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Received for review March 2, 1956. Accepted August 27, 1956. Division of Fertilizer and Soil Chemistry, 128th Meeting, ACS, Minneapolis, Minn., September 1955. Work supported by Iowa Engineering Experiment Station.

ATMOSPHERIC POLLUTION

Relationship among Exposure Periods, Foliar Burn, and Fluorine Content of Plants Exposed to Hydrogen Fluoride

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Low concentrations of fluorides from industrial gases have been found in the atmosphere of some agricultural areas. Observations of a pathological condition attributed to fluorides in a wide range of plant species resulted in initiation of controlled fumigation experiments to determine the effects of environmental variables upon the rate of foliar response to hydrogen fluoride fumigation. Forty plant varieties were exposed to atmospheric concentrations of 1.5, 5, and 10 parts per billion of hydrogen fluoride in daylight and darkness. Correlation between exposure factor and accumulated foliar fluoride level for family, genus, and species has been calculated. The varieties fumigated averaged 91.3% as responsive to hydrogen fluoride in darkness as in daylight. Varieties fumigated were somewhat more responsive to a daily low fumigation concentration than to twice weekly higher concentrations of approximately equivalent exposure factor.

OBSERVATIONS OF A PATHOLOGICAL CONDITION in a wide range of species of plants have been made in seven areas within the state of Washington within the past decade. In each of the affected areas, air pollution in the form of gaseous fluorides has been diagnosed as the primary contributing cause of the observed leaf scorch (*14, 17, 19, 21, 22, 24, 28*).

Numerous reports concerning field observations of the visible effects of fluoride upon certain types of vegetation have been reviewed by Miller, Johnson, and Allmendinger (*22*) and Thomas (*30*). Others have contributed descriptions of field observations of the effects of fluoric effluents upon vegetation (*9, 11, 13, 15, 20, 23, 26*). Several papers within the past 5 years have reported the effects of controlled hydrogen fluoride fumigation on plants conducted in a concentration range of 0.05 to 10 p.p.m. of fluoride (*12, 16, 30, 32*).

Extensive field sampling for atmospheric fluorides has been conducted by the Division of Industrial Research of the State College of Washington between 1949 and 1954 in Spokane, Wash. (*5*); Longview, Tacoma, and Camas, Wash. (*2*); and Utah and Salt Lake Counties in Utah (*1*). The results of these surveys indicated that average 4-hour atmospheric concentrations were less than 5 p.p.b., with occasional maximum 4-hour average concentrations in the order of 10 to 20 p.p.b. of hydrogen fluoride. Other investigators in the field of air pollution (*10*) show agreement with these data. As these concentrations were considerably lower than those used in most of the fumigation work which had been reported, a need existed for fumigation studies using concentrations which had actually been found in the field, and which had been blamed for observed pathological conditions in plants growing in the field.

It is of practical importance to obtain information regarding minimum concentrations and exposure times required to produce visible foliar fluoride burn on a wide variety of vegetation. The development of such data must be based

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upon a study of the influence of environmental factors which might conceivably affect the rate of response of a given variety of vegetation to hydrogen fluoride gas.

Therefore, in 1951, fumigation experiments were undertaken at the State College of Washington exposing a variety of plants to concentrations of hydrogen fluoride in the range of a few tenths of a part to 20 p.p.b. During the 1953 growing season, 40 varieties, including 34 species, were exposed to hydrogen fluoride gas at three different concentration levels in both daylight and darkness. The influence of light upon visible foliar response was chosen as one of the first variables to be studied because Katz and coworkers (*18*) had previously reported that plants exhibited an extremely low response to sulfur dioxide in darkness as contrasted to a response to equal concentrations in daylight. Furthermore, meteorological considerations, confirmed by field-air sampling data obtained in one of the major pollution areas indicated that many of the ground level fumigations occurred during the hours of darkness and early morning hours of low light intensity.

If a similar lack of foliar response to hydrogen fluoride in darkness should exist, then one would need only to consider daylight ground-level pollution concentrations in subsequent studies. In this report, however, test varieties showed nearly as great a response in darkness as in daylight.

Experimental Methods

Fumigation Equipment. Fumigation greenhouses, constructed of Fiberpane plastic, were used as enclosures in which varying concentrations of hydrogen fluoride were developed and maintained. The light intensity as measured within the chamber on a cloudless, summer day was in excess of 5000 foot-candles. The air in the greenhouses was exchanged approximately once every 2 minutes. The incoming air was passed through a large countercurrent water-spray washer and then passed into a 12-inch-diameter distributing duct which conducted the air to each of the five greenhouses. Each greenhouse duct was equipped with a damper which enabled the balancing of the air flow into the several chambers. The uniformity of air flow throughout each of the chambers was visually checked by hanging paper streamers at the average foliage level throughout the greenhouses. The incoming airflow baffles were adjusted so that an evenness of motion of the streamers was obtained.

Known and constant quantities of hydrogen fluoride were introduced into four of the five chambers. Scrubbed air without added fluorides was circulated through the fifth chamber, which served as the control unit. A 1 or 2% mixture of hydrogen fluoride with nitrogen was produced by introducing a weighed amount of anhydrous hydrogen fluoride into a dry, evacuated stainless steel pressure cylinder and then diluting with dry oil-pumped nitrogen. Each greenhouse fluoride-atmosphere producing system consisted of a series of pressure-reducing values which maintained a constant flow of the hydrogen fluoride–nitrogen mixture into the inlet duct of each fumigation chamber. All of the copper gas-conducting lines and the housing which contained the pressure cylinders and regulating valves were maintained at 120° F. to prevent condensation of hydrogen fluoride within the gas distribution systems.

