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INTERACTION OF FOSETYL-ALUMINUM FUNGICIDE AND COPPER FUNGICIDES ON CITRUS FRUIT AND FOLIAGE

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Abstract. **Studies were conducted to investigate reports of phytotoxicity when citrus leaves and fruits were sprayed with combinations of fosetyl-aluminum (fosetyl-Al) (Aliette) and copper fungicide. When fosetyl-Al and any of several copper fungicides were the only components of a spray mixture, phytotoxicity symptoms developed on fruits and young leaves. When copper fungicides were applied first and fosetyl-Al applied up to 14 days later on the same young citrus leaf, phytotoxicity symptoms were present. However, the symptoms were not as severe as when the fosetyl-Al and copper fungicides were applied in the same suspension. When fosetyl-Al was applied first, phytotoxicity symptoms were greatly reduced. As pH of spray suspensions were increased with various compounds, a reduction in phytotoxicity symptoms was measured on citrus leaves sprayed with the suspensions. In laboratory studies when 0.5 lb. a.i./100 gal fosetyl-Al all the copper was detected as free Cu^{++}.**

Fosetyl-aluminum (fosetyl-Al) has been found to be an effective fungicide in reducing losses in young citrus trees to *Phytophthora* spp. (2). Copper fungicides are effective in controlling several foliar diseases of citrus and are commonly used on Florida citrus (3). Some growers reported the occurrence of leaf burn on citrus foliage and blemishes on fruit when fosetyl-Al and copper fungicides were applied in the same spray suspension. No phytotoxicity was reported when combinations of fosetyl-Al and a copper hydroxide fungicide were applied on 17 different landscape ornamentals (4). Combining fosetyl-Al and copper fungicides would reduce application costs in commercial Florida citrus operations. Blemishes of fruit by copper sprays alone is discussed by Whiteside (6).

This investigation was conducted to determine the conditions associated with phytotoxicity symptoms on citrus leaves and fruits following spray applications of suspensions containing both fosetyl-Al and copper fungicides and what measures can be taken to prevent these occurrences.

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Materials and Methods

Field studies were conducted in commercial citrus groves or in groves at the University of Florida, Institute of Food and Agricultural Sciences, Agricultural Research and Education Center, Fort Pierce, FL (AREC-Ft. Pierce).

Fosetyl-Al (Aliette 80W) was obtained from Rhone-Poulenc AG Co. Copper fungicides used in the various experiments were Tribasic copper sulfate (TBCS) (Tennessee brand tri-basic copper sulfate, Tennessee Chem. Co.); Copper hydroxide (Kocide 101, Griffin Ag Products Co., Inc.); and Copper Count-N (Mineral Research and Development Corp).

'Marsh' grapefruit trees located at AREC-Ft. Pierce, with immature fruit and recently flushed foliage, were sprayed to run-off with suspensions containing fosetyl-Al (4 lb. a.i./100 gal), TBCS (1.0 lb/100 gal), and Naco 99% miscible oil (1/2 gal/100 gal), individually or in different combinations of these three ingredients. Spray applications were made at 300 psi with a hand-held spray gun attached to a small John Bean sprayer on 9 Sep. 1986. Trees had from 3-10 recently flushed terminals each. Wind speed was minimal with partial cloud cover present until 11:15 AM. A thunderstorm at 5:30 PM provided 3.2 inches of rain on the grove. The high and low temperatures for the day were 91 and 67 F. Ratings of phytotoxicity were made 11 days after treatment on leaves and stems on the most recently flushed terminals. The rating system was: 0 = no blemishes on leaves to 3 = all leaves with heavy necrosis. Fruit blemish readings were: 0 = no blemishes to 3 = all fruit with heavy surface necrosis.

