pH OF ACIDIC MIST SOLUTIONS

HCl		AR
pH	%	pH
1.0	0.500	1.0
1.7	0.100	1.5
2.2	0.025	2.0
2.6	0.012	2.5
3.2	0.003	3.0
3.7	0.001	3.5
5.2	water	5.2

[1]AR = simulated acidic rain solution of $HNO_3:H_2SO_4$ mixed 2.5:1

TABLE 44
FOLIAR INJURY AND HEIGHTS OF PINTO BEANS EXPOSED TO THREE WEEKLY ACIDIC MIST EPISODES

Treatment (pH)	Injury: Area[1] HCl	Injury: Area[1] AR[2]	Injury: No. leaves (%) HCl	Injury: No. leaves (%) AR	Height (cm) HCl	Height (cm) AR
1.0	11.8[3] a[4]	12.0 a	92 a	92 a	17.6 ab	15.6 b
1.5	9.0 b	10.5 ab	73 ab	89 a	17.0 ab	18.6 a
2.0	2.2 e	5.0 cde	39 cd	64 b	17.0 ab	17.4 ab
2.5	3.0 de	5.4 cd	30 cde	35 cde	15.3 b	16.0 b
3.0	3.5 cde	6.3 c	19 de	46 c	16.0 b	16.8 ab
3.5	5.4 cd	2.7 de	39 cd	28 cde	16.9 ab	17.0 ab
water	4.2 cde	3.5 cde	31 cde	17 e	16.2 b	16.3 ab

[1]Area injured was estimated on scale of 1 to 12

[2]AR refers to the $HNO_3:H_2SO_4$ (2.5:1 v/v) simulated acidic rain mist mixture

[3]Each value is mean of eight plants

[4]All 14 treatments were analyzed with a one-way ANOVA; means under each variable (e.g., Area) followed by the same letter(s) were not significantly different by Duncan's NMRT at $P < 0.05$

TABLE 45
FOLIAR INJURY AND HEIGHTS OF PINTO BEANS EXPOSED TO FIVE WEEKLY ACIDIC MIST EPISODES

Treatment (pH)	Injury: Area[1] HCl	Injury: Area[1] AR[2]	Injury: No. leaves (%) HCl	Injury: No. leaves (%) AR	Heights (cm) HCl	Heights (cm) AR
1.0	12.0[3] a[4]	12.0 a	91 ab	96 ab	17.8 ab	15.5 ab
1.5	4.8 c	6.0 b	91 ab	90 a	17.9 a	16.5 ab
2.0	3.9 d	3.2 d	50 e	72 cd	16.4 ab	17.7 ab
2.5	2.2 e	2.2 e	25 f	12 fg	15.3 b	16.1 ab
3.0	1.5 e	5.3 bc	15 fg	81 bc	16.2 ab	15.4 b
3.5	1.6 e	3.4 d	24 f	63 d	17.2 ab	17.4 ab
water	1.5 e	3.5 d	10 g	98 a	16.2 ab	17.1 ab

[1-4]Same as notes for Table 44

TABLE 46
FOLIAR INJURY ON PINTO BEANS EXPOSED TO
SIX WEEKLY ACIDIC MIST EPISODES

Treatment	Leaf area[1] injured		No. leaves injured (%)	
(pH)	HCl	AR[2]	HCl	AR
1.0	6.9[3]bc[4]	11.0 a	57 d[4]	88 ab
1.5	8.0 b	6.0 bc	91 a	92 ab
2.0	6.1 bc	5.4 cd	100 a	90 ab
2.5	4.9 cd	6.9 bc	73 bcd	98 a
3.0	4.9 cd	6.0 bc	89 ab	100 a
3.5	3.7 d	6.5 bc	67 cd	100 a
water	5.7 cd	5.2 cd	83 abc	100 a

[1-4]Same as notes for Table 44

Senescent or slightly injured leaves remained on the plants after exposure to mists of lower concentrations thereby increasing the injury value.

The strong acid treatment stimulated new leaf growth but this was not clearly apparent in the foliar data (Table 47). At harvest old and new leaves were not separated, and fallen dead leaves were not counted. Leaf area and weight, however, reflected the loss of significant leaf tissue following pH 1.0 treatments, particularly HCl mist. Areas and weights of plants exposed to the other HCl treatments tended to increase with pH.

Seed pods formed on all bean plants except those treated with pH 1.0 mist (Table 48). Numbers or weights of pods from plants exposed to all other treatments revealed no trends, although weight-per-pod seemed to increase with pH, particularly with the AR mist treatments.

Stem height at harvest reflected no changes from measurements made three weeks earlier (Table 49). Stem weight was reduced at pH 1.0 whereas heights of plants exposed to other treatments were statistically similar to the control plant heights.

Much variability was present in the experimental data. HCl and AR treatments at pH 1.0 were destructive, reducing plant growth, yield, and biomass. Lesser concentrations of acids also reduced leaf area and stem and leaf weights in many cases, but individual plant variability obscured significant results. Other variables were not routinely repressed in plants treated with mists less acidic than pH 1.0. Injury was noted for several treatments, but our techniques could not reliably detect differences in amounts of injury, particularly six weeks after exposures. Among other problems was the fact that stressed plants tended to produce new leaves at a faster rate than controls.

TABLE 47
LEAVES ON PINTO BEANS AFTER SIX WEEKLY ACIDIC EXPOSURES TO MIST

Treatment (pH)	No. leaves per plant		Leaf area (cm^2)		Leaf fresh weight (mg)	
	HCl	AR[1]	HCl	AR	HCl	AR
1.0	5.1[2]abc[3]	5.1 abc	9.5 c	10.9 c	161 c	205 c
1.5	5.2 abc	7.6 a	37.4 abc	59.5 ab	514 bc	1291 ab
2.0	3.9 bc	6.4 ab	34.8 bc	67.4 ab	611 abc	1519 a
2.5	4.8 bc	4.0 bc	58.1 ab	45.3 abc	1049 abc	915 abc
3.0	4.6 bc	3.9 bc	56.1 abc	40.3 abc	1036 abc	774 abc
3.5	3.6 bc	2.6 c	53.2 abc	23.0 bc	1240 ab	476 bc
water	5.2 abc	3.6 bc	82.3 a	30.5 bc	1571 a	653 abc

[1,2,3]Same as notes 2, 3, 4, respectively, Table 44

TABLE 48
PODS HARVESTED FROM BEAN PLANTS AFTER
SIX WEEKLY EXPOSURES TO ACIDIC MIST

Treatment (pH)	No. pods per plant		Dry weight (g)		Dry weight per pod	
	HCl	AR[1]	HCl	AR	HCl	AR
1.0	0.0[2]c[3]	0.0 c	0.0 d	0.0 d	0.00	0.00
1.5	2.1 b	1.8 b	0.5 bc	0.2 cd	0.24	0.11
2.0	3.1 a	2.5 ab	1.1 a	0.7 b	0.35	0.27
2.5	2.3 ab	2.4 ab	0.7 b	0.7 b	0.29	0.29
3.0	2.1 b	1.6 b	0.8 ab	0.6 b	0.37	0.36
3.5	1.8 b	2.1 b	0.6 b	0.7 b	0.32	0.33
water	2.3 ab	2.0 b	0.8 ab	0.8 ab	0.36	0.40

[1-3]Notes same as for Table 47

TABLE 49
STEMS HARVESTED FROM PINTO BEANS AFTER
SIX WEEKLY EXPOSURES TO ACIDIC MIST

Treatment	Height (cm)		Fresh weight (g)		Dry weight (g)	
(pH)	HCl	AR[1]	HCl	AR	HCl	AR
1.0	17.7[2]a[3]	15.6 ab	1.16 fg	0.93 g	0.15 de	0.13 e
1.5	17.3 ab	16.3 ab	1.28 def	1.40 cdef	0.24 cd	0.23 cd
2.0	16.9 ab	17.4 ab	1.88 a	1.77 ab	0.41 a	0.35 ab
2.5	15.1 b	16.0 ab	1.24 efg	1.56 abcde	0.24 cd	0.28 bc
3.0	16.0 ab	15.4 ab	1.43 bcdef	1.42 bcdef	0.29 bc	0.24 cd
3.5	17.0 a	16.8 ab	1.46 bcdef	1.67 abc	0.23 cd	0.30 bc
water	16.2 ab	16.8 ab	1.63 abcd	1.46 bcdef	0.34 ab	0.24 cd

[1-3]Same notes as for Table 47

Treated plants also lost old senescent leaves more readily than the control plants. No differences could be detected in the responses of plants to HCl mist compared to simulated AR mist.

EFFECTS ON LEMON LEAVES AND FRUIT

Leaves on twigs and ripe fruit were collected from mature orchard trees. The twigs were kept in water to prolong leaf health. Leaves were arranged so either upper or lower surface was exposed. Fruit was marked to identify the exposed surface. Leaves and fruit were exposed to HCl and simulated acidic rain (AR) mist with treatments ranging from pH 1.3 to 2.1 in pH 0.2 steps (Table 50).