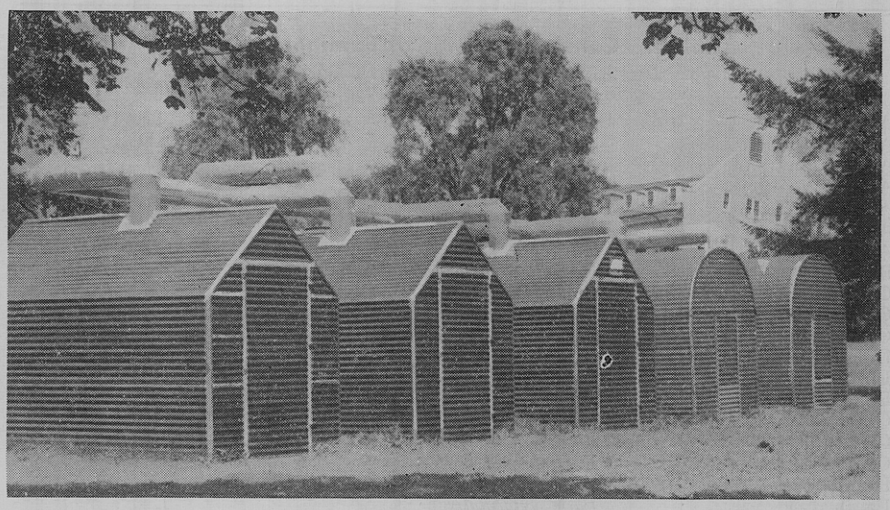

Figure 1. Fumigation chambers

The resultant hydrogen fluoride–air mixture entered the greenhouses at the top and impinged upon a baffle plate designed to force the air flow throughout the chamber. A pickup manifold surrounded the interior of the chamber at ground level and was equipped with a series of small holes arranged linearly along this duct. This gas removal manifold aided in forcing the fumigation atmosphere into a uniform dispersion pattern within the chamber.

The fumigation atmospheres were exhausted throughout a second countercurrent water-spray tower to prevent recirculation of contaminated air. The primary features of the fumigation equipment are illustrated in Figures 1 and 2.

Fumigation Specimens. The exposure plants were grown in pots up to 5 gallons in size containing uniform local soil. All specimens were either grown entirely outdoors, or, if started in a greenhouse, were hardened outdoors, for at least 2 weeks before initial exposure. All plants were watered daily. The plants were placed in the fumigation

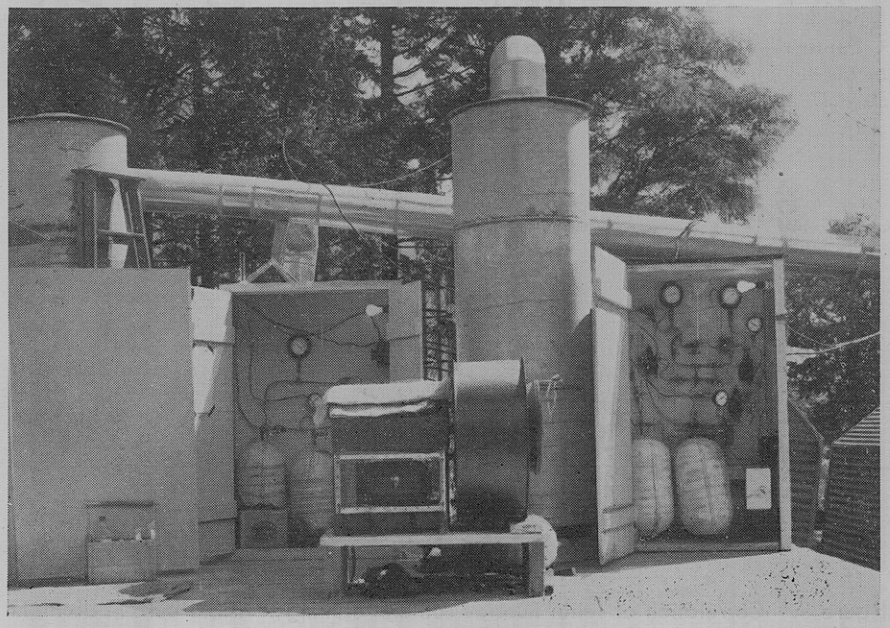

Figure 2. Air scrubber and hydrogen fluoride atmosphere controllers

Table I. Common Names of Fumigated Plants

Common Name	Scientific Name	Abbreviation[a]
Alfalfa	*Medicago sativa*	...
Apple, Delicious	*Malus sylvestris*	AD
Apple, Jonathan	*Malus sylvestris*	AJ
Apple, Wealthy	*Malus sylvestris*	AW
Apple, Winesap	*Malus sylvestris*	AWi
Apricot	*Prunus armenicaca*	Ap
Arbor Vitae	*Thuja orientalis*	AV
Blueberry	*Vaccinium carymbosum*	B
Carrots	*Daucus carota*	Ca
Cherry	*Prunus avium*	C
Corn	*Zea mays*	...
Douglas fir	*Pseudotsuga taxifolia*	...
Elm	*Ulmus oumila*	E
Engleman spruce	*Picea engelmannii*	...
Gladiolus	*Gladiolus hortulanus*	Gl
Grand fir	*Abies grandis*	...
Grape	*Vitis vinifera*	G
Hemlock	*Tsuga heterophylla*	...
Larch	*Larix occidentalis*	L
Laurel	*Kalmia latifolia*	...
Lilac	*Syringa vulgaris*	Li
Locust	*Robinia pseudoacacia*	...
Lodgepole pine	*Pinus contorta*	LPP
Maple	*Acer plamatum*	M
Mulberry	*Morus alba*	Mu
Parsnip	*Pastinaca sativa*	...
Peach	*Prunus persica*	Pe
Pepper	*Piper nigrum*	Pep
Petunia	*Petunia hybrida*	...
Ponderosa pine	*Pinus ponderosa*	PP
Prune	*Prunus hortulania*	P
Raspberry	*Rubus idaeus*	R
Rhododendron	*Rhodendron*	...
Rose	*Rosa dilecta*	...
Squash	*Cururbita maxima*	...
Sweet pea	*Lathyrus ordoratus*	...
Tomato	*Lydopersicon esculentum*	...
White pine	*Pinus monticola*	...
Willow	*Salix aurea*	W

[a] Abbreviations used in Figures 3 to 8.

greenhouses only during the exposure periods. Thus, all fumigation exposures were conducted on plants which approached field - hardened conditions. The common names of all varieties fumigated and the abbreviations used in subsequent figures are tabulated in Table I.

