Reprinted from
Proc. Fla. State Hort. Soc. 110:67-70. 1997.

COPPER FUNGICIDES—RESIDUES FOR DISEASE CONTROL AND POTENTIAL FOR SPRAY BURN

L. G. ALBRIGO AND L. W. TIMMER
Citrus Research and Education Center
University of Florida, IFAS
700 Experiment Station Road
Lake Alfred, FL 33850

K. TOWNSEND
Citrus Consultant
1001 4th St.
Vero Beach, FL 32962-2814

H. W. BECK
Agric. and Biological Eng.
University of Florida
PO Box 110570
Gainesville, FL 32611-0570

Additional index words. Spray volume, canopy position, initial deposition, fruit growth.

Abstract. **Spray application tests of copper fungicides were conducted to improve melanose and greasy spot control while minimizing the amount of copper (Cu) applied, particularly on grapefruit. Initial Cu deposition and weathering of Cu fungicides on fruitlets were determined in relation to spray volume, Cu concentration, fruit growth and weather conditions. Reducing spray volume to 1168 l/ha (125 gal/ac) increased deposition with no sacrifice of coverage. Generally, 1168 l/ha was more effective than 235 l/ha (25 gal/ ac) since 235 l/ha resulted in less coverage of fruit if the leaf canopy was dense. After application, Cu concentration decreased primarily as a function of fruit surface expansion. Weathering accounted for an average loss of 19% over the period of 10 to 16 days and 43% for periods of 19 to 22 days. Intervals between sprays may be adjusted to as frequently as 2 weeks shortly after bloom, when fruit surface area is small and percent surface expansion is greatest, to 4 week intervals later in the spring when percentage increase in surface area is less. Spray burn from Cu-oil sprays occurred in the early summer with the combination of 4.5 kg/ ha metallic Cu with oil at 46.5 l/ha in 235 l/ha water. A protocol of using less oil with higher Cu (9.3 l/ha oil with 4.5 kg/ha Cu) or higher oil with lower Cu (46.9 l/ha oil with 2.25 kg/ha Cu) in summer reduced spray burn and gave satisfactory melanose and greasy spot control.**

Introduction

Copper (Cu) fungicides are widely used in Florida citrus, particularly for melanose and greasy spot control (Knapp, 1997; Timmer and Zitko, 1996). Growers often report inadequate control (personal communications) or spray burns (Albrigo and Grosser, 1996) associated with Cu use. Spray burn from Cu is more likely to occur if it is applied with oil (Albrigo, 1978) or other potentially phytotoxic compounds (Albrigo and Grosser, 1996). Copper fungicides can cause a stippling burn (Schutte et al., 1997) or darken blemishes from other injuries (Brodrick, 1970).

Florida Agricultural Experiment Station Journal Series No. N-01538.

Mabbett and Phelps (1983) reported successful use of low volume sprays of Cu fungicides for greasy spot control on leaves. These Cu residues showed considerable resistance to rain and wind weathering. Less than 1 ppm Cu ions in solution are required for adequate control of bacteria (Mennkissoglu and Lindow, 1991) and the conidia of *Diaporthe citri* Wolf, the melanose organism (Timmer, unpublished). Generally, lower carrier volumes for canopy sprays result in higher concentrations of chemicals delivered to target leaves for pest control (Salyani and McCoy, 1989). At the same time, higher concentrations of phytotoxic chemicals increase the risk of spray burn (Albrigo and Grosser, 1996). Very little information is available regarding maintenance of Cu residues on fruitlets of citrus or other crops as they expand during early season growth when they are most susceptible to fungal diseases such as melanose on citrus (Timmer and Zitko, 1996). Timmer, Zitko and Albrigo (unpublished) found that more frequent applications of Cu with less copper per application were more effective than the same amount of Cu applied fewer times.

The studies reported here evaluate the effect of carrier spray volume on Cu deposition, the maintenance of Cu residue during fruit surface expansion and weathering, and the effect of various spray strategies to provide disease protection while minimizing spray burns. This information should be useful for decisions concerning spray volume, copper concentration and frequency to provide adequate protection and minimize chances of spray burn.

