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Proceeding Paper

Selected Mineral Interactions in Two Varieties of *Lycopersicum esculentum* L. Produced Organically and Enriched Naturally with Fe and Zn †

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Abstract: Plants need certain micronutrients for normal and healthy growth, namely iron and zinc. However, Fe and Zn have low kinetic mobility in soils and in plants. In fact, in tomato plants, Fe shows low mobility in phloem due to soil interactions that can reduce Fe uptake. Foliar spraying is one of the most effective strategies to deal with this soil–plant interaction. Foliar spraying with Zn causes an increase in Zn content in the edible part of plants. In this context, mineral interactions were monitored in two commercial varieties ("maçã" and "chucha") of *Lycopersicum esculentum* L. after two foliar sprays with a mix of two products of Fe and Zn (treatment 1 and 2), following an organic production mode. In leaves of the two varieties, Zn showed a higher content in treatment 1. Considering Fe, the "maçã" variety showed a higher content in treatment 1, unlike the "chucha" variety, which presented a higher content in treatment 2. Regarding tomatoes of the "maçã" variety, Zn showed an antagonistic trend with Ca, K and S. In conclusion, after two foliar sprays of Fe and Zn on tomatoes, it was possible to identify a nutrient interaction between other minerals mainly in the "maçã" variety, although both varieties were produced under the same soil conditions.

Keywords: biofortification; *Lycopersicum esculentum* L.; organic tomato production

1. Introduction

Plants need 16 essential nutrients for normal growth and development. Three of them (C, H and O) are obtained from the atmosphere and soil water, and the remaining elements, N, P, K, Ca, Mg, S, Fe, Zn, Mn, Cu, B, Mo and Cl, are collected from soil minerals, organic matter or though fertilizers [1]. Fe (required as Fe^{2+} and/or Fe^{3+}) and Zn (required as Zn^{2+}) are classified as micronutrients based on plants' requirements and fertilization needs [2]. Both elements have important roles in plants. Iron has a central role in plant metabolism (namely in photosynthesis and respiration [1]), in synthesis and maintenance of chlorophyll [1,2], in enzyme electron transfer [2] and protein metabolism [1]. Zinc is necessary for numerous different functions in plant metabolism; it has an important role in RNA and protein synthesis [1] and is involved in enzymes that regulate various metabolic activities within plants [2]. Additionally, both Fe and Zn have low kinetic mobility in soils [3] and plants [2,3]. However, some studies indicate that Zn translocation occurs though xylem [4–7] and phloem [4,5]. Fe presents low mobility in tomato plants, particularly in phloem [8,9], due to soil interactions that can reduce Fe uptake. Foliar spraying is considered one of the most effective strategies to improve Fe uptake [2,10]. In horticultural crops, foliar fertilization is widely used [11], being an important agricultural practice where nutrients are applied straight through plant foliage [12]. The application through leaves is a faster and more efficient way to provide essential nutrients for plants compared to soil applications [10,11]. Considering the important roles that both Zn and Fe have in plants, and tomato (*Lycopersicum esculentum* L.) being considered one of the most important horticultural crops globally (constituting an excellent source of minerals, vitamins and antioxidants) [13], we aimed to monitor nutrient interactions in two heavily consumed commercial tomato varieties ("maçã" and "chucha") after two foliar sprays with two mixtures of Fe and Zn, following an organic production mode.

2. Materials and Methods

2.1. Biofortification Itinerary

The experimental tomato-growing field, located in western Portugal (39°41′48.517″ N; 8°35′45.524″ W), was used to growth two tomato (*Lycopersicum esculentum* L.) varieties ("maçã" and "chucha"), following an organic production mode. The planting date was 12 June 2019 and the harvest date was 4 October 2019 (four foliar sprays were carried out during the agricultural period with 10–11-day intervals). The first foliar spray occurred on 5 September and the second after 11 days. The biofortification was performed with a mix of two products (Zitrilon-15% and Maxiblend); treatment 1 (low mix) corresponded to a mix of 0.40 kg·ha^{-1} Zitrilon (15%) and 1 kg·ha^{-1} Maxiblend and treatment 2 (high mix) corresponded to a mix of 1.20 kg·ha^{-1} Zitrilon (15%) and 4 kg·ha^{-1} Maxiblend. Both products can be used in organic farming. Zitrilon (15%) is a concentrated Zn fertilizer with 15% in chelated form (EDTA); it can be used in any type of crop and applied as a foliar fertilizer. Maxiblend is a commercial product made of a mixture of micronutrients (Fe, Mn, Zn, Cu, B, Mo, Mg) mostly constituted by Fe (5.3%); it is rapidly absorbed by plants and can be applied by foliar spraying. Control plants were not sprayed at any time with Fe or Zn. Each treatment was performed in quadruplicate. During the agricultural period, average air temperatures oscillated between 13 °C and 29.6 °C.

