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Interactions of Nutrients in Valencia Orange Leaves as Affected by the Composition of Manganese, Zinc, and Urea Sprays

C. K. Labanauskas

UNIVERSITY OF CALIFORNIA DIVISION OF AGRICULTURAL SCIENCES

The main effects and interactions of foliar applications of $MnSO_4$, $ZnSO_4$, and urea in factorial combinations on nutrients in Valencia orange leaves were studied. The presence of $MnSO_4$ in $ZnSO_4$ foliar sprays containing Na_2CO_3 as precipitating agent significantly decreased the concentration of soluble Zn ions in solution and, as a consequence, decreased the concentration of Zn in the leaves as compared with Zn concentration found in the spray solutions and leaves of trees sprayed with $ZnSO_4$ alone. The presence of $ZnSO_4$ plus Na_2CO_3 in $MnSO_4$-urea foliar sprays significantly increased the concentration of soluble Mn ions in solution, causing increased Mn concentration in the leaves of trees sprayed with this solution. Considering all Mn-urea treatments in this experiment, a positive interaction between Mn and urea foliar applications occurred: Mn concentration increased in the leaves of trees sprayed with $MnSO_4$-urea mixture. This increase in Mn concentration in the leaves may have been due to better uptake of Mn by the leaves when urea was present, since the concentration of Mn in the spray solution was not affected significantly by the presence or absence of urea in Mn foliar sprays.

THE AUTHOR:

C. K. Labanauskas is Professor of Horticultural Science, and Horticulturist at the Citrus Research Center and Experiment Station, Riverside.

C. K. Labanauskas

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INTRODUCTION

ONE ION, TAKEN UP BY THE PLANT, and its effect on the concentration of another ion in plant tissue has been the subject of numerous reports in the literature. Interpretation of these effects has varied widely, however, depending on the nature of the experiments. A common assumption is that these increases or decreases in the nutrient elements of foliage represent absorption or uptake of nutrients by the plant. This has led to the conclusion that certain ions must in some way retard the entrance of some ions and simultaneously assist still others in entering the plant root from the nutrient medium (Epstein, 1962).

Steyn and Eve (1956) studied the Zn and Cu interactions when applied either as a foliar spray to citrus or as a fertilizer mixture to the soil. They found that Cu depressed the uptake of Zn following both methods of application. Labanauskas *et al.* (1963) reported that MnO_2 foliar applications to Valencia orange trees reduced Cu and N concentrations in the leaves. The presence of urea of $ZnSO_4$ in $MnSO_4$ foliar sprays significantly increased Mn concentration in Valencia orange leaves (Labanauskas and Puffer, 1964). $MnSO_4$ foliar applications to lemon trees resulted in lower Zn and Cu concentrations in the leaves, as compared with concentrations in similar leaves from trees not sprayed with Mn (Labanauskas *et al.*, 1961).

Since commercial citrus orchards are sprayed annually with Mn, Zn, and urea, it is necessary to determine the effects of these nutrient sprays—not only on the concentrations in the leaves of the nutrients applied, but also on the concentrations of other nutrients and their interrelationships in the leaves. The effect of applied nutrients on the concentration of dissimilar nutrients in plant tissue is of fundamental importance in the understanding and interpretation of tissue analysis data. One must clearly distinguish between the influence of nutrients applied and the physiological factors within the plant not related to supply but still capable of affecting tissue composition.

MATERIALS AND METHODS

A Valencia orange orchard in Ventura County, California, showing leaf symptoms of Mn and Zn deficiency, was selected for this experiment. The factorial combinations of two levels, each of Mn, Zn, and urea, that comprised the eight treatments, are summarized in table 1. Each treatment was

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TABLE 1

NUTRIENT CONCENTRATIONS IN FOLIAR SPRAYS APPLIED JANUARY AND JULY, 1962 TO 1964, TO VALENCIA ORANGE TREES

Treatment*	Concentrations in foliar spray (lbs/100 gal.)			
	Na_2CO_3†	$ZnSO_4$ (36% Zn)	$MnSO_4$ (28% Mn)	Urea (46% N) (<.25% biuret)
$Mn_0 N_0 Zn_0$	....	...	...	...
$Mn_1 N_0 Zn_0$	....	...	2.0	...
$Mn_0 N_1 Zn_0$	....	...	...	7.5
$Mn_1 N_1 Zn_0$	....	...	2.0	7.5
$Mn_0 N_0 Zn_1$	0.25	1.5	...	...
$Mn_1 N_0 Zn_1$	0.25	1.5	2.0	...
$Mn_0 N_1 Zn_1$	0.25	1.5	...	7.5
$Mn_1 N_1 Zn_1$	0.25	1.5	2.0	7.5

* Subscript $_0$ treatment trees received no spray of the element indicated; subscript $_1$ denotes treatment.