Injury was estimated 48 hours after exposure. Foliar burn caused by HCl mist was not readily distinguishable from that caused by simulated AR mist. However, leaf injury (Table 51) was greater for AR than for HCl at the same pH. AR mist caused significant injury at pH 1.7 and lower whereas HCl-induced injury occurred at pH 1.5 for upper surface mistings and pH 1.3 for lower surface applications. Lemon fruit were spotted by the mist, but only at lowest pH levels (Table 52). No differences were detectable between the two kinds of acid.

Conclusions drawn from this study are that exposure to a short period of acidic mist will injure lemon leaves and fruit only if acid concentrations are high. Leaves were more sensitive to simulated AR mist than to HCl mist and were generally more sensitive when the top surface was exposed. Concentrations of pH 1.3 were necessary to produce injury on mature lemon fruit.

TABLE 50
pH AND CONCENTRATION OF ACIDIC MIST SOLUTIONS

Simulated acidic rain solution (pH)	HCl concentration for same pH (%)
1.3	0.25
1.5	0.20
1.7	0.10
1.9	0.05
2.1	0.03

TABLE 51
INJURY ON LEMON LEAVES EXPOSED TO HCl OR SIMULATED ACIDIC RAIN MIST

Treatment	Upper surface		Lower surface	
(pH)	HCl	AR[1]	HCl	AR
1.3	2.3[2]bcde[3]	6.3 a	2.7 bc	4.3 a
1.5	3.3 bc	5.2 a	1.8 cd	4.7 a
1.7	2.8 bcd	3.6 b	2.5 bcd	3.2 b
1.9	2.2 cde	2.2 cde	1.8 cd	2.3 bcd
2.1	2.2 cde	1.5 de	1.8 cd	2.0 bcd
Water	1.2 e		1.2 d	

[1]Acidic rain (AR) solutions prepared by mixing reagent grade HNO_3 and H_2SO_4 2.5:1 in distilled water and adjusting pH

[2]Leaf area injured was estimated on 1 to 12 scale, mean of 5 or 6 leaves

[3]Means for each leaf surface followed by same letter(s) were not significantly different at $P < 0.05$ by Duncan's NMRT

TABLE 52
INJURY ON LEMON FRUIT DUE TO ACIDIC MIST

Treatment (pH)	HCl	AR[1]
1.3	4.8[2]a[3]	4.7 a
1.5	1.7 b	1.8 b
1.7	1.7 b	1.2 b
1.9	1.7 b	1.3 b
2.1	1.5 b	1.7 b
Water	1.7 b	

[1-3]Same as notes for Table 51

EFFECTS ON TOMATO FRUIT

Ripe (red) unbruised cherry tomatoes were picked from glasshouse grown Tiny Tim plants. Fruit was rinsed with distilled water to remove dust and dirt then dried with paper towels to avoid water spotting. The fruit were placed on wire 1/2-inch mesh screen platforms during exposure to acidic mist created from HCl solutions of 1% (pH 0.7), 0.5% (pH 1.0), 0.1% (pH 1.5), or 0.05% (pH 1.8). The simulated acidic rain (AR) solutions were 2.5:1 mixtures of nitric and sulfuric acids at pH 1.5, 1.7, 1.9 and 2.1. Tap water control mists were pH 8.6. Ten fruit were exposed per pH treatment and treatments were replicated twice.

Following acidic misting, tomatoes were transferred to open egg cartons in the headhouse. Injury was assayed two and seven days after treatments.

Fruit showed little evidence of any injury even after exposure to HCl of pH 0.7 (Table 53). Some fruit had tiny chlorotic spots which were not necessarily due to the acid. Comparisons of means of injury ratings revealed no significant difference among the replicates or any of the treatments. Similarly, no differences existed when treatments were variously partitioned for analysis. No meaningful changes in injury were noted after seven days except that fruit had begun to dry and shrivel. No disease organisms were actively present two weeks after exposures.

Tomato fruit appeared resistant to short exposures of acidic mists strong enough to injure leaf surfaces. Natural acidity of the fruit may aid in its resistance to acidic pollutants.

TABLE 53
INJURY ON TOMATO FRUIT FOLLOWING ACIDIC MIST EXPOSURE

Treatment		Days after exposure	
Acid	pH	2	7
HCl	0.7	1.15[2]	1.40
HCl	1.0	1.40	2.50
HCl	1.5	2.10	2.05
HCl	1.7	1.90	1.65
AR[1]	1.5	1.15	1.30
AR	1.7	1.30	2.05
AR	1.9	1.05	1.55
AR	2.1	1.00	1.45
H_2O	8.6	1.20	1.55

[1]AR is simulated acidic rain mist of HNO_3 plus H_2SO_4 mixed 2.5:1

[2]Fruit area injury estimated on 1 to 12 scale, mean of two replicates of 10 tomato fruit each

EFFECTS ON CUT ZINNIA FLOWERS

Our research has shown that single episodes of acidic mist are unlikely to cause life-threatening injury to most healthy plants. However, if cut flowers are seriously injured, their economic value may be greatly jeopardized. In this test, sensitivity of blooming flowers to HCl or simulated acidic rain (AR) mist was determined. Blooming flowers of Scarlet Queen zinnia were cut from plants prior to exposure to 0.1, 0.5 or 1% HCl or to simulated AR mist of pH 1.9, 1.7 and 1.5. The flower stems, supported in a mesh screen, were in water. Seven flowers were exposed for each acid treatment and treatments were replicated three times.

Injury, following exposure to any of the three acid concentrations, was seen as petal necrosis described earlier (see DAMAGE TO INFLORESCENCES). Analysis of variance conducted on data for the seven treatments indicated injury on all acidic mist-treated flowers was significantly greater than senescence found on the controls (Table 54). Partitioning the treatments for analysis provided additional information: Combined acid treatments were more injurious than tap water. HCl treatments were more damaging than simulated AR treatments, an expected finding since HCl pH's were generally lower than AR solutions. However, simulated AR mist at pH 1.5 caused more injury than HCl at the same pH.

TABLE 54
INJURY ON ZINNIA FLOWERS EXPOSED TO ACIDIC MIST

Treatment (decreasing toxicity) Acid	pH	Estimated area injured
HCl	0.7	6.09 ± 0.08[2] u[3]
HCl	1.0	5.61 ± 0.23 v
AR[1]	1.5	5.09 ± 0.08 w
HCl	1.5	3.90 ± 0.35 x
AR	1.9	3.28 ± 0.24 y
AR	1.7	2.95 ± 0.17 yz
H_2O	8.7	2.71 ± 0.43 z

[1]AR is simulated acidic rain mist

[2]Floral area injured was estimated on 1 to 12 scale, mean and standard deviation of 21 flowers

[3]Means followed by the same letter(s) were not significantly different at $P < 0.05$ by Duncan's NMRT

Zinnia flowers were sensitive to injury when exposed to small amounts of HCl mist of pH 1.5 or to simulated AR mist of pH 1.9. These pH values have been known to occur in the field under certain specific conditions.

WEEKLY ACIDIC RAIN AND HCl MISTS

Plants usually recover from most single-episode acidic mist treatments. However, multiple exposures may occur. It was expected that repeated episodes would cause more permanent damage than single ones. Pinto bean plants were exposed weekly to mist treatments of HCl or simulated AR of pH 2.5 and 1.7 or to water. Plants were 20 days old when treated with the first of four weekly mists. Each acid-harvest-concentration treatment consisted of eight plants. Leaves were graded 48 hours after each weekly exposure. Representative plants harvested just prior to the next exposure were graded, weighed, and measured.

Injury ratings recorded 48 hours after misting showed certain trends which were consistent each week (Figure 7). The pH 2.5 acid treatments were generally no more injurious than water controls whereas pH 1.7 solutions caused significant amounts of injury. AR mist at pH 1.7 damaged leaves more than HCl at the same pH. Injury ratings recorded at each of the four harvests reflected the same trends (Figure 8).

