LOW-RESIDUE MICRONUTRIENT FOR CITRUS

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APPLICATIONS OF zinc, manganese, and copper compounds to alkaline California soils have not proven consistently effective in supplying these elements to citrus trees. However, commercially formulated compounds and mixtures containing zinc, manganese and copper in proper concentrations readily supply adequate amounts of these nutrients when used in foliar applications. Such sprays, in which precipitating agents are combined with $ZnSO_4$, $MnSO_4$ and $CuSO_4$, are relatively high in salts, but low in metallic ions in solution, as shown in tests reported here. Such sprays leave large amounts of residue on the leaves, and because of this undesirable effect, these studies were undertaken to develop safe, low-residue micronutrient sprays.

Laboratory experiments

The interacting effects of various ratios of metals and precipitating agents were studied. Metallic equivalents of 0.25, 0.50, 0.75, 1.00 lb of commercial grade sulfates of zinc manganese and copper respectively, were dissolved in 100-gallon equivalents of deionized water, to which given proportions of Na_2CO_3 were added. Each series contained one treatment to which no Na_2CO_3 was added. The pH values and ionic concentrations of zinc, manganese, and copper in these solutions were determined (table 1).

The data in table 1 show that in the absence of Na_2CO_3, ionic concentrations of zinc, manganese, and copper were directly proportional to the amount of metal sulfates dissolved. In the absence of Na_2CO_3, the pH values of the zinc and copper solutions did not change appreciably with increasing amounts of dissolved $ZnSO_4$ and $CuSO_4$, but, the pH of manganese solutions decreased with increasing amounts of $MnSO_4$ in solution. When the amount of metal was held constant and the Na_2CO_3 increased, the concentrations of the ions in the solution decreased, with differences only in degree. The metallic elements of the $ZnSO_4$, $MnSO_4$, and $CuSO_4$ solutions were removed from the solution as carbonate precipitates.

The degree of precipitation of these metals is dependent upon the pH and the amount of carbonates present in the solution. For practical consideration, the concentrations of zinc and manganese in separate solutions of 1 lb of $ZnSO_4$, and 1 lb of $MnSO_4$ per 100 gallons of water with no precipitating agent, are about the same as the zinc and manganese found in a solution containing 3 lbs of $ZnSO_4$, and 3 lbs of $MnSO_4$, with 3 lbs of Na_2CO_3. One pound of $CuSO_4$ (0.25 lb copper), without a precipitating agent, per 100 gallons of water resulted in 326 ppm copper (table 1).

TABLE 1. NA_2CO_3 EFFECTS ON CONCENTRATIONS OF SOLUBLE ZINC, MANGANESE, AND COPPER IONS IN NUTRITIONAL SPRAY SOLUTION

Na_2CO_3 applied	0.25		0.50		0.75		1.00	
	Zinc (lb/100 gal)							
(lb/100 gal)	ppm	pH	ppm	pH	ppm	pH	ppm	pH
0.00	331	4.7	645	4.7	952	4.7	1275	4.7
0.25	262	6.5	502	6.6	855	6.6	1050	6.6
0.50	177	6.7	387	6.7	735	6.7	960	6.7
0.75	90	8.6	255	6.9	615	6.8	870	6.8
1.00	19	9.3	184	7.0	487	6.9	750	6.8
1.25	15	9.7	70	7.4	312	6.9	573	6.8
1.50	7	9.9	30	8.2	225	7.0	492	6.9
	Manganese (lb/100 gal)							
	0.25		0.50		0.75		1.00	
	ppm	pH	ppm	pH	ppm	pH	ppm	pH
0.00	331	4.1	663	4.0	994	3.8	1326	3.7
0.25	263	8.3	536	8.3	903	8.3	1274	8.2
0.50	156	8.5	481	8.3	819	8.2	1170	8.1
0.75	66	9.0	361	8.6	695	8.4	1014	8.3
1.00	23	9.4	244	8.7	559	8.4	858	8.3
1.25	9	9.8	125	9.0	302	8.5	513	8.1
1.50	9	10.0	3	9.2	3	8.6	448	8.1
	Copper (lb/100 gal)							
	0.25		0.50		0.75		1.00	
	ppm	pH	ppm	pH	ppm	pH	ppm	pH
0.00	326	4.7	649	4.7	990	4.6	1298	4.6
0.25	55	5.9	374	5.7	803	5.5	1122	5.4
0.50	18	6.3	304	5.8	656	5.7	979	5.6
0.75	4	7.9	143	6.0	458	5.7	766	5.6
1.00	0	9.5	75	6.5	297	5.9	605	5.8
1.25	0	9.7	15	7.2	180	6.2	440	5.9
1.50	0	9.9	0	8.5	70	6.5	286	6.0

Solubility studies

The results obtained from the solubility studies in the laboratory were tested on Washington Navel orange trees under field conditions for correction of deficiency symptoms, toxicity of spray material, yield of oranges, and longevity of response. Washington Navel orange trees 45 years old on sweet orange rootstock at the Citrus Research Center, University of California at Riverside, were used for a field trial of the laboratory study. No noticeable zinc or copper deficiency symptoms appeared on the leaves but manganese deficiency symptoms were present on young leaves. In past years, these trees had responded favorably to sprays of zinc and manganese. Foliar applications were made in April, 1963 when the trees were in the late bloom stage and the new flush of leaves was

