



Article

Spatio-Temporal Disposition of Micronutrients in Green Bean Grown in Sandy Mulching Soils

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Abstract: Currently, there is no information available about the spatio-temporal distribution of micronutrients in sandy mulching soils widely used in the southeast of Spain; therefore, in this experiment, we aimed to characterize the spatio-temporal distribution of micronutrients in the wet bulb zone in two sand-mulched soils. Four different factors were considered over the experiment: (a) soil model, (b) time sampling, (c) distance from the emitter, and (d) depth. Each soil was divided into four blocks and the soil sample per block was composed of 20 subsamples. The micronutrient concentration was determined in each soil sample through atomic absorption spectrometry determinations. To establish the relationship between factors, a multifactor ANOVA test analysis was conducted. The results obtained reported a higher micronutrient concentration in the soil profile than in the sand layer. Moreover, in the soil profile, there was a decrease in micronutrient concentration in distance for Fe (from 10.4 to 7.9 mg kg $^{-1}$), Zn (from 4.0 to 3.5 mg kg $^{-1}$), Mn (from 23.9 to 16.2 mg kg $^{-1}$), and Cu forms (from 2.5 to 1.5 mg kg^{-1}). Moreover, there was a decrease in micronutrients with depth for Fe (from 10.5 to 8.0 mg kg $^{-1}$), Zn (from 4.0 to 3.7 mg kg $^{-1}$), Mn (22.0 to 17.2 mg kg $^{-1}$), and Cu (from 2.1 to 1.7 mg kg $^{-1}$). Higher micronutrient concentration after green bean crop harvest was related to the highest organic matter content, with the following values for Fe $(12.3 \text{ mg kg}^{-1})$, Zn (4.0 mg kg^{-1}) , Mn (23.6 mg kg $^{-1}$), and Cu (2.0 mg kg $^{-1}$) in the soil profile. The fertigation management of the crop did not modify the micronutrient concentrations in distance in the sand layer due to the reduced exchange capacity of the sand with micronutrients.

Keywords: *Phaseolus vulgaris*; organic matter content; sand layer; soil depth; time of sampling; trace elements



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1. Introduction

The importance of the horticulture crops is related to economic benefits due to the variety of crops [1,2]. One of the most relevant intensive horticulture areas in Europe is located in Almeria (Southern Spain), with 31,614 ha of greenhouses [3].

Some of the main characteristics of the soils used to cultivate in this area are the following: high levels of CaCO₃, basic pH, and a low organic matter content [4]. Due to these characteristics, the development of some crops may be affected by a reduction in yield and length of the root [5]. A common technique in the area to improve the soil is the use of sand-mulched soil, which is composed of a layer of sand, an intermediate organic matter layer usually mixed with the topsoil, and a natural soil with a changing texture, which can

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differ from clay to sandy loam [6,7]. There are some advantages of using mulches, such as: reduction in evaporation of the soil and some improvements in the root system reviewed by several authors [8,9]. Another important advantage from the mulching is the increase in soil fertility, crop production, soil erosion control [10,11], and the mitigation of post-wildfire erosion [12]. Another common practice in the greenhouse is the solarization that consists in a moisture-thermal process for soil disinfection of pests and pathogens, which also can improve the availability of nutrients and the content of soluble organic matter [13–15].

Micronutrients (Fe, Zn, Cu, and Mn) are taken up in a very small quantity for proper plant growth [16]. Nevertheless, they are essential from the metabolic point of view, since they are involved in the enzymatic regulation, playing essential roles in enzymatic activity or participating as coenzyme, as well as in redox functions [17].

The feasibility of micronutrients (Fe, Mn, Cu, and Zn) in soils depends on different aspects that can modify their distribution in the soil profile [18,19]. These factors are the following: clay content [20], moisture of the soil [21], pH, organic matter (OM) content [22], and cation exchange capacity (C.E.C.) [23].

After reviewing the previous literature, some authors have reported that Cu and Zn are immobile in clay soils [20], whereas others pointed out that the variability of Fe, Mn, Cu, and Zn increased with the moisture of the soil [21]. Regarding pH, Malavolta et al. [24] noted that the micronutrient availability decreased under higher pH because of the fact that the pH value determines mobility affecting the plants' uptake. Sharma et al. [25] reported that the increase in OM resulted in a higher micronutrient availability, since the OM generated soluble chelating agents, which increased the solubility of micronutrients. Soils with high C.E.C. can exchange micronutrient cations between soil solution and the negatively charged surfaces of clay and organic matter, so they protect trace elements from leaching [23].

Considering the micronutrient distribution in distance and depth, Mendieta et al. [26] noted that the highest Fe, Mn, Cu, and Zn concentration was near to the drip, and Gupta et al. [17] reported that the upper part of the soil had the highest Fe, Mn, Cu, and Zn concentration.

In this type of soil, the availability of micronutrients and their distribution in the soil profile have special relevance. Although there is a little information about micronutrients' distribution in soil, it is necessary to highlight that the knowledge about this topic in sandy mulched soil is rather scarce. Therefore, in this experiment, we assessed the spatio-temporal distribution of micronutrients in the wet bulb zone in two representative horticultural sand-mulched soils fertigated with drippers.