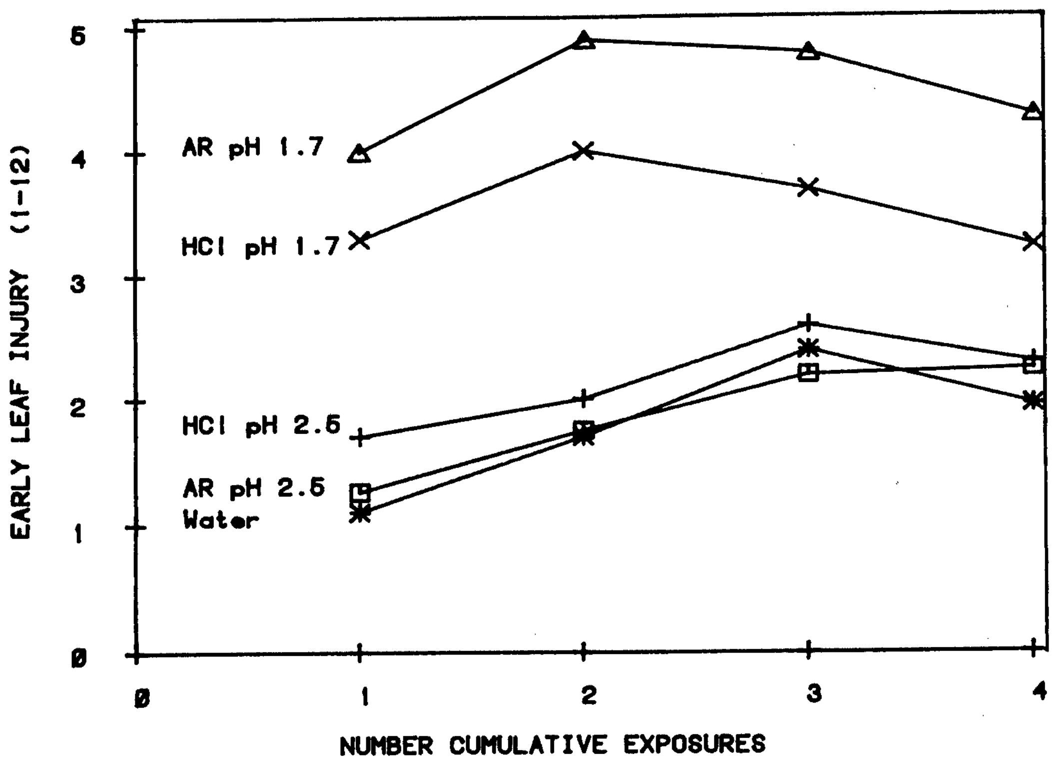


Figure 7. Leaf injury estimated on bean plants 48 hours after weekly exposures to HCl or simulated AR mist.

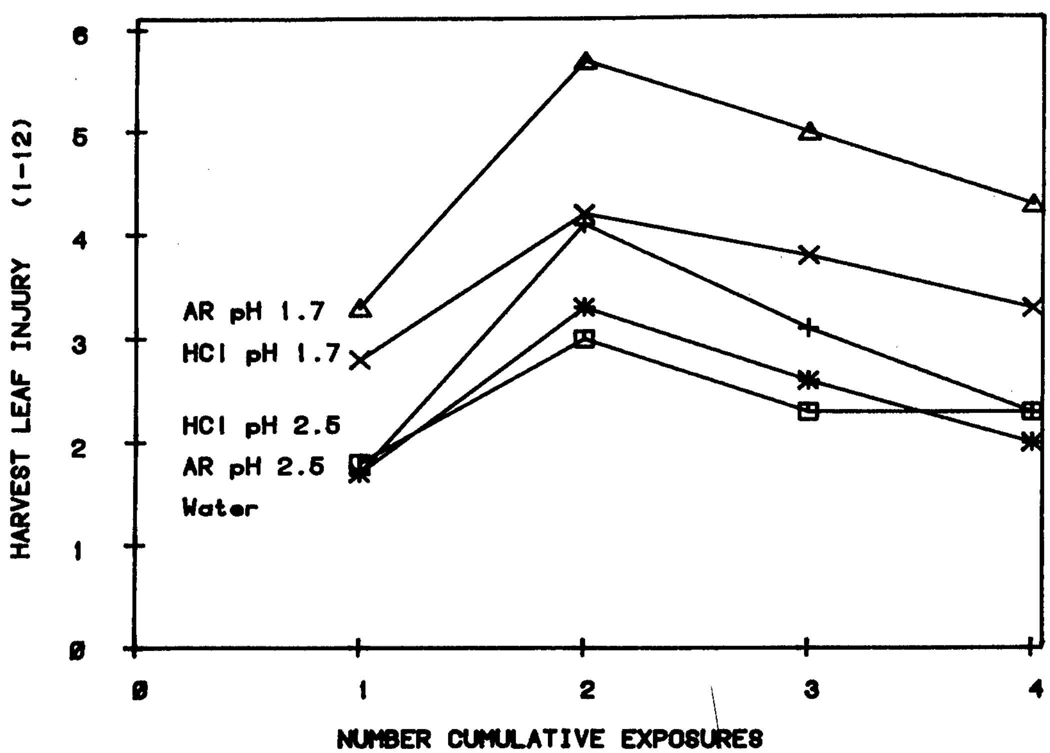


Figure 8. Leaf injury estimated on bean plants exposed to acidic mists. Eight plants harvested and graded one week after 1 to 4 exposures to HCl or simulated AR mists.

Treatments were compared over the four weeks of the experiment using two-way analyses of variance of harvest data. Injury recorded at harvest and averaged for the harvests (40 plants) or the treatments (32 plants) revealed the trend discussed above for treatments (Table 55). Plants harvested after the first exposure had least injury whereas plants harvested after the second week had highest injury values. Injury may have accumulated during the first two weeks then plant growth may have resumed and/or the reproductive cycle of the plant may have begun.

Analysis of leaf area and leaf numbers yielded nearly the same mean separations for all treatments (Tables 56 and 57). However, when leaf area per leaf was calculated, small leaves were associated with plants exposed to AR mist of pH 1.7 while large leaves were associated with those exposed to pH 2.5 (Table 58). Similarly, leaves collected at the second harvest were largest. Leaf senescence may have begun by the third week. Similar results were obtained for leaf weights (Table 59).

Treatments did not influence stem weights similarly analyzed by two-way ANOVA (Table 60). The harvest data indicated that stems increased in weight from first to third week. Loss in weight by the fourth harvest may be due to senescence or to movement of stored materials to reproductive structures.

Flowers were formed on the plants by the second and third harvests and pods developed by the third and fourth harvests (Table 61). More flowers occurred on plants exposed to AR mist than on those plants exposed to HCl or water. Pod numbers did not differ among treatments.

TABLE 55
BEAN HARVEST TWO-WAY ANALYSIS OF INJURY

Harvests (n=40)		Treatments (n=32)	
No.[1]	Injury	Acid & pH	Injury
1	2.25[2] d[3]	HCl 1.7	3.49 b
2	4.04 a	HCl 2.5	2.78 c
3	3.33 b	AR 1.7	4.45 a
4	2.81 c	AR 2.5	2.36 d
		H_2O 4.3	2.45 cd

[1]Weekly harvest made 1-4 weeks after exposure

[2]Average estimated injured leaf area, mean of 40 or 32 plants

[3]Means in columns followed by the same letter(s) were not significantly different by Duncan's NMRT

TABLE 56

BEAN HARVEST TWO-WAY ANALYSIS OF LEAF AREA

Harvests (n=40)		Treatments (n=32)	
No.[1]	Leaf area (cm^2)	Acid & pH	Leaf area (cm^2)
1	366[2]b[3]	HCl 1.7	412 ab
2	531 a	HCl 2.5	435 ab
3	485 a	AR 1.7	373 b
4	304 b	AR 2.5	472 a
		H_2O 4.3	418 ab

[1-3]Same notes as for Table 55 except average leaf area

TABLE 57

BEAN HARVEST TWO-WAY ANALYSIS OF LEAF NUMBERS PER PLANT

Harvests (n=40)		Treatments (n=32)	
No.[1]	No. leaves	Acid & pH	No. leaves
1	7.4[2]b[3]	HCl 1.7	8.7 a
2	9.4 a	HCl 2.5	9.0 a
3	9.8 a	AR 1.7	8.4 a
4	8.1 b	AR 2.5	8.8 a
		H_2O 4.3	8.5 a

[1-3]Same notes as for Table 55 except average number of leaves

TABLE 58
BEAN HARVEST TWO-WAY ANALYSIS OF LEAF AREA PER LEAF

Harvests (n=40)		Treatments (n=32)	
No.[1]	Area (cm^2)	Acid & pH	Area (cm^2)
1	47.9[2]b[3]	HCl 1.7	44.9 bc
2	55.2 a	HCl 2.5	47.0 bc
3	49.1 b	AR 1.7	43.0 c
4	36.8 c	AR 2.5	53.0 a
		H_2O 4.3	48.3 b

[1-3]Same notes as for Table 55 except average leaf area per leaf

TABLE 59
BEAN HARVEST TWO-WAY ANALYSIS OF LEAF WEIGHTS

Harvests (n=40)			Treatments (n=32)		
No.[1]	FW (g)	DW (g)	Acid & pH	FW (g)	DW (g)
1	8.7[2]b[3]	1.5 b	HCl 1.7	9.0 b	1.6 b
2	11.8 a	2.1 a	HCl 2.5	9.7 ab	1.7 ab
3	10.5 a	1.9 a	AR 1.7	8.5 b	1.5 b
4	6.9 c	1.2 c	AR 2.5	10.7 a	1.9 a
			H_2O 4.3	9.6 ab	1.7 ab

