Application of Calcium Sprays for the Protection of Citrus from Atmospheric Fluorides

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Abstract. Bearing 'Valencia' orange trees growing in a commercial orchard adjacent to a known source of fluoride air pollution were sprayed periodically over a 3-year period with $Ca(OH)_2$ and $CaCl_2$ sprays. These materials in spray and dust forms have been used successfully in the Pacific Northwest to protect gladiolus and peaches from the harmful effects of fluoride-containing atmospheres. It has been postulated that calcium reacts with fluoride gases to produce insoluble and therefore nontoxic CaF_2.

Results of these studies indicated that under conditions of high fluoride air pollution, application of lime sprays may improve citrus fruit production, but the mechanism of protection or improvement was not as simple as previously postulated. Immediately adjacent to the source where fluoride air pollution was at a maximum, applications of both $Ca(OH)_2$ and $CaCl_2$ were associated with increased internal fluoride accumulation by 'Valencia' orange foliage. With increased distance and therefore diminishing air pollution, an apparent reversal in effect was observed with the calcium sprays resulting in reduced internal accumulation of fluoride.

Although the effects of $CaCl_2$ sprays on fluoride accumulation closely paralleled those obtained with $Ca(OH)_2$, fruit production was not improved where $CaCl_2$ sprays were applied, possibly as a result of induced chloride toxicity.

INTRODUCTION

Fluoride air pollution damage to ornamental and agricultural crops is a common and often serious problem in areas adjacent to industries which heat fluorine-containing fuels or ores to high temperatures. Aluminum reduction, steel and phosphate manufacture and ceramics production are examples of fluoride-emitting industries.

Young citrus foliage, when repeatedly exposed to atmospheres containing 1 or 2 parts gaseous fluoride per billion parts air, will gradually accumulate 100 to 200 parts per million F on a dry weight basis. Toxicity symptoms commonly associated with excess fluoride accumulation in citrus include interveinal and marginal chlorosis leading to marginal necrosis under extreme conditions, smaller leaf size and reduced fruit production (3, 4).

Lime sprays have been found very effective in preventing fluoride damage to gladiolus (1), pine trees (7) and peach fruit (2). The protection afforded by the lime was ascribed to the formation of insoluble CaF_2 on the surface of the leaf. As a result of spray trials with peaches, Benson (2) suggested that increased internal Ca content of peach tissue might also be involved. He also found $CaCl_2$ sprays as effective if not more effective than lime sprays or dusts for protecting sensitive peach varieties against fluoride-induced soft suture, a physiological disorder of peach fruits.

Attempts by Leonard and Graves[2] to reduce fluoride-induced chlorosis on citrus foliage in the field in Florida through the use of lime sprays have met with only partial success. Significant regreening was achieved only when a mixture containing manganese sulfate and urea, as well as hydrated lime, was applied to the citrus foliage and this treatment was followed by a prolonged dry period. Effects of these treatments on tree growth or fruit yields were not reported by the Florida workers.

Beginning in 1960 and continuing to the present, various materials and techniques of application have been tested under both field and greenhouse conditions in California in an attempt to find an effective means of preventing fluoride accumulation in citrus foliage and thereby reducing fluoride damage. This paper describes the results of a spray trial under field conditions.

MATERIALS AND METHODS

Beginning in March, 1960, and continuing until October of 1963, $Ca(OH)_2$ and $CaCl_2$ sprays were applied at 72 bearing 'Valencia' orange trees situated ¼ to ¾ mile downwind from tile and brick kilns near El Cerrito, California. Half of the trees (nine 4-tree plots) were sprayed twice monthly from March 1 until October and once per month during the remainder of the year with lime spray containing 5 lb. $Ca(OH)_2$ per 100 gal of water. An equal number of trees were sprayed on the same dates with a solution containing 2.5 lb $CaCl_2$ per 100 gal. Eight ounces of 'Tide' detergent were added as a wetting agent to each 100 gal of spray solution. An additional 36 trees in the same area, but separated from the sprayed trees by at least one guard tree, were selected as controls and were sprayed with detergent only in the same tap water used in making up the lime and $CaCl_2$ spray solutions.

Spring cycle leaves collected before each spraying were analyzed for fluoride content using a modification (4, 5) of the classic Willard-Winter (9) steam distillation technique for separating the F from interfering substances. The separated F was titrated with standard thorium nitrate in the presence of Chrome Azurol S indicator. Prior to analysis, all of the leaves were washed with Ivory soap, rinsed briefly first in 0.3*N* HCl, then in distilled water, wiped dry with cloth toweling, and ground while fresh in a domestic type food grinder. The freshly ground green leaves were quick frozen and stored at −10° F in a deep freeze prior to analysis.