2. Materials and Methods

2.1. Plant Material and Location

The experiment was conducted in two greenhouses in Agrarian Research and Training Institute ubicated in Almería (latitude: 36°47′14″ N and longitude: 02°42′15″ W). The plant material was *Phaseolus vulgaris* L. c.v. Mantra RZ (Figure 1). The experimental period lasted 90 days (short-cycle crop). The climatic conditions over the experiment were recorded with HOBO Sensors, as well as wet bulb air temperature (HOBO U12 Onset Computer Corp., Bourne, MA, USA). The recordings obtained over the experimental period showed mean, maximum, and minimum temperature ranging from 22 to 30 °C (Figure 1), 40 to 50 °C, and 10 to 15 °C; respectively, and a relative humidity ranging from 60 to 80%.

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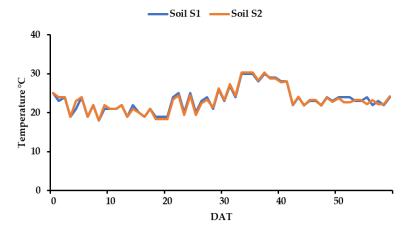


Figure 1. Plant material, greenhouse facilities, and mean temperature of two greenhouses (soil S_1 and soil S_2).

2.2. Treatments and Experimental Design

To perform the experiment, two representative horticultural soils of the greenhouse production in the southeast of Spain covered with sand $(S_1 \text{ and } S_2)$ were chosen. Considering the properties of the soil included in Table 1, both soils were classified as Cumulic anthrosols. The comparison between both soils reported that the soil S_1 has lower OM, CEC, micronutrients, silt, stoniness, and apparent density than soil S_2 .

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Table I. Physicochemica	l composition of l	ooth soils (S ₁ and S ₂	at the start of the experiment.

	S_1	S_2	
Chemical soil properties			
рН	8.1 ± 0.28	8.0 ± 0.33	ns
EC	1.30 ± 0.14	1.35 ± 0.11	ns
Organic matter content (%)	$1.00\pm0.08\mathrm{b}$	2.50 ± 0.18 a	*
C.E.C. (meq 100 g^{-1})	$9.80 \pm 0.88 \mathrm{b}$	14.50 ± 1.17 a	*
Nutrients (mg kg $^{-1}$)			
Fe	$4.71 \pm 0.52 \mathrm{b}$	10.62 ± 1.14 a	*
Zn	$3.54 \pm 0.43 \mathrm{b}$	4.31 ± 0.51 a	*
Cu	$0.52 \pm 0.10 \mathrm{b}$	1.53 ± 0.21 a	*
Mn	$19.21\pm1.86~b$	$25.12 \pm 2.32 \ a$	*
Physical soil properties			
Texture	loamy-sandy	loamy-sandy	

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Table 1. Cont.

	S ₁	Sa	
	<u> </u>	52	
Particle size distribution (%)			
Sand	73 ± 5 a	$58\pm4\mathrm{b}$	*
Silt	$12\pm1\mathrm{b}$	30 ± 4 a	*
Clay	15 ± 1	13 ± 2	ns
Stoniness $(g.g^{-1})$	$0.30 \pm 0.04 \mathrm{b}$	0.51 ± 0.06 a	*
Apparent density (g.cm ⁻³)	$1.52 \pm 0.08 \mathrm{b}$	1.71 ± 0.07 a	*

The same lowercase letters or ns indicates nonsignificant differences. * indicates significant differences at $p \le 0.05$.

Both soils in the experiments were composed of sand mulching and original soil profile. This system is based on the incorporation of some materials to the original soil. The system consists of three layers: (1) top layer of grave-sand of 0.05 to 0.10 m (granulometry composed of particle sizes from <1 mm to 5 mm), (2) an intermediate layer of organic amendment of manure (0.01 to 0.02 m) located between the grave-sand layer and the soil, and (3) the soil profile. It is important to highlight that sometimes the sandy mulching soil can be the original soil or an incorporated soil with a texture of clay loam to sandy loam (range from 0.1 to 0.4 m) (Figure 2). Below the 0.4 m, there was a raw soil without tillage [27].

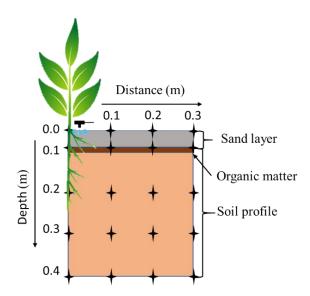


Figure 2. Layout of the sampling points in the experiment.

The amounts of fertilizers applied over the experiment were 67 and 189 kg ha⁻¹ of N and K, respectively, following the advice given by other scientists under similar conditions [28]. The fertigation of the crop in both soils was carried out with drippers with a flow of L h⁻¹. The nutrient solution supplied has EC and pH values of 0.92 dS m⁻¹ and 8.02, respectively. The chemical composition of the nutrient solution was the following: 0.20 mM carbonates (CO₃²⁻), 3.30 mM bicarbonates (HCO₃⁻), 1.17 mM chloride (Cl⁻), 3.80 mM sulphates (SO_4^{2-}), 1.87 mM nitrates (NO_3^-), 1.75 mM ammonium (NH_4^+), 3.72 mM potassium (K⁺), 2.09 mM calcium (Ca²⁺), 3.40 mM magnesium (Mg²⁺), and 1.03 mM sodium (Na⁺). The sources of N and K for the fertigation of the crop were: NH₄NO₃ (33.5% N, 50% NH_4^+ -N, and 50% NO_3^- -N) and K_2SO_4 (52% K_2O and 45% SO_3). The chemical analysis of the soil showed higher P concentration, resulting in nonapplication of P fertilizers over the experiment. In order to maintain the initial conditions of the experiment, micronutrients were not applied to the soil via fertigation. The irrigation schedule was based on the ETc values and the timing of the irrigation through the use of tensiometers (-20 KPa of matric potential) at different depths (0.15 and 0.30 m). Over the experimental period, the total water volume was 24 L m⁻² in preplanting and 134 L m⁻² during the cycle of the crop. Agriculture **2022**, 12, 1066 5 of 11

The yield of green bean in both soils was similar without significant differences, showing values of 2.47 and 2.36 kg m⁻² in soils S₁ and S₂, respectively.