† Irrigation water used for making up these solutions contained appreciable but unknown quantities of carbonates. Under certain environmental conditions one pound of $ZnSO_4$ per 100 gal. of water may cause some injury to young citrus leaves, if it is not precipitated with Na_2CO_3 in quantities equal to 1/6 the weight of $ZnSO_4$.

replicated eight times on two-tree plots in a Latin square design. In January and July of 1962, 1963, and 1964, the foliar applications of $ZnSO_4$, $MnSO_4$, and urea—alone, and in factorial combinations—were applied. In October of those years, 60 fully-expanded, spring-cycle, terminal leaves per treatment were sampled, hand-washed, dried, ground, and chemically analyzed, according to the procedures described by Labanauskas *et al.* (1965). Treatment effects on variables were analyzed statistically, and the differences between the means were evaluated by a multiple range test (Duncan, 1955).

RESULTS

One month after foliar applications of Mn and Zn, leaves no longer showed symptoms of Mn and Zn deficiency. The sprayed leaves became dark-green and shiny, while unsprayed leaves were dull, light-green, and characterized by pale areas between the main veins and dark-green areas along the veins (Labanauskas and Puffer, 1964).

Foliar application of $MnSO_4$ increased Mn concentration in sprayed leaves, while the concentrations of K, Ca, and Zn were decreased. Significant interaction was noted between $MnSO_4$ and urea foliar sprays on the Mn concentration in the leaves.

Foliar applications of $ZnSO_4$ increased the concentrations of Zn, Mn, and Na in the sprayed leaves, while N, Ca, Mg, and Cu were decreased. The concentrations of P, K, B, Cl and Fe in the leaves were not influenced by $ZnSO_4$ sprays. Significant interaction occurred between $ZnSO_4$ and $MnSO_4$ foliar sprays on the Zn concentration in the leaves.

Applications of urea increased Mn concentration in the leaves. However, the main effect of urea sprays on Mn concentrations in the leaves was not so important in this study as the effects of urea and Mn treatments on Mn concentrations.

A significant decrease in the concentration of Zn ions in both solution and leaves occurred with $MnSO_4$ present in $ZnSO_4$ sprays—as compared with Zn ion concentrations in sprays and leaves when $ZnSO_4$ was used alone (table 3). The concentration of Mn in the leaves was significantly greater with urea present in $MnSO_4$ foliar sprays than

TABLE 2

MAIN EFFECTS OF FOLIAR SPRAYS OF $MnSO_4$, UREA, AND $ZnSO_4$ ON THE YIELD AND NUTRIENT CONCENTRATIONS IN LEAVES OF VALENCIA ORANGE TREES (1962 TO 1964)

Treatment*	Mean effects† on:												
	Yield: Field boxes/tree	Leaves (dry weight)											
		N	P	K	Ca	Mg	Na	Cl	Zn	Mn	Cu	B	Fe
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*
Mn_0	4.64	2.72	0.14	1.17	4.14	0.40	0.05	0.03	53.0	13.0	5.8	289.0	57.0
Mn_1	5.48	2.72	0.14	1.04	4.07	0.39	0.05	0.03	44.0	94.0	5.8	299.0	56.0
Level of significance	.01	NS	NS	.01	.05	NS	NS	NS	.01	.01	NS	NS	NS
$Urea_0$	4.95	2.72	0.14	1.09	4.12	0.40	0.05	0.03	49.0	51.0	5.6	294.0	57.0
$Urea_1$	5.18	2.72	0.14	1.12	4.08	0.39	0.05	0.03	48.0	56.0	5.7	291.0	56.0
Level of significance	NS	NS	NS	NS	NS	NS	NS	NS	NS	.01	NS	NS	NS
Zn_0	5.19	2.74	0.14	1.13	4.14	0.40	0.04	0.03	15.0	52.0	6.0	296.0	57.0
Zn_1	4.93	2.69	0.14	1.08	4.07	0.39	0.06	0.03	82.0	55.0	5.2	293.0	56.0
Level of significance	NS	.01	NS	NS	.05	.05	.01	NS	.01	.05	.01	NS	NS
Coefficient of variability	.20	.05	.10	.19	.05	.12	.22	.24	.20	.21	.17	.11	.27

* Subscript $_0$ treatment trees received no spray of the element indicated; subscript $_1$ denotes treatment.
† Each value is a mean of 96 individual determinations.

when leaves were sprayed with $MnSO_4$ alone (table 3).

