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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 tomatoes plants, Fe showed low mobility in phloem and 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. Nevertheless, foliar sprayings with Zn presented an increase in its 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. Yet, considering Fe, "maçã" variety also showed a higher content in treatment 1, unlike "chucha" variety, which presented a higher content in treatment 2. Regarding tomatoes of "maçã" variety, Zn showed an antagonistic trend with Ca, K and S. In conclusion, after two foliar sprays of Fe and Zn, in tomatoes, there was possible to identify a nutrient interaction between other minerals mainly in "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, being 3 of them (C, H and O) obtained from the atmosphere and soil water, whereas the remain elements are 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]. Regarding 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 job in plant metabolism (namely in photosynthesis and respiration [1]), in synthesis and maintenance of chlorophyll [1,2], and in enzyme electron transfer [2] and protein metabolism [1]. Zinc it's necessary for numerous different functions in plant metabolism, has an important role in RNA and protein synthesis [1] and it's involved in enzymes that regulated 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 occurred though xylem [4–7] and phloem [4,5]. Regarding Fe, presents a low mobility in tomato plants, namely in phloem [8,9] and due to soil interactions, that can reduce Fe uptake, foliar spraying is considered one of the most effective strategies [2,10]. Nevertheless, 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]. In fact, considering the important roles that both Zn and Fe perform in plants and being tomato (*Lycopersicum esculentum* L.) considered one of the most important horticultural crops globally (constituting an excellent source of mineral, vitamins, and antioxidants) [13], this study aimed to monitor nutrition interactions in two commercial varieties ("Maçã" and "Chucha") heavily consumed after two foliar sprays carried out with a mix of two products of Fe and Zn, following an organic production mode.

2. Materials and Methods

2.1. Biofortification Itinerary

The experimental tomato-growing field, located in the Western of 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. Planting date was on 12 June and harvest date on 4 October 2019 (four foliar sprays were carried out during the agricultural period with 10–11 days interval). 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), in which treatment 1 (Low mix) corresponds to a mix of 0.40 kg.ha^{-1} Zitrilon (15%) and 1 kg.ha^{-1} Maxiblend and treatment 2 (High mix) corresponds to a mix of 1.20 kg.ha^{-1} Ziltrilon (15%) and 4 kg.ha^{-1} Maxiblend. Both products used 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 crops and can be applied as a foliar fertilizer. Maxiblend is commercial product made up of a mixture of micronutrients (Fe, Mn, Zn, Cu, B, Mo, Mg) mostly constituted by Fe (5.3%), being rapidly absorbed by plants and can be foliar applied. Control plants were not sprayed at any time with Fe and Zn. Each treatment was performed in quadruplicate. During the agricultural period air temperatures oscillated between an average of 13–29.6 °C.

2.2. Mineral Content in Soils, Tomatoes, and Leaves

Mineral contents were determined in soil samples (33 samples, 100 g picked up 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 a XRF analyzer (model XL3t 950 He GOLDD+,Thermo Fisher Scientific MA, USA) under He atmosphere.

2.3. Statistical Analysis

Data were statistically analyzed using a One-Way ANOVA to assess differences among treatments in each variety, followed by a Tukey's 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. As such, the chemical composition of soil of 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, it was verified the presence of contaminating mineral elements: Pb and As.

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 *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 "maçã" and "chucha" varieties after two foliar sprays with Fe and Zn (Table 2). In fact, both varieties showed a significantly higher content of Zn in low mix treatment, compared to control. However, considering Fe, "maçã" variety also showed a higher content in low mix treatment, unlike "chucha" variety, which presented a higher content in high mix treatment, compared to control leaves. In "maçã" leaves, Ca, K, and S showed a significantly higher content in high mix treatment, relatively to control. Yet, in "chucha" leaves, only Ca and K also showed a significantly higher content in high mix treatment (S showed a lower content in high mix treatment and a higher content in 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 2nd foliar spraying with Fe and Zn. Different letters indicate significant differences, between treatments, in each variety (statistical analysis using the Scheme 0. Foliar spray was carried out with two concentrations (Low mix and High mix). 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, mineral content of tomatoes was also assessed after two foliar sprays with Fe and Zn (Table 3). Regarding "maçã" variety, Zn showed a significantly higher content in high mix treatment and control, despite the highest content were obtained in high mix treatment. Yet, also showed an antagonistic trend with Ca, K, and S, considering that in low mix treatment (lowest Zn content), these minerals presented a significantly higher content compared to the remain treatments and showed a decrease of content in high mix treatment and control (where Zn content was higher). Regardless, control showed a higher content of Zn in "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 2nd 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 spray was carried out with two concentrations (Low mix and High mix). 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 influences 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 is 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 presence of contaminating mineral elements in the soil (As and Pb) are below the limits. According to Portuguese law [19] the Pb content is below the limit of 110 mg kg^{-1} for pH > 7.0 (the pH of tomato-growing field is higher than 7 (data not shown)). Regarding As, in uncontaminated soil the concentration can be vary between 0.2 and 40 mg kg^{-1}[20], being our content within range. Additionally, according to Portuguese law [18] the content of Zn in soils needs to be under 450 (for pH >7.0) to be used for agriculture, having obtained a Zn content much lower than the limit value (Table 1).

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

Regarding Fe content in tomatoes of both varieties, was below the device's detection limit (<35 ppm), not being possible to concluded about the treatments applied (Table 3). Yet, considering Zn, in both varieties showed significantly lower content in low mix treatment and in "maçã" variety presented a higher content in high mix treatment, unlike "chucha" variety that showed a higher content in control. Nevertheless, in both varieties, Ca, K (except in "chucha" variety") and S (except in "chucha" variety") showed a higher content in low mix treatment. Additionally, "maçã" variety showed a Zn 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 and Zn or probably due to synergetic interactions between N and K in the soil (the increased of K uptake can be related to the increase of N) [22]. Yet, in "chucha" variety there is no clear trend regarding the mineral interaction and did not biofortified at this stage, although both varieties were produced in the same region and under the same soil conditions. Considering high mix treatment in "maçã" variety, seems that Zn are redistributed by xylem and phloem [4,5].

5. Conclusions

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

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