2.3. Soil Sampling

The distribution of micronutrients at spatial and temporal levels were assessed in both soils considering four factors: soil type (S_1 and S_2 (ST)), time sampling (at the beginning and at the end of the experiment period (90 DAT) (TS)), distance of the sample from the emitter (0.1, 0.2, and 0.3 m (DE)), and depth (D) (0–0.1 m, sand layer; 0.1–0.2, 0.2–0.3, and 0.3–0.4 m (soil profile)), and their relationships (Figure 3). Due to the high variability between samples in soil, each greenhouse was split into four blocks. To obtain a representative soil sample per block, each sample was composed of 20 subsamples corresponding with 20 random points of soil.

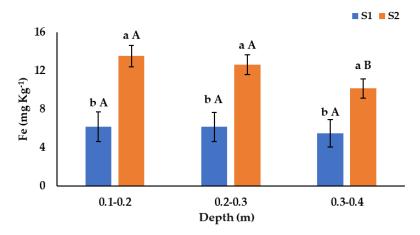


Figure 3. Interaction between depth (D) and soil type (ST) for soil Fe concentration (mg kg $^{-1}$). The comparison between the soil type in each depth is assessed with lowercase letters. The comparison between each type of soil at different depths is assessed with capital letters.

2.4. Micronutrient Analysis

The methodology for micronutrient extraction was carried out following the protocol reported by Lindsay and Norvell [29]. Soil sample (10 g) was placed into an Erlenmeyer flask of 125 mL and 20 mL of reagent (5 mM DTPA, 0.01 M CaCl₂, and 100 mM triethanolamine (TEA) [(HOCH₂CH₂)₃N] (pH 7.30). Afterwards, it was centrifuged at $120 \times g$ rpm for 2 h and filtered under vacuum flask using filter paper. Then, the solution extracted (5 mL) was diluted with 20 mL of deionized water. Concentrations of Fe, Cu, Zn, and Mn were assessed with atomic absorption spectrometry determinations (UNICAM 969 AA) at 248.8, 213.9, 279.5, and 324.6 nm, respectively.

2.5. Statistical Analysis

To determine the relationship between the different factors, a multifactor ANOVA test (least significant difference (LSD) $p \le 0.05$) was carried out. Three different tests were performed: sand layer (2 × 2 × 3 factorial), soil profile (2 × 2 × 3 × 3 factorial), and the last one comparing the sand layer and the soil profile. All the statistical analysis was carried out with Statgraphics Plus v. 5.1 (Statgraphics, Warrenton, VA, USA).

3. Results

3.1. Micronutrient Concentration in Sand Layer

The concentration of Fe, Cu, Zn, and Mn in the sand layer and the interaction between ST, TS, and DE is shown in Table 2. Comparing both ST, the concentration of Fe, Zn, Cu, and Mn in the soil S_2 was greater in 30, 29, 33, and 45 % compared with soil S_1 . Moreover, there was a significant increase in the concentration at the end of the crop with 65, 29, 47,

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and 60 % for Fe, Zn, Cu, and Mn, respectively, compared to the beginning of the experiment. At the distance from the dripper, no differences in micronutrient concentration were found in the sand layer.

Table 2. Average concentration of Fe, Zn, Cu, and Mn (mg kg $^{-1}$) in sand layer and the interaction between the different factors. Soil type (ST), time sampling (TS), and distance of the sample from the emitter (DE).

Factor		Fe	Zn	Mn	Cu
A: ST		*	*	*	*
	S_1	$2.0 \pm 0.2 \mathrm{b}$	0.7 ± 0.05 b	$1.8\pm0.2\mathrm{b}$	$1.1\pm0.1~\mathrm{b}$
	S_2	$2.6 \pm 0.2 a$	0.9 ± 0.05 a	2.4 ± 0.2 a	1.6 ± 0.2 a
B: TS		*	*	*	*
	Initial	$1.7\pm0.2\mathrm{b}$	$0.7 \pm 0.05 \mathrm{b}$	$1.7 \pm 0.2 \mathrm{b}$	$1.0\pm0.1~\mathrm{b}$
	Final	2.8 ± 0.3 a	0.9 ± 0.05 a	2.5 ± 0.2 a	1.6 ± 0.2 a
C: DE		ns	ns	ns	ns
	0.1	2.2 ± 0.2	0.8 ± 0.05	2.1 ± 0.2	1.3 ± 0.1
	0.2	2.3 ± 0.2	0.7 ± 0.05	2.1 ± 0.2	1.3 ± 0.1
	0.3	2.3 ± 0.2	0.7 ± 0.05	2.1 ± 0.2	1.3 ± 0.1
Interaction					
	ST x TS	ns	ns	ns	ns
	ST x DE	ns	ns	ns	ns
	TS x DE	ns	ns	ns	ns

The same lowercase letters or ns indicates nonsignificant differences. * indicates significant differences at $p \le 0.05$.

