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Foliar Application of $ZnSO_4$ and $CuSO_4$ Affects the Growth, Productivity, and Fruit Quality of Washington Navel Orange Trees (*Citrus sinensis* L.) Osbeck

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Abstract: The goal of this study was to examine how to improve the vegetative growth, nutritional status, productivity, and fruit quality of Washington navel orange trees by examining the effect of foliar application of $ZnSO_4$ (0, 300, and 600 mg/L) solutions in combination with $CuSO_4$ (0, 200, and 400 mg/L) solutions on Washington navel orange trees, which were 11 years old and grown in clay loam soil with a surface irrigation system. The results showed that all the investigated measurements responded specifically to each investigated factor. $ZnSO_4$ elicited a stronger and more effective response than $CuSO_4$. Nonetheless, the response varied only slightly or moderately from one measurement to the next. In terms of the interaction effect between $ZnSO_4$ and $CuSO_4$ concentrations, the effect of each investigated factor was directly reflected in its combinations, with $ZnSO_4$ (600 mg/L) and $CuSO_4$ (200 and 400 mg/L) being the most effective for the majority of the measurements under consideration. When the highest level of $ZnSO_4$ was combined with the highest level of $CuSO_4$, the highest values for the various vegetative growth parameters shoot length and diameter, number of leaves per shoot, leaf area, and total assimilation area per shoot were obtained. As a result, the nutritional status (the highest total leaf chlorophyll and leaf mineral contents) was significantly coupled with the treatment of 600 mg/L $ZnSO_4$ in combination with 400 mg/L $CuSO_4$. Moreover, the combinations of the highest $ZnSO_4$ concentration (600 mg/L) and $CuSO_4$ concentration (400 mg/L) exhibited the greatest statistical values of the measurements of fruiting aspects as well as fruit quality. Consequently, it can be recommended that using 600 mg/L $ZnSO_4$ in combination with 400 mg/L $CuSO_4$ as a foliar spray on monthly basis during the period from March to July could be safely recommended under similar environmental conditions and horticulture practices adopted in the present experiment.

Keywords: foliar application; nutritional status; fruit quality; vegetative growth; Washington navel orange; zinc and copper sulfate

1. Introduction

Plants require micronutrients, such as zinc, manganese, copper, boron, and molybdenum. Except for molybdenum, all micronutrients are unavailable in Egypt. Zinc added to alkaline soil is typically adsorbed or precipitated on the surface and does not easily pass to the root region, according to research. Furthermore, because citrus is a deep-rooted tree, applying micronutrients to the soil may be ineffective [1]. Zn foliar application increased sweet orange fruit yield compared with the control treatment [2].

Plant nutrients are easily absorbed through the surface of the leaves; as a result, Swietlik [3] stated that the mineral nutrients reached the leaf in three stages: (1) penetration through the cuticle and epidermal walls, (2) adsorption on the surface of the plasmalemma, and (3) passage through the plasmalemma to the cytoplasm. Foliar treatments are also required in cases of immobilization processes, which render the application to soils ineffective. Nutrient absorption is determined by several influences, including plant types, leafage, nutrient type and concentration, product formulation, climatic conditions, and plant nutritional status [4]. Citrus development has also been affected by micronutrients such as zinc (Zn) and copper (Cu) applications. These components influence the biochemical functions of the plant system. Zn is an important micro factor essential for plants because of its role in tryptophan synthesis, a precursor to indole acetic acid synthesis [5].

Citrus trees are the most economically important fruit crop in Egypt in terms of cultivated area, output, and export potential. Egypt is considered to be the world's largest orange exporter and is ranked as the sixth-largest producer. The orange is the major species of citrus in Egypt. Where an area of approximately 133,236 hectares was planted, accounting for about 69% of the total citrus area, producing about 2.9 million tons, and representing about 71% of the total citrus harvest, orange exports were about 1.1 million tons, accounting for about 92% of the total citrus exports [6]. There are different problems with navel orange productivity in the Delta zone, such as (1) a lack of sufficient quantity of fertilizers, still, mostly no prescribed fertilization programmers; (2) vast areas that have had low productivity due to the orange crop, with some of these orchards planted more than 50 years ago; (3) low productivity of different orchards (around 22 tons/ha); and (4) most orchards in the Delta area having mixed varieties within the same field [7].

Zn is needed for the action of different enzymes, such as dehydrogenases, aldolases, isomerases, transphosphorylases, and RNA and DNA polymerases [8]. It has an essential function in the metabolism of starch and serves as a co-factor for several enzymes, and it influences photosynthesis reactions, nucleic acid metabolism, and protein biosynthesis [9]. Bergmann [10] indicated that zinc is assumed to be involved in chlorophyll synthesis because of its effect on protein, carbohydrate, and energy metabolism. Taiz and Zeiger [11] stated that several enzymes needed zinc ions (Zn^{2+}) for their function, and zinc may be required for chlorophyll biosynthesis in some plants.

Cu is involved in the stimulation of lignification of all plant cell walls, photosynthesis, and electron carriers in plant enzyme systems [12]. It plays an essential function in the synthesis and/or stabilization of other plant pigments in chlorophyll soil. Copper also participates in various physiological processes and is an important cofactor for certain metalloproteinases, but complications occur when excess copper is found in cells [13].

As a result, the purpose of this study was to determine the effect of spraying 'Washington' navel orange trees with varying concentrations of $ZnSO_4$ and $CuSO_4$ on vegetative growth, nutritional status, yield, and fruit quality.

2. Materials and Methods

During the 2019 and 2020 experimental seasons, 11-year-old Washington navel orange trees budded on Sour orange rootstock were planted 5 × 5 meters apart (168 trees/fed.) in a private orchard under surface irrigation located in the Toukh region, Qalyubia Governorate, Egypt. The experimental area was located at an altitude of 45 m above mean sea level between the 30.45 N latitude and 31.10 E longitude. The same horticultural practices were applied to all trees as recommended by the Ministry of Agriculture and implemented in the region. This study was designed to determine the effects of different $ZnSO_4$ and $CuSO_4$ concentrations on the growth, nutritional status, and fruiting aspects of Washington navel orange trees. Before the start of the first season (2019) a mechanical and chemical analysis of the orchard soil surface (40 cm depth) was carried out according to [14], as shown in Table 1 below.

Table 1. Physical and chemical properties of the soil under investigation.

Physical Analysis	Value	Chemical Analysis			
		Cations meq/L		Anions meq/L	
Coarse sand	11%	Ca^{2+}	8.8	$CO_3{}^{2-}$	Zero
Fine sand	19.4%	Mg^{2+}	3.25	$HCO_3{}^{-}$	4.5
Silt	19.0%	Na^{+}	4.30	Cl^{-}	6.45
Clay	49.4%	K^{+}	1.08	$SO_4{}^{2-}$	8.00
Texture class	Clay loam	Available N 24.5 mg/kg			
Soil pH	7.3	Available P 11.94 mg/kg			
E.C, ds/m	1.65	Available K 170.5 mg/kg			
Organic matter	3.6%				

The nine treatments involved in this study can be summarized as follows:

1—Tap water (control), 2—$CuSO_4$ 200 mg/L,
3—$CuSO_4$ 400 mg/L, 4—$ZnSO_4$ 300 mg/L,
5—$ZnSO_4$ 300 mg/L + $CuSO_4$ 200 mg/L, 6—$ZnSO_4$ 300 mg/L + $CuSO_4$ 400 mg/L,
7—$ZnSO_4$ 600 mg/L, 8—$ZnSO_4$ 600 mg/L + $CuSO_4$ 200 mg/L,
9—$ZnSO_4$ 600 mg/L + $CuSO_4$ 400 mg/L

Considering that the forms of zinc and copper added were copper sulfate and zinc sulfate solutions, the molecular weight of $CuSO_4$ was 159.61 and the molecular weight of copper was 63, and the molecular weight of $ZnSO_4$ was 161.47 and the molecular weight of zinc was 65.21.

2.1. *Experiment Layout*

The nine investigated fertilization treatments were organized using a complete randomized block design with three replications, with a single tree representing each replicate. As a result, 27 healthy fruitful Washington navel orange trees that were healthy, disease-free, and in the on-year state were carefully selected. The chosen trees were divided into three categories (blocks) on the basis of their growth vigor, with each block containing nine similar trees, each of them received one of the nine foliar spray treatments investigated (a single tree was randomly subjected to one treatment). During each season, the dedicated trees for each treatment were sprayed five times with the corresponding solution in one-month intervals beginning at full bloom. Considering that spraying treatments were used to cover the entire foliage of each tree canopy, 5 liters were found to be sufficient in this regard. In the second year, all treatments were repeated with different trees in the same experiment area. Climatic data presented in Table 2 showing the different weather data for the experimental area.

During the first and second seasons of study, four main branches (limbs/scaffolds) well-distributed around each tree's periphery were carefully selected and tagged late in March 2019 and 2020. In addition, 20 newly developed spring shoots were labeled.

Table 2. Weather data on the air temperature, rainfall, and relative humidity of the study area: Toukh Qalubia, Egypt (2019–2020 growing years and long-term data).

Month	Min Temp.	Max Temp.	Humidity	Wind	Sun	Rad	Eff. Rain	ETo
	°C	°C	%	km/Day	Hours	MJ/m^2/Day	mm	mm/Day
January	7.2	20.8	51	206	7.8	13.5	1.1	2.83
February	7.6	23.9	42	245	8.6	17.0	1.2	3.80
March	10.6	24.8	38	276	8.9	20.0	1	5.12
April	14.8	30.7	30	277	9.2	22.6	1	6.90
May	18.5	35.3	31	262	10.2	25.1	0	8.02
June	21.2	36.9	33	271	11.4	26.7	0	8.81
July	22.2	39.1	39	223	11.3	26.2	0	8.00
August	22.4	37.4	32	205	10.4	25.1	0	7.42
September	19.4	33.2	44	214	9.5	22.2	0	6.21
October	17.2	31.3	47	213	9.2	18.1	0	5.12
November	10.6	24.5	53	180	8.3	14.5	0	3.53
December	7.6	20.7	57	193	7.8	13.1	0.58	2.70

Abbreviation explanations: Min Temp—minimum temperature recorded during the night; Max Temp—maximum temperature recorded during the day; Humidity—total amount of vapor in the atmosphere, Wind—the wind speed in km/h; Sun—sun hours; Rad—radiation amount per day; Eff. rain—total amount of rain during the month in mm; ETO—evapotranspiration per day in mm. Source: Meteorological Station of Qalubia, Egypt.

2.2. Vegetative Growth Measurements

In the middle of October, the following vegetative growth parameters were determined during the first and second experimental seasons.

In this regard, the average number of newly developed shoots per one meter of each tagged limb, average length and thickness, and the number of leaves per labeled shoot were estimated. In addition, the average leaf area (cm^2) on a weight basis was also determined. Hence, 20 mature leaves from the previously labeled shoots per limb were randomly collected. Then, 20 disks from each centimeter of the area were taken and oven-dried, together with the leaves, at 80 °C until a constant weight was achieved. Using a known dry weight of leaves with a known surface area, i.e., 20 leaf discs on one hand and the total weight of 20 leaves on the other, the average leaf area in centimeters was calculated. Moreover, the assimilation area per shoot was calculated according to the following equation: Assimilation area = leaf area x No. of leaves per one shoot.

2.3. Biochemical Analysis

2.3.1. SPAD Chlorophyll

The total chlorophyll content in fresh leaves was determined using Minolta meter SPAD-502.