Fosetyl-Al (4 lb. a.i./100 gal), and TBCS (1.6 lb/100 gal) were applied to run-off separately on separate 'Marsh' grapefruit shoot terminals with expanded but not hardened leaves. The alternate fungicide, fosetyl-Al on TBCS-sprayed terminals or TBCS on fosetyl-Al-sprayed terminals, were applied 3, 6, 10 or 14 days after the initial spray application. Mixtures of fosetyl-Al and TBCS were applied to separate shoot terminals on the day the experiment was initiated and 3, 6, 10 and 14 days later. Water was applied to previously unsprayed shoot terminals at 0, 3, 10 and 14 days. There were 5 replicate shoot terminals on separate trees for each treatment. Shoots were rated for phytotoxicity symptoms 17 days after the experiment was initiated. The rating system used was: 1 = no blemish to 12 = severe necrosis with twig dieback.

Preliminary studies indicated that various buffering compounds including hydrated lime (CaO) and $MgCO_3$, when added to fosetyl-Al + copper compound suspensions reduced or eliminated phytotoxicity symptoms. Shoots of 'Marsh' grapefruit at the AREC-Ft. Pierce grove with recent flush and immature fruit about 2.5 inch diameter were sprayed with fosetyl-Al, 4 lb. a.i./100 gal, and copper fungicides, Kocide 101 (1 lb./100 gal), TBCS (1.4 lb./100 gal) and Copper Count-N (0.5 gal/100 gal) individually, and in combinations. Other aliquots of fosetyl-Al and copper fungicide mixtures were amended with CaO or $MgCO_3$. The suspensions were applied with a hand held sprayer to shoots and fruits. In a second, similar test, fosetyl-Al (4 lb. a.i./100 gal), Kocide 101 (4 lb./100 gal), TBCS (4 lb./100 gal) Copper Count-N (3 gal/100 gal), individually, and in mixtures of fosetyl-Al and copper compounds as well as aliquots of the fosetyl-Al and copper fungicide mixtures with hydrated lime (1 lb./100 gal) were applied to run-off. The experiment was conducted in a commercial 'Marsh' grapefruit grove near Stuart, FL. A single nozzle (SS8006), CO2-powered sprayer was used to apply suspension of the materials at 100 gal/acre rate. Suspensions were made up to simulate 100 gallons per acre concentration but were applied at about 300-500 gallons per acre rate. Conditions at the time of application were 85 F, 80% RH, and a 3 mph easterly wind. Suspensions were made up with tap water, pH 7.6. Estimates were made of percent fruit surface affected on replicate fruit clusters, percent leaf area affected and percent leaf drop. There were 3 replicates of each treatment. The data was statistically analyzed and means separated by Duncan's multiple range test.

Fosetyl-Al 4 lb. a.i., Kocide 101 4 lb. formulation and hydrated lime 1 lb. were added to 50, 100 and 200 gal of water individually and in the following combinations: fosetyl-A1 + Kocide 101 and fosetyl-Al + Kocide 101 + hydrated lime. The experiment was conducted in a commercial 'Marsh' grapefruit grove near Stuart, FL. Treatments were applied to run-off with a single nozzle CO2-powered sprayer. Data was taken as an estimate of % fruit surface blemished.

Fosetyl-Al, 4 lb. a.i./100 gal and Kocide 101, 4 lb. formulated was mixed in suspensions. Suspension pH was measured with a Fisher 13-620-83 electrode. Copper activity of the suspension was measured in millivolts with a Orion 942900 cupric ion electrode and a Orion 900200 double junction reference electrode attached to an American Scientific pH/ISE meter. Millivolt readings were converted into parts per million free cupric ion by referring to a standard curve produced with a copper standard.

Results

Phytotoxicity symptoms ranged from light brown stains to severe dark necrosis, defoliation or fruit drop when fosetyl-Al and copper compounds were combined. In most cases, phytotoxicity symptoms were more common on young leaves than on older leaves. In a few cases, no symptoms were observed on fruit with the combination.

All leaf or shoot terminal phytotoxicity ratings were made on the most recent flush. The severity of the phytotoxicity symptoms was greater when spray oil was added to the combination of fosetyl-Al and TBCS (Table 1). The phytotoxicity symptoms were more severe on leaves and fruit on the southside (sun-exposed side) of the trees.