Materials and Methods

In the 1995-96 season in a test near Haines City, FL, 4.5 kg/ha (4 lbs/ac) metallic Cu (Kocide DF) was sprayed on mature grapefruit or Murcott trees. Mature grapefruit trees in two blocks in the Vero Beach area were sprayed with 4.5 kg/ha metallic Cu (COC) on various dates during the spring fruit growth period. Details of these tests are presented in Table 1. Curtec™ sprayers were used for low volume applications (235 l/ha) and speed sprayers were used to deliver the higher water volumes. The spray volume rates used in various tests were 235, 1168, 1869, 2336 or 4673 l/ha, and these equal 25, 125, 200 250, and 500 gal/ac. Samples of fruitlets were analyzed for initial Cu deposits and then for residues 10 to 22 days after application. Cu residues were obtained by washing fruit samples in 1% HCl in water. Samples of fruit were obtained at 1.2 to 1.8 m (1.5 avg) or 2.4 to 3 m (2.7 avg) above the ground and from outside (0 to 0.3 m) and/or inside (0.6 to 1.2 m) the canopy. Four replicate plots were sampled with 2 sub-samples for each plot. Fruit volume was determined by water displacement and surface area of these fruit was calculated on the assumption that they were spheres. Generally, the trees were resprayed every 2 to 3 weeks depending on weather, with a shorter interval to respraying if rain occurred.

In the 1996-97 season, after observing spray burn from 4.5 kg/ ha Cu with 46.5 l/ha (5 gal/ac) oil in 235 l/ha water the previous year, a protocol of applying either 2.25 (2 lb/ac) or 4.5 kg metallic Cu (Kocide DF) with less than 9.3 l/ha (1 gal/ac) oil during melanose season was used. During the greasy spot control period 46.5 l/ha of oil was used only with the 2.25 kg rate of Cu while 4.7 l/ha oil was continued with the 4.5 kg/ha Cu rate. General details of 2 tests on mature grapefruit trees are presented in Table 1. Two dou-

Table 1. Summary of the test conditions for spray application tests of fungicidal Cu with or without spray oil and at various spray carrier rates of water on mature trees in the Ridge or Indian River District.

Year	Test #	Location County	Fruit Type	Cu Rate kg/ha	Oil Rate l/ha	Spray Vol l/ha	Sample Height M
1995	1	Polk	Murcott	4.5	0	235, 1877	1.5[z], 2.7
		Polk	Grapefruit	4.5	0	235, 1877	1.5, 2.7
	2	Indian River	Grapefruit	4.5	<9.3	235, 1173, 2347, 4693	1.5, 2.7
	3	St. Lucie	Grapefruit	4.5	<9.3	1173, 2347, 4693	1.5, 2.7
1996	4	Indian River	Grapefruit	2.25	9.3	235, 1173	1.5, 2.7
				4.5	46.5		
	5	Indian River	Grapefruit	2.25	9.3	235, 1173	1.5, 2.7
				4.5	46.5		

[z]At the 1.5 meter height samples were collect from the outer canopy (0 to 0.3 m) and inside the canopy (0.6 to 1.2 m depth).

ble row beds were treated for each Cu-spray volume combination. Each bed was divided in half to provide 4 plots per treatment, and for each spray test period, 2 fruit samples per tree position per plot were collected. Fruit samples were collected in each plot from the same tree positions as in 1995-96 one day after and 10 to 22 days after application depending on the test. The grower determined when to spray and resampling for Cu residues after weathering and fruit expansion was done just before the next spray was applied.

From the fruit samples described above, Cu solutions were collected from the surfaces by washing fruit twice for 2 min each time with 250 ml aliquots of 1% HCl solution. Solutions were further acidified to 5% HCl, filtered and Cu determined by Atomic Absorption Spectrophotometry. Washed surfaces per sample ranged from approximately 10 cm^2 (25 fruit) for samples taken just after petal fall to about 250 cm^2 (12 to 18 fruit) for samples taken in May.

The location and concentration of Cu deposition on exposed (outside) and protected (inside or backside) fruit surfaces of outer canopy fruit were assessed by x-ray analysis using a Kevex™ 8000 on an Scanning Electron Microscope (SEM, Hitachi™ S530). Fruit were harvest with stems, carefully set on Styrofoam carriers, and transported to the lab. Exposed or inside surfaces were removed with a stainless steel razor blade, mounted on stubs, coated with carbon and counted for 100 sec in each SEM field at 100× mag. Either 4 or 1 count areas per fruit surface were done since the standard deviations were equal.

In 1995-96, fruit were graded for melanose lesions and copper spray burn. In 1996-97 at harvest 2 samples of 100 fruit per plot (400 per treatment) were graded for fresh fruit grade and the blemishes of melanose and spray burn were evaluated.