Fruit production data for each of the 108 trees used in this experiment were recorded for crops picked in June 1960, 1961, and 1963. In the Spring of 1962, the orchard was pruned so severely that most of the year's crop was lost. In the Fall of 1963, most of the trees used in these trials were

Table 1. Fruit production in field boxes per tree for field-grown 'Valencia' orange trees sprayed with calcium hydroxide (A), calcium chloride (B), and tap water (C).

Treatment blocks	Distance from kiln	Boxes of fruit per tree[y]								
		1960			1961			1963		
		A	B	C	A	B	C	A	B	C
A, B, C.......	¼ mile	2.06	2.16	2.10	2.62	1.56	1.92	1.39	1.33	1.27
D, E, F.......	½ mile	2.77	2.64	2.69	3.70	2.41	2.81	1.94	1.46	1.79
G, H, I.......	¾ mile	2.81	2.73	2.98	3.39	2.66	3.13	1.70	1.94	2.33
Treatment mean—all blocks[x] . .		2.55_{ns}	2.51_{ns}	2.59_{ns}	3.24_a	2.21_b	2.62_b	1.68_{ns}	1.58_{ns}	1.79_{ns}

[y] Values which do not share the subscript letters a, b, and c are significantly different at the 5% level of probability using Snedecor's (8) multiple range test of mean differences; ns—not significant.

[x] There was no crop in 1962.

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[1] Department of Soils and Plant Nutrition and Statewide Air Pollution Research Center.

[2] Leonard, C. D. and H. B. Graves, Jr., 1965. Final report, air pollution research at the Florida Citrus Experiment Station, August 1962–August 1965. *Univ. of Fla. Citrus Exp. Sta. Mimeo.*

removed, thereby ending the experiment. The reduction in level of fluoride air pollution in this orchard during the course of this experiment was due to modifications in kiln processing methods and the substitution of clays of lower F content.

Results and Discussion

No significant effects of the lime or calcium chloride treatments were observed when the 1960 crop was harvested in June, 1960. Approximately 15 months are required in southern California between 'Valencia' fruit set and maturity. The 1960 crop, therefore, had been on the trees nearly a year when the spray treatments were begun in March, 1960. In 1961, there was a significant increase in fruit production associated with the lime spray treatment but no significant response to the $CaCl_2$ sprays (Table 1). Although the yield differences were not statistically significant at the 5% level, there was a trend towards reduced fruit production where $CaCl_2$ was applied. The 1962 crop was lost when the orchard was pruned back severely to make room for newly interplanted young trees. In 1963, the fruit crop was comparatively light and there was no significant influence of the spray treatments on fruit production. By this time, however, the general level of fluoride air pollution in the area as indicated by accumulation in citrus foliage (Table 2) was only one-fourth the prevailing level in 1960.

Table 2 contains mean maximum fluoride analysis data for spring cycle 'Valencia' orange leaves receiving the 3 different spray treatments. Since the foliage was thoroughly washed with soap and then rinsed in dilute HCl previous to analysis, these concentrations represent only the internal or absorbed fluoride content. Unwashed leaves contained twice as much F as washed leaves. Rinsing briefly with dilute HCl solution removed an additional 20 to 30% of the fluoride present in unwashed samples.

The most surprising result of these treatments was the general increase rather than decrease in fluoride content of the citrus leaves sprayed with $Ca(OH)_2$ or $CaCl_2$. Only when the level of pollution was sufficiently low to produce an accumulation of less than 70 ppm fluoride in untreated or water-sprayed control foliage was the lime spray treatment effective in reducing fluoride uptake. Calcium chloride sprayed trees accumulated the most F at higher F levels but were essentially equal to the controls in this respect at lower levels of pollution. Comparison of fruit yields and fluoride contents of foliage from water-sprayed control trees and unsprayed adjacent guard trees indicated that the control treatment had no measurable effect on fruit production or fluoride accumulation. None of the treatments had a significant effect on fruit quality criteria—size of fruit, citric acid, specific gravity, vitamin C or juice content.

Calcium content of sprayed and unsprayed foliage (Table 3) failed to establish any straightforward relationship between the treatments and internal calcium content. Apparently very little of the calcium applied to the surface as $Ca(OH)_2$ or $CaCl_2$ found its way to the interior of the citrus leaf. This would cast doubt on the importance of the internal precipitation mechanism as proposed by Benson (2) in this instance.