When TBCS was sprayed onto young terminal shoots and these terminals oversprayed with fosetyl-Al 3-14 days later, phytotoxicity symptoms decreased with increase in time between the initial TBCS application and application of fosetyl-Al (Fig. 1). Little or no phytotoxicity symptoms occurred on young terminal shoots initially sprayed with fosetyl-Al and oversprayed with TBCS 3-14 days later. No phytotoxicity symptoms occurred on leaves sprayed with TBCS only, fosetyl-Al only or water only.

When fosetyl-Al and TBCS were mixed in the same suspension, pH ranged from pH 4.2 to 4.8. When 0.5 lb. a.i./100 gal basic copper sulfate was mixed in suspension with 4 lb. a.i./100 gal fosetyl-Al, cupric ion selective electrode readings indicated that all of the copper added was present as free Cu^{++}.

When CaO or $MgCO_3$, were applied with fosetyl-Al + copper fungicide mixtures, phytotoxicity symptoms on young leaves and fruits were greatly reduced or eliminated (Table 2). Hydrated lime added to mixtures of fosetyl-Al with TBCS, Kocide 101, and Copper Count N reduced or eliminated phytotoxicity symptoms in a second experiment (Table 3).

As the gallonage of water used to produce suspensions of fosetyl-Al and Kocide 101 was reduced, increasing the concentration of fosetyl-Al and Kocide 101 but not their ratio, fruit surface blemishing increased (Table 4).

Table 1. Phytotoxicity ratings on young leaves and on fruit of 'Marsh' grapefruit following treatment with Aliette, Tribasic copper sulfate or spray oil, alone or in combinations.

Treatment[z]	Phytotoxicity rating[y]	
	Leaves	Fruit
Water	0 a[x]	0 a
Tribasic copper sulfate	0 a	0 a
Oil	0 a	0 a
Aliette 80W	0 a	0 a
Aliette + oil	0 a	0 a
Aliette + TBCS	0.6 b	0.2 a
Aliette + TBCS + oil	2.0 c	0.9 b

[z]Amount of materials used per 100 gallon water: Aliette 80W, 5 lb formulated; Tribasic copper sulfate, 1.0 1b formulated; and Naco 99% miscible oil, 1/2 gal.
[y]Rating system: 0 = no blemishes on leaves to 3 = all leaves with heavy necrosis. Fruit blemish rating system 0 = no blemishes on fruit to 3 = heavy surface blemish on fruit.
[x]Mean separation in columns by Duncan's multiple range test, 5% level.

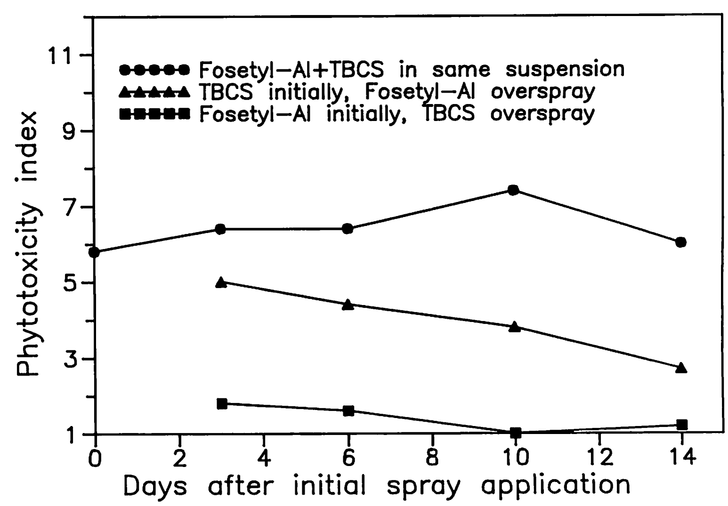

Fig. 1. Effect of combination of fosetyl-Al and basic copper sulfate combinations on terminal shoots of "Marsh" grapefruit. Fosetyl-Al + TBCS mixtures were applied on the day experiment was initiated and 3, 6, 10 or 14 days. For treatments receiving an initial TBCS application or fosetyl-Al application, a single overspray with the alternate compound was applied 3, 6, 10 or 14 days after initial application. The phytotoxicity rating system used was 1 = no blemish to 12 = leaves and stem with heavy necrosis with all leaves abscised.