[1-4]Same notes as for Table 55 except average fresh (FW) or dry (DW) leaf weights per plant

TABLE 60
BEAN HARVEST TWO-WAY ANALYSIS OF STEM WEIGHTS

Harvests (n=40)			Treatments (n=32)		
No.[1]	FW (g)	DW (g)	Acid & pH	FW (g)	DW (g)
1	5.5[2] b[3]	0.8 c	HCl 1.7	6.6 a	1.5 a
2	7.6 a	1.6 b	HCl 2.5	6.9 a	1.6 a
3	7.3 a	1.9 a	AR 1.7	6.8 a	1.5 a
4	7.1 a	1.8 ab	AR 2.5	7.4 a	1.6 a
			H_2O 4.3	6.6 a	1.5 a

[1-3] Same notes as for Table 59 except average stem weights per plant

TABLE 61
NUMBER OF FLOWERS AND PODS PER PLANT

Treatment Acid & pH	Harvest 1	2	3	4
HCl 1.7	0 (0)[1]	0.8 (0)	0.5 (4.3)	0 (4.1)
HCl 2.5	0 (0)	0.8 (0)	0.3 (4.9)	0 (4.2)
AR 1.7	0 (0)	3.0 (0)	0.8 (4.9)	0 (4.4)
AR 2.5	0 (0)	2.1 (0)	0.4 (5.2)	0 (4.1)
H_2O 4.3	0 (0)	0.8 (0)	0.2 (4.8)	0 (4.5)

[1] Average number of bean flowers and pods (in parentheses) on harvested plants, mean of eight plants

In conclusion, brief acidic mists of pH 1.7 applied weekly to bean seedlings caused significant visible leaf injury. Injury was greater for simulated AR mist of $HNO_3:H_2SO_4$ mixtures than for HCl. Mists of pH 2.5 caused no more leaf injury than distilled water. Some reduction was noted for leaf area and weight for plants exposed to pH 1.7 mists, particularly for AR solutions. Injury or weight reductions did not seem to accumulate beyond the second week of treatments although senescence and development of reproductive structures (flowers and pods) may have obscured additive effects.

A possible stimulation of growth may be indicated by the greater leaf area on plants exposed to pH 2.5 AR mist and by a greater number of flowers on plants exposed to pH 1.7 AR mist. The mists may provide small amounts of sulfur and nitrogen as fertilizer. Injury was found on plants exposed to HCl mists of moderately high acid concentrations, however, accumulation of injury or growth changes was not observed.

FACTORS ALTERING PLANT RESPONSE TO HCl MIST

OZONE AND MIST

The possibility exists that plants may be impacted by both acidic mists and gaseous air pollutants such as ozone, sulfur dioxide, nitrogen dioxide, and peroxyacetyl nitrate (PAN). In one experiment, pinto bean seedlings were exposed to 0.5, 0.1, 0.025, 0.012 or 0.0% HCl mist in the morning and the same plants were fumigated for three hours of 0.0 or 0.3 ppm ozone that same afternoon. Continuous stir tank reactor chambers were used for the ozone treatments (as described in Granett and Taylor, 1977).

Foliar injury was recorded 48 hours after the treatments. Although HCl-induced injury, usually recognized as necrotic lesions, could be distinguished from the brown spotting caused by ozone, only overall injury was estimated. Amount of leaf area with injury and the percent number of leaves injured per plant were recorded. The pH of HCl treatment was more useful in some calculations than percent concentration.

The experiments were repeated three times; analysis showed no significant difference between these blocks at $P < 0.001$. Similarly, no injury differences existed between the tap water (0.0% HCl) and the dry, un-misted controls so the latter treatment was not used in most analyses.

Ozone-treated plants were significantly more injured than non-fumigated plants. When HCl alone was considered by combining ozone treatments, certain differences existed (Table 62). The estimated leaf area injured data best fit a quadratic curve whereas the ratio data (of injured/total leaves) best fit a cubic function (Figure 9).

Separating the ozone factor allowed some generalizations to be made (Table 63). Ozone-exposed plants incurred greater injury than those not so treated. Further, ozone exposure appeared to increase the injury response of plants treated with HCl at concentrations below 0.025% HCl mist (pH 2.09) while having little effect on those plants treated at higher HCl concentrations. This might be expected since plants exposed to elevated HCl concentrations were considerably damaged; acid-induced injury predominates and little tissue remained to be injured by the ozone. The nature of the response was seen in graphic form (Figure 10). Curves of best fit were calculated using the data (Table 64). Note that no significant curve existed for the estimated leaf area injured (EAI) data for ozone-fumigated plants. More than two ozone concentrations would be required to satisfactorily include ozone in an injury equation.

TABLE 62

RESPONSE OF BEAN PLANTS TO HCl COMBINING ALL OZONE TREATMENTS

Treatment		Injury	
pH	% HCl	Estimated area	Leaf ratios (%)
0.975	0.500	6.4[1] y[2]	96.7[3] x
1.507	0.100	3.6 z	94.2 x
2.093	0.025	3.1 z	64.9 y
2.383	0.012	2.7 z	43.3 z
7.857	0	2.9 z	40.0 z
(-)[4]	(dry)	(2.9 z)	(38.6 z)

[1]Mean of leaf area injured estimated on 1 to 12 scale, average of six plants

[2]Means in columns followed by the same letter(s) were not significantly different at $P < 0.05$ by Duncan's NMRT

[3]Mean of percent leaves injured per plant, average of six plants

[4]Ozone was only treatment

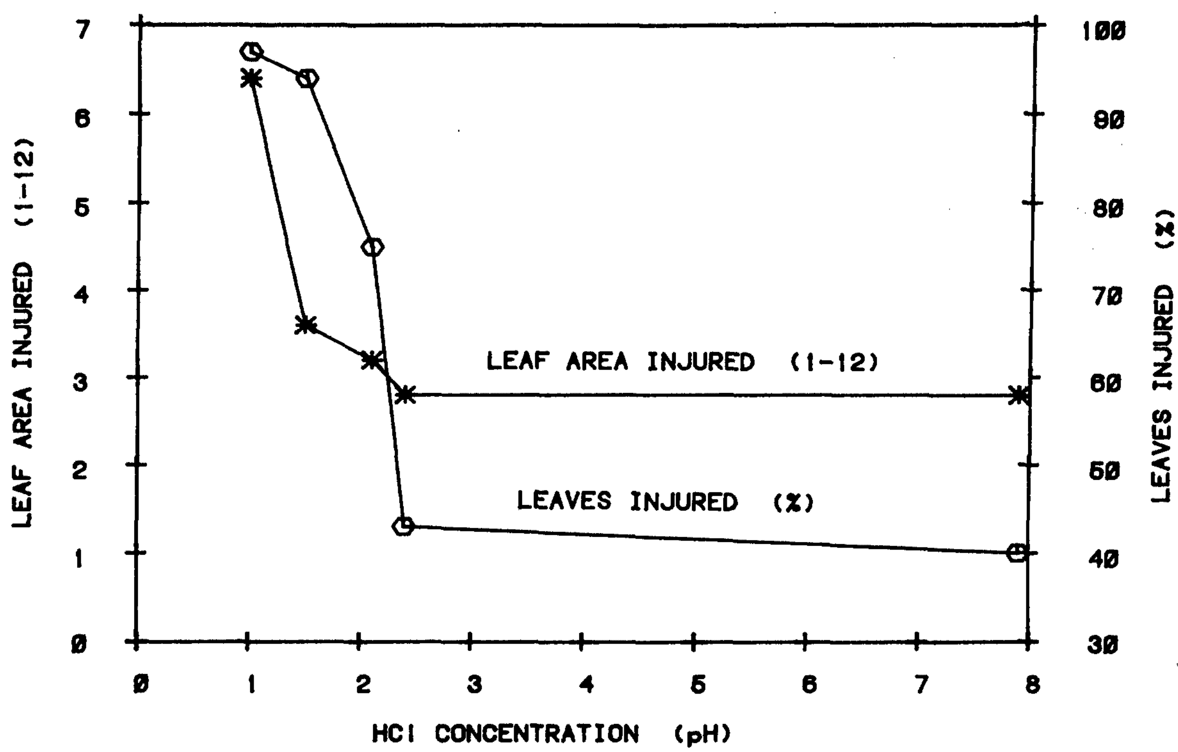


Figure 9. Foliar injury on pinto bean leaves exposed to HCl mist and ozone. Ozone treatments combined.