Fumigation Procedures. The experiments herein reported were begun on July 27 and continued through August and September 1953. Three concentration levels were utilized in these studies: 1.5, 5 and 10 p.p.b. of hydrogen fluoride. The sequence of exposure of replicated groups of plants at each concentration level was arranged so that an approximately equivalent exposure was given to each group during each week. Plants at the 5- and 10-p.p.b. levels were exposed for 8 and 4 hours, respectively, twice weekly. All plants at the 1.5-p.p.b. level were exposed 8 hours daily, 5 days per week. All plants were examined daily for development of foliar-fluorosis symptoms before they were transferred to the fumigation chambers. All plants showing symptoms of burn were then removed from the experiment. The fumigation-exposure intensity for each fumigation sequence was expressed as an empirical value called the "exposure factor." This term is defined as the sum of the products of each daily total exposure in hours and each average daily atmospheric concentration in parts per billion of hydrogen fluoride.

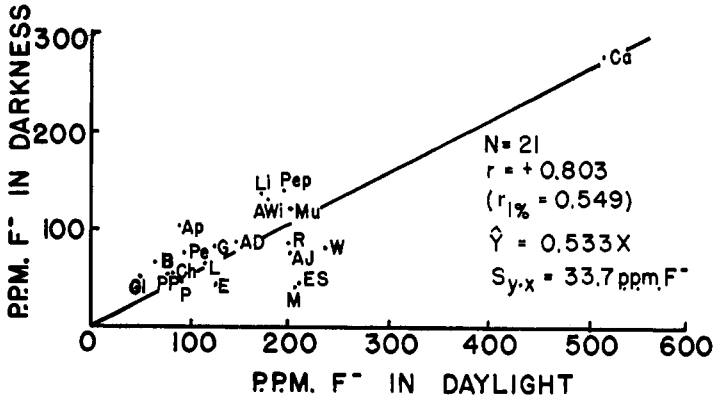

Figure 3. Correlation of foliar fluoride content resulting in visible burn in daylight and darkness at equivalent fumigation levels

Analytical Methods. Air samples were continuously withdrawn over a 2-hour period from each fumigation chamber throughout each exposure period. The Tygon sample-tube inlets were suspended within the chambers at average foliage level. The atmosphere sampling equipment for each chamber was located adjacent to each chamber, thus requiring a minimum of sampling tubing. The absorption towers used have been described (*5*). The fluoride content of the absorption liquid was determined by direct high-salt–thorium nitrate titration (*4, 29*).

Foliage samples for the fumigated test plants were collected 3 days after completion of a fumigation exposure, placed in 1-quart containers with 4 grams of Fisher "low in fluorine" lime, and shaken. The samples were dried in an oven for 24 hours at 70° C. and the dry weight was determined. The entire sample was then placed in an Inconel crucible, a slurry made with water, and the sample placed on a hot plate under infrared heat lamps. Following this partial ashing, the final ashing was accomplished in a muffle furnace at 600° C. for 30 minutes. The ash was then fused with sodium hydroxide according to the procedures of Remmert and coworkers (*25*) and Rowley, Grier, and Parsons (*27*) and the fused ash distilled from perchloric acid by slightly modified procedures previously described (*8, 31*). An aliquot of the distillate was titrated according to a modified high-salt-thorium titration (*4, 29*).

Results

Relative Rate of Foliar Uptake of Fluoride in Daylight and Darkness. Four replicated sets of fumigation specimens were exposed to atmospheres containing approximately 1.5 and 5 p.p.b. of hydrogen fluoride in daylight and in darkness. The plants exposed to the hydrogen fluoride in the dark were placed in a blacked-out greenhouse at the same time and on the same days as the comparable daylight sets. Individual plants were removed from the fumigation experiment upon observa-

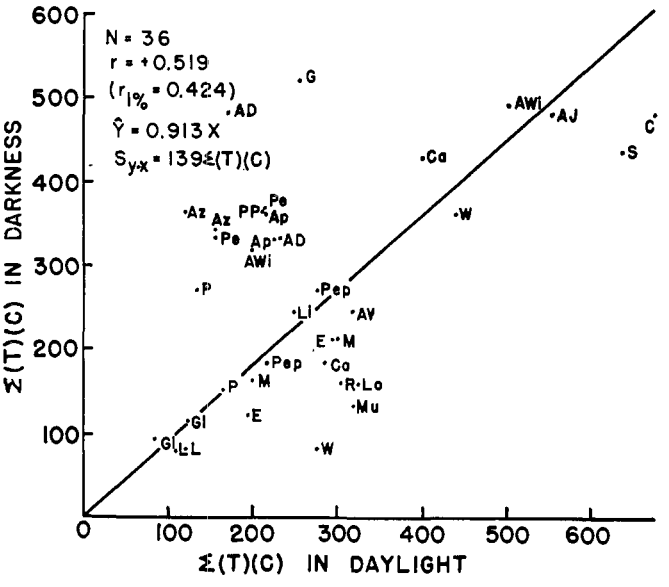

Figure 4. Correlation of visible foliar burn produced in daylight and darkness at equivalent fluoride fumigation levels