In many respects, the results obtained in this experiment agree with those obtained by Benson (2) working with peaches. Citrus, unlike peaches, however, responded more favorably to lime than to calcium chloride.

Although frequent applications of lime sprays substantially increased 'Valencia' fruit production in an orchard subjected to rather severe fluoride air pollution, the mechanism of protection or improvement is not apparent from the data obtained. At high levels of fluoride air pollution, application of lime sprays increased fluoride accumulation but improved yields. At lower levels of pollution, lime sprays decreased fluoride uptake but had no significant influence on fruit production. This seems to rule out the possibility of lime sprays having a beneficial effect not related to fluoride accumulation. The fact that total calcium content of citrus foliage was not appreciably influenced by the calcium spray treatments also confuses the picture. It may be that high levels of fluoride accumulation in the absence of added lime internally fixes sufficient calcium to interfere with normal growth and fruit production. The fact that fluoride toxicity symptoms on citrus are not unlike calcium deficiency symptoms would support this possibility. Several attempts to demonstrate that water-soluble calcium contents are associated with fluoride accumulation have not been successful to date.

The fact that $CaCl_2$ sprays had approximately the same effects as $Ca(OH)_2$ on fluoride accumulation but did not improve fruit production is probably due to the potential toxicity of absorbed chloride ion on citrus growth and production. Citrus is relatively sensitive to chloride ion, especially when dilute chloride salts are applied to the foliage. Harding and co-workers (6) have observed considerable foliage damage on citrus trees wetted repeatedly by low-head-type sprinklers.

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Table 2. Maximum fluoride content of spring cycle foliage collected from 'Valencia' orange trees growing near brick and tile kilns. $Ca(OH)_2$ (A), $CaCl_2$ (B), and tap water (C) sprays were applied twice monthly beginning March 1, 1960. All concentrations are expressed in parts per million on a dry weight basis.

Treatment blocks	Distance from nearest kiln[a]	Fluoride content (ppm)											
		1960			1961			1962			1963		
		A	B	C	A	B	C	A	B	C	A	B	C
A, B, C	¼ mile	284	306	204	126	135	93	87	92	76	34	49	61
D, E, F	½ mile	201	242	178	107	106	88	74	81	70	27	44	42
G, H, I	¾ mile	190	199	128	33	40	44	33	39	41	17	33	35

[a] A second kiln devoted to tile pipe manufacture was located ¼ mile distant from the brick kiln.

Table 3. Calcium content of 'Valencia' orange foliage sprayed with lime, calicum chloride, or tap water.

Spray treatment	Calcium content of foliage (%)
5 lb. $Ca(OH)_2$/100 gal	2.41
2.5 lb. $CaCl_2$/100 gal	1.98
H_2O only	2.30

Rest Intensity of Dormant Peach and Apricot Leaf Buds as Influenced By Temperature, Cold Hardiness and Respiration[1]

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Abstract. A bell shaped, rest-intensity curve as a function of time was obtained for 'Elberta' peach and 'Chinese' apricot leaf buds growing in the field. Rest was not closely associated with fluctuating environmental temperatures, cold hardiness, or rate of respiration.

Apricot leaf buds reached the peak of their rest before peach leaf buds, and it was not as intense or as deep as it was with the peach buds. Rest was completed by both species at the same time in early January.

INTRODUCTION

THROUGHOUT the world, growers of deciduous fruit may experience crop failures because of an unusually warm winter, a severely cold winter, or intermittent warm and cold weather during the winter. A warm winter may result in an incomplete rest period, thus prolonging dormancy in the spring, and causing trees neither to leaf out nor to grow properly (7). Conversely, severe cold temperatures may kill the flower buds or even the tree. Growers try to avoid such winter conditions by proper site selection, but nevertheless, most deciduous fruit tree plantings are threatened almost every year by cold weather in the spring, particularly when the temperatures have alternated widely between warm and cold. Tree growth is minimal during the rest period regardless of the environmental temperatures, so they can withstand relatively severe cold until the rest period is completed in mid-winter. Subsequently, however, growth may occur during warm periods resulting in killing of buds if the temperature then reverts to below the critical level.

The purpose of this study was to learn more about the rest period. Trees have been referred to as being in deep rest, but whether or not rest intensity actually changes with the duration of the resting period has not been determined, to our knowledge. In addition to measuring intensity of rest, a second objective was to observe the cold hardiness level and rate of respiration as influenced by the tree being in or out of rest.