TABLE 63

RESPONSE OF BEAN PLANTS EXPOSED TO HCl MIST AND OZONE

Treatment		Estimated area		Leaf ratios (%)	
		Ozone		Ozone	
pH	% HCl	0.0 ppm	0.3 ppm	0.0 ppm	0.3 ppm
0.975	0.500	6.2[1] w[2]	6.5 w	95.0 a	98.3 a
1.507	0.100	3.6 y	3.6 y	95.0 a	93.3 a
2.093	0.025	2.0 z	4.3 xy	52.0 c	77.8 b
2.383	0.02	1.2 z	4.3 xy	11.7 d	75.0 b
7.857	0	1.1 z	4.8 x	5.0 d	75.0 b
(-)[3]	(dry)	(1.1 z)	(4.8 x)	(5.0 d)	(72.2 b)

[1]Estimated area and leaves injured, mean for three plants

[2]All 12 means for a particular variable were analyzed together. Means followed by the same letter(s) were not significantly different at $P < 0.05$ by Duncan's NMRT

[3]Ozone was only treatment

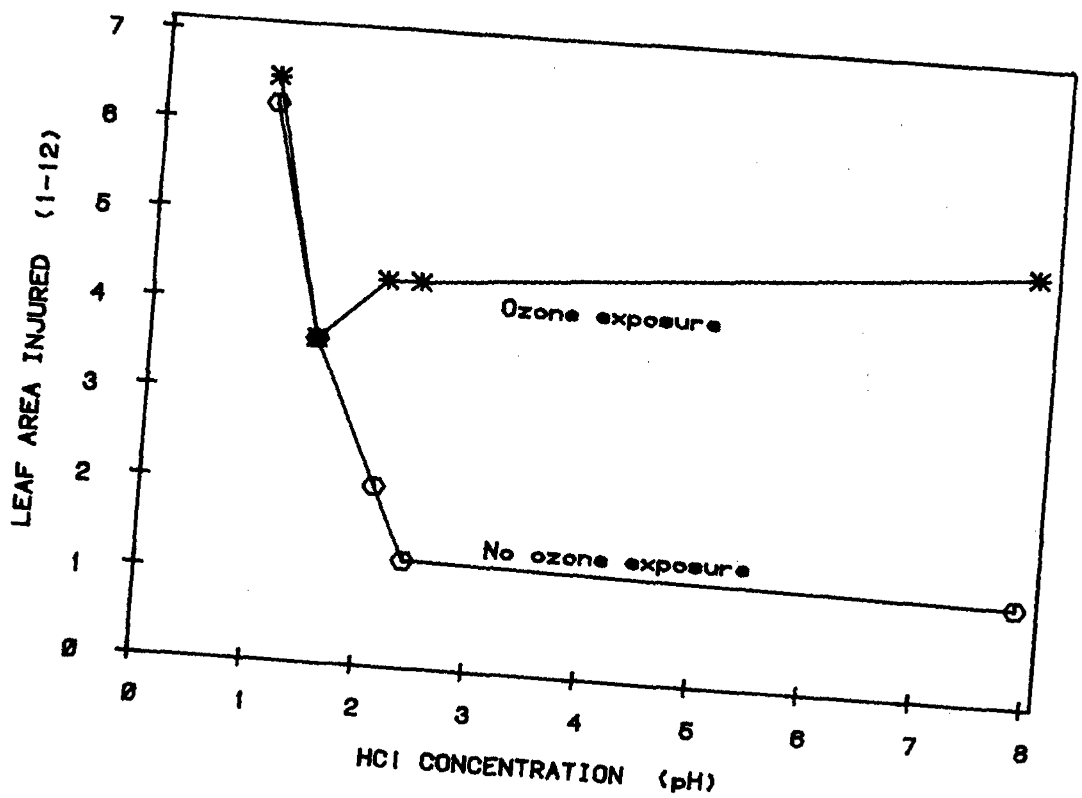
TABLE 64

SUMMARY OF CURVES RELATING FOLIAR INJURY TO HCl MIST CONCENTRATION WITH OR WITHOUT OZONE

Treatment	Equation	Function	r^2
No ozone	EAI[1] = $10.82 - 5.40\,(pH)^3 + 0.58\,(pH)^2$	Quadratic	0.76
No ozone	LI[2] = $173.0 - 66.0\,(pH) + 0.86\,(pH)^3$	Cubic	0.89
Ozone	LI = $118.9 - 19.8\,(pH) + 0.28\,(pH)^3$	Cubic	0.88

[1]EAI = Estimated leaf area injured on 1 to 12 scale; pH = HCl concentration expressed as pH value

[2]LI = Leaves injured in percent



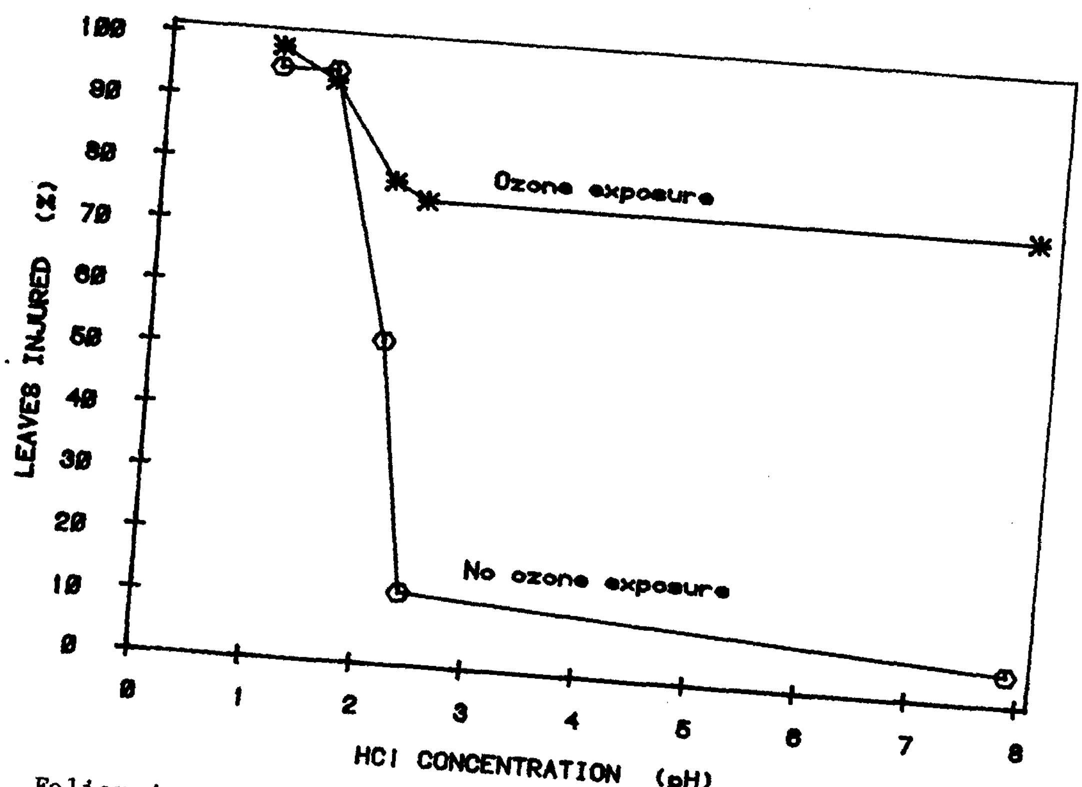


Figure 10. Foliar injury induced by HCl and ozone. 10a. (above) Estimated area injured. 10b. (below) Ratio of injured leaves per plant.

TIME OF DAY OF TREATMENT

Physiological states in plants vary with time. Activities change with temperature and light and are often coupled with a daily time cycle. Simple tests were conducted to determine whether the time of day when plants were exposed to HCl might influence response.

Pinto bean seedlings were exposed to HCl mist at 0700, 1200, or 1900 hours PST. Plants were thus in darkness or subdued natural light during the 0700 and 1900 hour exposures. HCl mist was generated from solutions of 0.5, 0.1, 0.025, and 0.0% HCl. Eight plants were exposed per treatment with replicates conducted on three separate days. Plants were harvested one week after exposure. Split-plot analyses were performed on estimated injury, number and area of leaves per plant, and leaf and stem weights (Table 65).

Both acid concentration and time of day were important when considering estimated leaf area injured (Tables 66 and 68). The 0.025% HCl treatment was no more injurious to leaves than the water control. Mist treatment in the subdued evening light at 1900 hours was significantly less damaging than treatments made at the other two times. Replicates were not significant. When the percent leaves injured variable was considered, the results were similar to estimated area (Tables 67 and 68). More separation occurred between acid concentration means with percent leaves than with estimated area data. Evening exposures at 1900 hours appeared less harmful than exposures at 0700 or 1200 hours.

Leaf area was significantly smaller at harvest only for plants treated with the most concentrated HCl mist and time of day was not an important factor (Table 69). Leaf and stem weight results were comparable to leaf area in that only the most acidic mist preparation created weight reductions at harvest and time of day did not influence harvested weight (Table 70). Log transformation of the weight data did not change the analyses.