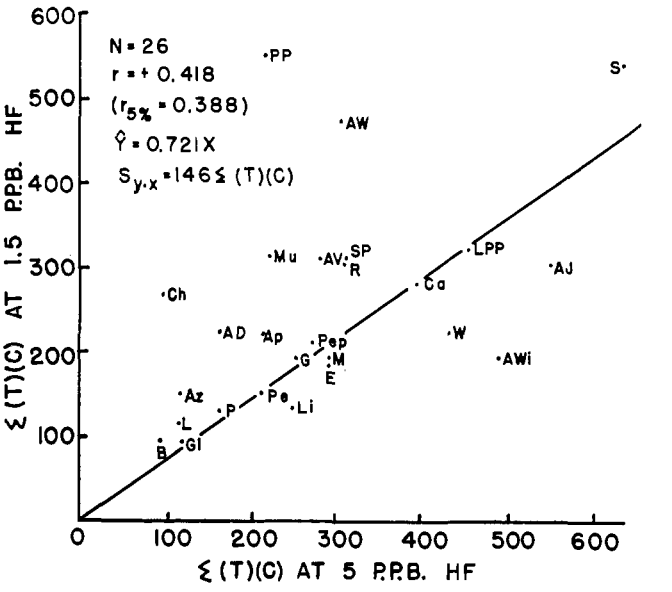

Figure 5. Correlation of visible foliar burn produced at 1.5 and 5 p.p.b. hydrogen fluoride in daylight

tion of the first symptoms of foliar fluorosis. Figure 3 is a plot of the average foliar fluoride levels in parts per million on a dry weight basis for all plants of each variety exposed to the point of visible injury in the daylight against similar levels developed in plants exposed in darkness. The slope of the regression line of the daylight foliar fluoride levels on the darkness foliar fluoride levels indicates that on the average 53.3% as much foliar fluoride was required to produce equivalent injury in darkness as in daylight. The correlation coefficient was found to be $r = +0.803$, which is in excess of that required for significance at the 1% probability level.

Relative Rate of Foliar Response of Plants in Daylight and Darkness. Correlation of the average exposure factors of the replicated fumigation specimens exposed to atmospheres containing approximately 1.5 and 5 p.p.b. of hydrogen fluoride in daylight and in darkness is shown in Figure 4. A consideration of the exposure factors, the product of the hours exposed and the fumigation concentration in parts per billion of hydrogen fluoride, indicates that plants exposed in darkness were on the average 91.3% as responsive to fluoride in the production of visible foliar injury in the darkness as in the daylight. The correlation coefficient between daylight and darkness injury indexes was found to be $r = +0.537$, which is greater than that required for significance at the 1% probability level.

Relative Rate of Response of Plants Exposed at Different Concentration Levels. Replicated sets of fumigation specimens were exposed in daylight to atmospheres containing approximately 1.5, 5, and 10 p.p.b. of hydrogen fluoride. Individual plants were removed from the fumigation experiment upon observation of the first symptoms of foliar fluorosis. Figure 5 is a plot of the average exposure factors for all plants of each variety which were exposed to the point of visible foliar burn at the 5-p.p.b. hydrogen fluoride level against the average exposure factors for plants similarly exposed at the 1.5-p.p.b. hydrogen fluoride level. The slope of the regression line of the 1.5-p.p.b. exposure level on the 5-p.p.b. level indicates that the varieties fumigated were, on the average, 73.8% as responsive to foliar fluorosis at the 5-p.p.b. level as they were at the 1.5-p.p.b. level. The correlation coefficient for this comparison was found to be $r = +0.458$, which is greater than that required for significance at the 5% probability level.

Similarly, the average exposure factors for all plants of each variety which were exposed at the 1.5- and 5-p.p.b. hydrogen fluoride levels in darkness to the point of initial appearance of visible injury were plotted aginst each other in Figure 6. The slope of the regression line of the 1.5-p.p.b. exposure level on the 5-p.p.b. level indicates that the varieties fumigated were, on the average, 70.0% as responsive to foliar fluorosis at the 5-p.p.b. level as at the 1.5-p.p.b. level. The correlation for this darkness comparison was calculated

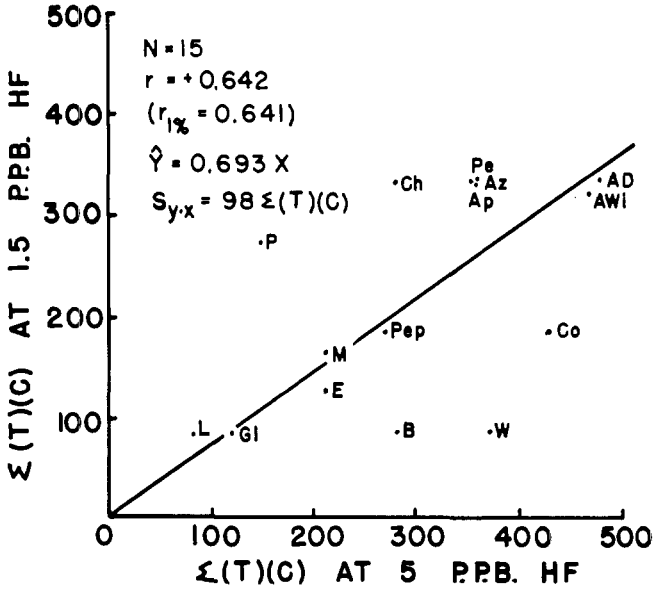

Figure 6. Correlation of visible foliar burn produced at 1.5 and 5 p.p.b. hydrogen fluoride in darkness

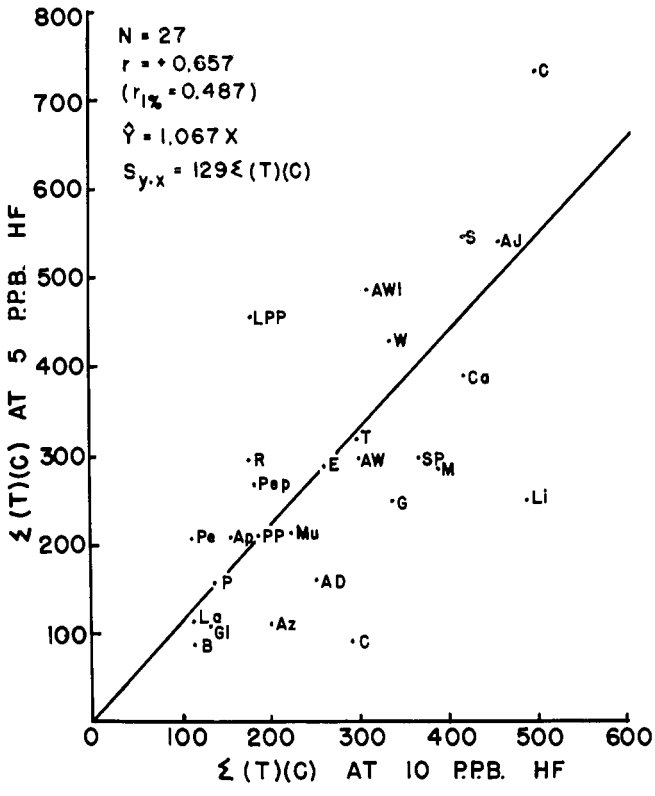

Figure 7. Correlation of visible foliar burn produced at 5 and 10 p.p.b. hydrogen fluoride in daylight