3.2. Micronutrient Concentration in Soil Profile

The interaction (ST, TS, DE, and D) and the micronutrient concentration of both soils are shown in Table 3. All micronutrients studied present similar behavior, being affected by all factors assessed. Soil S₂ showed 108, 18, 52, and 18 % higher concentrations of Fe, Zn, Cu, and Mn, respectively, than soil S₁ and, also, there was an increase in Fe (from 8.6 to 9.6 mg kg $^{-1}$), Zn (from 3.5 to 4.0 mg kg $^{-1}$), Cu (from 18.1 to 21.0 mg kg $^{-1}$), and Mn (from 1.7 to 2.1 mg kg $^{-1}$) at the final stage of crop cycle. Moreover, there was a significant decrease in concentration in the DE for Fe (from 10.4 to 7.9 mg kg $^{-1}$), Zn (from 4.0 to 3.5 mg kg $^{-1}$), Mn (23.9 to 16.2 mg kg $^{-1}$), and Cu (from 2.5 to 1.5 mg kg $^{-1}$). In addition, there was a significant decrease in the concentration of Fe (24%), Zn (15%), Cu (22%), and Mn (19%) in depth.

Table 3. Average concentration of Fe, Zn, Cu, and Mn (mg kg $^{-1}$) in soil profile and the interaction between the different factors. Soil type (ST), time sampling (TS), distance of the sample from the emitter (DE), and depth (D).

Factor	•	Fe	Zn	Mn	Cu
A: ST		*	*	*	*
	S_1	$5.9 \pm 0.6 \mathrm{b}$	$3.4 \pm 0.2 \mathrm{b}$	$15.5\pm1.4~\mathrm{b}$	$1.7\pm0.1~\mathrm{b}$
	S_2	12.3 ± 1.2 a	4.0 ± 0.3 a	23.6 ± 2.2 a	2.0 ± 0.1 a
B: TS		*	*	*	*
	Initial	$8.6\pm0.5\mathrm{b}$	$3.5 \pm 0.2 \mathrm{b}$	$18.1\pm1.1~\mathrm{b}$	$1.7\pm0.1~\mathrm{b}$
	Final	9.6 ± 0.4 a	4.0 ± 0.2 a	21.0 ± 1.2 a	2.1 ± 0.2 a
C: DE		*	*	*	*
	0.1	10.4 ± 0.6 a	4.0 ± 0.1 a	23.9 ± 1.3 a	2.5 ± 0.2 a
	0.2	$8.9 \pm 0.4 \mathrm{b}$	$3.6 \pm 0.2 \mathrm{b}$	$18.5\pm1.2\mathrm{b}$	$1.6\pm0.1~\mathrm{b}$
	0.3	7.9 ± 0.4 c	$3.5 \pm 0.2 \mathrm{b}$	$16.2\pm1.4~\mathrm{c}$	$1.5\pm0.1~\mathrm{b}$
D: D		*	*	*	*
	0.1-0.2	10.5 ± 0.4 a	4.0 ± 0.1 a	22.0 ± 1.0 a	2.1 ± 0.10 a
	0.2 - 0.3	$9.3 \pm 0.5 \mathrm{b}$	$3.7 \pm 0.1 \text{ b}$	$19.4\pm0.9~\mathrm{b}$	$1.8\pm0.04~\mathrm{b}$
	0.3 – 0.4	$8.0 \pm 0.4 \mathrm{~c}$	3.4 ± 0.1 c	$17.2\pm0.9~\mathrm{c}$	$1.7\pm0.04~\mathrm{c}$

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Table 3. Cont.

Factor	•	Fe	Zn	Mn	Cu
Interaction					
	$ST \times TS$	ns	ns	ns	ns
	$ST \times DE$	ns	ns	ns	ns
	$ST \times D$	*	ns	ns	ns
	$TS \times DE$	ns	ns	ns	ns
	$TS \times D$	ns	ns	ns	ns
	$DE \times D$	ns	ns	ns	ns

The same lowercase letters or ns indicates nonsignificant differences. * indicates significant differences at p < 0.05.

There was an interaction between TS and D sample in soil Fe concentration (Figure 3). The soil S_2 showed higher Fe concentration than soil S_1 and a decrease in depth. The depth distribution of Fe in the soil S_2 showed similar trends as Zn, Mn, and Cu (decreasing from 13 to 10 mg kg⁻¹); however, the soil S_1 showed similar soil Fe concentration at different depths.

3.3. Micronutrient Concentration Comparative between Sand Layer and Soil Profile

A comparison of the soil and sand layer properties in the two different soils at both sampling times is reported in Table 4. At the beginning of the crop cycle, the sand layer showed a lower concentration in both soils. The micronutrient concentration for Fe, Zn, Cu, and Mn in soil $\mathbf{S_1}$ (206, 433, 100, and 825 %) and in soil $\mathbf{S_2}$ (521, 363, 38, and 1078 %) were higher than the soil profile. Similar trends were found at the end of the crop cycle in all the micronutrients in soil $\mathbf{S_1}$ (187, 433, 375, and 632 % higher concentration of Fe, Cu, Zn, and Mn compared to the sand) and soil $\mathbf{S_2}$ (294, 310, 33, and 790 % higher concentration of Fe, Cu, Zn, and Mn compared to the sand).

Table 4. Comparison of average concentration of Fe, Zn, Cu, and Mn (mg kg^{-1}) in sand and soil profile at the start and final stage of the crop cycle.