TABLE 65
SPLIT-PLOT ANALYSIS OF TIME-OF-DAY DATA

Source of Variation	df
Blocks (day replicates)	2
HCl treatments	3
Error A (Blocks x HCl)	6
Time of day	2
Blocks x Time interaction	4
HCl x Time interaction	6
Error B	11
Total	35

TABLE 66

INJURY ON BEANS EXPOSED TO HCl MIST AT DIFFERENT TIMES OF DAY

HCl concentration (%)	Time of day (hours PST)		
	0700	1200	1900
0.5	8.2[1] u[2]	8.2 u	5.8 v
0.1	3.4 w	3.3 wx	2.6 wx
0.025	2.3 xy	2.3 wxy	1.4 yz
0.0	1.3 z	1.2 z	1.2 z

[1]Estimated leaf area injured, mean of 24 plants

[2]Any means in table followed by same letter(s) were not significantly different at $P < 0.05$ by Duncan's NMRT

TABLE 67

LEAVES INJURED ON BEANS EXPOSED TO HCl MISTS MORNING, NOON, OR NIGHT

HCl concentration (%)	Time-of-day (hours PST)		
	0700	1200	1900
0.5	75[1] v[2]	81 v	80 v
0.1	52 wx	58 w	55 wx
0.025	48 x	48 x	23 y
0.0	14 z	12 z	8 z

[1]Percent leaves injured per plant, mean of 24 plants

[2]Same as note 2, Table 66

TABLE 68

ACID CONCENTRATION AND TIME EFFECTS ON HCl MIST INJURY ON BEANS

Concentration effect			Time-of-Day effect		
	Leaves injured			Leaves injured	
HCl concentration (%)	Estimated area	Numbers (%)	Time (hours PST)	Estimated area	Numbers (%)
0.5	7.4[1] x[2]	78[3] w[2]	0700	3.8[4] a[2]	47[5] a[2]
0.1	3.1 y	55 x	1200	3.8 a	49 a
0.025	2.0 z	39 y	1900	2.7 b	42 b
0	1.2 z	11 z			

[1]Estimated area injured, mean of 72 plants

[2]Means in each column followed by the same letter were not significantly different by Duncan's NMRT

[3]Percent leaves injured, mean of 72 plants

[4]Same as note 1, but mean of 96 plants

[5]Same as note 3, but mean of 96 plants

TABLE 69

AREA OF LEAVES EXPOSED TO HCl MIST AT DIFFERENT TIMES OF DAY

Concentration effect		Time-of-day effect	
HCl concentration (%)	Leaf area (cm^2)	Time (hours PST)	Leaf area (cm^2)
0.5	66.1[1] z[2]	0700	98.5[3] a
0.1	104.2 y	1200	94.5 a
0.025	114.9 y	1900	102.4 a
0.0	108.7 y		

[1]Area of leaves, mean of 72 plants

[2]Same as note 2, Table 68

[3]Same as note 1, but mean of 96 plants

TABLE 70
WEIGHTS OF LEAVES AND STEMS OF BEAN PLANTS EXPOSED TO HCl MIST AT DIFFERENT TIMES OF DAY

HCl concentration (%)	Fresh weight (g)		Dry weight (g)	
	Leaf	Stem	Leaf	Stem
0.5	1.45[1] z[2]	1.49 z	0.25 z	0.12 z
0.1	2.58 y	1.81 y	0.33 y	0.19 y
0.025	2.85 y	1.91 y	0.37 y	0.21 y
0.0	2.68 y	1.81 y	0.36 y	0.21 y
Time-of-day (hrs)				
0700	2.38[3] a	1.79 a	0.32 a	0.18 a
1200	2.28 a	1.73 a	0.32 a	0.17 a
1900	2.51 a	1.75 a	0.34 a	0.19 a

[1] Weight, mean of 72 plants

[2] Means in groups followed by same letter were not significantly different at $P < 0.05$ by Duncan's NMRT. Note that none of the time-of-day means were statistically different

[3] Weight, mean of 96 plants

The time of day when plants were exposed to mist had some effect on amount of subsequent injury: exposure to mist in the evening was less injurious to bean plants than exposures made earlier. This effect of time did not apply to leaf area, numbers, or leaf and stem weights of plants harvested a week after exposure. All variables were influenced by the acid concentration of the mist with the most concentrated treatments always causing greater injury or reduction than the others.

ACIDIC MIST DILUTION ON LEAVES

Rationale

Even very acidic mists require a certain residence period on the leaf surface before injury can occur. Leaves wetted by neutral liquids before or after HCl mist exposure may be more tolerant to the acid since the HCl may become diluted.

Rinsing Leaves Before Mist Treatments

The relative tolerance of wet leaves to acid injury was tested. Leaves of three-week-old pinto bean seedlings were rinsed with tap water (pH 7.7) or were left dry just prior to exposure to HCl mist. Rinse water was applied gently with a garden hose spray nozzle until all leaf surfaces were thoroughly wet. Pot soil was protected from drenching. Wet and dry plants were then exposed to 0.0, 0.1, or 0.5% HCl mist.

Plants were injured in response to HCl mist acidity (Table 71). Amount of injury on wet leaves was not significantly different than on dry leaves nor did the nature of injury differ. Thus, water on the leaves at time of exposure to mist did not influence development of injury.

Rinsing Leaves After Mist Treatments

Rinsing leaves with water after HCl mist treatment was also investigated. Pinto bean seedlings were exposed without pretreatments to acidic mists generated from 0.0, 0.1 or 0.5% HCl solutions. Following the application period, plants were rinsed for three minutes with tap water spray so that leaf surfaces but not soil were wetted. Delay between completion of mist exposures and start of rinse treatments was 0, 2.5, 5, or 10 minutes. Plants receiving neither rinses nor acidic mist treatments served as controls. Leaf injury was estimated 48 hours after treatments.

Rinsing plants reduced foliar injury due to acidic mist. Significant interactions between replicates, acid treatments, and rinse treatments necessitated the use of one-way analysis of variance on each treatment. Results of the analyses (Table 72) and of further two-way ANOVA tests with partitioning indicated that all of the rinse treatments decreased injury such that the rinsed plants statistically had no more damage than the no-acid controls. More injury occurred with 0.5% HCl mists than with 0.1% but, even at the higher concentration, rinses reduced injury.

Tap water effectively washed off or diluted the HCl mist solutions and reduced or prevented leaf injury from occurring. Rinsing could be delayed for at

TABLE 71
INFLUENCE OF PRETREATMENT RINSE ON INJURY INDUCED BY HCl MIST

Plant pretreatment	HCl concentration (%)		
	0.0	0.1	0.5
Dry	1.62 ± 0.12[1] a[2]	3.10 ± 0.45 b	5.69 ± 0.59 c
Wet (pH 7.8)	1.43 ± 0.19 a	3.03 ± 0.05 b	5.21 ± 0.60 c

[1]Injury on scale of 0 to 12, mean and standard deviation of three replications of seven plants each

[2]Means in rows followed by same letter were not different at $P < 0.05$ by Duncan's NMRT

TABLE 72

FOLIAR INJURY ON PINTO BEAN PLANTS RINSED AFTER EXPOSURE TO HCl MIST

Delay between mist and rinse treatments (minutes)	HCl mist treatments			
	Replicate 1		Replicate 2	
	0.1%	0.5%	0.1%	0.1%
0.0	1.79[1] b[2]	1.96 bc	2.04 b	2.51 b
2.5	1.96 b	1.94 bc	2.10 b	2.43 b
5.0	1.81 b	2.09 bc	2.09 b	2.99 b
10.0	2.06 b	2.39 b	2.04 b	2.29 b
no rinse	3.97 a	10.23 a	5.74 a	9.19 a
no acid	1.43 b	1.37 c	1.59 b	2.36 b

[1] Average estimated leaf injury, mean of primary leaves on seven plants

[2] Means of replicates followed by the same letter(s) were not significantly different at $P < 0.05$ by Duncan's NMRT

least ten minutes. This may be a satisfactory method for reducing injury in specific, high-cost crops impacted by acid solutions.

DETECTING ALUMINUM OXIDE ON LEAF SURFACES

RATIONALE

The detection of the exhaust ground cloud after a shuttle rocket launch may be of great importance. Although the ground cloud might precipitate acidic mist, injury symptoms on plants might not be present or specific enough to provide positive proof-of-passage. Aluminum oxide dust also precipitates from the cloud. The feasibility of detecting aluminum on leaves was considered since the dust was likely to be distributed over many plants in the path of the cloud and would adhere to the leaf surfaces.