Since the concentrations of nutrients found in the sprayed leaves are directly proportional to the concentrations of nutrients applied (Labanauskas *et al.*, In Press), it was necessary to determine the concentrations of Zn and Mn in these spray solutions. (See table 4). As shown in table 4, addition of $MnSO_4$ to $ZnSO_4$ (plus Na_2CO_3) sprays, in the presence or absence of urea, significantly reduced the concentrations of Zn in the spray solution, consequently, lower concentrations of Zn were found in the leaf tissue sprayed with this mixture. On the other hand, when $ZnSO_4$ was added to the $MnSO_4$-urea spray solution, the concentration of Mn in the solution was increased; therefore, higher concentrations of Mn were found in the leaves sprayed with this solution than they were when sprayed with $MnSO_4$-urea alone.

Concentrations of soluble Mn ions in

TABLE 3

INTERACTION EFFECTS (IN THE PRESENCE OF Na_2CO_3) OF $MnSO_4$ AND $ZnSO_4$ ON Zn CONCENTRATIONS—AND $MnSO_4$ AND UREA ON Mn CONCENTRATIONS—IN SPRAYED VALENCIA ORANGE LEAVES

Treatment*	Element concentrations in oven-dried leaves†	
	Zn	Mn
	ppm	*ppm*
Zn_0 Mn_0	15	...
Zn_0 Mn_1	15	...
Zn_1 Mn_0	91	...
Zn_1 Mn_1	74	...
N_0 Mn_0	...	13
N_1 Mn_0	...	13
N_0 Mn_1	...	88
N_1 Mn_1	...	99
Level of significance	.01	.01

* Subscript $_0$ treatment trees received no spray of the element indicated; subscript $_1$ denotes treatment.

† Each value is a mean of 48 individual determinations, made over a period of three years. The test consisted of two treatments and 8 replications.

TABLE 4

MEAN CONCENTRATIONS OF Zn AND Mn IONS IN THE SPRAY SOLUTION AND IN 6-MONTH-OLD OVEN-DRIED LEAVES (1962 TO 1964)

Treatment*	Na_2CO_3 (precipitant for $ZnSO_4$)	Mean concentrations of:			
		Zn in:		Mn in:	
		Spray†	Leaves‡	Spray†	Leaves‡
	lbs/100 gal	*ppm*	*ppm*	*ppm*	*ppm*
Mn_0 N_0 Zn_0	....	....	15x	....	13x
Mn_1 N_0 Zn_0	....	....	15x	335x	89y
Mn_0 N_1 Zn_0	....	....	15x	....	12x
Mn_1 N_1 Zn_0	....	....	15x	352x	92y
Mn_0 N_0 Zn_1	0.25	518y	91z	....	14x
Mn_1 N_0 Zn_1	0.25	260x	74y	715y	87y
Mn_0 N_1 Zn_1	0.25	556y	90z	....	14x
Mn_1 N_1 Zn_1	0.25	239x	75y	770y	106z
Level of significance	....	.01	.01	.01	.01

* Applied in January and July of 1962 through 1964: $ZnSO_4$, 36% Zn; $MnSO_4$, 28% Mn; urea, 46% N, less than 0.25% biuret. Subscript $_0$ treatment trees received no spray of the element indicated; subscript $_1$ indicates treatment.

† Each value is a mean of 8 individual determinations.

‡ Each value is a mean of 24 individual determinations, consisting of one treatment, 8 replications. Letters x, y, and z after mean values indicate statistical populations. Mean values are statistically significant only if they do not have a letter in common.

TABLE 5
ANNUAL VARIATIONS IN NUTRIENT CONCENTRATIONS IN VALENCIA ORANGE LEAVES AND YIELD OF ORANGES (1962 TO 1964)

Item	Year*			Level of significance	Coefficient of variability
	1962	1964	1965		
N (per cent, dry wt.)	2.56x	2.78y	2.82y	.01	.04
P (per cent, dry wt.)	0.15y	0.13x	0.15y	.01	.07
K (per cent, dry wt.)	1.08x	1.07x	1.17y	.01	.09
Ca (per cent, dry wt.)	3.97x	4.30y	4.04x	.01	.06
Mg (per cent, dry wt.)	0.41y	0.38x	0.40y	.01	.09
Na (per cent, dry wt.)	0.07z	0.05y	0.04x	.01	.14
Cl (per cent, dry wt.)	0.03	0.03	0.03	NS	.38
Zn (ppm, dry wt.)	68.0y	37.0x	41.0x	.01	.21
Mn (ppm, dry wt.)	94.0y	32.0x	34.0x	.01	.17
Cu (ppm, dry wt.)	5.1x	5.5y	6.4z	.01	.14
B (ppm, dry wt.)	368.0z	264.0y	251.0x	.01	.08
Fe (ppm, dry wt.)	61.0y	60.0y	49.0x	.05	.14
Yield: field boxes/tree	4.44x	5.94y	4.80x	.01	.20

* Each value is a mean of 64 individual determinations, consisting of 8 treatments and 8 replications. Letters x, y, and z after mean values indicate statistical populations. Mean values are statistically significant only if they do not have a letter in common after values.

solution in the presence of urea were not increased significantly (table 4), although there was a trend in that direction. Similarly, the presence of urea in the individual $MnSO_4$ sprays did not increase significantly the concentrations of Mn in the leaves sprayed with $MnSO_4$-urea mixture; however, there was also a trend in that direction.