Table 2. Buffering compounds effect on pH of various combinations of fosetyl-Al + copper fungicide suspensions and phytotoxicity to young citrus leaves.

Treatment[z]	pH	Phytotoxicity rating[y]	
		Leaf	Fruit
water	7.2	0 a[x]	0 a
Fosetyl-A	3.9	0 a	0 a
Kocide 101	7.0	0 a	0 a
Kocide 101 + Fosetyl-Al	4.2	6.8 cd	1.2 b
Kocide 101 + Fosetyl-Al + CaO	6.2	0 a	0 a
Kocide 101 + Fosetyl-Al + $MgCO_3$	5.2	0 a	0 a
Basic copper sulfate (BCS)	7.3	0 a	0 a
BCS + Fosetyl-Al	4.0	7.2 d	1.6 c
BCS + Fosetyl-Al + CaO	5.6	0 a	0 a
BCS + Fosetyl-Al + $MgCO_3$	5.8	0 a	0 a
Copper Count-N (CCN)	7.7	1.6 b	0 a
CCN + Fosetyl-Al	4.0	6.2 c	1.0 b
CCN + Fosetyl-Al + CaO	6.4	0.2 a	0 a
CCN + Fosetyl-Al + $MgCO_3$	5.0	0 a	0 a

[z]Amount of materials used per 100 gallon water: Aliette 80W, 5 lb formulated; Tribasic copper sulfate, 1.0 lb formulated; Kocide 101, 1.0 lb; Copper Count-N, 0.5 gal; CaO, 2.2 lb; and $MgCO_3$, 2.2 lb.
[y]Leaf phytotoxicity rating system: 0 = no blemish to 10 = severe injury with twig dieback. Fruit phytotoxicity rating system: 0 = no blemish to 10 = fruit with heavy necrosis.
[x]Mean separation in columns by Duncan's multiple range test, 5% level.

Discussion

Phytotoxicity symptoms were observed on fruit and young citrus leaves in most cases when fosetyl-Al and copper fungicides were applied in the same spray suspension. The extent of phytotoxicity was about the same for combinations of fosetyl-Al with several common copper-containing fungicides used to control fungal diseases in citrus. Several small scale tests not reported above showed a similar but less severe response when fosetyl-Al and various nutrient mixes containing copper were applied together.

Laboratory studies showed that the combination of fosetyl-Al and copper fungicides released large amounts of free Cu^{++} ions. Free Cu^{++} ions are generally regarded as the active copper form involved in various biological activities (5). The release of free Cu^{++} ions appears to be a pH affect. When copper fungicides were alone in suspension, the pH ranged from about pH 7.0 to 8.5. When fosetyl-Al was added, the pH of the combinations ranged between pH 4.0 and 5.0, where most copper compounds are readily soluble. The detection of large amounts of free $Cu++$ in these combination suspensions, with the copper electrode indicates that fosetyl-Al does not complex Cu^{++}.

Table 3. Effect of Fosetyl-Al and copper fungicides and combinations on fruit and leaves of 'Marsh' grapefruit.

Treatment[z]	pH	Fruit surface blemish (%)	Leaf burn %
Untreated	7.6	0 a[y]	0 a
Fosetyl-Al (F-Al)	3.4	0 a	0 a
Kocide 101	7.2	0 a	0 a
Tribasic copper sulfate	7.4	0 a	0 a
Copper Count-N	7.5	12 b	0 a
F-Al + Kocide 101	4.8	30 d	0 a
F-Al + TBCS	4.2	35 d	7.6 b
F-Al + Copper Count-N	5.7	23 c	0 a
F-Al + Kocide 101 + lime	5.6	0 a	0 a
F-Al + TBCS + lime	4.8	10 b	0 a
F-Al + Copper Count–N + lime	6.7	13 b	0 a

[z]Amount of fungicide and buffering materials used on a per 100 gallon basis: Fosetyl-Al, 4 lb. a.i., Kocide 101, 4 lb. formulated; Tribasic copper sulfate, 4 lb. formulated; Copper Count-N, 3 gal and hydrated lime, 1 lb.
[y]Mean separation in columns by Duncan's multiple range test, 5% level.