2.2. Mineral Content in Soils, Tomatoes and Leaves

Mineral contents were determined in soil samples (33 samples, 100 g taken at 30 cm depth in the experimental field), following [14], before the implementation of the culture. Following [14,15], quantification of mineral elements in tomatoes and leaves after two foliar sprays was carried out by X-ray fluorescence, using an XRF analyzer (model XL3t 950 He GOLDD+, Thermo Fisher Scientific, Waltham, MA, USA) under He atmosphere.

2.3. Statistical Analysis

Data were statistically analyzed using a one-way ANOVA to assess differences between treatments in each variety, followed by Tukey's test for mean comparison. A 95% confidence level was adopted for all tests.

3. Results

Soil is the original supply of nutrients to grow plants, being an essential part of agriculture success. Thus, the chemical composition of the soil in the tomato-growing field was analyzed (Table 1). The mineral composition of the soil showed a higher content of Ca, followed by K and Fe. Regarding the minerals presented in smaller quantities, S showed a higher content, followed by Zn. However, the presence of the contaminating mineral elements Pb and As was verified.

Table 1. Mean values ± S.E. (n = 33) of mineral elements of the soil of the experimental tomato-growing field selected for Fe and Zn biofortification of *Lycopersicum esculentum* ("maçã" and "chucha" varieties).

Ca	**K**	**Mg**	**P**	**Fe**	**S**	**Zn**	**Pb**	**As**
		%				**ppm**		
9.96 ± 1.53	2.28 ± 0.16	0.21 ± 0.06	0.17 ± 0.01	1.14 ± 0.15	56.6 ± 3.80	29.4 ± 4.56	16.1 ± 2.71	17.1 ± 1.61

Mineral content of tomatoes leaves was assessed in the "maçã" and "chucha" varieties after two foliar sprays with Fe and Zn (Table 2). Both varieties showed a significantly higher content of Zn in the low mix treatment compared to the control. However, considering Fe, the "maçã" variety showed a higher content in the low mix treatment, unlike the "chucha" variety, which presented a higher content in the high mix treatment compared to control leaves. In "maçã" leaves, Ca, K and S showed significantly higher contents in the high mix treatment relative to the control. In "chucha" leaves, Ca and K showed significantly higher contents in the high mix treatment (S showed a lower content in the high mix treatment and a higher content in the control).

Table 2. Mean values ± S.E. (n = 4) of Fe, Zn, Ca, K and S in dry leaves of *Lycopersicum esculentum* ("maçã" and "chucha" varieties) after the second foliar spraying with Fe and Zn. Different letters indicate significant differences between treatments in each variety (statistical analysis using the Scheme 0). Foliar spraying was carried out with two concentrations (low mix and high mix). The control was not sprayed.

Variety	**Treatments**	**Fe (ppm)**	**Zn (ppm)**	**Ca (%)**	**K (%)**	**S (%)**
"Maçã"	Control	206c ± 5.6	230c ± 1.9	6.71b ± 0.02	1.70b ± 0.01	1.30a ± 0.01
	Low mix	347a ± 2.9	318a ± 0.8	5.64c ± 0.00	1.54c ± 0.01	1.03b ± 0.01
	High mix	224b ± 1.3	296b ± 1.3	7.94a ± 0.04	1.90a ± 0.01	1.30a ± 0.02
"Chucha"	Control	199b ± 1.5	85c ± 2.0	7.68c ± 0.01	1.68b ± 0.00	1.71a ± 0.02
	Low mix	68c ± 8.4	635a ± 3.9	8.14b ± 0.00	1.65b ± 0.00	1.49b ± 0.02
	High mix	267a ± 3.1	252b ± 0.6	8.62a ± 0.02	2.38a ± 0.01	1.37c ± 0.01

Additionally, the mineral content of tomatoes was assessed after two foliar sprays with Fe and Zn (Table 3). Regarding the "maçã" variety, Zn showed a significantly higher content in the high mix treatment and control, with the highest Zn content obtained in the high mix treatment. Zn also showed an antagonistic trend with Ca, K and S; in the low mix treatment (lowest Zn content), the latter minerals presented significantly higher content compared to the remaining treatments and showed a decrease in content in the high mix treatment and control (where Zn content was higher). Regardless, the control showed a higher content of Zn in the "chucha" variety, and there is no clear trend regarding the mineral interaction between Zn, Ca, K and S.