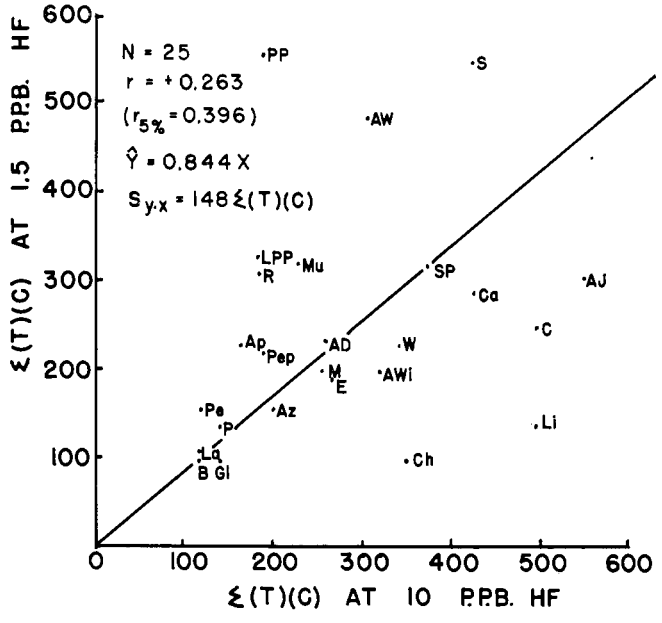

Figure 8. Correlation of visible foliar burn produced at 1.5 and 10 p.p.b. hydrogen fluoride in daylight

to be $r = +0.625$, which is greater than that required for significance at the 1% probability level.

Figure 7 shows a plot of all average exposure factors for all plants exposed to the point of initial visible injury at the 5- and 10-p.p.b. hydrogen fluoride levels in daylight. The slope of the regression line of the 5-p.p.b. level on the 10-p.p.b. level indicates that the varieties fumigated were on the average, 109.7% as responsive to foliar fluorosis at the 10-p.p.b. level as at the 5-p.p.b. level. The correlation coefficient for this daylight comparison was $r = +0.608$ which is greater than that required at the 1% probability level.

Figure 8 is a comparison of the relationship between the average exposure factors for all plants of each variety fumigated to the point of initial foliar fluorosis at the 1.5- and 10-p.p.b. hydrogen fluoride levels in daylight. The slope of the regression line of the 1.5-p.p.b. level on the 10-p.p.b. level indicates that the varieties fumigated were, on the average, 78.6% more responsive at the 10-p.p.b. level as at the 1.5-p.p.b. level. The correlation coefficient for the comparison was calculated to be $r = +0.468$, which is greater than that required for significance at the 5% probability level.

Table II. Correlation Coefficients of Exposure Factors vs. Foliar Fluorine Content by Family

		Daylight Exposure			Darkness Exposure		
Family Name	*Common Names*	*N*	*r*	*Significance level*	*N*	*r*	*Significance level*
All plants exposed		266	0.373	[a]	70	0.125	[b]
Ericaceae	Blueberry Laurel Rhododendron	25	0.030	[b]	3	0.750	[b]
Leguminoseae	Alfalfa Locust Sweet pea	18	0.138	[b]	4	0.778	[b]
Pinaceae	Douglas fir Grand fir Hemlock Lodgepole pine Ponderosa pine Spruce White pine	59	0.013	[b]	15	−0.184	
Rosaceae	Apple (4 var.) Apricot Cherry Peach Prune Raspberry Rose	77	0.709	[a]	18	0.256	[b]
Solanaceae	Tomato Petunia	15	0.321	[b]	5	0.393	[b]
Umbelliferae	Carrots Parsnips	17	0.050	[b]	7	0.743	[c]

[a] Significant at 1% probability level.
[b] Not significant at 5% probability level.
[c] Significant at 5% probability level.

Correlation of Exposure Factor with Foliar Fluoride Content. Five replicated sets of specimens were exposed, respectively, to atmospheres of 1.5, 5, and 10 p.p.b. of hydrogen fluoride in daylight and 1.5 and 5 p.p.b. of hydrogen fluoride in darkness. The correlation coefficient of the foliar fluoride content of all varieties of plants exposed in daylight at the three different atmospheric fluoride levels against their exposure factors was found to be $r = +0.373$, which is greater than that required for significance at the 1% probability level.

The correlation coefficient for foliar fluoride content of all varieties of plants exposed *vs.* their exposure factors for all darkness exposures was calculated to be $r = +0.125$. The correlation coefficient required for significance at

the 5% probability level for $N = 70$ is $r = 0.232$.

The correlation coefficients of the foliar fluoride content for all plants from each family have been calculated individually and are indicated in Table II. With the exception of the members of the family Rosaceae, the correlations of foliar fluoride content *vs.* exposure factor were of relatively low statistical significance. Even in the case of the family Rosaceae, removal of the large number of individual apple values from the consideration (the genus *Prunus*) produced a marked drop in statistical significance in relationship between foliar fluoride content and exposure factor. This change may also be attributed to the variations in response of the remaining members of this family to foliar fluorosis—i.e., apricot and prune are extremely sensitive, while cherry and rose are resistant to foliar fluoride burn. Other families showing low correlation between foliar fluoride content and exposure factor include Pinaceae, Ericaceae, and Umbelliferae, all of which include varieties which are widely separated on a "scale of relative fluoride sensitivity."