Table 4. Effect of suspension concentrations of Aliette + Kocide 101 on phytotoxicity symptoms on 'Marsh' grapefruit fruit and the effect of lime on incidence of phytotoxicity.

Treatment[z]	Fruit surface blemish (%)		
	50 GPA[y]	100 GPA	200 GPA
Control	0 a[x]	0 a	0 a
Fosetyl-Al	0 a	0 a	0 a
Kocide 101	0 a	0 a	0 a
Fosetyl-Al + Kocide	73 d	50 c	30 b
Fosetyl-Al + Kocide + lime	7 a	0 a	0 a

[z]The same amount of fungicide and buffering material used for 50 gal, 100 gal and 200 gal of water; Fosetyl-Al 4 lb. a.i., Kocide 101 4 lb. formulation and hydrated lime 1 lb.
[y]GPA = projected gallons per acre of spray material.
[x]Mean separation in columns by Duncan's multiple range test, 5% level.

Phytotoxic symptoms were present on young leaves sprayed with separate applications of fosetyl-Al and copper fungicides, even when copper was sprayed 14 days before. The phytotoxicity symptoms decreased with time between application of Kocide 101 and the subsequent fosetyl-Al overspray. Although no studies were conducted to determine if the same phenomenon occurs on fruit, care should be taken to avoid applying fosetyl-Al to young leaves and fruits that have been recently sprayed with copper compounds. It would be advisable to apply a buffering compound (for example hydrated lime) with fosetyl-Al on citrus even if fosetyl-Al is sprayed alone to avoid possible phytotoxicity.

Observations throughout the experiment indicated that surfaces sprayed with the combination of fosetyl-Al and copper fungicides and exposed to the sun were more likely to have phytotoxicity symptoms. Young leaves and fruits inside the canopy or on the northside of the trees had less severe symptoms. In addition, in other field studies conducted by M. Vathakos phytotoxicity symptoms were not observed on young fruit from November through June. Further study is needed to determine the reasons for these differences.

Further examples of added phytotoxicity symptoms with the addition of spray oil to fosetyl-Al and copper fungicide combinations were also described in tests by Sonoda and Vathakos but not reported in the present paper. Spray oil by itself has been implicated as a causal agent of phytotoxic symptoms, when temperatures are high or when trees are under stress (6). Combinations of spray oil and liquid copper fungicides have also been reported to produce a phytotoxic response on citrus fruit surfaces (6).

The alleviation of phytotoxicity symptoms with the addition of compounds that shift pH upward indicate that Cu^{++} may be less available with the addition of these compounds. Measurement of free Cu^{++} in suspensions to which these compounds have been added has not been done.

Literature Cited

1. Albrigo, L. G. 1978. Occurrence and identification of preharvest fruit blemishes in Florida citrus groves. Proc. Fla. State Hort. Soc. 91:78-81.
2. Davis, R. M. 1982. Control of *Phytophthora* root and foot rot of citrus with systemic fungicides metalaxyl and fosetyl aluminum. Plant Dis. 66:218-220.
3. Knapp, J. L., D. P. H. Tucker, J. W. Noling, and V. V. Vandiver. 1989. Florida citrus spray guide. Fla. Coop. Ext. Ser. Circ 393-0. 30 pp.
4. Simone, G. W., and D. E. Short. 1987. Compatibility and plant safety of fosetyl aluminum fungicide with other landscape ornamental pesticides. Proc. Fla. State Hort. Soc. 100:369-373.
5. Sunda, W. G. and P. A. Gillespie. 1979. The response of a marine bacterium to cupric ion and its use to estimate cupric ion activity in seawater. J. Marine Res. 37:761-777.
6. Whiteside, J. O., S. M. Garnsey, and L. W. Timmer. 1988. Compendium of citrus diseases. APS Press. St. Paul, MN.