2.3.2. Estimation of Certain Minerals

During both seasons, representative samples of the fourth and fifth leaves from the bases of spring shoots were collected from each replicate in October. The samples were thoroughly washed with tap water, rinsed twice with distilled water, oven-dried at 80 °C until they reached a constant weight, and finely ground. A 250 mL digestion flask previously washed with acid and distilled water was filled with 0.2 g of ground plant material. A 6 mL mixture of concentrated (5 mL) sulfuric acid and (1 mL) perchloric acid (70%) in a 5:1 (v/v) ratio was added. The samples were digested on an electric heater until dense white fumes appeared, at which point the solution became clean and a volume of about 2.5 mL was obtained. The samples were then allowed to cool before being quantitatively transferred into a 50 mL volumetric flask and diluted with distilled water. The distilled water was used to reach the required volume. The modified micro Kjeldahl method described by [15] was used to determine the total Nitrogen content (N). The total phosphorus (P) was determined by wet digestion of plant materials using sulfuric and perchloric acid, as recommended by [16]. The total potassium in the digested material (total leaf K) was determined photometrically using the method described in [17]. Following [18], the calcium and magnesium percentages, as well as the iron, manganese, and zinc contents, were determined using an atomic absorption spectrophotometer (Perkin Elmer-3300).

2.4. Productivity Measurements

2.4.1. Fruit Set Percentage

During each experimental season, the number of perfect flowers per tagged limb was counted at full blooming after estimating of 75% of the petal fall fruit set as a percentage of perfect flowers utilizing the following equation:

$$\text{Fruit set\%} = \frac{\text{Number of set fruitlets}}{\text{Number of perfect flowers}} \times 100$$

Fruit retention %:

During each experimental season, the percentage of retained fruits was estimated in late December using the following equation:

$$\text{Fruit}'\text{s retention\%} = \frac{\text{Number of presented (remained) fruits at a given date}}{\text{Number of set fruitlets}} \times 100$$

2.4.2. Yield Attributes

Fruits from each tree were harvested separately in late December 2019 and 2020, then counted and weighed. The number or weight (in kilograms) of fruits harvested per tree was used to estimate tree productivity (yield), and furthermore, the yield per tree.

2.4.3. Fruit Quality

Fruit Physical Properties

At harvest time, 15 healthy fruits were taken from each treatment to estimate the fruit's physical properties. The fruit's physical properties investigated in this case were the average fruit weight (g), dimensions (polar and equatorial diameters, i.e., length and width in centimeters), fruit shape index (length: width), juice weight and juice %, and peel thickness (mm).

Fruit Chemical Characteristics

The total soluble solids percentage (TSS %) of fruit juice was determined using a Carl Zeins hand refractometer. Following [19], fruit total acidity (grams of citric acid per 100 mL of juice) and ascorbic acid (V.C) content (milligrams of ascorbic acid per 100 mL fruit juice) were determined. The total soluble solids/acid ratio was calculated as well. Following [19], the ascorbic acid/vitamin C content was determined by titration with a 2,6-dichlorophenol-indophenol indicator. Furthermore, the percentage of total sugar was calculated using the method described by [20].

2.5. Statistical Analysis

All data collected during both experimental seasons were subjected to an analysis of variance, and significant differences between means were determined using the formula in [21]. Letters were used for distinguishing between the means of specific effects of two investigated factors, i.e., $ZnSO_4$ and $CuSO_4$ concentrations and the interaction between them, according to Duncan's multiple test range [22].

3. Results

The influence was assessed by comparing the responses of the various parameters under study to each investigated factor ($ZnSO_4$ and $CuSO_4$) separate with the responses to different concentrations of these factors is a specific effect. In addition, the interaction effect of $ZnSO_4$ with $CuSO_4$ concentrations (combinations).

3.1. Vegetative Growth Measurements

The investigated growth parameters in response to the different treatments were the number of developed shoots per meter of each tagged main branch (limb/scaffold), the average shoot length and diameter, the number of leaves/shoots, the average leaf area, and the total assimilation area/shoot. Figures 1 and 2 displays data collected during the 2019 and 2020 seasons.

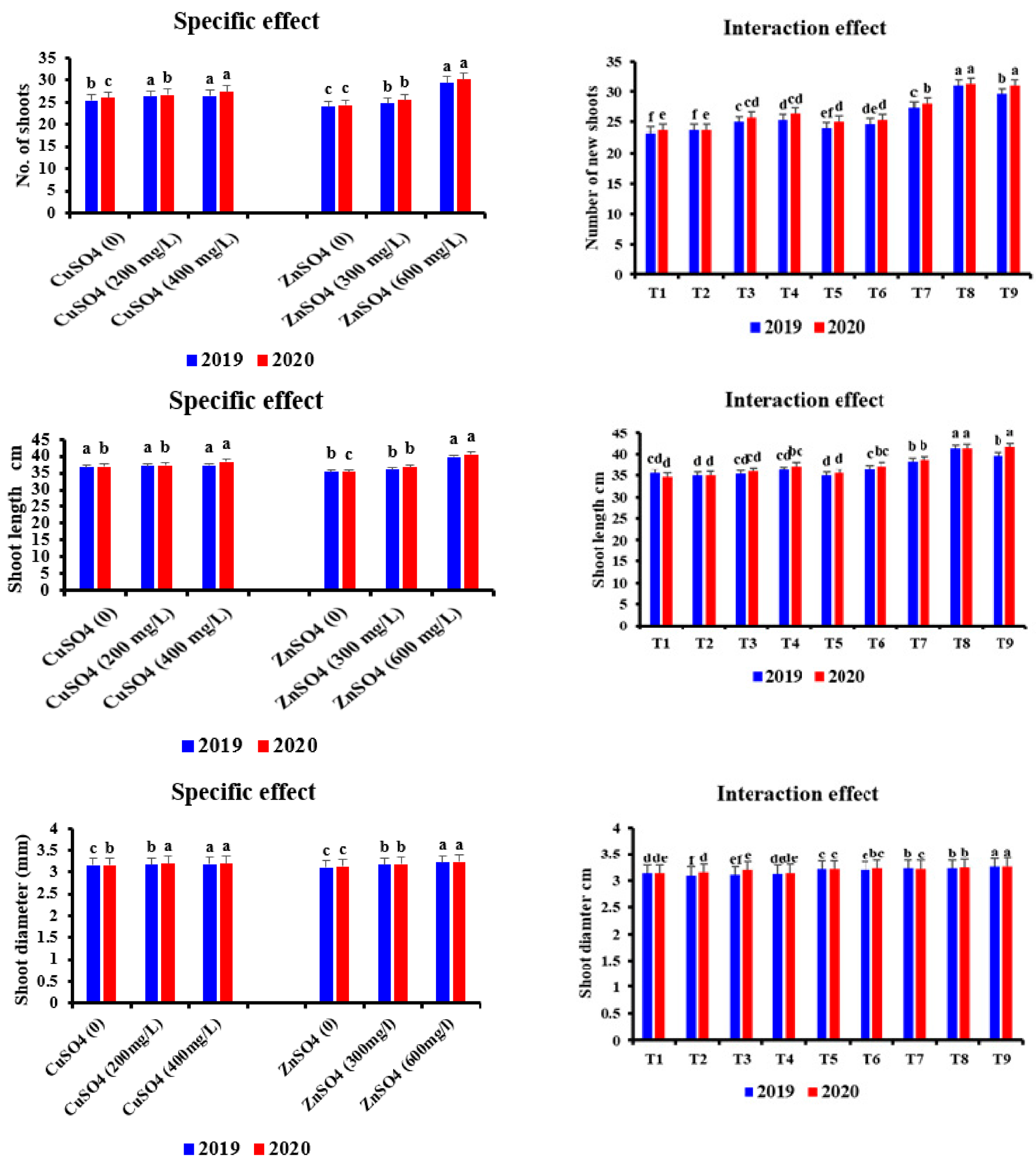

Figure 1. Shoot length (cm), shoot diameter (cm), and number of leaves/shoots of Washington navel orange trees in response to specific and interaction effects of different $ZnSO_4$ and $CuSO_4$ concentrations during the 2019 and 2020 seasons. The means of specific and interaction effects followed by the same letters did not significantly differ at the 5% level. Note: T1 = control, T2 = $CuSO_4$ 200 mg/L, T3 = $CuSO_4$ 400 mg/L, T4 = $ZnSO_4$ 300 mg/L, T5 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 200 mg/L, T6 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 400 mg/L, T7 = $ZnSO_4$ 600 mg/L, T8 = $ZnSO_4$ 600 mg/L+ $CuSO_4$ 200 mg/L, and T9 = $ZnSO_4$ 600 mg/L + $CuSO_4$ 400 mg/L.

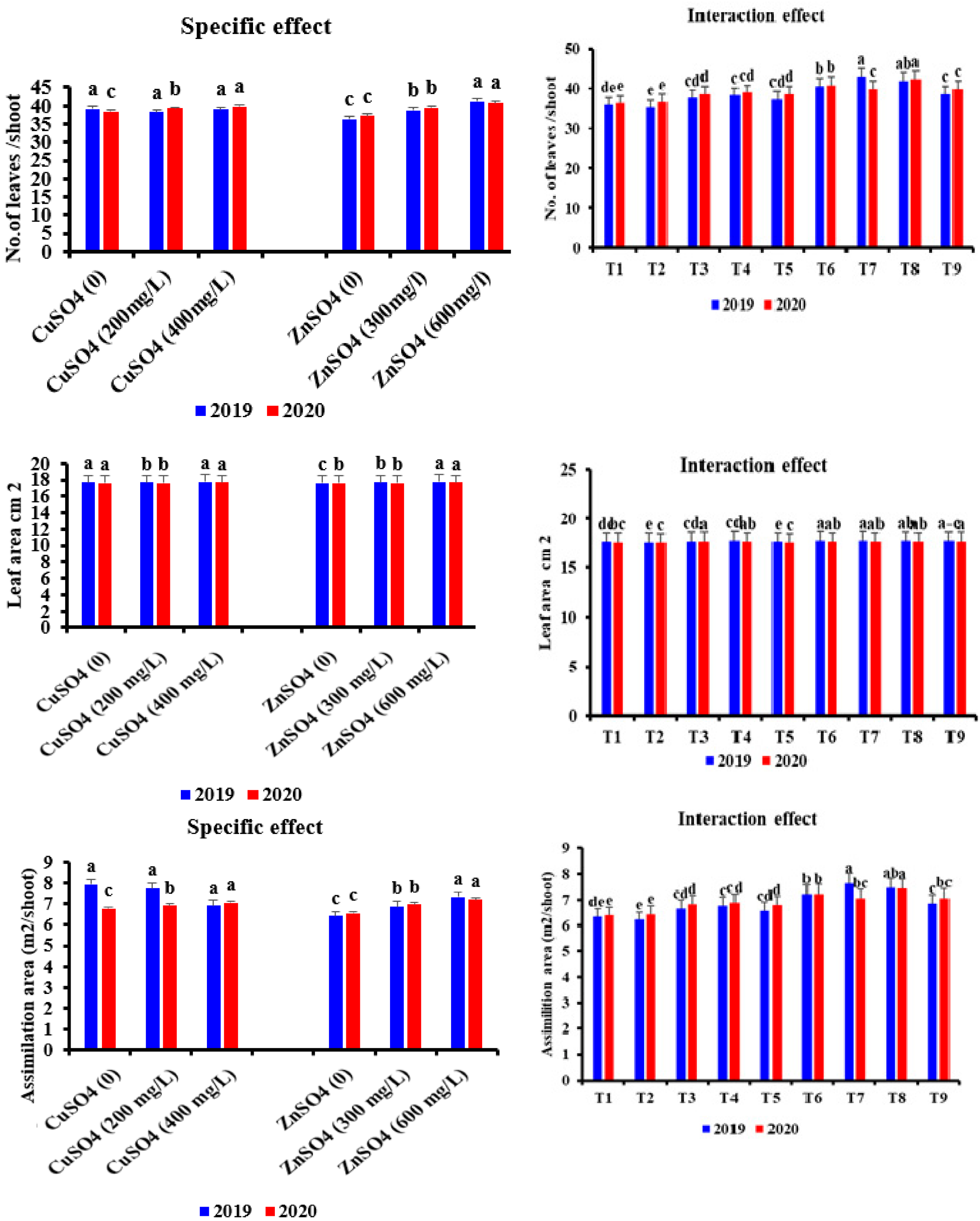

Figure 2. Number of new shoots, leaf area (cm^2), and assimilation area m^2/shoot of Washington navel orange trees in response to specific and interaction effects of different $ZnSO_4$ and $CuSO_4$ concentrations during the 2019 and 2020 seasons. The means of specific and interaction effects followed by the same letters didn't significantly differ at the 5% level. Note: T1 = control, T2 = $CuSO_4$ 200 mg/L, T3 = $CuSO_4$ 400 mg/L, T4 = $ZnSO_4$ 300 mg/L, T5 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 200 mg/L, T6 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 400 mg/L, T7 = $ZnSO_4$ 600 mg/L, T8 = $ZnSO_4$ 600 mg/L + $CuSO_4$ 200 mg/L, and T9 = $ZnSO_4$ 600 mg/L + $CuSO_4$ 400 mg/L.