Table III. Correlation Coefficients of Exposure Factors vs. Foliar Fluoride Content by Genus

Genus Name	Common Name	Daylight Exposure N	Daylight Exposure r	Daylight Exposure Significance level	Darkness Exposure N	Darkness Exposure r	Darkness Exposure Significance level
Pinus	Lodgepole pine Ponderosa pine White pine	22	0.478	[a]	5	−0.269	[b]
Prunus	Apricot Cherry Peach Prune	29	0.268	[b]	8	0.413	[b]

[a] Significant at 5% probability level.
[b] Not significant at 5% probability level.

The correlation coefficients for foliar fluoride content *vs.* exposure factors for all plants exposed within each genus are listed in Table III. By decreasing the number of varieties considered for each correlation, some increase in significance of these measurements is attained—viz., through elimination of most of the extremely resistant members of the family Pinaceae, the correlation coefficient calculated for the members of the genus *Pinus* was increased to $r = +0.487$, which is significant at the 5% probability level where $N = 22$.

Table IV indicates the correlation coefficients for the foliar fluoride content *vs.* exposure factors for all plants exposed when classified according to species. Two effects are noted as the consideration of correlation coefficients is made by narrowing the classification from family to genus to species. In the case of species which are represented by larger numbers of plants in the fumi-

Table IV. Correlation Coefficients of Exposure Factors vs. Foliar Fluoride Content by Species

Genus and Species		Common Name	Daylight Exposure N	Daylight Exposure r	Daylight Exposure Significance r	Darkness Exposure N	Darkness Exposure r	Darkness Exposure Significance level
Morus	*alba*	Mulberry	6	0.100	[a]	2		
Prunus	*armeniaca*	Apricot	7	0.027	[a]	2		
Salix	*aurea*	Willow	7	0.946	[b]	2		
Prunus	*avium*	Cherry	8	0.580	[a]			
Daucus	*carota*	Carrots	6	0.116	[a]	4	0.615	[a]
Vaccinium	*carymbosum*	Blueberry	8	0.369	[a]	2		
Pinus	*contorta*	Lodgepole pine	8	0.357	[a]	2		
Rosa	*bilecta*	Rose	8	0.910	[b]	2		
Picea	*engelmannii*	Engleman spruce	6	−0.154	[a]	2		
Lycopersiocon	*esculentum*	Tomato	6	0.021	[a]	2		
Abies	*grandis*	Grand fir	8	0.889	[b]	2		
Tsuga	*heterophylla*	Hemlock	3	0.870	[c]	0		
Gladiolus	*hortulanus*	Gladiolus	6	0.023	[a]	2		
Prunus	*hortulania*	Prune	7	0.396	[a]			
Petunia	*hybrida*	Petunia	9	0.594	[a]	3		
Rubus	*idaeus*	Raspberry	7	0.274	[a]	2		
Kalmia	*latifolia*	Laurel	7	0.108	[a]	2		
Curcubita	*maxima*	Squash	5	−0.628	[a]	1		
Zea	*mays*	Corn	5	0.869	[c]	1		
Pinus	*monticola*	White pine	7	0.105	[a]	2		
Piper	*nigrum*	Pepper	7	0.266	[a]	3		
Larix	*occidentalis*	Larch	6	−0.759	[a]	2		
Lathyrus	*ordoratus*	Sweet pea	6	0.637	[a]	2		
Thuja	*orientalis*	Arbor vitae	7	0.368	[a]	2		
Ulmus	*oumila*	Elm	2					
Prunus	*Persica*	Peach	7	0.018	[a]	2		
Acer	*plamatum*	Maple	4	0.377	[a]	1		
Pinus	*ponderosa*	Ponderosa pine	7	0.138	[a]	2		
Robinia	*pseudoacicia*	Locust	7	0.136	[a]	0		
Medicago	*sativa*	Alfalfa	5	0.870	[b]			
Pastinaca	*sativa*	Parsnips	11	0.791	[b]	3		
Malus	*sylvestris*	Red delicious apple Red Jonathan apple Wealthy apple Winesap apple	31	0.715	[b]	8	0.465	[a]
Pseudotsuga	*taxifolia*	Douglas fir	7	−0.328	[a]	2		
Vitis	*vinifera*	Grape	7	0.146	[a]	2		
Syringa	*vulgaris*	Lilac	6	0.213	[a]	2		
Rhodendron		Rhododendron	8	0.343	[a]	2		

[a] Not significant at 5% probability level.
[b] Significant at 1% probability level.
[c] Significant at 5% probability level.

gation exposures—such as apples, Figure 9—there was an increase in the significance of the calculated correlation coefficients. In many of the species in which N was less than 10, correlation coefficients were of less significance than the correlation coefficients obtained in the corresponding genus or family considerations.

Average Exposure Factors and Foliar Fluoride Levels. The data developed through the replicated exposure of approximately 40 different species and/or varieties of plants to three levels of hydrogen fluoride gas under conditions of daylight and darkness have been compiled in Table V. This table records the average exposure factor and average fluoride level in the tissue of plants exposed under the five different fumigation conditions to the point of foliar injury and for those plants for which fumigation was discontinued before the production of visible symptoms.

Discussion

The relationship which was obtained between the foliar fluoride levels in plants exposed to the point of initial injury in daylight and the fluoride levels associated with plants similarly exposed in darkness would tend to indicate that

Table V. Average Exposure Factors and Foliar Fluoride Concentrations Developed at Several Hydrogen Fluoride Fumigation Levels