MATERIALS AND METHODS

Dormant 'Gleason Elberta' peach and 'Chinese' apricot trees that were 10 and 15 years old respectively were used for this study. Eighty twigs 9 inches long of each species were collected weekly from October 6, 1966 through March 6, 1967. Each twig contained 10 to 20 leaf and flower buds. The twigs were chosen at random from each of 8 peach and 8 apricot trees. They were wrapped in moistened newspaper and placed in a polyethylene bag to avoid desiccation before use.

Rest intensity study. Twenty-four twigs each week of each species were used to study rest intensity. Preliminary experiments had shown that gibberellic acid did break the rest of peach leaf buds, but that different

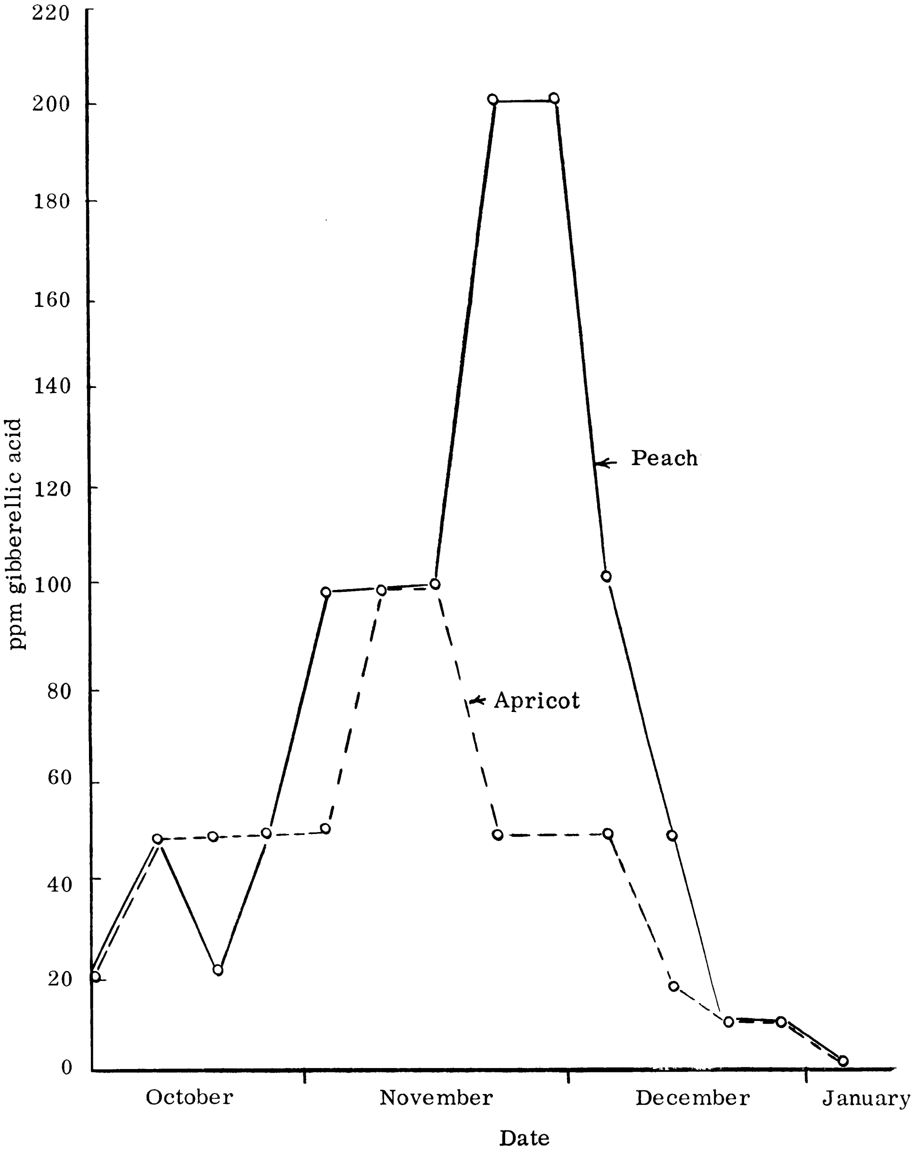

Fig. 1. The rest intensity changes of Chinese apricot and Gleason Elberta peach trees during the winter of 1966–67. Intensity was measured by the concentration of gibberellic acid needed to cause resting leaf buds to start growing.

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[1] Received for publication November 6, 1968. Published with the approval of the Director of Research as paper number 839 of the journal series.

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