3.1.1. Specific Effect

It is quite clear that all the above-mentioned vegetative growth parameters were specific to each investigated factor. Nevertheless, not only did the grade of response vary from one vegetative growth measurement to the next, but the rates of difference of the investigated measurements exhibited by $ZnSO_4$ were more pronounced than those exhibited by $CuSO_4$. Moreover, it is noted in Figures 1 and 2 that the highest values for the different vegetative growth parameters were recorded when the highest level of $ZnSO_4$ or the highest level of $CuSO_4$ was used. This was true for all growth measurements taken over two seasons.

3.1.2. Interaction Effect

The results showed that in both seasons, the recorded vegetative growth parameters were all favorably influenced by the different $ZnSO_4$ and $CuSO_4$ treatments. Moreover, the values recorded for the different parameters showed steady significant increases when raising the application rates of $ZnSO_4$ and/or $CuSO_4$. Accordingly, the highest values for the different parameters were recorded when the highest level of $ZnSO_4$ was combined with the highest rate of $CuSO_4$.

3.2. Total Chlorophyll and Macro and Micronutrient Contents in the Leaves

The data presented in Figures 3–5 indicates that the total chlorophyll content together with the nutritional status of Washington navel orange trees, i.e., N, P, K, Ca, Mg, Fe, Mn, Zn, and Cu contents, were influenced by specific and interaction effects of different concentrations of $ZnSO_4$ and $CuSO_4$ and their combinations during 2019 and 2020 seasons.

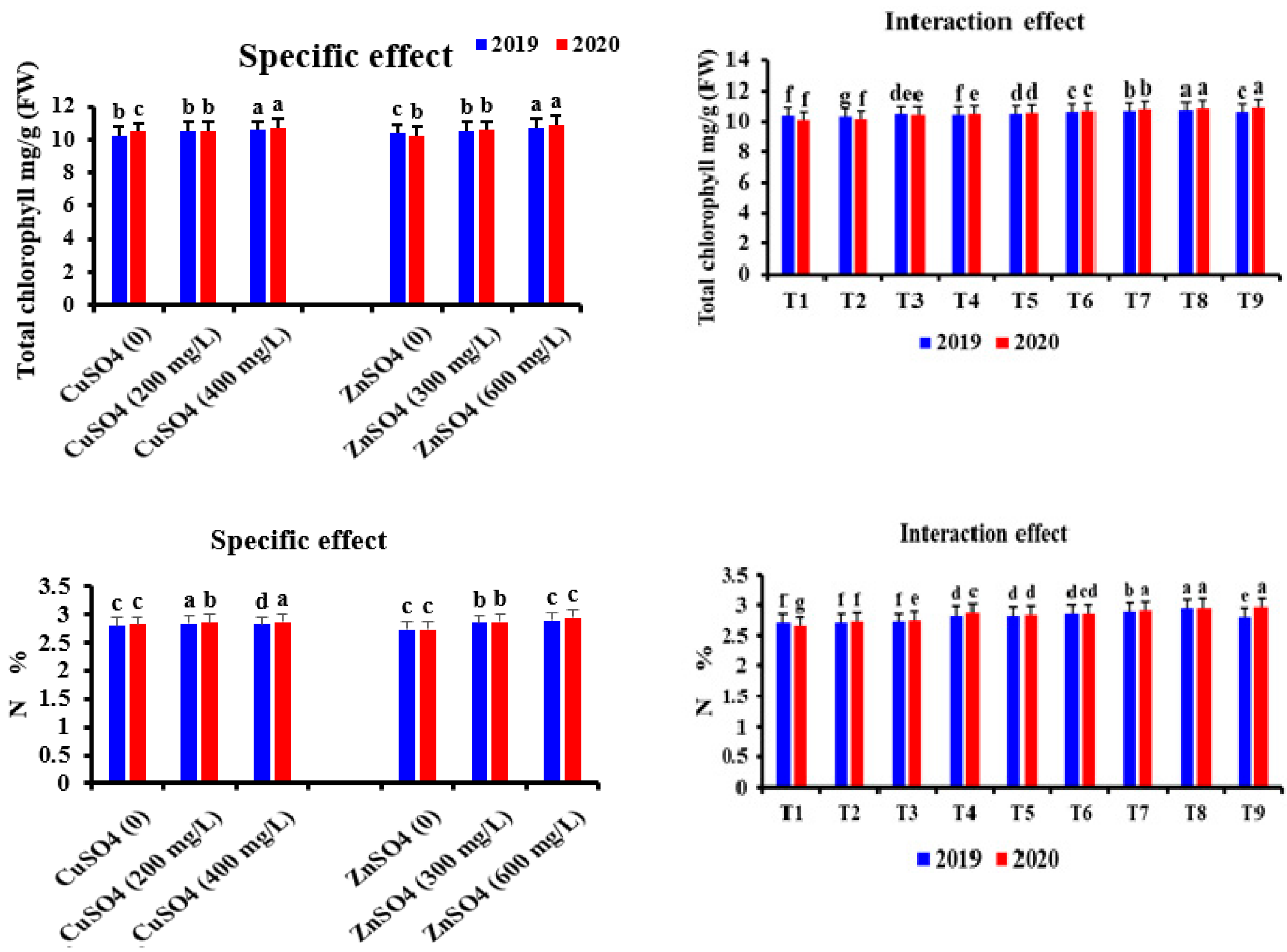

Figure 3. *Cont.*

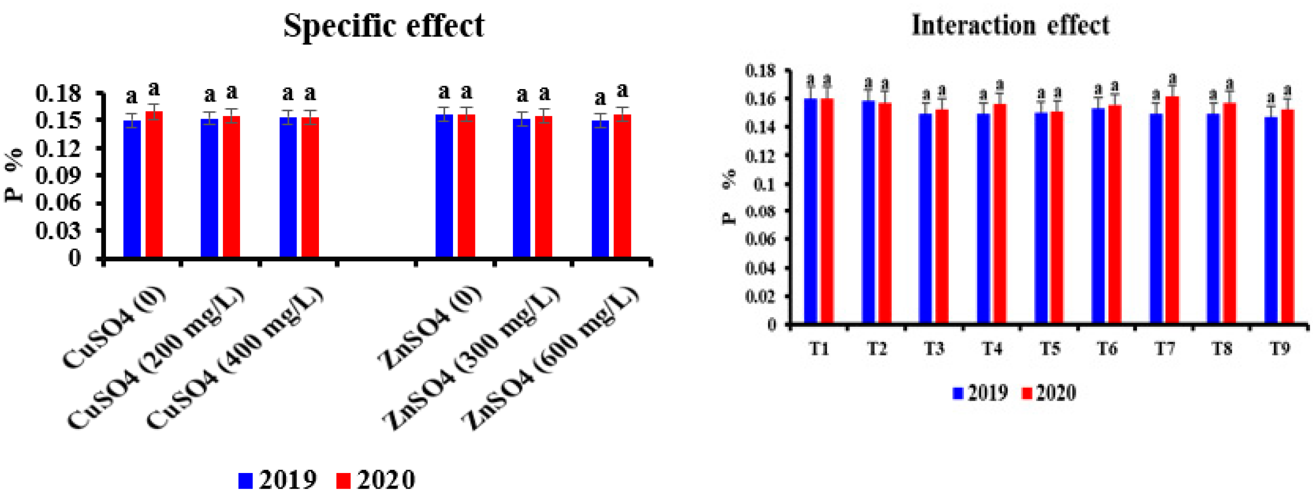

Figure 3. Total leaf chlorophyll (mg/g F.W.), N, and P contents of Washington navel orange trees in response to the specific and interaction effects of different $ZnSO_4$ and $CuSO_4$ concentrations during the 2019 and 2020 seasons. The means of specific and interaction effects followed by the same letters did not significantly differ at the 5% level. Note: T1 = control, T2 = $CuSO_4$ 200 mg/L, T3 = $CuSO_4$ 400 mg/L, T4 = $ZnSO_4$ 300 mg/L, T5 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 200 mg/L, T6 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 400 mg/L, T7 = $ZnSO_4$ 600 mg/L, T8 = $ZnSO_4$ 600 mg/L + $CuSO_4$ 200 mg/L, and T9 = $ZnSO_4$ 600 mg/L + $CuSO_4$ 400 mg/L.