		S_1			S_2		
Parameter	T. Sampling	Sand	Soil Profile		Sand	Soil Profile	
Fe	Initial Final	$1.7 \pm 0.2 \text{ b}$ $2.3 \pm 0.2 \text{ b}$	$5.2 \pm 0.5 \text{ a}$ $6.6 \pm 0.6 \text{ a}$	*	$1.9 \pm 0.2 \mathrm{b}$ $3.2 \pm 0.3 \mathrm{b}$	11.8 ± 1.2 a 12.6 ± 1.3 a	*
Zn	Initial Final	$0.6 \pm 0.1 \text{ b} \\ 0.8 \pm 0.1 \text{ b}$	$3.2 \pm 0.3 \text{ a} \\ 3.8 \pm 0.4 \text{ a}$	*	$0.8 \pm 0.1 \text{ b}$ $1.0 \pm 0.1 \text{ b}$	3.7 ± 0.4 a 4.1 ± 0.4 a	*
Cu	Initial Final	$0.8 \pm 0.1 \text{ b} $ $1.3 \pm 0.1 \text{ b}$	$1.6 \pm 0.2 \mathrm{b}$ $1.8 \pm 0.2 \mathrm{a}$	*	$1.3 \pm 0.1 \text{ b}$ $1.8 \pm 0.2 \text{ b}$	$1.8 \pm 0.2 \text{ a} $ $2.4 \pm 0.2 \text{ a}$	*
Mn	Initial Final	$1.6 \pm 0.2 \text{ b}$ $2.2 \pm 0.2 \text{ b}$	14.8 ± 1.3 a 16.1 ± 1.4 a	*	$1.8 \pm 0.2 \text{ b}$ $2.9 \pm 0.3 \text{ b}$	$21.2 \pm 2.2 \text{ a} \\ 25.8 \pm 2.4 \text{ a}$	*

The same lowercase letters or ns indicates nonsignificant differences. * indicates significant differences at $p \leq 0.05$.

4. Discussion

Fageria et al. [30] reported critical levels ranging from 2.5 to 5 mg kg $^{-1}$, 0.1 to 2 mg kg $^{-1}$, 0.1 to 2.5 mg kg $^{-1}$, and 1 to 5 mg kg $^{-1}$ of Fe, Zn, Cu, and Mn, respectively, in soils using extractant DTPA. Our values in the soil profiles (S₁ and S₂) were the following for Fe (6 to 12 mg Kg $^{-1}$), around 4 mg Kg $^{-1}$ in Zn, from 16 to 24 mg Kg $^{-1}$ in Mn and around 2 mg Kg $^{-1}$ in Cu. The microelements Fe, Zn, and Mn were in the upper part of that the critical levels range proposed by Fageria et al. [30]. These variations reported in our experiment can be ascribed to previous soil management. The low bioavailability of Cu in the soil can be related with two factors: the calcareous chemical composition of the soil and the copper deficiency which can be ascribed to antagonistic interactions with Fe in waterlogged soil, as reported by Hooda [31]. Comparing the critical level ranges

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mentioned above with the sand layer, our values range from 2.0 to 2.6 in Fe, 0.7 to 0.9 in Zn, 1.8 to 2.4 Mn, and 1.1 to 1.6 mg Kg^{-1} (S₁ and S₂). It is important to highlight that all the micronutrients were in critical levels due to the low retention capacity of the Fe, Zn, Cu, and Mn associated to the texture (sandy soil) and the low OM content [31].

In this experiment, the micronutrient concentration increased under higher organic matter (OM) content at the end of the experiment (S_2) . This can be associated to two factors: the high capacity of the OM in the soil for sorption of trace elements and the formation of strong soluble complexes improving trace element solubility [32] and the cation exchange capacity (C.E.C.) that is the ability to exchange micronutrient cations between soil solution and the negatively charged surfaces of clay and organic matter, protecting trace elements from leaching [23]. According to our results, many researchers have also reported this relationship in different types of soils [22] and that the higher availability of microelements was generated by higher organic matter content and the process of mineralization of the soil. For instance, the values reported by Yaro et al. [33] were the following (r = 0.91, 0.32, 0.41, and 0.39 for Fe, Zn, Mn, and Cu) and they also reported micronutrient concentrations above the critical values (Fe: 4.5 mg kg^{-1} , Zn: 0.8 mg kg^{-1} , Mn: 1.0 mg kg⁻¹, and Cu: 0.2 mg kg⁻¹). Moreover, Rai et al. [34] showed a significant positive correlation of 0.32 (Cu concentration ranging from 0.16 to 1.86 mg Kg^{-1}) and 0.28 (Fe ranging from 6.66 to 34.76 mg Kg^{-1}). It is necessary to mention that the pH shows similar values in the soil profile; therefore, there is no contribution into the modifications in micronutrient distribution associated to it [23]. On the other hand, some authors found negative correlation between pH and Fe, Zn, Mn, and Cu concentrations [35–37].

As a consequence of the high micronutrient availability in the soil profile S_2 , the sand layer also showed a high micronutrient concentration because of the retention of micronutrients by sand in the evaporation process, as reported by Bachmann et al. [38]. On the same hand, similar results were reported by Llanderal et al. [39] with NO_3^- , NH_4^+ -N, K, and electrical conductivity (EC).