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COMPARISON OF VARIOUS SPRAY OILS FOR CONTROLLING GREASY SPOT ON GRAPEFRUIT LEAVES AND FRUIT

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Abstract. **Oils with 435 (distillation temperature °F) specifications have long been used in Florida citrus groves to control greasy spot (*Mycosphaerella citri* Whiteside), as well as various pests. Now, because of improvements in the refining of spray oils, which may reduce risks of phytotoxicity, consideration is being given to the possible use of spray oils with higher distillation temperatures (heavier oils), to take advantage of their superior pesticidal action. In two out of five trials conducted in 1987 and 1988, 455 oil gave better control of greasy spot on leaves than 435 oil, but neither oil controlled greasy spot rind blotch (GSRB) effectively. A copper fungicide at 0.4 lb. Cu/100 gal (dilute application rate), applied either alone or mixed with 0.5 gal 435 oil/100 gal, controlled GSRB well, and provided better control of greasy spot on leaves than 455 or 476 oil alone at 0.5 gal/100 gal, and sometimes better control on leaves than 455 or 476 oils at 1.0 gal/100 gal.**

Emulsified petroleum oils have long been used in Florida citrus groves as insecticides and acaricides, as well to remove deposits of sooty mold and to reduce the severity of greasy spot, caused by *Mycosphaerella citri* Whiteside. In earlier years, spray oils often had adverse effects on the tree and fruit due to the variable quality of the oils then available. Unsuitable oils cause leaf and fruit drop, delayed coloring of fruit and poor internal fruit quality, and they render the tree more susceptible to freeze injury (3).

Research was begun at the Citrus Experiment Station, Lake Alfred, Florida in 1962 by Trammel and Simanton (1, 2, 3) to determine the relative effectiveness of different oils as pesticides and to define the properties needed for optimum pest control without adversely affecting the tree or fruit. The temperature at which 50% of an oil distills at 10 mm Hg was determined as the most reliable indicator of pesticidal efficiency and safety (1). Oils of higher distillation temperatures (DT) were referred to as being heavier than those of lower DT. Oils with a DT below 400°F were considered too inefficient for greasy spot control (2). Greasy spot control was best at the highest DT tested, which was 480°F. However, detrimental effects to tree and fruit were sometimes recorded with oils above 440°F DT (3).

In 1966, 2 types of spray oil were recommended and approved for use in Florida citrus groves (1). One type of oil, designated as FC 412-66 was a lighter oil for use in the fall or winter if a serious pest infestation should occur at this time of year. It was intended to minimize the risk of rendering the trees more prone to freeze damage or of affecting fruit quality. The other type of oil, designated as FC 435-66, was a heavier oil for normal summer use. More recently, it has been suggested that the 435 DT specification might be too rigid and that it might be possible to use oils of somewhat higher DT to utilize their superior pesticidal action without experiencing adverse side effects. Improvements in the refining techniques have increased the unsulfonated residue value of the oils available today, which should lower the risks of causing adverse physiological effects on the tree. R. F. Brooks (Univ. of Florida, personal communication) concluded that oils of 455 DT could be safely used on 'Valencia' orange trees, even if applied 3 times per year.

Oils with 435 DT specifications need to be supplemented with copper fungicides to provide a better assurance of greasy spot control, particularly when greasy spot pressure is heavy (6). Also, because 435 oil provides little or no control of greasy spot rind blotch (GSRB) (5), a copper fungicide is commonly added to the oil spray in grapefruit groves intended for fresh market fruit production. GSRB is generally too insignificant on other citrus cultivars to require the routine inclusion of copper fungicides in the summer oil spray to control this form of greasy spot (4). While heavier oils were known to provide better control of greasy spot on leaves (2), no information was previously available on the effect of heavier oils on GSRB.

This paper reports the results of spraying experiments on grapefruit trees to determine: 1) if heavier oils could control GSRB and 2) if the use of a heavier oil could dispense with the need for a copper fungicide to provide a better assurance of greasy spot control on leaves.

Materials and Methods

The experiments were conducted on 'Marsh' grapefruit trees at Lake Alfred and Davenport, Florida. In the

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