	Daylight Exposure									Darkness Exposure					
	Fumigation Level														
	1.5 p.p.b.			5 p.p.b.			10 p.p.b.			1.5 p.p.b.			5 p.p.b.		
Common Name	Σ(T)(C)[a]	p.p.m.[b]	Injury[c]	Σ(T)(C)	p.p.m. F	Injury	Σ(T)(C)	p.p.m. F	Injury	Σ(T)(C)	p.p.m. F.	Injury	Σ(T)(C)	p.p.m. F	Injury
Alfalfa	356	149	...	506	203	...	506	182	...	250	25	...	522	132	...
Apple, Delicious	230	183	X	165	112	X	258	142	X	336	72	X	486	106	X
	234	49	...												
Apple, Jonathan	301	143	X	548	259	X	461	194	X	362	48	...	486	79	X
Apple, Wealthy	480	234	X	304	173	X									
	202	74	...							362	35	...	522	37	...
Apple, Winesap	196	153	X	494	204	X	319	152	X				486	133	X
	271	97	...							321	44	...			
Apricot, Morpark	225	58	X	213	83	X	163	107	X	336	130	X	368	84	X
Arbor vitae	318	138	X	286	104	X									
	225	76	...				501	60	...	250	38	...	522	59	...
Blueberry	97	53	X	92	72	X	118	64	X	82	34	X	288	103	X
Carrots	284	323	X	398	723	X	425	307	X	188	250	X	430	309	X
Cherry	275	62	X	98	53	X	350	126	X	336	51	X	288	51	X
Corn				747	178	X	496	47	X						
	592	151	...	695	133	...	506	85	...				367	99	...
Douglas fir	168	238	...	340	200	...	317	212	...	214	102	...	358	103	...
Elm	192	265	X				261	160	X	124	18	X	216	72	X
Englemen spruce	282	80	...	310	245	...	372	149	...				370	31	...
				358	210	X				163	57	X			
Gladiolus	97	37	X	119	46	X	137	57	X	82	59	X	122	44	X
Grand fir	252	71	...	375	155	...	384	140	...	214	43	...	370	41	...
Grape				252	138	X	344	122	X				522	84	X
	592	117	..							362	51	...			
Hemlock				292	133	..									
Larch	107	53	X	119	147	X	118	106	X	82	62	X	83	73	X
Laurel	262	35	...	346	42	...	501	58	...	188	34	...	400	21	..
Lilac	138	123	X	248	216	X							245	138	X
	381	267	...	381	230	...	506	123	...	250	116	...			
Locust	212	113	...	505	153	...	501	80	...						
Lodgepole pine	325	39	X	460	73	X	181	70	X				522	32	...
	234	26	..				506	106	...				216	55	X
Maple				297	209	X									
	225	80	...				397	129	...						
Mulberry	319	273	X	203	213	X				139	122	X			
	177	129	..	422	144	..							358	128	...
Parsnip							312	172	X						
	315	177	...	433	479	...	401	208	...	214	218	...	466	146	...
Peach	151	92	X	213	89	X	118	94	X	336	54	X	368	101	X
Pepper	218	149	X	274	203	X	188	244	X	188	136	X			
							401	154	...						
Petunia	315	84	...	433	362	...	399	148	...	214	66	...	466	273	...
Ponderosa pine	551	83	X	213	72	X	187	80	X				368	54	X
	271	46	...							362	19	...			
Prune	132	64	X	165	90	X	140	107	X	272	42	X	152	60	X
Raspberry	306	243	X	306	216	X	183	162	X	163	88	X			
				438	176	...							320	104	...
Rhododendron				360	85	X									
	277	44	...				351	30	...	250	45	...			
Rose	346	120	...	646	244	...	500	176	...	362	80	...	522	61	...
Squash				631	134	X	421	179	X						
				695	85	...	496	99	...	362	114	...			
Sweet pea	313	327	X	307	148	X	374	141	X						
				422	118	...							430	144	...
Tomato				327	278	X	302	207	X						
	442	231	...	551	291	...	506	171	...	250	247	...	522	123	...
White pine	202	70	...	665	138	...	496	67	...	367	136	...			
							109	41	X				83	73	X
Willow	227	144	X	438	271	X	340	270	X	82	65	X	368	98	X

[a] Exposure factor is product of hours of exposure times atmospheric concentration in p.p.b. HF.
[b] Fluoride concentration in exposed leaves on dry weight basis.
[c] X. Plant removed from fumigation upon initial observance of foliar burn.
... No visible burn upon completion of fumigation.

plants are generally more susceptible to foliar fluorosis when exposed to the hydrogen fluoride fumigant in darkness. Application of the concept of exposure factor to the study of the relative susceptibility of plants to hydrogen fluoride in daylight and darkness, however, indicates that a longer exposure at equivalent fumigation levels is required to produce the observed injury under the experimental conditions employed. Consideration of two concepts, foliar fluoride levels and exposure factors, shows that although the plant tends to develop foliar fluorosis at lower tissue-fluoride levels in the darkness than in daylight, they are, on the average, absorbing or metabolizing fluoride approximately twice as rapidly in daylight as in darkness under comparable conditions of temperature and humidity.

Field conditions in many areas of fluoride pollution normally associate conditions of lower temperature and higher humidity with the hours of darkness. The effect of these variables upon the relative susceptibility of plants to hydrogen fluoride in daylight and darkness should be considered before final conclusions are drawn regarding the relative susceptibility of field grown plants to hydrogen fluoride in the day and night.

Comparison of the rate of foliar response of plants under conditions of 1.5 p.p.b. daily exposure to hydrogen fluoride gas and twice-weekly exposure at 5 and 10 p.p.b. tends to indicate that plants exposed more frequently to the minimum level employed developed foliar fluorosis at lower total exposures (exposure factors) than did plants exposed twice weekly at the 5- and 10-p.p.b. levels. This variation in plant response which was observed both in daylight and darkness between the 1.5-, and 5- and 10-p.p.b. fumigation levels suggested the possibility of the existence of innate powers of recuperation within the plant structure which influence the rate at which foliar fluorosis develops.

In this study of the relative susceptibility of plants to foliar fluorosis, it is suggested that the exposure factor associated with the incidence of leaf injury is a more accurate criterion of susceptibility than is the foliar fluoride level associated with the injury. The exposure factor is a measure of the rate of absorption of atmospheric fluorides to the threshold of injury level and is therefore more important in the study of relative susceptibility than is the actual threshold foliar-fluoride level associated with the production of the visible injury.