TABLE 2. MEAN CONCENTRATION OF ZINC, MANGANESE, AND COPPER IONS IN THE SPRAY SOLUTION, IN SPRAYED AND NEW FLUSH LEAVES, AND THE YIELD OF WASHINGTON NAVEL ORANGES†

	Zinc		Manganese		Copper	
	Control	Zn_1	Control	Mn_1	Control	Cu_1
Spray solution (ppm)	–	441	–	440	–	371
Concentration in oven-dried leaves Sprayed (ppm)	100	133**	14	58**	7	27**
New flush (ppm)	19	19NS	8	10**	5.6	6.4**
Yield (lb/tree)	187	154NS	149	193*	187	149NS

NS—indicates that the differences between means are not significant.
* Significant at the 5% level.
** Significant at the 1% level.
† Each value is a mean of 24 individual determinations.

about one-third developed. Five rates (0.25, 0.50, 1.00, 1.50, and 2.00 lbs per 100 gallons of water) of zinc, manganese, and copper were applied to foliage in a factorial combination.

Seven days after treatment with $ZnSO_4$, $MnSO_4$, and $CuSO_4$, the trees were inspected for leaf injuries and drop. It was found that concentrations greater than 0.50 lb, of metallic copper per 100 gallons of water severely defoliated the trees. Therefore, only results from the 0.25 lb and 0.50 lb rates of zinc, manganese, and copper per 100 gallons of water are presented in table 2. No visual leaf drop was observed on these trees sprayed with 0.25 lb and 0.50 lb of copper per 100 gallons of water; however, excessive blossom drop did result.

Excess blossom drop

The effect of this excess blossom drop from 0.25 and 0.50 lb of Cu per 100 gallons of spray material reduced the yield numerically but not enough to be statistically significant (see table 2). The higher concentrations of copper reduced the yield by more than 95%. These data are not presented in this paper but are available upon request. Applications of zinc and manganese at rates of 0.25, 0.50 or 1.00 lb per 100 gallons of water produced no observable injuries. Two lbs of metallic zinc per 100 gallons of water caused leaf injury. The only visible deposit from these sprays which was very light, resulted from the zinc and manganese salts themselves.

Spring flush leaves sprayed in April, 1963, were sampled in June. The yield was obtained in February, 1964. In June, 1964, samples of the new flush of leaves, comparable in age and size to the previous year's sampling, were obtained from the treatment trees.

Foliar applications of zinc with a mean concentration of 441 ppm (for the 0.25-lb and 0.50-lb rates) in the spray solution increased zinc concentration in the sprayed leaves, but did not increase the concentration in unsprayed leaves that developed the following year (table 2). Addition of manganese and copper separately or together, to zinc foliar sprays reduced the zinc concentration in the leaves sampled two months after spraying. Although the sprayed leaves were adequately supplied with zinc, the concentrations of zinc in the new flush of leaves sampled the following spring were only slightly above the deficiency range. This substantiated previous observations that zinc from previously sprayed leaves was not materially translocated into a following new flush (table 2).

Foliar applications of manganese having a mean conecntration (for the 0.25 lb- and 0.50-lb rates) of 440 ppm, increased manganese concentration in the leaves, corrected manganese deficiency symptoms, increased yield, and caused no adverse effects (table 2). New leaves sampled the following spring from trees which were manganese-spray treated contained a slightly higher manganese concentration than new leaves from the previously unsprayed control trees. This indicated a slightly higher rate of movement of manganese than of zinc from the sprayed leaves into the following year's new flush.

Foliar applications

Foliar applications of copper with no precipitant present, and with a mean concentration (for 0.25-lb and 0.50-lb rates) of 371 ppm, increased copper concentration in the sprayed leaves and caused excessive blossom drop without causing any injury to the young leaves. The yield was consequently reduced numerically by the copper sprays. The new flush of leaves sampled the following spring, June, 1964, from trees previously sprayed with copper contained slightly higher concentrations of copper than leaves from trees not sprayed with copper. This indicates that copper also moved somewhat more readily than zinc from the sprayed leaves into the new flush.

Additional experiments

The findings from these experiments have been successfully tested commercially during the past 10 years in five different climatic locations in California, including the Citrus Research Center at Riverside. In these applications, 1 lb each of $ZnSO_4$ (36% Zn) and $MnSO_4$ (28% Mn) per 100 gallons of water, singly or in combination, corrected the respective deficiency symptoms with no injury to the fruit or foliage. In early spring shortly after the major spring bloom and flush is about expanded, 7.5 lbs of urea (46% N) may be added to the $ZnSO_4$ and $MnSO_4$ mixture to supply additional nitrogen if needed by the trees. Urea should be omitted in summer sprays on orange trees because of the adverse effect on fruit quality. Urea should contain less than 0.25% biuret.

In addition to reducing the total residue on the leaves, application of micronutrients without Na_2CO_3 as a precipitating agent avoids addition of undesirable Na^+ ion, and reduces the amounts of $SO_4^=$ ion. This latter reduction may be of particular importance where SO_4-excess problems already exist.

One pound of $CuSO_4$ (25% Cu) per 100 gal of water (about 230 ppm Cu^{++}) alone, or in combination with $ZnSO_4$ and $MnSO_4$ without a precipitating agent increased the copper concentration in the sprayed leaves by up to 30 ppm and caused excessive bloom drop. Since copper is very phytotoxic to parts of citrus plants, it should not be applied to citrus trees without a precipitating agent, regardless of the amount used.

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