Results and Discussion

Generally, the lowest spray volume (235 l/ha) resulted in lower initial deposits (Table 2). The exception to this was for Murcott in the Haines City grove (Test 1). The grapefruit trees had a very thick canopy and presumably the leaves captured most of the spray at the low volume. The Murcott trees had just been hedged and had very thin canopies. Grapefruit trees in the Vero Beach area (Test 2) had canopies of intermediate density which apparently still hindered spray penetration as much as did the grapefruit tree canopies near Haines City. The Cu deposition from 235 l/ha was significantly less than for 1168, 2336 or 4673 l/ha of spray volume (Table 2, Test 2). In tests on leaves, Cu deposition was greatest for lower spray volumes for exposed leaves (Mabbett and Phelps, 1983, Salyani and McCoy, 1989) but less at lower volumes for interior leaves (Salyani and McCoy, 1989). In our 1995 tests, both interior and exterior fruit showed reduced deposition with the lowest volume (235 l/ha), but highest deposition at the next lowest volume (1168 l/ha).

Table 2. Initial deposition of Cu on fruitlets from application of 4.5 kg/ha of metallic Cu at various spray volumes - 1995.

Spray volume l/ha	Cu Deposit (µg/cm^2) Test 1, Murcott	Test 1, Gpft	Test 2, Gpft	Test 3, Gpft	Avg/Gpft
235	6.3 A	3.1 B	2.5 c	—	2.8
1168	—	—	9.3 a	12.5 a	10.9
1869	4.0 B	6.3 A	—	—	6.3
2336	—	—	8.3 ab	5.8 c	7.1
4673	—	—	7.3 b	7.0 b	7.1

Mean separation in columns by Duncan Multiple Range; upper case, P = 1%; lower case, P = 5%.

Table 2. Initial deposition of Cu on fruitlets from application of 4.5 kg/ha of metallic Cu at various spray volumes - 1995.

Mean separation in columns by Duncan Multiple Range; upper case, P = 1%; lower case, P = 5%.

In 1996 and with a different grove site for one of the tests, deposition was equal or greater for 235 compared to 1168 l/ha for 2.25 or 4.5 kg/ha Cu (Table 3). In location 1, the 4.5 kg/ha Cu resulted in higher initial deposits of Cu than the 2.25 kg/ha rate, but results

Table 3. Initial deposition of Cu on fruitlets from various spray volumes and Cu amounts in the spray solution - 1996.

Spray volume l/ha	Cu deposit (µg/cm^2) Test 4: 2.25 kg Cu	Test 4: 4.5 kg Cu	Test 5: 2.25 kg Cu	Test 5: 4.5 kg Cu	Avg Cu/ Spray Vol
235	9.9 B	13.0 A	12.5	6.8	10.6
1168	3.9 C	14.2 A	11.7	27.0	14.2
Avg Cu (ug)/ Cu Rate	6.9 B’	13.6 A’	12.1	16.9	

Mean separation by Duncan Multiple Range; P = 1%, Rows & Columns test 4; Test 5 not significant.

at location 2 were too variable and differences were not significant.

Table 4. Cu deposition (µg/cm² of fruit surface) by tree position for all tests in 1995 and 1996.

Tree Position	Test 1-Murcott	Test 1-Gpft	Test 2-Gpft	Test 3-Gpft	Test 4-Gpft	Test 5-Gpft	Avg Cu mg/cm²
1.5 m Outside	4.2 B	5.6	8.3 B	7.1 a	10.9	20.6	9.5
1.5 m Inside	3.5 C	4.8	6.0 C	5.9 b	—	—	5.1
2.7 m Outside	6.4 A	5.1	10.9 A	7.4 a	10.1	10.9	7.5
2.7 m Inside	—	— N. S.	—	—	9.7 N. S.	12.1 N. S.	10.9

Mean separation by Duncan Multiple Range, upper case = 1%, lower case = 5%.

For all tests over 2 years at 4.5 kg/ha Cu and including all fruit positions in the canopy, the deposition was 6.4 µg/cm² fruit surface for 235 l/ha and 15.8 µg/cm² for 1168 l/ha spray volume. Since Cu deposition on leaves is greater at ultra low volume such as 235 l/ha (Salyani and McCoy, 1989; Mablett and Phelps, 1983), leaf surfaces are interfering with spray movement to the fruit.