Previously reported work (*3, 6, 7*) has indicated that higher levels of foliar fluorides were required to produce foliar injury when the first fumigation exposures were begun after the leaves had matured for a portion of the growing season. The data herein reported were developed for fumigation experiments which were begun on July 27 and continued until mid-September, at which time all exposures were concluded regardless of whether foliar injury had been produced. Fluoride levels producing foliar fluorosis as reported in Table V were those levels required to produce injury in leaves which were 2 to 3 months old when first exposed and were over 5 months old in the cases of plants removed from fumigation in September. Since the levels reported were those producing injury on mature leaves, these data cannot be considered to furnish a suitable criterion for conclusions regarding the fluoride-tolerance levels of these species which might be observed under field conditions where exposures to fluoride-containing gases might take place much earlier in the leaf maturing process.

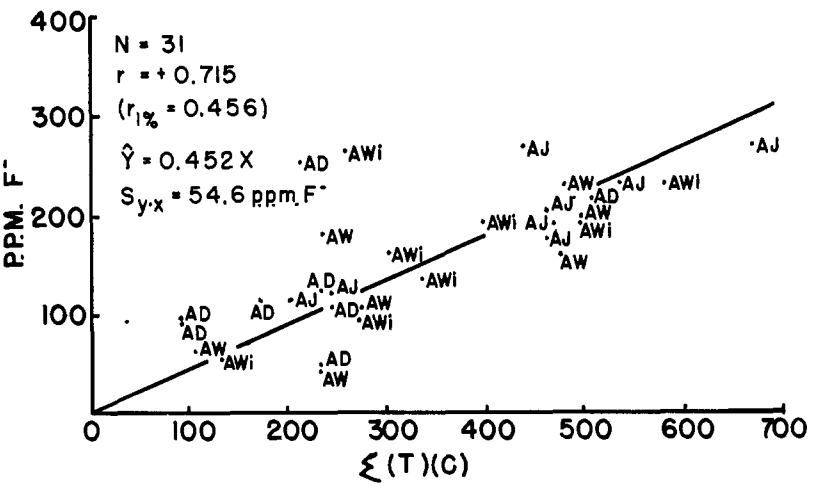

Figure 9. Correlation of foliar fluoride content with exposure factor for apples

Conclusions

The fumigation-exposure intensity for a given fumigation sequence has been defined as an "exposure factor." This term is an empirical value defined as the sum of the products of each daily total exposure in hours and each average daily atmospheric concentration in parts per billion of hydrogen fluoride and is a measure of the rate at which an exposed plant is accumulating fluoride toward the threshold of visible injury level.

Replicated sets of plants representing 40 different varieties, including 34 species, exposed to two levels of atmospheric fluoride were found to be on the average 91.3% as sensitive to foliar fluoride burn in darkness as in daylight.

Replicated sets of plants exposed to three levels of atmospheric fluoride in daylight and two levels in darkness exhibited greater response to fluoride when fumigated daily for 8 hours at 1.5 p.p.b. of hydrogen fluoride than when fumigated either 8 hours every third day at 5 p.p.b. of hydrogen fluoride or 4 hours every third day at 10 p.p.b. of hydrogen fluoride. Plants exposed at 5 p.p.b. of hydrogen fluoride were almost as responsive to the fumigant as were the plants exposed at the 10-p.p.b. hydrogen fluoride level. It is postulated that plants exposed at the higher levels every third day had an opportunity to attain a measure of recovery from the effects of each fumigation during the 2 days following each exposure. Plants exposed at the lowest level on a daily basis had less opportunity to recover between fumigations.

The obtained correlation coefficients of exposure factor *vs.* foliar fluoride content for the fumigation of all exposed plants at three atmospheric fluoride levels and in daylight and darkness were generally found to increase in significance as the plant classifications were narrowed from family to genus to species.

The threshold levels for the production of foliar injury herein reported cannot be considered the minimum toxic levels for these species as the leaves of the exposed plants had matured for 2 to 3 months prior to initial exposure to hydrogen fluoride gas. These conditions are not comparable to field conditions wherein leaves may be exposed to fluoride-containing effluents at any time following their initial emergence from the bud. Leaves in the immature partially expanded condition have previously shown to be more susceptible to foliar fluorosis than mature leaves.

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Received for review September 15, 1954. Accepted October 16, 1956. Presented in part before the Air Pollution Symposium, Division of Water Sewage and Sanitation, 126th meeting, ACS, New York, September 1954. Scientific Paper R Series No. 44 Washington State Institute of Technology, Project 108, Scientific Paper No. 1564 Washington Agricultural Experiment Stations. Project No. 1322.

FUNGICIDES

Toxic Action of Metal Ions to Fungus Spores

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Quantitative studies have been carried out on the interactions between metal ions and spores of representative fungi. Silver is taken up rapidly by fungus spores, so that germination can be completely inhibited after a contact time of 1 minute or less. Only mercury(I) and (II), and to a lesser extent copper, offer serious competition. The toxicity of silver is unaffected by chloride, but reduced by bromide, and prevented by iodide. Silver has a marked effect on the permeability of spores as measured by the outward movement of phosphorus compounds from cells labeled with phosphorus-32. Copper, zinc, and cadmium reduce germination appreciably only after some hours of contact with the spores. About 75% of the zinc content of spores grown in the presence of zinc-65 is exchanged with nonradioactive zinc within 10 minutes. Materials move inward and outward more readily with fungus spores than was supposed.

METAL IONS have long been of interest because of their fungicidal properties. Copper and mercury are important commercially as components of fungicidal preparations and zinc, cadmium, and silver have either found commercial use or been extensively investigated in laboratory studies.

Laboratory evaluations of the toxicity of metal ions have been concerned chiefly with effects on the germination of fungus spores and prevention of the growth of mycelium on agar plates. Comparisons of toxicity have usually been based on the concentrations in the media required to bring about a certain response. No information is obtained by these procedures on the innate toxicity of the materials, because the quantities required by the spores or mycelium remain unknown.

In these studies toxicity has been expressed, whenever possible, on a spore-weight. The ions investigated differ markedly in their toxicity and in the speed with which they act when brought into contact with spores. There are also