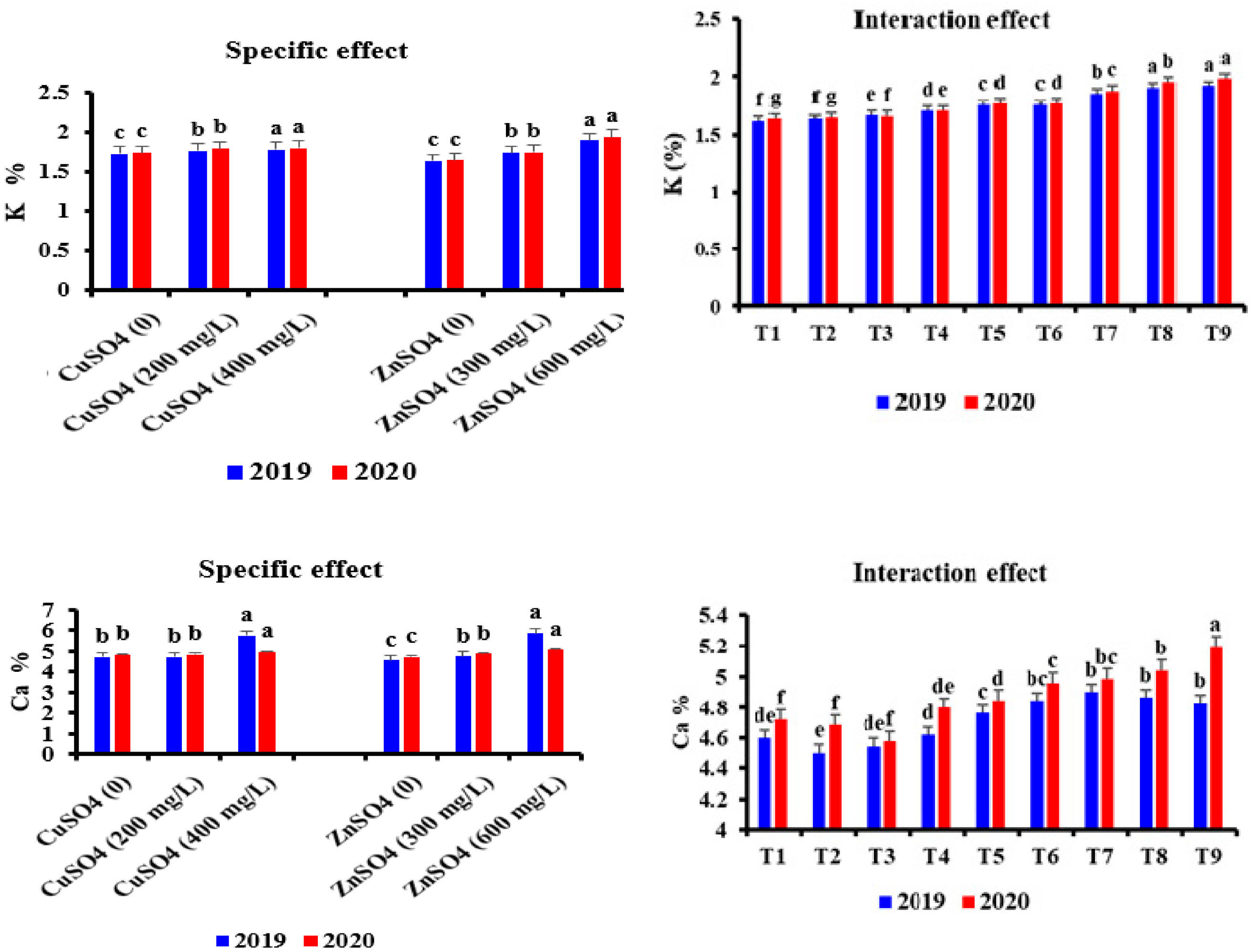

Figure 4. *Cont*.

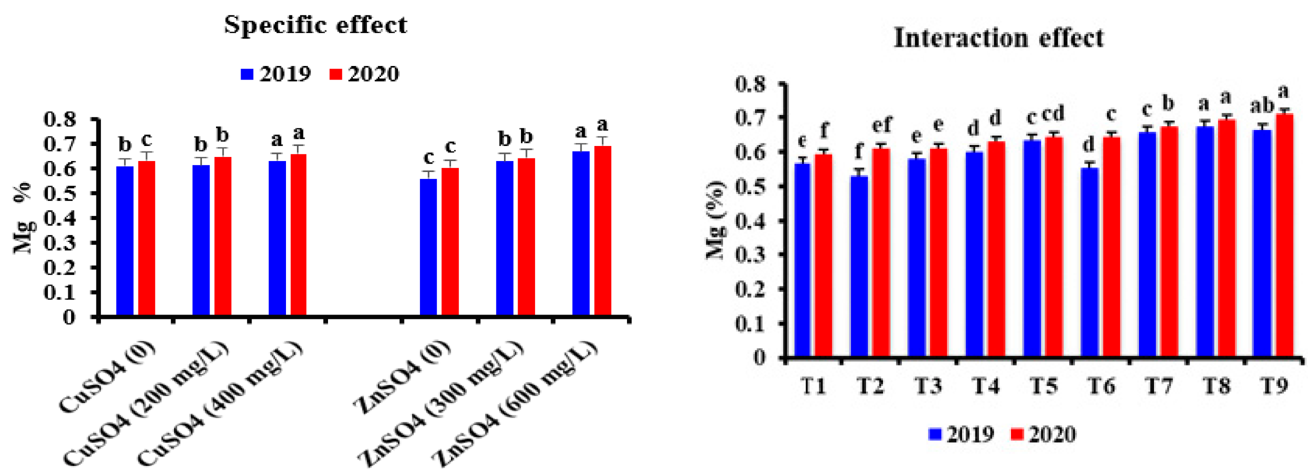

Figure 4. Leaf K, Ca, and Mg contents of Washington navel oranges in response to specific and interaction effects of different $ZnSO_4$ and $CuSO_4$ concentrations during the 2019 and 2020 seasons. The means of specific and interaction effects followed by the same letters did not significantly differ at the 5% level. Note: T1 = control, T2 = $CuSO_4$ 200 mg/L, T3 = $CuSO_4$ 400 mg/L, T4 = $ZnSO_4$ 300 mg/L, T5 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 200 mg/L, T6 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 400 mg/L, T7 = $ZnSO_4$ 600 mg/L, T8 = $ZnSO_4$ 600 mg/L + $CuSO_4$ 200 mg/L, and T9 = $ZnSO_4$ 600 mg/L + $CuSO_4$ 400 mg/L.

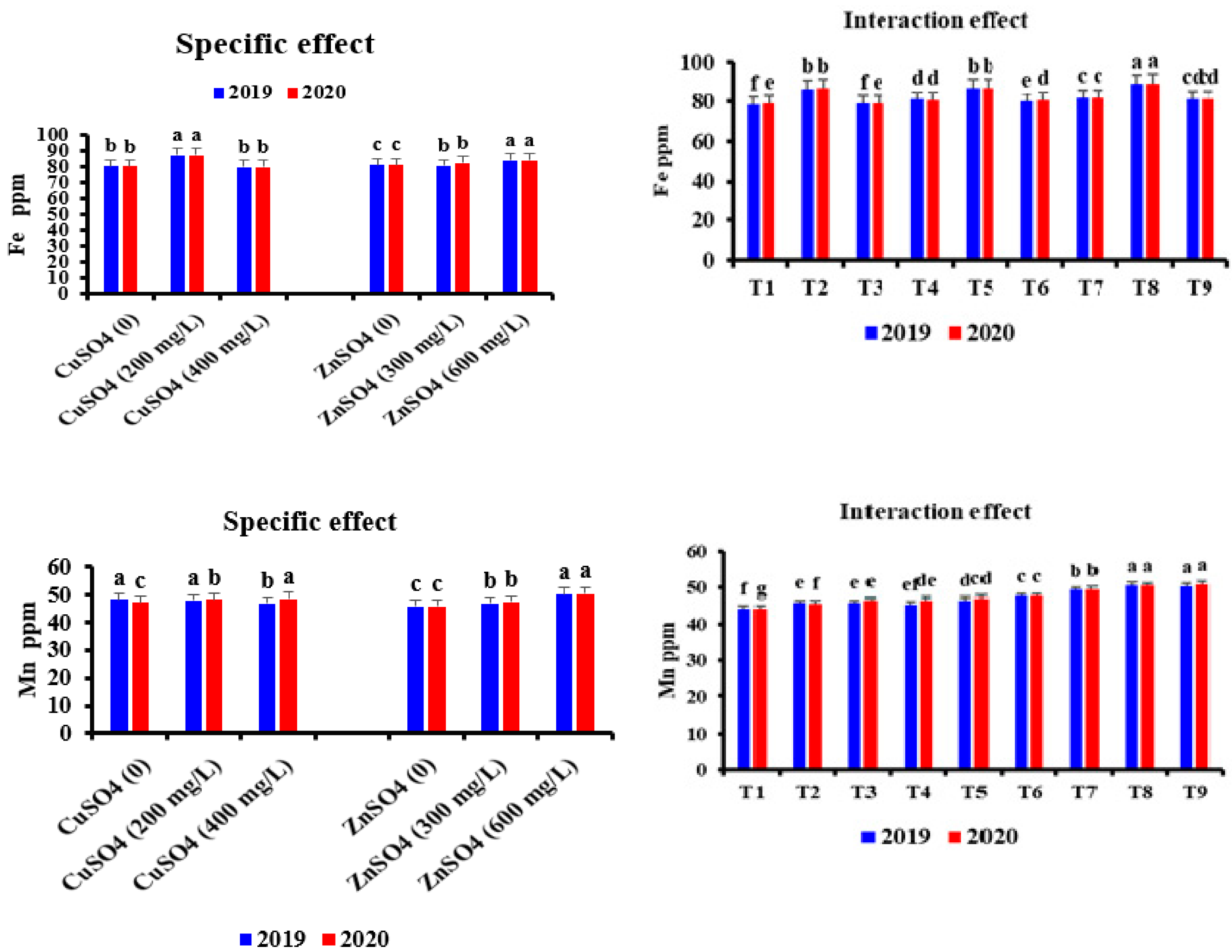

Figure 5. *Cont.*

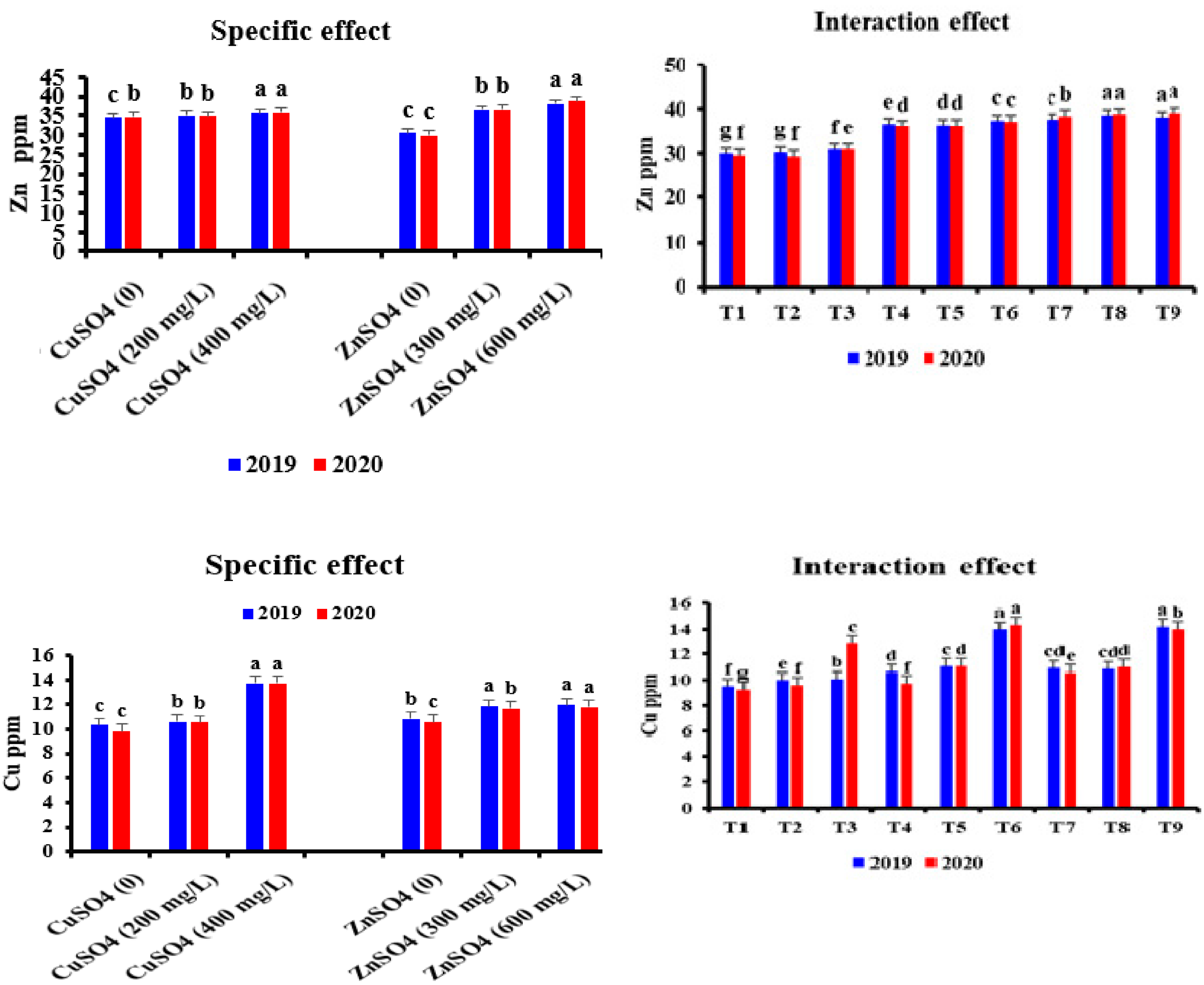

Figure 5. Fe, Cu, Zn, and Mn contents of Washington navel oranges in response to specific and interaction effects of different $ZnSO_4$ and $CuSO_4$ concentrations during the 2019 and 2020 seasons. The means of specific and interaction effects followed by the same letters did not significantly differ at the 5% level. Note: T1 = control, T2 = $CuSO_4$ 200 mg/L, T3 = $CuSO_4$ 400 mg/L, T4 = $ZnSO_4$ 300 mg/L, T5 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 200 mg/L, T6 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 400 mg/L, T7 = $ZnSO_4$ 600 mg/L, T8 = $ZnSO_4$ 600 mg/L + $CuSO_4$ 200 mg/L, and T9 = $ZnSO_4$ 600 mg/L + $CuSO_4$ 400 mg/L.