The soil and the sand layer showed different trends in distribution for the micronutrients in distance. A homogenous distribution of the micronutrient concentration in the sand layer could be due to the lateral movement of the water, which develops wet strips. Consequently, these micronutrients are more soluble and, together with the low-capacity retention of the sand layer, allow a uniform distribution of the trace elements [40–42]. In addition, the information about the retention and lateral distribution of the micronutrients in the sand layer are limited. Regarding soil profile, there was a decrease in micronutrient concentration in distance showing the highest values near to the dripper. Similar results were found by [19], reporting a decrease in Fe, Zn, Mn, and Cu concentration of 65, 86, 94, and 85 %, respectively [19]. This fact can be ascribed to the highest root density near to the dripper, which results in a higher availability of the micronutrients due to the formation of chelates through root exudates and the exudation of acidic compounds by roots into the rhizosphere [31,42].

As far as micronutrient concentration in depth was concerned, our results showed a significant decrease in both soil profiles. Being in line with our results, Franzluebbers and Hons [43] and Verma et al. [44] also reported higher micronutrient concentrations in the top of a bare soil. Moreover, Nadaf et al. [45] found a similar trend for Zn, Mn, and Cu decreasing the concentration of the micronutrient from 0.52 to 0.34, 4.16 to 2.14, and 5.99 to 4.89 mg kg $^{-1}$, respectively. The reduction in micronutrient concentration in depth in the soil profile may be due to the decomposition of soil OM and crop residues located in the top layer [46], as most residues are reduced in a short period of time after deposition [47].

Moreover, the CEC of the soil avoids the trace elements leaching [23]. In addition to this, the root distribution and depth has a crucial role in the profile of micronutrients, since nutrients are absorbed by deeper roots, and then translocated to the aerial parts of the plant [48,49].

On the other hand, Fe concentration showed the same values in depth in the soil S_1 , which may be attributed to the movement of finer fractions to lower horizons during

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the process of illuviation, as reported Verma et al. [44]. Similar trends were found by Fageria et al. [30], who described that Fe can be leached in sandy soils (S_1 have a 75% of sand in the particle distribution size of the soil). On the other hand, the increase in the trace element at the end of the experiment can be related to the different process of abovementioned in-depth distribution and, also, with organic matter mineralization. Moreover, it is important to mention that the mulching increased the mineralization of the organic matter due to better conditions for mineralization process compared to a bare soil [50].

Comparing the sand and soil layer, it can be reported that the highest micronutrient concentration was found in the soil layer, and this can be due to the high OM content associated to the high cationic exchangeable capacity of the soil compared to the sand layer [44,51].

5. Conclusions

According to these results, the microelements showed a similar behavior. The concentration of the trace elements (Fe, Zn, Mn, and Cu) increased with the content of OM in the soil profile compared to the sand layer. There was also an accumulation of micronutrients closer to the neck of the plant but decreasing in distance and in depth in the soil. The micronutrients showed lateral movement in the sand layer due to the low retention capacity of the sand. There was also a mobility of micronutrients without significant variations in distance. The lower concentration in the sand layer compared with the soil profile can be due to the major C.E.C. of the soil profile. These results suggest more studies on the distribution of micronutrients in the wet bulb to improve its characterization, since the previous information was very scarce. Nevertheless, it is important to carry out experiments comparing the micronutrients' distribution in a sandy mulching soil with a bare soil, and also considering the application of chelated micronutrients via fertigation.

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References

- 1. Zulfiqar, F.; Navarro, M.; Ashraf, M.; Akram, N.A.; Munné-Bosch, S. Nanofertilizer use for sustainable agriculture: Advantages and limitations. *Plant Sci.* **2019**, 289, 110270. [CrossRef]
- 2. Ayyub, C.M.; Wasim Haidar, M.; Zulfiqar, F.; Abideen, Z.; Wright, S.R. Potato tuber yield and quality in response to different nitrogen fertilizer application rates under two split doses in an irrigated sandy loam soil. *J. Plant Nutr.* **2019**, 42, 1850–1860. [CrossRef]
- 3. Duque-Acevedo, M.; Belmonte-Ureña, L.J.; Plaza-Úbeda, J.A.; Camacho-Ferre, F. The management of agricultural waste biomass in the framework of circular economy and bioeconomy: An opportunity for greenhouse agriculture in Southeast Spain. *Agronomy* **2020**, *10*, 489. [CrossRef]
- 4. Rashid, A.; Ryan, J. Micronutrient constraints to crop production in soils with Mediterranean-type characteristics. *J. Plant Nutr.* **2004**, 27, 959–975. [CrossRef]
- 5. Rajeswar, M.; Rao, C.S.; Balaguravaiah, D.; Khan, M.A. Distribution of available macro and micronutrients in soils of Garikapadu. *J. Indian Soc. Soil Sci.* **2009**, *57*, 210–213.
- 6. Segura, M.L. Fertirrigación de Cultivos Hortícolas en Condiciones Salinas con Sistema Enarenado y Sustratos Alternativos. Comarca Agrícola de Almería. Ph.D. Dissertation, University Autonomous of Madrid, Madrid, Spain, 1995; p. 271.
- 7. Lao, M.T. The mulching sandy soil and their management fergation in horticultural production. *Trends Soil Sci.* 2004, 3, 71–82.
- 8. Adnan, M.; Asif, M.; Khalid, M.; Abbas, B.; Sikander Hayyat, M.; Raza, A.; Ahmad Khan, B.; Hassan, M.; Awais Bashir, M.; Shakeel Hanif, M. Role of mulches in agriculture: A review. *Int. J. Bot. Std.* **2020**, *3*, 309–314.