Table 3. Mean values ± S.E. ($n = 4$) of Zn, Ca, K and S in dry tomatoes of *Lycopersicum esculentum* ("maçã" and "chucha" varieties), after the second foliar spraying with Fe and Zn. Different letters indicate significant differences between treatments in each variety (statistical analysis using the single factor ANOVA test, $p \leq 0.05$). Foliar spraying was carried out with two concentrations (low mix and high mix). The control was not sprayed.

Variety	Treatments	Fe (ppm)	Zn (ppm)	Ca (%)	K (%)	S (%)
"Maçã"	Control	<35	16.7a ± 0.76	0.14c ± 0.00	4.78c ± 0.01	0.14b ± 0.00
	Low mix	<35	14.2b ± 0.25	0.28a ± 0.00	5.60a ± 0.02	0.17a ± 0.00
	High mix	<35	17.1a ± 0.45	0.24b ± 0.01	5.33b ± 0.03	0.14b ± 0.01
"Chucha"	Control	<35	14.8a ± 0.77	0.15b ± 0.00	4.81b ± 0.01	0.13a ± 0.00
	Low mix	<35	10.2b ± 1.05	0.16a ± 0.00	3.82c ± 0.02	0.11b ± 0.01
	High mix	<35	13.0ab ± 0.34	0.15b ± 0.00	5.16a ± 0.02	0.13a ± 0.01

4. Discussion

The acquisition of nutrients (namely, macro and micro elements) by plants is affected by soil, type of plant and environment [16]. However, mineral structure and the state of dispersion also influence soil properties beyond the chemical composition of soil [17]. The tomato-growing field (organic soil) showed a higher content of Ca, followed by K, Fe, Mg, P, S, Zn, As and Pb (Table 1). The higher Ca content in the soil was due to the parent rock being a calcareous unit, corresponding to the Turonian stage of the Cretaceous (C2–3), with intercalations of limestones and marls [18]. The contaminating mineral elements in the soil (As and Pb) were below the limits according to Portuguese law [19]. The Pb content was below the limit of 110 mg kg^{-1} for pH > 7.0 (the pH of the tomato-growing field was higher than 7 (data not shown)). Regarding As, in uncontaminated soil, the concentration can vary between 0.2 and 40 mg kg^{-1} [20]; our content was within this range. Additionally, according to Portuguese law [18], the content of Zn in soils needs to be under 450 (for pH > 7.0) for the soil to be used for agriculture; in this experiment, we obtained a Zn content much lower than the limit value (Table 1).

Moreover, the significantly higher content of Zn obtained in the low mix treatment (and not in the highest treatment applied—high mix treatment) in tomato leaves of both varieties (Table 2) can be related to Zn's limited mobility in leaves [21] or due to external factors when applying the two foliar sprays. In leaves of the "maçã" variety, Fe also showed a higher content in the low mix treatment, probably due to the low mobility within the plant [2]. The differences between both varieties in Fe content can be dependent on the variety and its different mineral needs (that vary in mobility within the plant) [2].

Fe content in tomatoes of both varieties was below the measuring device's detection limit (<35 ppm); thus, it was not possible to draw conclusions about the treatments applied in this regard (Table 3). Zn in both varieties showed significantly lower content in the low mix treatment, and in the "maçã" variety, Zn presented a higher content in the high mix treatment, unlike the "chucha" variety, which showed a higher Zn content in the control. Nevertheless, in both varieties, Ca, K (except in "chucha") and S (except in "chucha") showed a higher content in the low mix treatment. Additionally, Zn in the "maçã" variety showed an antagonistic relationship with Ca, K and S. This relationship can be due to the low mobility of Ca and S [2]; due to antagonism with one of the cations Ca, Fe or Zn; or due to the synergetic interactions between N and K in the soil (the increased K uptake can be related to the increase in N) [22]. In the "chucha" variety, there is no clear trend regarding the mineral interaction, and it was not biofortified at this stage, although both varieties were produced in the same region and in the same soil conditions. Considering the high mix treatment in the "maçã" variety, Zn appears to be redistributed by xylem and phloem [4,5].

5. Conclusions

Through two foliar sprays with Fe and Zn at the two concentrations reported in this study, leaves and tomatoes of the "maçã" and "chucha" varieties can be enriched, following an organic production mode. However, although both varieties were produced in the same soil conditions, we observed an antagonistic relationship between Zn and Ca, K and S in tomatoes of the "maçã" variety. Additionally, in the "chucha" variety, there were no clear trend regarding the mineral interaction between the minerals analyzed.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/IECPS2021-11935/s1.

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