As for the specific effect of $ZnSO_4$ spray solutions, all concentrations significantly increased all investigated leaf chemical compositions compared with the control. Such a trend was seen during both seasons. Moreover, the most effective $ZnSO_4$ was significantly coupled with its highest concentration (600 mg/L) in terms of the response of total chlorophyll content and macro and micronutrient contents. However, the high concentration of $CuSO_4$ (400 mg/L) resulted in a slight increase in the total leaf chlorophyll content and level of macro and micronutrient contents.

3.3. Interaction Effect

Concerning the interaction effect between $ZnSO_4$ concentrations and $CuSO_4$ concentration on the total leaf chlorophyll, and furthermore on the macro and micronutrients contents. The data presented in Figures 3–5 indicates that the different combinations varied in terms of their effect on the leaf chemical compositions of Washington navel orange trees. However, the most effective combinations were generally in a relationship with those between the highest concentration of $ZnSO_4$ (600 mg/L) and the highest $CuSO_4$ concentration (400 mg/L). Moreover, the trend of response varied greatly or slightly from one leaf chemical constituent to another. The highest leaf mineral contents were significantly coupled with the treatment of 600 mg/L$ZnSO_4$ with 400 mg/L$CuSO_4$ in both seasons. On the contrary, the lowest values of all or most leaf chemical constituents were usually concomitant with combinations between the lowest $ZnSO_4$ concentration (0 mg/L) and other $CuSO_4$ concentration (200 mg/L and 400 mg/L). In addition, other combinations were in the middle of the aforementioned two extremes. The obtained results can explain the basis of the more pronounced response of various nutritional status measurements to the specific effect of $ZnSO_4$ concentration rather than the specific effect of $CuSO_4$ concentration.

3.4. Some Fruiting Characterization in Response to $ZnSO_4$ and $CuSO_4$ Foliar Application

The data obtained for the fruit set %, fruit retention %, number of fruits/tree, average fruit weight (g), yield/tree (kg), and yield/ha (ton) as productivity measurements in response of the two evaluated factors during the 2019 and 2020 seasons are presented in Figures 6 and 7.

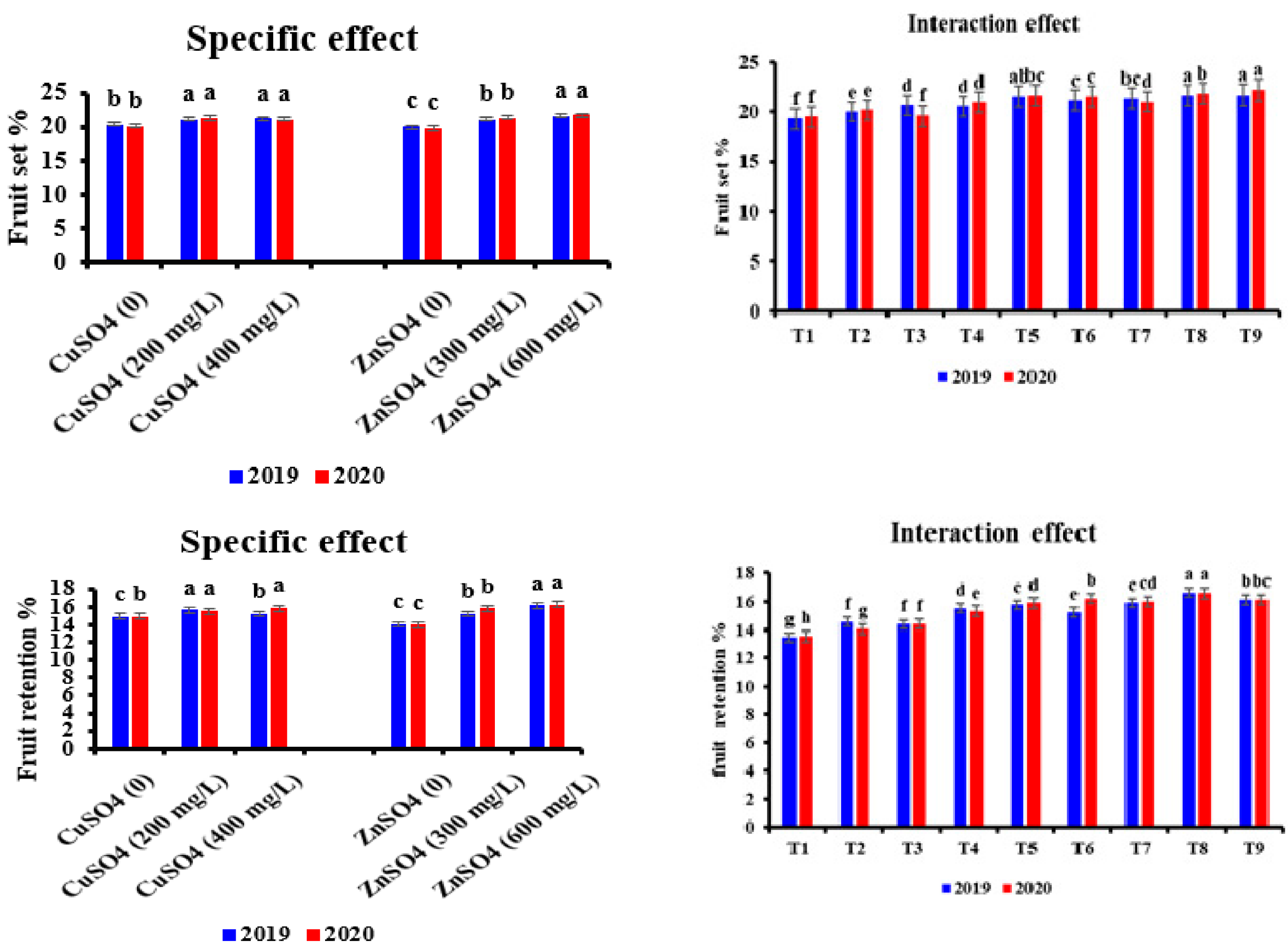

Figure 6. *Cont.*

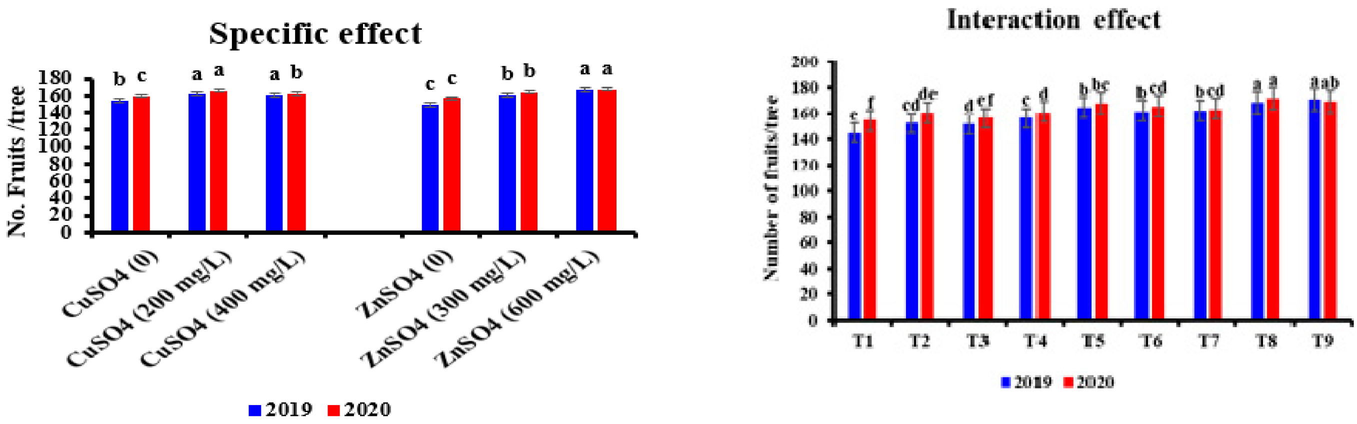

Figure 6. Fruit set %, number of fruits/tree, and fruit retention % of Washington navel orange trees in response to specific and interaction effects of different $ZnSO_4$ and $CuSO_4$ concentrations during the 2019 and 2020 seasons. The means of specific and interaction effects followed by the same letters did not significantly differ at the 5% level. Note: T1 = control, T2 = $CuSO_4$ 200 mg/L, T3 = $CuSO_4$ 400 mg/L, T4 = $ZnSO_4$ 300 mg/L, T5 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 200 mg/L, T6 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 400 mg/L, T7 = $ZnSO_4$ 600 mg/L, T8 = $ZnSO_4$ 600 mg/L + $CuSO_4$ 200 mg/L, and T9 = $ZnSO_4$ 600 mg/L + $CuSO_4$ 400 mg/L.