Agriculture **2022**, 12, 1066 10 of 11

9. Iqbal, R.; Raza, M.A.S.; Valipour, M.; Saleem, M.F.; Zaheer, M.S.; Ahmad, S.; Nazar, M.A. Potential agricultural and environmental benefits of mulches-a review. *Bull Natl. Res. Cent.* **2020**, *44*, 75. [CrossRef]

- 10. Jordán, A.; Zavala, L.M.; Gil, J. Effects of mulching on soil physical properties and runoff under semi-arid conditions in southern Spain. *Catena* **2010**, *81*, 77–85. [CrossRef]
- 11. Fernández, C.; Vega, J.A. Are erosion barriers and straw mulching effective for controlling soil erosion after a high severity wildfire in NW Spain? *Ecol. Eng.* **2016**, *87*, 132–138. [CrossRef]
- 12. Fernández, C.; Vega, J.A. Effects of mulching and post-fire salvage logging on soil erosion and vegetative regrowth in NW Spain. *For. Ecol. Manag.* **2016**, *375*, 46–54. [CrossRef]
- 13. Scopa, A.; Candido, V.; Dumontet, S.; Miccolis, V. Greenhouse solarization: Effects on soil microbiological parameters and agronomic aspects. *Sci. Hortic.* **2008**, *116*, 98–103. [CrossRef]
- 14. Katan, J.; Gamliel, A. Plant health management: Soil solarization. In *Encyclopedia of Agriculture and Food Systems*; Elsevier: Amsterdam, The Netherlands, 2014; pp. 460–471.
- 15. Al-Shammary, A.A.G.; Kouzani, A.; Gyasi-Agyei, Y.; Gates, W.; Rodrigo-Comino, J. Effects of solarisation on soil thermal-physical properties under different soil treatments: A review. *Geoderma* **2020**, *363*, 114137. [CrossRef]
- 16. Vukašinović, I.Ž.; Todorović, D.J.; Đorđević, A.R.; Rajković, M.B.; Pavlović, V.B. Depth distribution of available micronutrients in cultivated soil. *J. Agric. Sci.* **2015**, *60*, 177–187.
- 17. Gupta, U.C.; Kening, W.U.; Liang, S. Micronutrients in soils, crops, and livestock. Front. Earth Sci. 2008, 15, 110–125. [CrossRef]
- 18. Kumar, M.; Babel, A.L. Available micronutrient status and their relationship with soil properties of Jhunjhunu Tehsil, District Jhunjhunu, Rajasthan. *Ind. J. Agric. Sci.* **2011**, *3*, 97–106. [CrossRef]
- 19. Belanović, S.; Ćakmak, D.; Kadović, R.; Beloica, J.; Perović, V.; Alnaass, N.; Saljnikov, E. Availability of some trace elements (Pb, Cd, Cu and Zn) in relation to the properties of pasture soils in Stara Planina mountain. *Bull. Fac. Forest.* **2012**, *106*, 41–56. [CrossRef]
- 20. Kingery, W.L.; Wood, C.W.; Delaney, D.P.; Williams, J.C.; Mullins, G.L. Impact of long-term land application of broiler litter on environmentally related soil properties. *J. Environ. Qual.* **1994**, 23, 139–147. [CrossRef]
- 21. Katyal, J.C.; Sharma, B.D. DTPA-extractable and total Zn, Cu, Mn, and Fe in Indian soils and their association with some soil properties. *Geoderma* **1991**, 49, 165–179. [CrossRef]
- 22. Herencia, J.F.; Ruiz, J.C.; Morillo, E.; Melero, S.; Villaverde, J.; Maqueda, C. The effect of organic and mineral fertilization on micronutrient availability in soil. *Soil Sci.* **2008**, *173*, 69–80. [CrossRef]
- 23. Chatzistathis, T. Micronutrient Deficiency in Soils and Plants; Bentham Science Publishers: Sharjah, Arabia, 2014; p. 183.
- 24. Malavolta, E.; Vitti, G.C.; Oliveira, S. *Avaliação do estado nutricional das plantas: Princípios e aplicações*; Associação Brasileira para Pesquisa da Potassa e do Fosfato: Piracicaba, Brasil, 1997; p. 201.
- 25. Sharma, R.P.; Singh, M.; Sharma, J.P. Correlation studies on micronutrients vis-à-vis soil properties in some soils of Nagaur district in semi-arid region of Rajasthan. *J. Ind. Soc. Soil Sci.* **2003**, *51*, 522–527.
- 26. Mendieta, L.A. Distribución Espacial de Nutrimentos en la Solución del Suelo para la Producción Intensiva de Fresa. Master Thesis, Postgrado de edafología, Colegio de Postgraduados, Montecillo, Texcoco, Estado de México, Mexico, 2011; p. 86.
- 27. Llanderal, A. Study of Diagnostic Methods and Evaluation of Nutritional Parameters in the Intensive Horticulture Cropping Systems as Basis for a Sustainable Management of the Fertigation. Ph.D. Thesis, Universidad de Almería, Ctra. Sacramento s/n, La Cañada de San Urbano, Almeria, Spain, September 2017; p. 177.
- 28. Segura, M.L.; Granados, M.R.; Contreras, J.I.; Martín, E.; Rodríguez, J.M. Greenhouse management of the potassium fertilization of a green bean crop. *Acta Hortic.* **2006**, 700, 145–148. [CrossRef]
- 29. Lindsay, W.L.; Norvell, W.A. Development of a DTPA test for zinc, iron, manganese and copper. *Soil Sci. Soc. Am. J.* **1978**, 42, 421–428. [CrossRef]
- 30. Fageria, N.K.; Baligar, V.C.; Clark, R.B. Micronutrients in crop production. Adv. Agron. 2002, 77, 185–268.
- 31. Hooda, P.S. Trace Elements in Soils; John Wiley & Sons Ltd.: Chichester, UK, 2010; p. 546.
- 32. Alloway, B.J. Sources of heavy metals and metalloids in soils. In *Heavy metals in soils*; Springer: Dordrecht, The Netherlands, 2013; pp. 11–50.
- 33. Yaro, D.T.; Kparmwang, T.; Raji, B.A.; Chude, V.O. Extractable micronutrients status of soils in a plinthitic landscape at Zaria, Nigeria. *Commun. Soil Sci. Plant Anal.* **2008**, *39*, 2484–2499. [CrossRef]
- 34. Rai, A.P.; Mondal, A.K.; Kumar, V.; Samanta, A.; Wali, P.; Kumar, M.; Dwivedi, M.C. Status of DTPA-extractable micronutrients in soils of Samba district of Jammu and Kashmir in relation to soil properties. *Ann. Plant Soil Res.* **2018**, *20*, 139–142.
- 35. Dhaliwal, S.S.; Naresh, R.K.; Mandal, A.; Singh, R.; Dhaliwal, M.K. Dynamics and transformations of micronutrients in agricultural soils as influenced by organic matter build-up: A review. *Environ. Sustain. Indic.* **2019**, *1*, 100007. [CrossRef]
- 36. Kumar, R.; Mandal, J. Vertical distribution of micronutrients and heavy metals. J. Pharmacogn. Phytochem. 2020, 9, 1526–1531.
- 37. Naskar, P.; Das, D.K.; Ghosh, D. Distribution of cationic micronutrients in relation to different soil properties and fractions of phosphorus in coastal soils of West Bengal. *J. Indian Soc. Soil Sci.* **2021**, *69*, 147–155. [CrossRef]
- 38. Bachmann, J.; Horton, R.; Van Der Ploeg, R.R. Isothermal and nonisothermal evaporation from four sandy soils of different water repellency. *Soil Sci. Soc. Am. J.* **2001**, *65*, 1599–1607. [CrossRef]