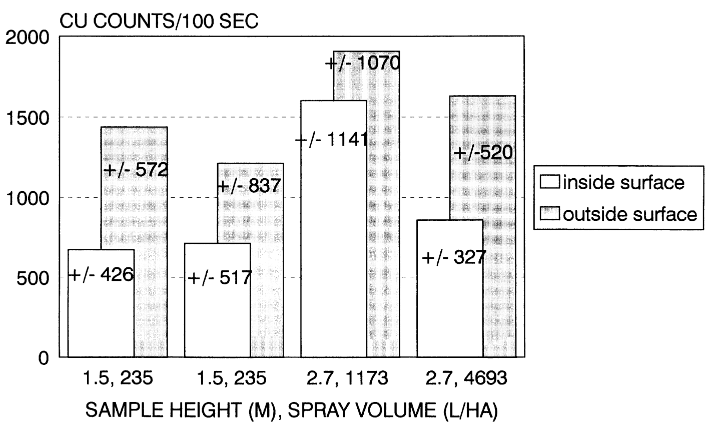

Figure 1. X-ray analysis of Cu deposits on the exposed and inside surfaces of grapefruit at different tree heights and spray volumes using 4.5 kg/ha Cu.

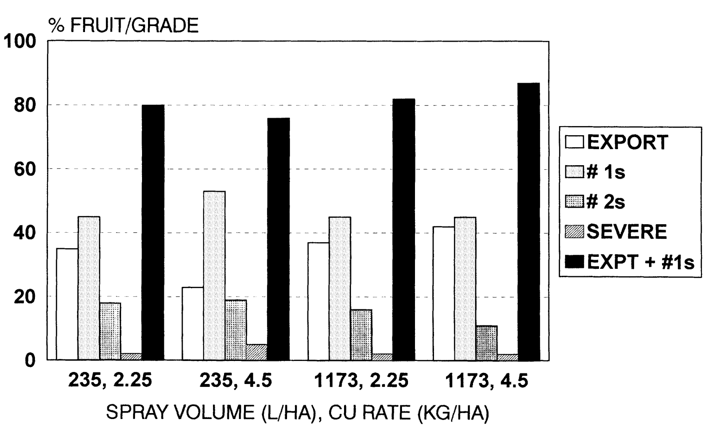

Figure 2. Fruit grades from grapefruit plots receiving 2.25 or 4.5 kg/ha Cu and sprayed at 235 or 1168 l/ha water. The final greasy spot spray received 46.5 l/ha spray oil with the 2.25 kg Cu rate. All other sprays were with 9.3 l/ha oil.

Inside fruit usually had reduced initial deposits compared to outside fruit (Table 4, Test 1-Murcott, Tests 2 & 3). Deposits on the outside fruit at 2.7 m were equal to or higher than those at 1.5 m. These fruit may have received more coverage on their interior surface since the spray would travel upward to reach them (Fig 1. 2.7 m fruit samples). Deposition in the top of the tree was not determined, but may have been less since these fruit are further away from the spray nozzles.

On individual fruit, Cu deposits were highly variable but outside surfaces of exposed fruit usually had twice the copper than the backside (inside) of the same fruit (Fig. 1). Average deposits were comparable to data in Table 2 with a trend of highest deposits on