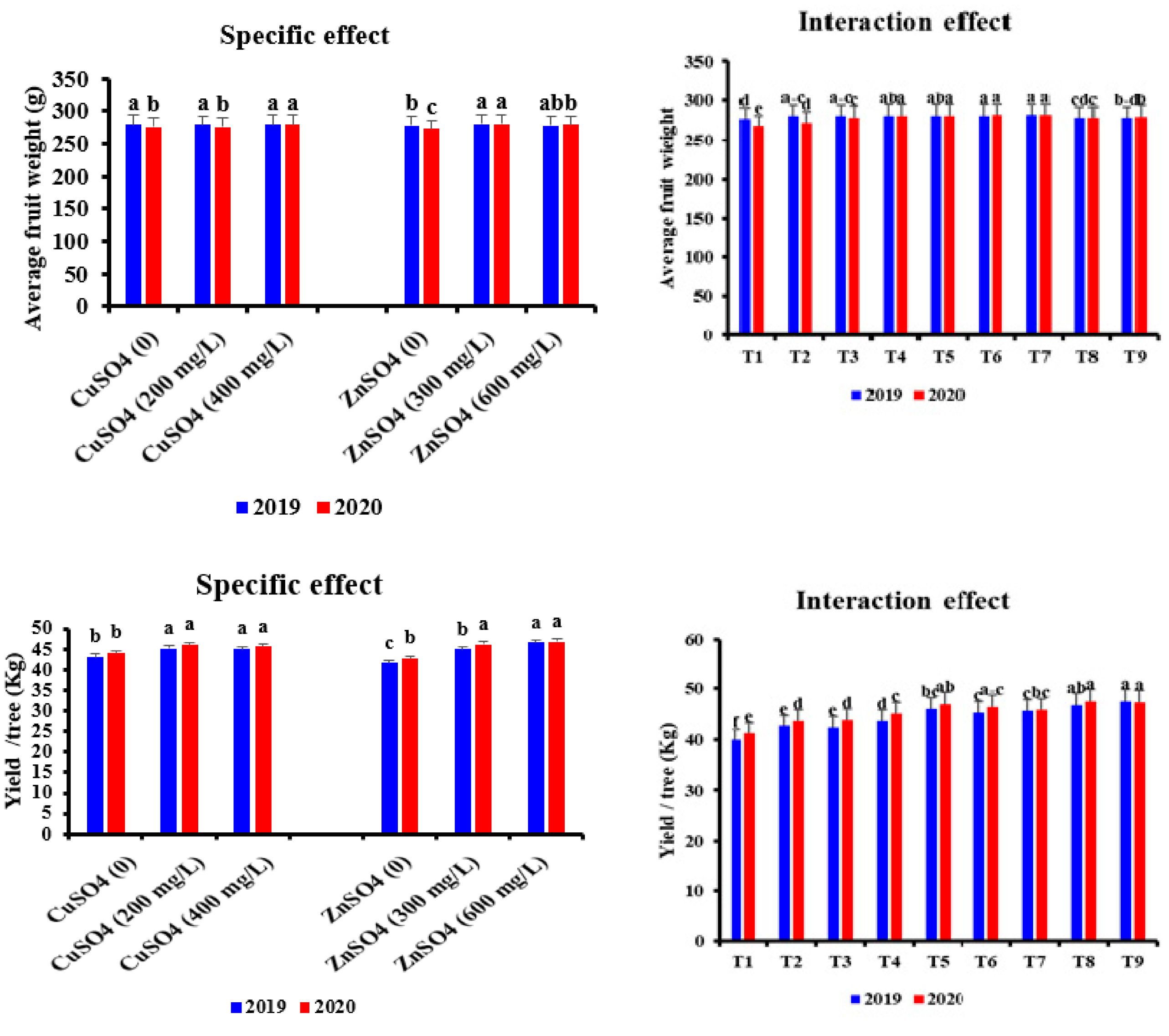

Figure 7. *Cont.*

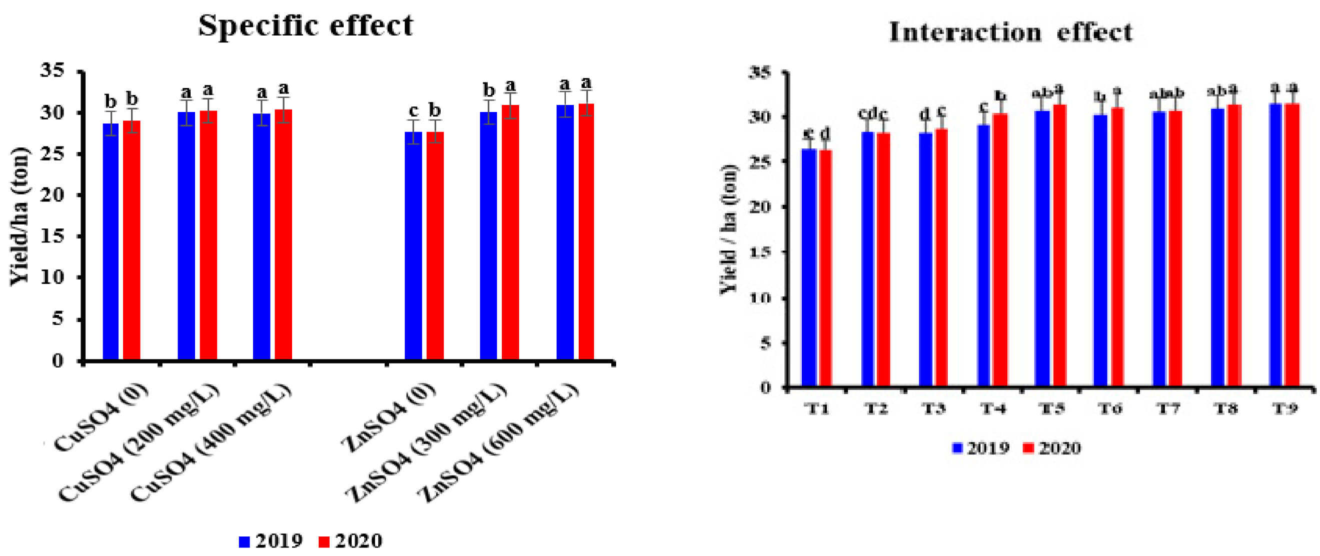

Figure 7. Average fruit weight (g), yield/tree (kg), yield/ha (ton) of Washington navel orange trees in response to specific and interaction effects of different $ZnSO_4$ and $CuSO_4$ concentrations during the 2019 and 2020 seasons. The means of specific and interaction effects followed by the same letters did not significantly differ at the 5% level. Note: T1 = Control, T2 = $CuSO_4$ 200 mg/L, T3 = $CuSO_4$ 400 mg/L, T4 = $ZnSO_4$ 300 mg/L, T5 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 200 mg/L, T6 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 400 mg/L, T7 = $ZnSO_4$ 600 mg/L, T8 = $ZnSO_4$ 600 mg/L + $CuSO_4$ 200 mg/L, and T9 = $ZnSO_4$ 600 mg/L + $CuSO_4$ 400 mg/L.

3.4.1. Specific Effect

It is undeniable that all the aforementioned fruiting measurements responded specifically to each investigated factor. Even so, not only did the grade of response vary from one fruiting parameter to another, but the rates of difference in the investigated measurements exhibited by $ZnSO_4$ were also more pronounced than the corresponding ones produced by $CuSO_4$. However, in general, the two $ZnSO_4$ spray solutions (300 and 600 mg/L) significantly increased all fruiting measurements compared with the control (water spray). Such a trend was seen with all fruiting measurements during the two seasons. The response of these fruiting parameters to the specific effect of $ZnSO_4$ and $CuSO_4$ concentrations emphasized unequivocally that the highest values of such measurements were significantly close to the highest $ZnSO_4$ and $CuSO_4$ concentrations (600 and 400 mg/L).

3.4.2. Interaction Effect

Figures 6 and 7 clearly show that in both seasons, the recorded fruiting parameters (fruit set %, fruit retention %, number of fruits/tree, average fruit weight/tree, yield/tree, and yield per hectare) were all favorably influenced by the different concentrations of $ZnSO_4$ and $CuSO_4$. Moreover, the values recorded for the different parameters showed steady significant increases when raising the application rates of $ZnSO_4$ and/or $CuSO_4$. Accordingly, the highest values for the different parameters were recorded when the highest level of $ZnSO_4$ was combined with the highest level of $CuSO_4$.

In addition, all investigated fruiting parameters that responded specifically to any investigated factor were also influenced by the factors' combinations. Consequently, a combination of the highest $ZnSO_4$ concentration (600 mg/L) and either $CuSO_4$ concentration (200 and 400 mg/L) exhibited, statistically, the greatest values of such measurements.

3.5. Fruit Quality

3.5.1. Fruit Physical Properties

The fruit dimensions (equatorial and polar diameters), fruit shape index, peel thickness, juice %, and weight were the evaluated fruit physical properties of Washington navel oranges in response to the differential investigated foliar spray treatments. The data obtained during both the 2019 and 2020 experimental seasons are presented in Figures 8 and 9.

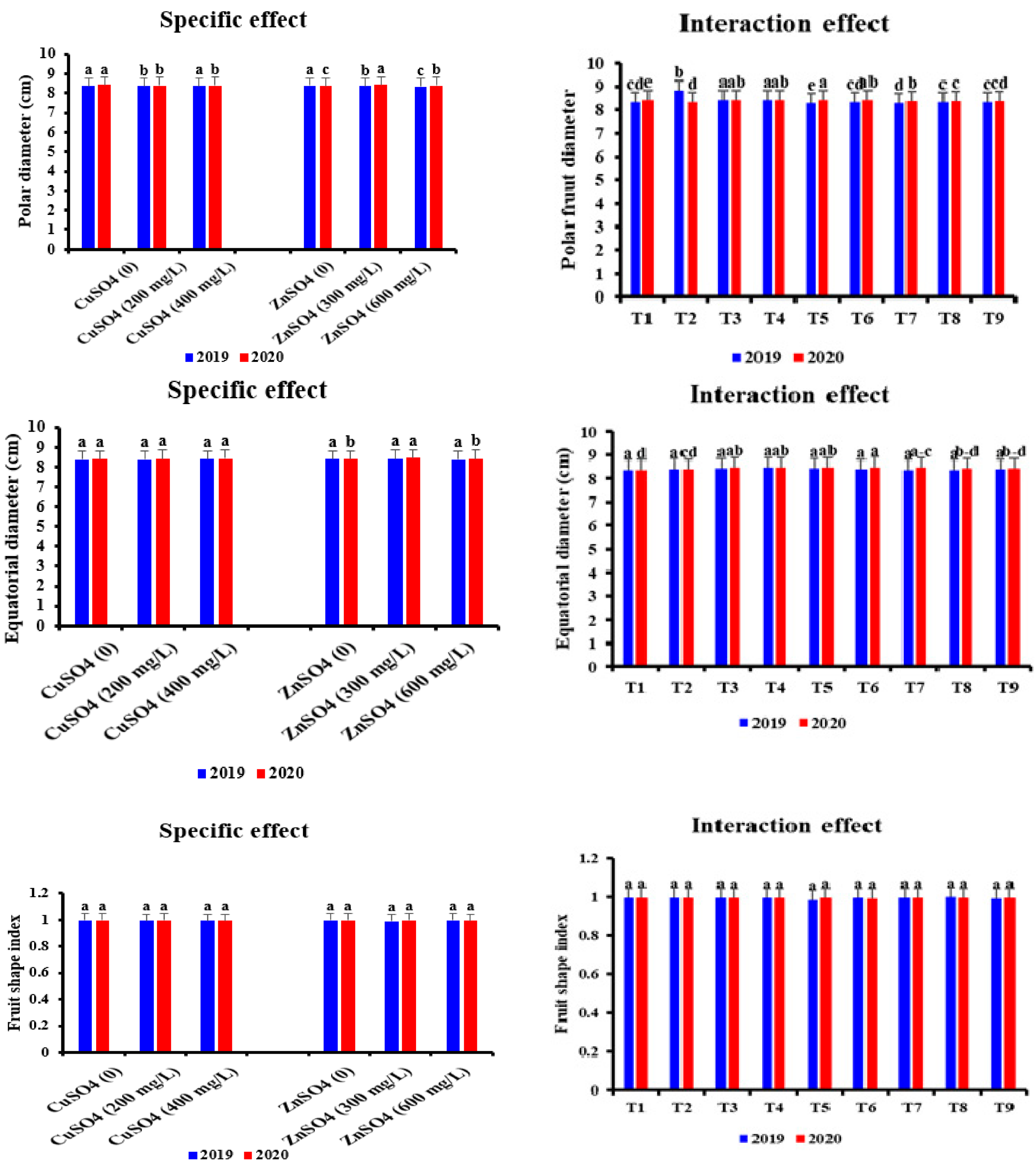

Figure 8. Polar diameter (cm), equatorial diameter, and fruit shape index of Washington navel oranges in response to specific and interaction effects of different $ZnSO_4$ and $CuSO_4$ concentrations during the 2019 and 2020 seasons. The means of specific and interaction effects followed by the same letters did not significantly differ at the 5% level. Note: T1 = Control, T2 = $CuSO_4$ 200 mg/L, T3 = $CuSO_4$ 400 mg/L, T4 = $ZnSO_4$ 300 mg/L, T5 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 200 mg/L, T6 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 400 mg/L, T7 = $ZnSO_4$ 600 mg/L, T8 = $ZnSO_4$ 600 mg/L + $CuSO_4$ 200 mg/L, and T9 = $ZnSO_4$ 600 mg/L + $CuSO_4$ 400 mg/L.