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39. Llanderal, A.; Garcia-Caparros, P.; Contreras, J.I.; Lao, M.T.; Segura, M.L. Spatial Distribution and Mobility of Nutrients on Sand Mulching Soil for Fertigated Green Bean Crops under Greenhouse Conditions in Southern Spain: (I) Macronutrients. *Agronomy* **2021**, *11*, 842. [CrossRef]

- 40. Resh, H.M. *Hydroponic Food Production: A Definitive Guide of Soilless Food-Growing Methods;* Woodbridge Press Publication: Beaverton, OR, USA, 2001; p. 462.
- 41. Contreras, J.I. Optimización de las Estrategias de Fertirrigación de Cultivos Hortícolas en Invernadero Utilizando Aguas de Baja Calidad (Agua Salina y Agua Regenerada) en Condiciones del Litoral de Andalucía. Ph.D. Dissertation, University Almeria, Almeria, Spain, 2014; p. 258.
- 42. Tisdale, S.L.; Nelson, W.L.; Beaton, J.D. *Soil Fertility and Fertilizers*; Collier Macmillan Publishers: Springfield, OH, USA, 1985; p. 346.
- 43. Franzluebbers, A.J.; Hons, F.M. Soil-profile distribution of primary and secondary plant-available nutrients under conventional and no tillage. *Soil Till. Res.* **1996**, *39*, 229–239. [CrossRef]
- 44. Verma, V.K.; Setia, R.K.; Sharma, P.K.; Singh, C.; Kumar, A. Pedospheric variations in distribution of DTPA-extractable micronutrients in soils developed on different physiographic units in central parts of Punjab, India. *Int. J. Agric. Biol.* 2005, 7, 243–246.
- 45. Nadaf, S.A.; Amara, D.M.K.; Patil, P.L. Distribution of Micronutrients in Selected Pedons of Sugarcane Growing Vertisols in Northern Karnataka State of India. *Open J. Soil Sci.* **2022**, *12*, 1–12. [CrossRef]
- 46. Wright, A.L.; Hons, F.M.; Matocha, J.E. Tillage impacts on microbial biomass and soil carbon and nitrogen dynamics of corn and cotton rotations. *Appl. Soil Ecol.* **2005**, 29, 85–92. [CrossRef]
- 47. Zibilske, L.M.; Materon, L.A. Biochemical properties of decomposing cotton and corn stem and root residues. *Soil Sci. Soc. Am. J.* **2005**, *69*, 378–386. [CrossRef]
- 48. Jiang, Y.; Zhang, Y.G.; Zhou, D.; Qin, Y.; Liang, W.J. Profile distribution of micronutrients in an aquic brown soil as affected by land use. *Plant Soil Environ.* **2009**, *55*, 468–476. [CrossRef]
- 49. García, S.; Gómez-Rey, M.X.; González-Prieto, S.J. Availability and uptake of trace elements in a forage rotation under conservation and plough tillage. *Soil Till. Res.* **2014**, *137*, 33–42. [CrossRef]
- 50. Ibrahim, M.; Khan, A.; Ali, W.; Akbar, H. Mulching techniques: An approach for offsetting soil moisture deficit and enhancing manure mineralization during maize cultivation. *Soil Till. Res.* **2020**, 200, 104631. [CrossRef]
- 51. Urrestarazu, M. Tratado de Cultivos Sin Suelo; Mundi-Prensa: Madrid, Spain, 2004; p. 874.