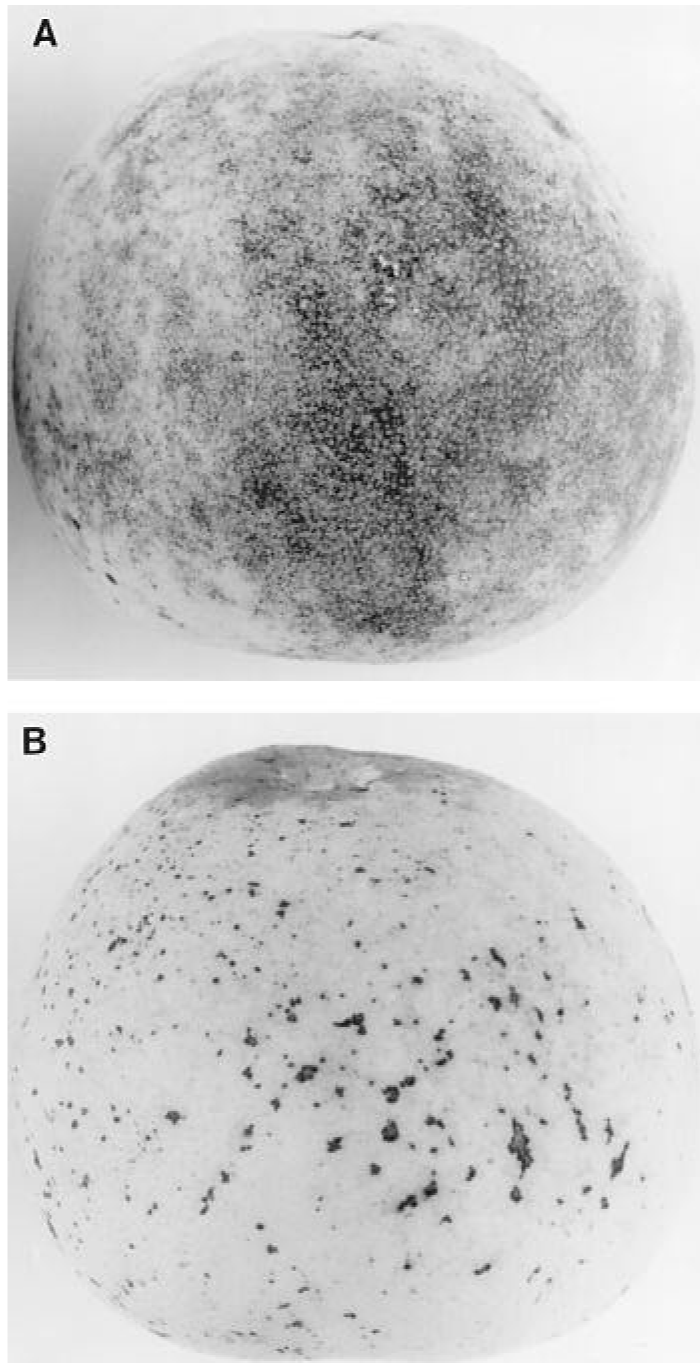

Figure 3. Typical spray burn patterns on exposed fruit surfaces when 4.5 kg metallic Cu and 46.5 l oil per ha were sprayed in 235 l/ha water.

fruit sprayed with 1168 l/ha of spray solution. The deposits were highly variable from location to location on the fruit with a stan-

Table 5. Changes in Cu residues over time as affected by fruit expansion and weathering.

Character	Test 1-Murcott	Test 1-Gpft	Test 2-Gpft	Test 3-Gpft	Test 4-Gpft	Test 5-Gpft
Original Conc. (μg/cm ^{2})	1.8	4.1	8.5	8.2	13.0	7.0
Ending Conc. (μg/cm ^{2})	1.0	0.35	2.0	1.9	4.5	3.0
Surface Expansion	2.9 ×	6.7 ×	3.3 ×	3.7 ×	1.9 ×	9.1 ×
Weather losses - %	45	38	23	15	33	57
Measured Period	22 days	22 days	10 days	16 days	19 days	19 days
& Rainfall	13.7 cm	13.7 cm	0.6 cm	2.7 cm	2.8 cm	2.3 cm

dard deviation equal to H the average values. Salyani and McCoy (1989) reported high coefficients of variability for Cu deposition data on leaves and the highest variability occurred at the lowest spray volumes.

For the various spray treatment combinations of Cu rate and spray volume in the 1996-97 season, the more marketable grapefruit grades of export plus (# 1) were 76 to 87% of the total fruit (Fig. 2). The lowest export percentage was for the 4.5 kg/ha Cu using 235 l/ha spray volume. The reduced grade was due to a small amount of spray burn even though only 9.3 l/ha oil was combined with this Cu rate for all the sprays that season. Although this injury was slight and left the fruit mostly in the #1 grade, a small increase in severe blemish grade was noted. The data indicates that 4.5 kg/ha or higher Cu rates should only be sprayed at carrier volumes higher than 235 l/ha.

When 4.5 kg/ha Cu was combined with 46.5 l/ha oil and sprayed in 235 l/ha water, the outer surface of exposed fruit was severely burned (Fig. 3). Although our data indicates that, on average, fruit sprayed with 235 l/ha volume had less deposition of Cu due to leaf interference with coverage, fully exposed fruit surfaces should have higher deposits as was demonstrated for leaves (Salyani and McCoy, 1989).

Initial deposition on the fruit surface is important for adequate protection, but maintenance of residue is the important factor as time passes after spraying. The decrease in concentration of surface deposits was primarily due to surface expansion as the fruit enlarged (Table 5). Cu loss per fruit accounted for 15 to 57 percent for the 10 to 22 day weathering periods for all tests. For the four tests carried out over a comparable test period (19 to 22 days), the range of weathering loss was 33 to 57%. Rainfall did not appear to be the deciding factor in the variability in loss per fruit. Fruit expansion during the period may have been more related (Test 4 vs Test 5, grapefruit). Physical dislodgment of Cu particles due to surface growth underneath the deposits may be more important than rain solubilization or direct rain dislodgment. The Murcott vs grapefruit weathering in Test 1 did not reflect this idea, however, since the Murcott fruit expanded only half as much as the grapefruit but had slightly more weathering.

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