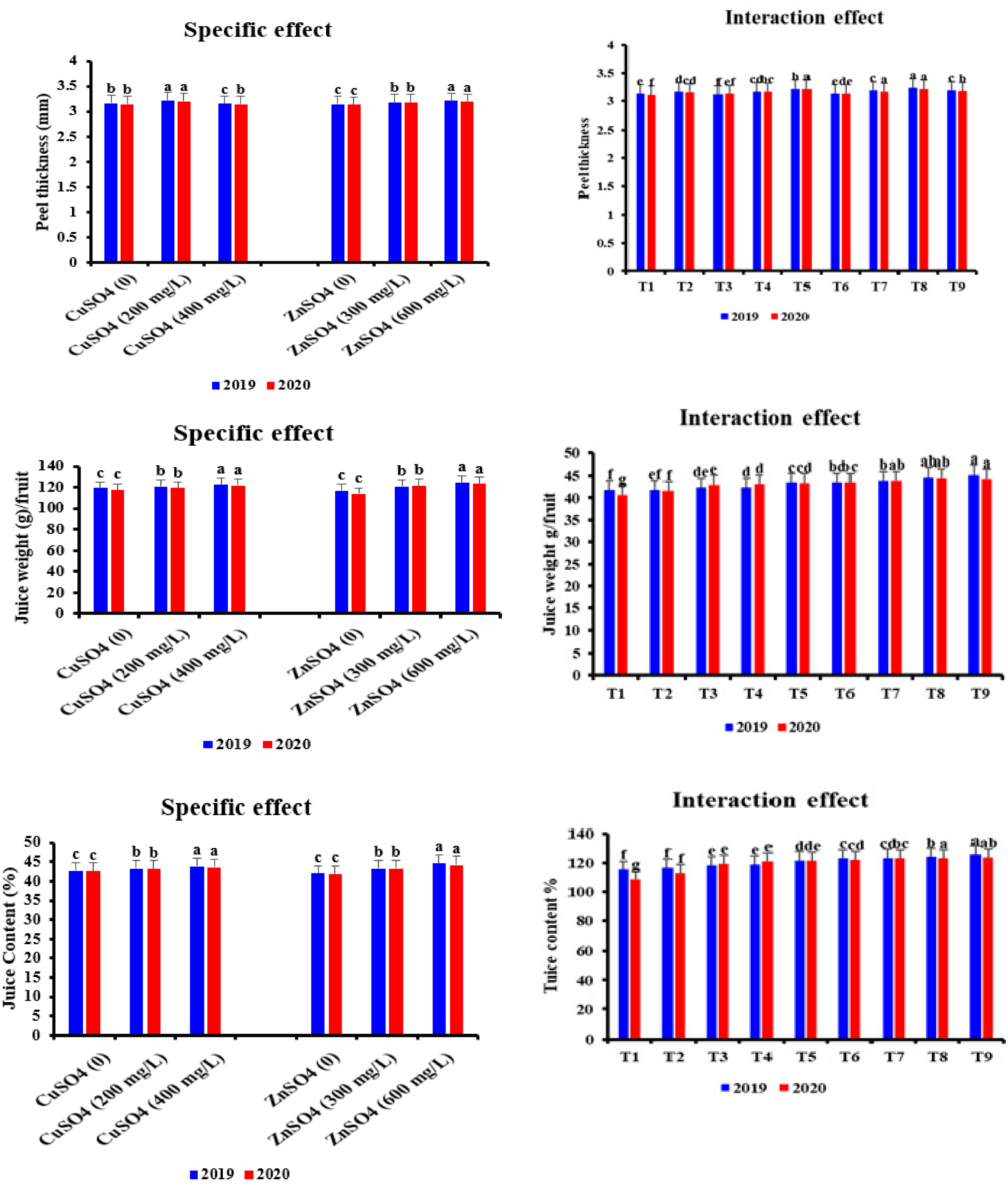

Figure 9. Peel thickness, juice content %, juice weight g/fruit of Washington navel oranges in response to specific and interaction effects of $ZnSO_4$ & $CuSO_4$ concentrations during 2019 & 2020 seasons. Means of specific and interaction effects followed by the same letters didn't significantly differ at the 5% level. Note: T1 = Control, T2 = $CuSO_4$ 200 mg/L, T3 = $CuSO_4$ 400 mg/L, T4 = $ZnSO_4$ 300 mg/L, T5 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 200 mg/L, T6 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 400 mg/L, T7 = $ZnSO_4$ 600 mg/L, T8 = $ZnSO_4$ 600 mg/L + $CuSO_4$ 200 mg/L and T9 = $ZnSO_4$ 600 mg/L + $CuSO_4$ 400 mg/L.

3.5.2. Specific Effect

It is abundantly clear that all the above-mentioned fruiting measurements responded specifically to each investigated factor. However, not only did the grade of response vary from one fruiting measurement to the next, but the rates of difference of the examined parameters exhibited by $ZnSO_4$ were greater than the analogous ones exhibited by $CuSO_4$. In general, the two $ZnSO_4$ spray solutions (300 and 600 mg/L) and $CuSO_4$ spray solutions (200 and 400 mg/L) significantly increased all fruit physical properties compared with the control (water spray). Such a trend was observed for all fruit physical properties during the two seasons with only one exception is the fruit shape index, and a significant difference between all $ZnSO_4$ and $CuSO_4$ concentrations was absent. The response of these fruit physical properties to the specific effects of $ZnSO_4$ and $CuSO_4$ concentration pointed out that these parameters were in a significantly strong relationship with the highest $ZnSO_4$ and $CuSO_4$ concentrations.

3.5.3. Interaction Effect

Concerning the interaction effect of different combinations among $ZnSO_4$ and $CuSO_4$ concentrations on the differential abovementioned parameters of Washington navel oranges, the data presented in Figures 8 and 9. In addition, all investigated fruit physical parameters that responded specifically to any investigated factor. Consequently, the combinations of the highest $ZnSO_4$ concentration (600 mg/L) and $CuSO_4$ concentration (400 mg/L) exhibited, statistically, the greatest values of such measurements exactly (fruit dimensions (equatorial and polar diameters), fruit shape index, peel thickness, and juice % and weight).

On the contrary, the lowest values of the previous parameters were always in a close relationship with the control ($ZnSO_4$ concentration (0 mg/L) and $CuSO_4$ concentrations (0 mg/L). Such a trend was seen during both seasons, with only one exception, the fruit shape index, which did not significantly respond to any investigated combination.

3.6. Fruit Chemical Characteristics

TSS %, total acidity %, TSS/acid ratio, total sugar %, and ascorbic acid (vitamin C) contents, the five investigated fruit juice chemical properties for Washington navel orange cv., were influenced by different concentrations of $ZnSO_4$ and $CuSO_4$ and their combinations. The data obtained during both the 2019 and 2020 experimental seasons are displayed in Figures 10 and 11.

3.6.1. Specific Effect

It is noted in Figures 10 and 11 that the highest values for the different fruit chemical characteristics were recorded when the highest level of $ZnSO_4$ or the highest level of $CuSO_4$ was used. In addition, the rates of difference of the investigated parameters resulting from $ZnSO_4$ treatment were more noticeable than the analogous ones resulting from CuSO4 treatment. Such a trend was observed with all fruit chemical characteristics during the 2019 and 2020 experimental seasons.

3.6.2. Interaction Effect

Concerning the interaction effect of different combinations among $ZnSO_4$ and $CuSO_4$ concentrations on the different investigated fruit chemical characteristics of Washington navel orange cv., Table 5. In each case, all investigated fruit chemical characteristics that responded specifically to any investigated factor were also influenced by these factors' combinations. Consequently, the combinations of the highest $ZnSO_4$ concentration (600 mg/L) and the highest concentration of $CuSO_4$ (400 mg/L) exhibited, statistically, the greatest values of such measurements, especially fruit chemical characteristics (TSS%, TSS/acid ratio, and total sugar and vitamin C contents). On the contrary, the lowest values of the previous measurements were always in strong relationship with these combinations, which are representative of the lowest concentration (0.05%), particularly when combined with

$ZnSO_4$ at 0 mg/L + $CuSO_4$ at 0 mg/L or the control treatment. In addition, the other combinations were situated in the middle of the aforementioned extremes. Such a trend was observed during both seasons, with only one exception, the total acidity of fruit juice, whose trend showed opposite effect.