Table 5 shows that concentrations of the 12 nutrients were strongly influenced by climatic and cultural factors that may have varied from year to year. These factors were not studied.

The effects of Mn, Zn, and urea sprays on concentrations of other nutrients in Valencia orange leaves were not significant. Nutrient concentrations still remained within the normal range and did not affect the yield or fruit quality.

DISCUSSION

In the present study, interactions in the presence of Na_2CO_3 were found between Mn and Zn, and between Mn and urea on Mn concentrations in the leaves. Since the effectiveness of micronutrient sprays is positively correlated with the concentrations of free ions in solution (Labanauskas *et al.,* In Press), it was necessary to determine the concentrations of free Zn and Mn ions in the spray solutions. The data showed that $MnSO_4$, when added to $ZnSO_4 + Na_2CO_3$ spray, in the presence or absence of urea, reduced free Zn ion concentration in the spray solution, and thus decreased uptake merely through an effect on the solubility of Zn in the system. On the other hand, when $ZnSO_4$ was added to the $MnSO_4$ spray solution, in the presence of Na_2CO_3 and urea, the concentration of free Mn ions in solution was increased; therefore, higher concentration of Mn was found in the leaves sprayed with $MnSO_4$-urea-$ZnSO_4$ solution than with that containing $MnSO_4$-urea.

These interactions between $MnSO_4$ and $ZnSO_4$ in the spray solution on the concentrations of Zn and Mn ions in solution can occur when (a) the precipitating agent is Na_2CO_3, (b) when normal irrigation water contains carbonates, or (c) some other compound is used which can serve as a precipitating agent for Zn and Mn. Zn ions in solution will be precipitated before Mn, since $ZnCO_3$ is less soluble than $MnCO_3$, and thus lower concentration of free Zn ions in solution will be found. In irrigation water, there is always some carbonate that will precipitate some Zn before Mn.

On the other hand, data obtained in a previous experiment (Labanauskas and Puffer, 1964) and the present experiment (table 3) show that considering all Mn-urea treatments, there was a positive interaction between Mn and urea foliar applications in increasing Mn concentration in the leaves of trees sprayed with $MnSO_4$ and urea mixtures. These overall increases in Mn concentrations in the leaves may have been due to the accumulative effect of urea on Mn or to slightly better absorption of Mn by the foliage when urea was present in $MnSO_4$ sprays.

However, the reduction in K and Ca concentrations in the leaves of trees sprayed with $MnSO_4$ spray solution is difficult to explain. This and previous experiments have proved that Mn foliar sprays applied to Mn-deficient orange trees increased the yield of oranges (Labanauskas *et al.*, 1963; Labanauskas and Puffer, 1964). Possibly, by thus increasing the yield of oranges, the concentrations of K and Ca in the leaves were reduced. On the other hand, the concentrations of N, P, Mg, Na, Cl, Cu, B, and Fe were not affected by this increase in yield due to Mn spray.

In this experiment and several others, Zn foliar sprays did not have any significant effect on yield, but did significantly reduce the concentrations of N, Ca, Mg, and Cu—while Na and Mn were increased in the leaves. The increase in Na concentration in the leaves can be attributed to the very small amount of Na_2CO_3 as the precipitating agent for $ZnSO_4$.

Data obtained in the present experiment partially confirmed and explained results of earlier studies (Labanauskas *et al.*, 1961, 1963; Labanauskas and Puffer, 1964) indicating that when Mn and Zn sprays, in the presence of Na_2CO_3 as a precipitating agent, are applied to citrus leaves, an interrelationship occurs among the nutrients in the spray solution. This interrelationship thus affects the concentrations of these nutrients in the leaves, particularly between Mn and Zn, K, Ca, Na, and between Zn and N, Ca, Mg, Na, Cl, Mn, and Cu. These data revealed that the concentrations of soluble-free Zn and Mn ions in the spray solution are responsible for some of these interactions between Zn and Mn in the leaf tissue. It appears that nutrients, such as Mn and Zn, when taken up by the leaves, may affect uptake and distribution of other nutrients, as shown by Cain (1948, 1953*a*, *b*). In addition, the high concentrations of Zn and Mn in the leaves may change the physiological activity of the leaf and affect the metabolic processes of nutrients within the leaf.

Thus, a low concentration of an element in plant tissue can occur not only from a low supply of the element in question, but also from another element which has been applied to the plant. This latter element may have a depressing effect on another ion, or it may affect the distribution of ions within a plant.

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