OBSERVATION OF PLANT TISSUE FROM KENNEDY SPACE CENTER

National Aeronautics and Space Administration (NASA) personnel collected plant tissue in the vicinity of the launch pad hours after lift-off of the fifth shuttle mission (STS-5) on November 11, 1982. Leaves were packaged with moist paper towels in "Zip loc" plastic bags, and transported to California by Air Force Space Division personnel. The samples were kept chilled for most of the period between collection and delivery to the Riverside campus four days after collection. One set was made up of green leaves and another set consisted of gray-brown colored leaves.

The green leaves were from six plant species collected 0.5 miles north of the launch pad, along an access road. All leaves had colorless, 100-400 µm long crystals on their upper and lower surfaces (Table 73). Many leaves had five or six necrotic or chlorotic 1-5 mm diameter spots. The necrotic spots penetrated through the leaf. In the depressions formed by some of the spots, a white lumpy powder was found. This powder may be residue of dissolved Al_2O_3. Similar white powder was found in areas away from the burn spots on some leaves.

The gray-brown leaves were from the sea ox eye plant, Borrichia frutescens, and were collected about 100 meters north of the launch pad perimeter fence. Plant tissue in this packet had the strong, sweet odor of dying vegetation. The leaves appeared watersoaked and necrotic, presumably due to exposure to the large concentrations of HCl gas generated during lift-off. Neither burn holes nor white powder were visible on these leaf surfaces. However, the two crystal types described above were found when the leaves dried.

MICROSCOPY AND ELEMENT ANALYSIS OF LEAF TISSUE

Borrichia frutescens leaves described above were air dried. Small pieces measuring 5 x 5 mm were mounted with double-stick cellophane tape on carbon stubs. The material was coated with evaporated carbon under vacuum. Specimens were viewed at 25-250 times magnification using a Jeolco model U3 scanning electron microscope (SEM) with an accelerating voltage of 0.5-5 KEV. Images seen were very poor and the crystals found tended to evaporate during viewing (Figure 11). The SEM was equipped with a United Scientific X-Ray Microtrace. When the X-ray probed certain crystalline structures on the leaf surface, the scan indicated large amounts of aluminum, chlorine, silicon and calcium (Figure 12). Sulfur, potassium, and iron were found in smaller amounts.

GENERATION OF ALUMINUM OXIDE BY SOLID FUEL COMBUSTION

The collected leaves were compared to leaves exposed to materials emitted from pieces of burning solid rocket fuel. Fuel pieces were mounted on ignition wires and placed in a screened enclosure in a 1.1 m^3 continuous stirred tank reactor chamber. The chamber was sealed during fuel combustion, but exhaust vents were opened later. During some tests, paddles rotated at 120 rpm to help mix the chamber air. A spinning disk applicator, attached to a brace mounted beneath the paddles, generated a fine water mist when activated. Pinto bean plants, serving as biological indicators, became injured when exposed to fuel-generated gas or mist. Hydrion pH paper placed in the chamber registered mist acidity.

On fuel ignition, a white cloud of gas and dust particles appeared in the chamber. The cloud was thicker and more opaque if the mist generator was operating and appeared more evenly distributed throughout the chamber if the paddles were rotating. Mist deposits were composed of smaller (but unmeasured) droplets if the paddles were stirring the air. Mist registered between pH 0.5 to 1.0 on paper within 2 to 5 seconds of fuel ignition with mister and paddles on whereas reaction was delayed to 8 seconds with paddles off.

TABLE 73

OBSERVATIONS OF LEAVES COLLECTED NEAR SHUTTLE LAUNCH PAD AFTER STS-5

Leaf	Identification	Findings
1[1]	Reed or grass without trichomes Saw palmetto Sevena repens	White powdery spots No HCl damage Clear 150-200 μm crystals
2	Broad leaf	5 HCl burn spots 1-5 mm diameter Burn spots penetrate leaf No white powder Clear 150-300 μm crystals
3	Narrow lanceolate leaf Sunflower type weed Helianthus spp	7 HCl spots, two with light 3.5 mm center surrounded by darker 7 mm region Other burn spots 1-2 mm dia. No white powder Clear 100-400 μm crystals
4	Sclerophyllous, shiny leaf Oak species Quercus sp	Chlorotic red and blue spots on upper leaf surface ca. 0.5-1 mm dia. Leaf tip red with white powder Four other white powder spots ca. 1-2 mm dia. Clear 100-500 μm crystals
5	Cordate leaves Morning glory (?) Convolvulus sp	5 necrotic burn spots, 1-6 mm diameter 5 chlorotic areas 1-2 mm dia. on top surface only No white powder Clear 150-350 μm crystals
6	Round serrate leaves pennywort Hydrocotyl sp.	5 necrotic burns 1-5 mm dia. Small necrotic spots less than 0.5 mm Clear 100-400 μm crystals
7[2]	Lanceolate leaves with trichomes Sea ox eye Borrichia frutescens	White 32-380 μm crystals Clear 51-385 μm crystals No burn holes or spots Over-all necrosis, watersoaking

[1]Species 1 to 6 collected 800 m north of launch pad

[2]Species 7 collected 100 meters from pad perimeter fence

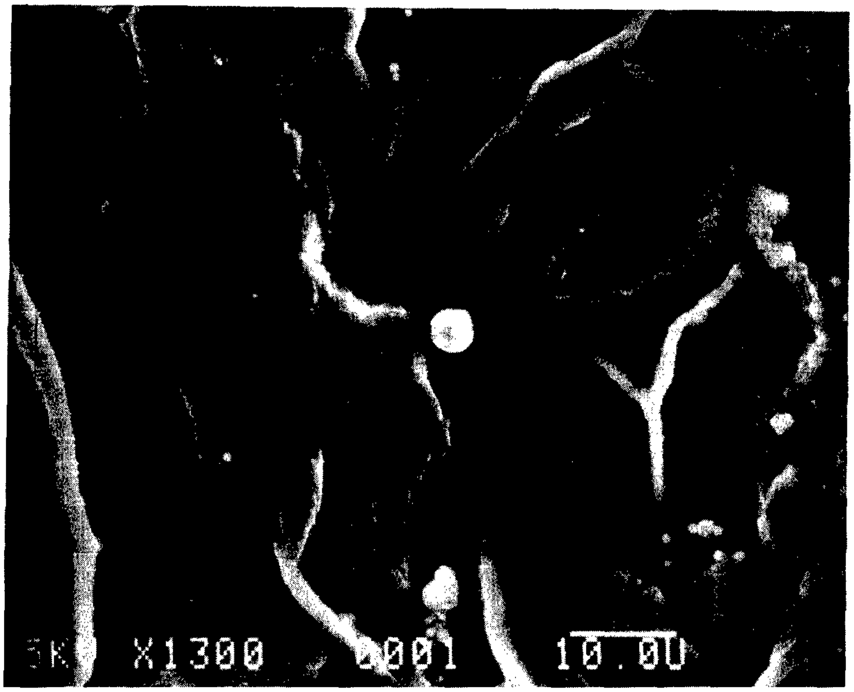


Figure 11. Scanning electron micrograph of leaf surface showing stomata and spherical crystal. Magnification is about 1300 times, marker is 10 μm.

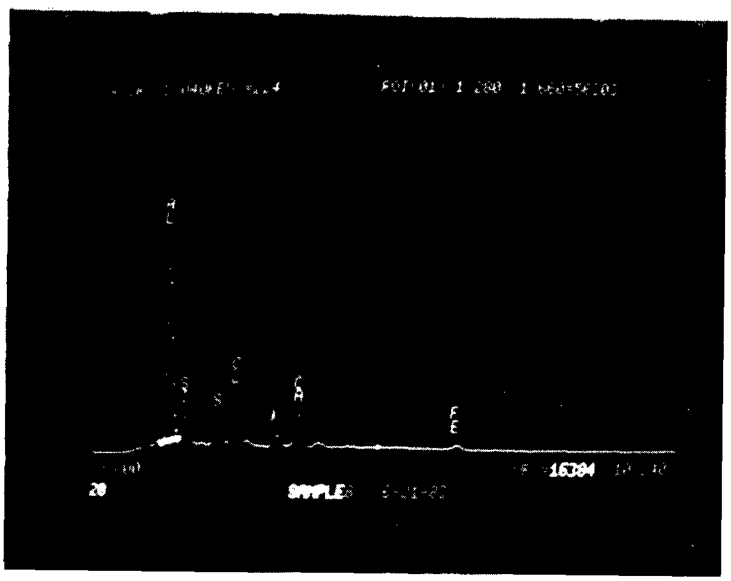


Figure 12. X-ray microtrace of crystal on exhaust-exposed leaf collected from the field. Peaks, 1 to r, are aluminum, silicon, sulfur, chlorine, potassium, calcium, and iron.