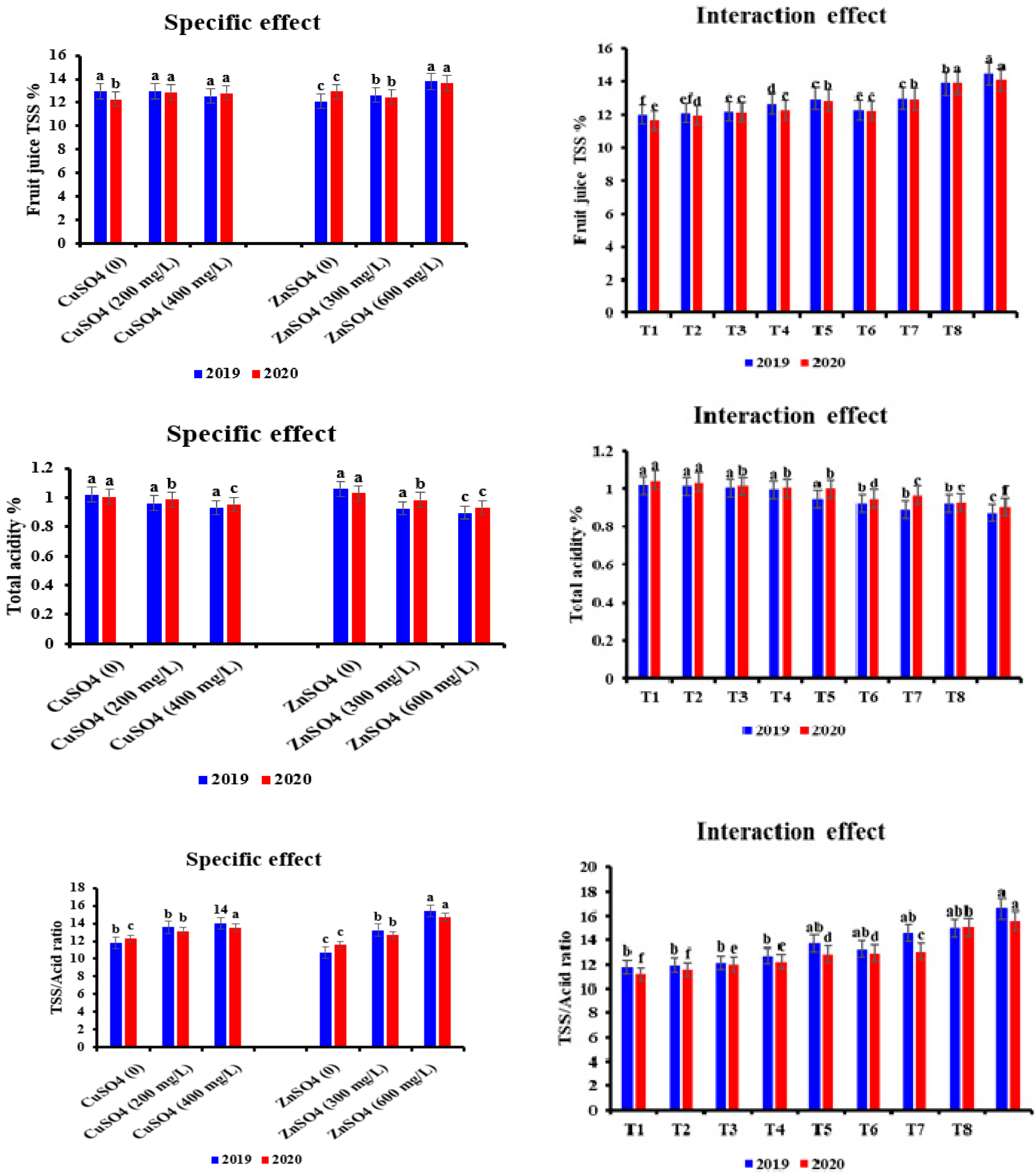

Figure 10. Fruit juice TSS %, acidity, and TSS acid ratio of Washington navel oranges in response to specific and interaction effects of different $ZnSO_4$ and $CuSO_4$ concentrations during the 2019 and 2020 seasons. The means of specific and interaction effects followed by the same letters did not significantly differ at the 5 % level. Note: T1 = control, T2 = CuSO4 200 mg/L, T3 = CuSO4 400 mg/L, T4 = ZnSO4 300 mg/L, T5 = ZnSO4 300 mg/L + CuSO4 200 mg/L, T6 = ZnSO4 300 mg/L + CuSO4 400 mg/L, T7 = ZnSO4 600 mg/L, T8 = ZnSO4 600 mg/L + CuSO4 200 mg/L, and T9 = ZnSO4 600 mg/L + CuSO4 400 mg/L.

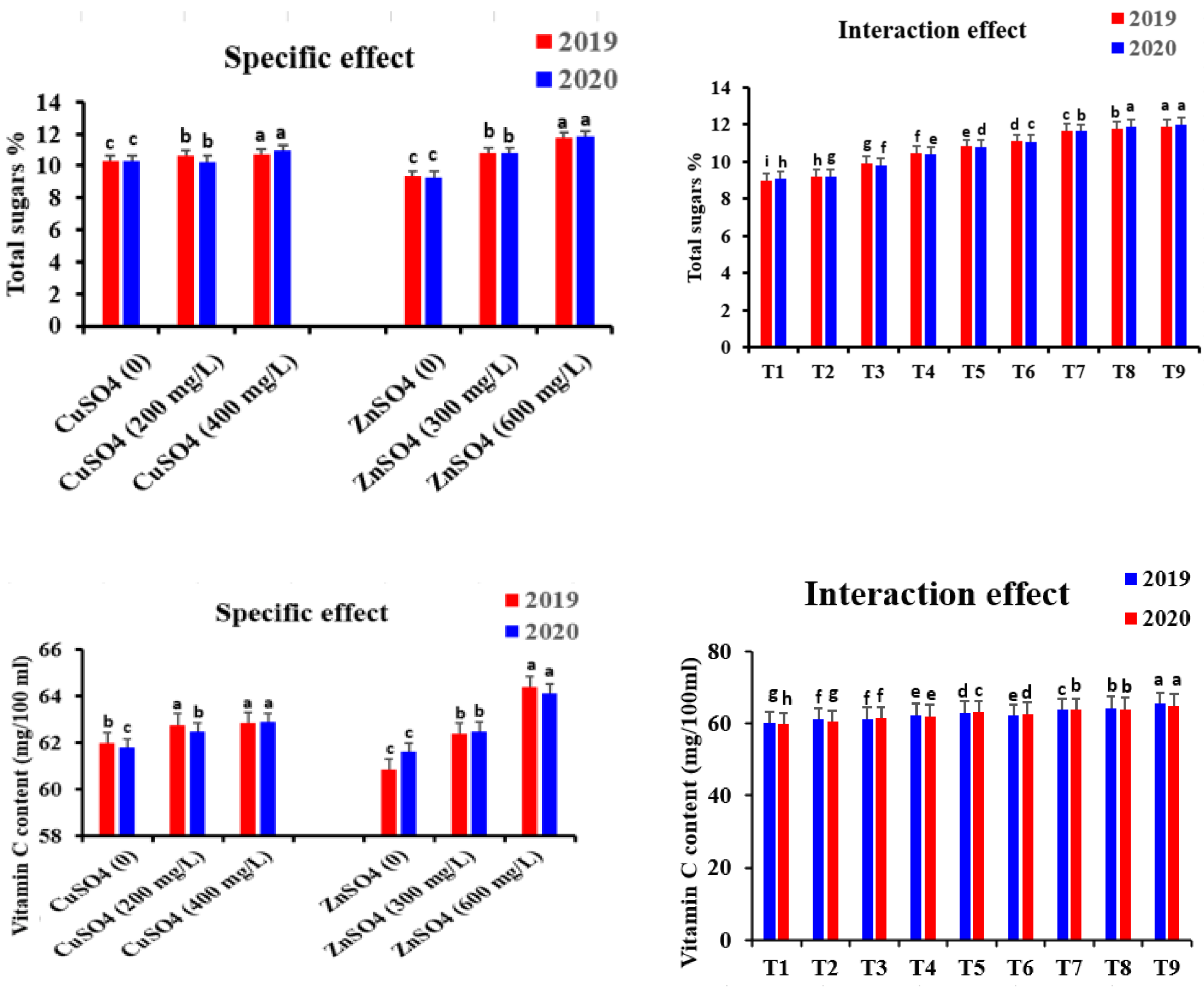

Figure 11. Total sugar % and vitamin C (mg/100 mL) of Washington navel oranges in response to specific and interaction effects of different $ZnSO_4$ and $CuSO_4$ concentrations during the 2019 and 2020 seasons. The means of specific and interaction effects followed by the same letters did not significantly differ at the 5% level. Note: T1 = Control, T2 = $CuSO_4$ 200 mg/L, T3 = $CuSO_4$ 400 mg/L, T4 = $ZnSO_4$ 300 mg/L, T5 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 200 mg/L, T6 = $ZnSO_4$ 300 mg/L + $CuSO_4$ 400 mg/L, T7 = $ZnSO_4$ 600 mg/L, T8 = $ZnSO_4$ 600 mg/L + $CuSO_4$ 200 mg/L, and T9 = $ZnSO_4$ 600 mg/L + $CuSO_4$ 400 mg/L.

4. Discussion

These findings could theoretically be interpreted based on the following three facts. 1—The more pronounced effect of $ZnSO_4$ relative to the comparatively mild reaction to $CuSO_4$ is a real explanation to understand the pattern of the response of the majority of the measurements under examination. 2—Simultaneous reaction rates were observed for both fruit measurements (polar and equatorial diameters), while both were similar in their response to a given spray treatment (combination) and were thus assumed to be the most responsible for the shortage of meaning between the various combinations. 3—Fruit juice total acidity reduction by various $ZnSO_4$ and $CuSO_4$ concentration combinations may be due either to the dilution effect, arising from a rise in fruit juice weight by different spray treatments ($ZnSO_4$ & $CuSO_4$ combinations), or to a reduction in fruit juice total acidity, typically associated with an earlier fruit maturity combined with a reduction in fruit juice total acidity.

There have been several studies published on citrus micronutrient deficiencies, and extensive research has been conducted on the effect of micronutrient application. The foliar application of these nutrients resulted in noticeable changes in several aspects of citrus species growth, flowering, fruit set, yield, and quality [23]. Nutrient application to the foliage often produces a faster response than application to the soil [24,25].

Citrus growth, on the other hand, is affected by the application of micronutrients, such as Zn, Boron (B), Manganese (Mn), and Cu. These elements have an impact on the metabolic functions of the plant system. Zn is an important microelement that is required by plants because it is involved in the production of tryptophan [5].

Zn is required for dehydrogenase activity, as well as isomerases, transphosphorylases, and RNA and DNA polymerases [8,9]. It is important in starch metabolism and acts as a cofactor for several enzymes. According to [10,11], many enzymes require zinc ions (Zn^{2+}) to function, and zinc. Copper (Cu) is involved in plant cell wall lignification, photosynthesis, and electron transport in plant enzyme systems [12]. It is essential for the formation and stability of chlorophyll and other plant pigments. Copper is involved in the biosynthesis of lignin and thus in the stabilization and lignification of cell walls, according to Bergmann [10,26]. Copper affects the chemical composition and formation of cell walls. Furthermore, [27,28] discovered that copper salts, such as the Bordeaux mixture, have long been used for spraying in horticulture. Fruit cracking was reduced by spraying with a $CuSO_4$ solution.

According to Bouazizi et al. [29], fluorescence microscopy revealed increased thickening of the secondary cell walls for both copper concentrations tested (50 and 75M $CuSO_4$).

In this regard, the fruit set is considered one most important indices of improved response fruit yield; [30,31] reported that fruit set and yield in citrus were significantly influenced by Zn fertilization. In addition, Cu deficiency is common in citrus trees that do not bear fruits during the first years after orchard establishment because of the increase in plant vigor through the application of high levels of nitrogen-containing fertilizers [32–35]. Zinc, on the other hand, is required for the production of auxin, the plant hormone responsible for cell elongation and growth [36].

Citrus fruit quality improved after 0.5% zinc sulfate (zinc sulfate) fertilization [37], whereas guava fruit quality improved after being micro-fertilized with copper sulfate (cupric sulfate), and the lowest deciduous fruit and best fruit quality were obtained by administering 0.5 percent copper sulfate through the leaves [38].

Zn participates in the activity of several enzymes (RNA, DNA polymerases, and dehydrogenases), as well as the maintenance of membrane structure and cell division [39–41]. Moreover, [42] demonstrated that providing B and Zn through foliar application to orange plants increased nutrient concentrations in leaves and promoted plant growth. Micronutrients are essential macronutrients for plant growth, yield, and quality. Plants only require trace amounts of it [43,44]. In addition, foliar application of combined micronutrients in Khasi Mandarin with {Zn (0.5%) & Cu (0.4%) + B(0.1%)} resulted in the highest fruit set percentage, number of fruits/plant, yield, total fruit retention %, total sugar percentage, and ascorbic acid content, compared with using {Zn (0.5%) + Mn (0.4%) + Cu (0.4%)}. As a result, it was determined that treatment with {Zn (0.5%) + Cu (0.4%) + B (0.1%)} was the best in terms of fruit growth and development [45].

5. Conclusions

In conclusion, the data obtained show that spraying Washington navel orange trees grown under comparable environmental conditions and horticulture practices every month from March to July with 600 mg/L $ZnSO_4$ or 400 mg/L $CuSO_4$ alone improved all the studied parameters, particularly productivity and fruit quality. However, spraying Washington navel orange trees with 600 mg/L $ZnSO_4$ in combination with 400 mg/L $CuSO_4$ or 600 mg/L $ZnSO_4$ in combination with 200 mg/L $CuSO_4$ every month from March to July offered the best results in terms of vegetative growth, nutritional status, productivity, yield, and fruit quality. This combination increased the yield by up to 17%.

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draft, R.S.; A.A.M.A.-M. and K.A.I.; review and editing, R.M.Y.Z. All authors have read and agreed to the published version of the manuscript.

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