Various elements were detected when fuel-exposed leaf pieces were analyzed using the X-ray microtrace. Aluminum and chlorine, which composed a major part of the fuel, were found in large amounts. Potassium and calcium were also present in significant quantities (Table 74). Some relationships could be established based on the quantity of aluminum found (Figure 13). Dry conditions provided the least amount of aluminum deposition in ten minutes (Figure 13a) whereas larger mist droplets, generated when the paddle fans were not rotating, apparently scavenged more aluminum than smaller droplets. Virtually no aluminum was associated with unexposed leaves (0 mg fuel) or on the leaf under-surface (Figure 14).

TABLE 74
ELEMENT ANALYSIS OF AREAS ON BEAN LEAF SURFACE AFTER EXPOSURE TO SRF

Conditions					Analysis			
Time[1] (min)	SRF[2] (mg)	Mist	Paddles[4]	No.[5]	Al	Cl	K	Ca
10	1200	yes[3]	on	1	81[6]	3,187	7,086	15,010
10	1800	yes	on	4	133	2,960	11,838	10,132
10	0	no	on	10	0	2,459	16,091	12,634
10	800	no	on	8	0	5,211	5,060	17,261
10	1200	no	on	2	27	970	1,981	3,228
10	1800	no	on	3	104	29,312	41,200	16,566
3	1800	yes	off	5	0	221	1,946	3,306
7.5	1800	yes	off	6	483	5,543	11,297	12,258
12	1800	yes	off	7	679	3,483	9,055	4,796

[1]Time plants were exposed to SRF in chamber

[2]Solid rocket fuel (SRF), pre-ignition mass

[3]Water mist generated at ca 15 mℓ min^{-1} with spinning disk applicator

[4]Paddles in chamber, stirring or not

[5]Number specimens analyzed

[6]Counts of element on monitor

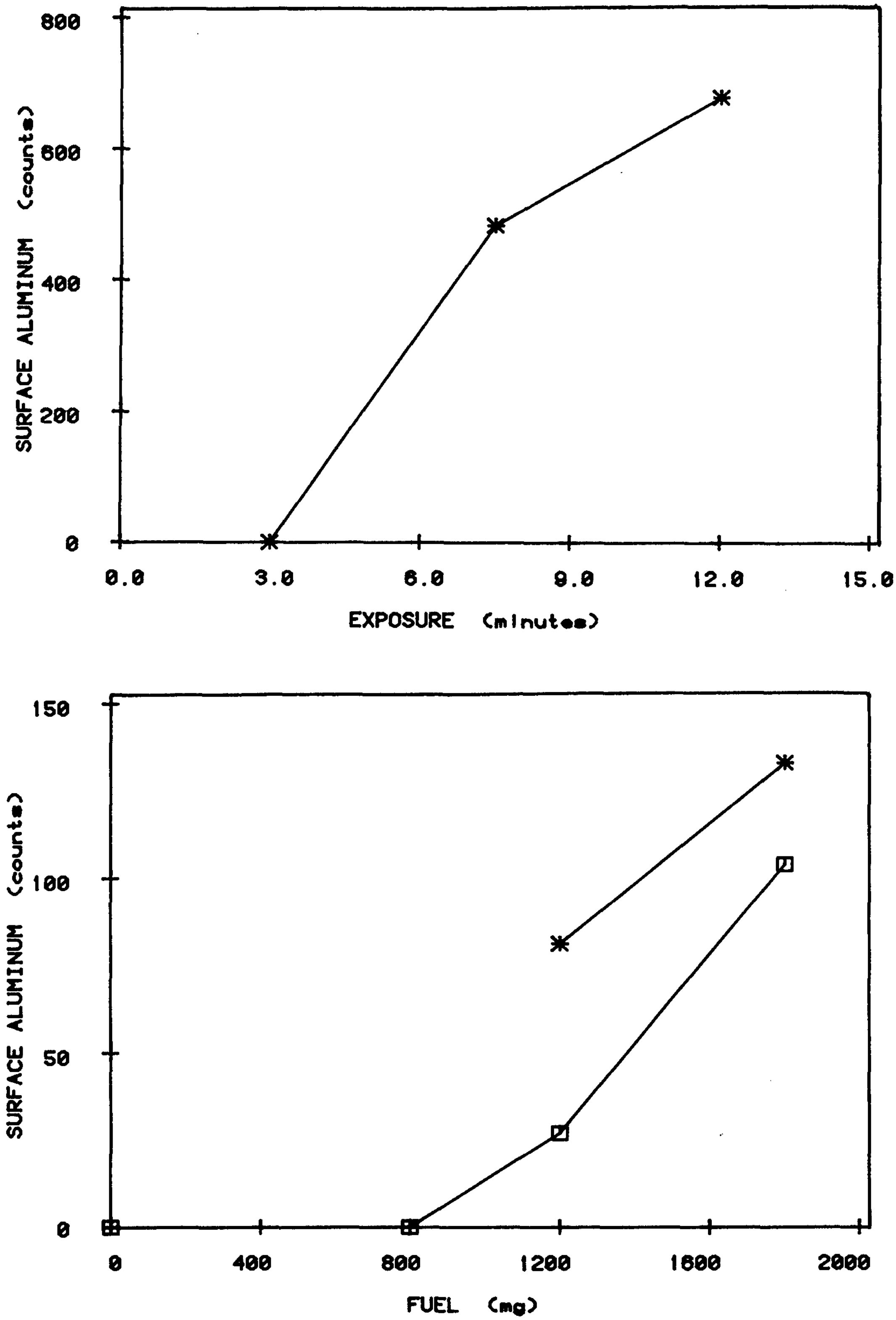


Figure 13. Aluminum counts detected on bean leaf upper surfaces. 13a. (above) Fuel constant at 1800 mg but exposure time increased. 13b. (below) Fuel increased while exposure time constant at 10 minutes, with (squares) or without (stars) paddles mixing chamber air.

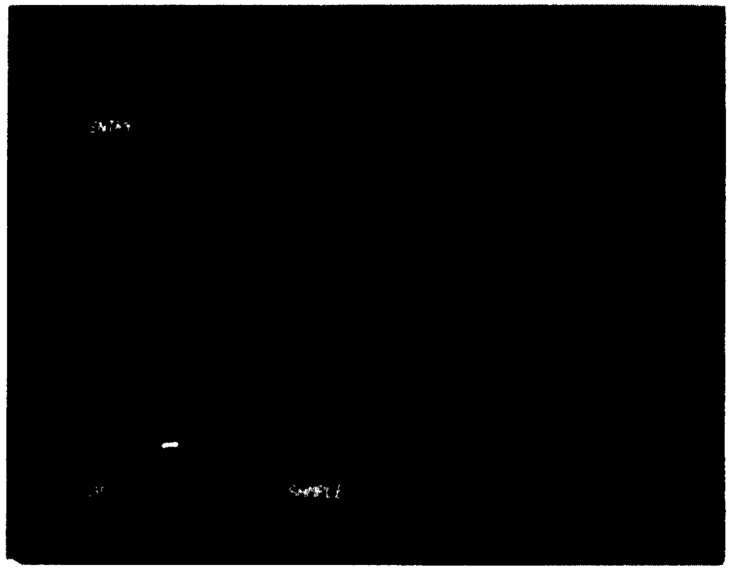


Figure 14. X-ray microtrace of unexposed bean leaf. Little aluminum is present on bean leaf piece unexposed to rocket fuel.

CONCLUSIONS

Tests and experiments conducted during the period covered by this report show that HCl mists at the acid concentrations found following a shuttle launch will be phytotoxic. Although the mist will injure most vegetation on which it falls, the Kennedy Space Center experience showed that not all plants will be impacted (Knott 1981). Our studies further indicate that some species will be more tolerant than others. Current tests also showed that aluminum oxide dust was not injurious to plant foliage but was present on many plants under the path of the ground cloud. Aluminum can be detected on leaf surfaces at periods after a launch and could be a desirable marker to signal the passage of the ground cloud. Further investigations correlating the occurrence and detection of surface aluminum are suggested.

Acidic rain mist, consisting of mixtures of sulfuric and nitric acids, was compared to HCl mist. Injury from either acid source was similar on the plants tested. Acidic rain injury was not likely to be confused with HCl-caused injury under field conditions near shuttle launches. Ambient acidic rain has never been recorded below pH 2.7, and single exposures at that concentration cause minimal amounts of injury.

Injury caused by ozone, an ambient air pollutant gas, can be distinguished from foliar injury induced by HCl mist. The effects of ozone and HCl are possibly additive up to a certain pollutant level above which no further injury can occur. HCl mist contributes more to the injury at high levels than does ozone.

HCl mist generally caused foliar injury on species tested and rarely posed a threat to the health of the impacted plant. Two other phytotoxic symptoms were noted. Flowers and fruits of some species could be discolored or pitted following exposure. Such injury would be cosmetic and could jeopardize the commercial value of some products. Marigold flowers exposed to HCl mist during fertilization produced seeds which had lower germination rates than seeds from water-treated flowers. The implication of this finding is still unclear.

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