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Research Article

Fruit mineral nutrient contents of field and greenhouse grown tomatoes and comparison with standard values

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Abstract

Tomato (*Solanum lycopersicum* L.) is a significant member of the Solanaceae family with substantial worldwide production. The nutritional content of vegetables affects their metabolic and quality characteristics positively or negatively in many aspects and is one of today's important research areas. In this study, grown tomato samples collected from fields and greenhouses in nine different cities of Türkiye were analysed for boron, calcium, copper, iron, potassium, magnesium, manganese, sodium, and zinc concentrations using spectroscopy, compared with available studies in terms of fertilization/nutrient uptake status and it was decided whether there is a difference between tomato samples grown in the field and the greenhouse. The study revealed that there are differences between macro and microelement contents of the field and greenhouse-grown tomatoes. Greenhouse tomatoes have greater nutritional element contents since they are protected from external effects and pesticides, growing in a healthy and nutritionally rich manner. The lowest and highest concentrations (mg kg^{-1} dry weight) of mineral elements were boron (18.13-28.30), calcium (1277-1836), copper (4.60-9.45), iron (18.86-27.33), potassium (20384-22305), magnesium (1870-2107), manganese (10.12-23.27), Sodium (119.65-209.11) and zinc (15.55-25.41). As a result, tomatoes produced in Türkiye for export to various countries were found to be containing adequate macronutrients according to the relevant literature except for potassium, and micronutrients contents were found to be within the safe limits. Also, considering the percentage of daily Recommended Dietary Allowance values it provides, it can be said that tomatoes are a good source of micronutrients.

Keywords: field; greenhouse; ICP-OES; macronutrients; micronutrients; *Solanum lycopersicum* L.

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Introduction

Tomato (*Solanum lycopersicum* L. $2n = 24$) is one of the most widely cultivated (conventionally, greenhouse or soilless agriculture) and important agricultural products among the members of the Solanaceae family as well as all vegetables. It exhibits an amazing adaptation capability, growing in any available agricultural area throughout the world despite originating from a single local region of South America (Peru, Chile, Ecuador, and Bolivia) (Aguirre *et al.*, 2017), a semitropical zone. Despite its widespread distribution potential, commercially cultivated varieties are very fragile against abiotic and biotic stresses (Sahu and Chattopadhyay, 2017). It is widely grown in the regions where the Mediterranean climate is common (Rodríguez-Ortega *et al.*, 2019). Tomatoes depend on highly stable average daily temperatures, especially during out-season production, even under favourable growing conditions (Ramírez-Arias *et al.*, 2011). Greenhouses are ideal places for providing favourable growing conditions for the production of tomatoes and some other vegetables such as cucumber, melon, eggplant, capsicum, cabbage, etc. due to the strictly controlled growing environment, unaffected by the external climate conditions, being a sustainable system (water and fertilizer management) and having maximum production efficiency with minimum input.

Also, tomato plays a significant role in healthy dietary nutrition with its ingredients such as lycopene which gives its natural colour and is an abundant free radical scavenger, protecting the cell and cellular processes from oxidative damage (Nasir *et al.*, 2015; Saini *et al.*, 2015), is strongly associated with the anti-inflammatory effects and support the organization of the human cell cytokine production (Hortelano, 2009; Ku and Lin, 2013), whereas the anthocyanine contents of tomatoes help in reducing the risk of cardiovascular diseases and various types of cancer (Mirto *et al.*, 2018), in addition to its rich dietary source of vitamin C and E (García-Closas *et al.*, 2004). Due to the increase in the socio-economic status of people, the demand for tomatoes has risen both in terms of quantity and quality (EI-Bassiony *et al.*, 2014). Therefore, consumers nowadays are expecting fruits bearing organoleptic quality (size, shape, and colour), taste quality (organic acid, sugar, and acid ratio, soluble sugar content, and total soluble solid contents), and nutritional quality (lycopene and vitamin C) (Ripoll *et al.*, 2014). Fertilizers with K play an important role in tomato production since the number of quality components in tomatoes depends on these fertilizers as much as growing conditions. Doug et al. reported that up to a certain dosage, K fertilization improved the marketable properties of tomatoes increasing Fe and Mg uptake, whereas excessive K fertilization decreased Na, Zn, and Ca uptake (Daoud *et al.*, 2020). Unfortunately, growing tomatoes in soil cultures intensively in the same greenhouse soil for extensive periods have some setbacks such as degradation of soil quality (such as Olsen-P, total N, and available K (Fu *et al.*, 2017)) and pH nature, decreased efficiency of microbial activity in the soil (Zhang *et al.*, 2015), increased risk of contamination within the soil and vegetables (Hu *et al.*, 2017), and decreased sustainability of greenhouses soil (Wang and Xing, 2017). Furthermore, heavy metal concentrations in greenhouse soils are found to be much higher than those of open fields (Hu *et al.*, 2014; Xu *et al.*, 2015). Therefore, soil properties and fertilization is a significant parameter for yield, mineral content and fruit quality. The following research reported that tomato fertilization with Mg, and B during the growing period has considerably increased total yields, fruit production, and some fruit characteristics (Kocevsky *et al.*, 1996). In supporting this research, tomato fertilization with N during the growing period has also increased colour parameters, soluble solid contents, and chemical contents like quality properties (Petropoulos *et al.*, 2020).

Turkey is one of the largest tomato producers in the world after China, India and the USA. As it is known, carbohydrates, proteins and fats are the essential nutrients of life. The protein quality and quantity of the seeds are basic factors for the selection of nutritive values of plants (Sá *et al.*, 2020). In addition to these, ash and fiber contents, moisture, the energy value of a vegetable and/or plant (food) are important for human diet and also soil quality (Armesto *et al.*, 2020). Mineral nutrients taken from the soil are incorporated into a variety of important compounds with structural and physiological roles in the plant, and thus the nutrient analysis of edible fruits and vegetables plays a crucial role in assessing their nutritional significance (Sotomayor *et al.*, 2019). B, Ca, Cu, Fe, K, Mg, Mn, Na and Zn are important macro and micronutrients that participate in several metabolic processes, such as primary and secondary metabolism, signal transduction, cell defence, hormone perception, energy metabolism, and gene regulation (Vatansever *et al.*, 2017). In this fashion, our primary aim is to i) determine the mineral nutrient status of edible tomato fruits from various origins of a significant producer country (Turkey) and ii) to compare the differences with tomatoes grown with different methods (cultivation methods such as greenhouses, field, hydroponic, etc.) in terms of basic mineral contents. For this purpose, fully grown tomato fruit samples were collected from both fields and greenhouses in nine different provinces of Turkey during the vegetation period and analysed for B, Ca, Cu, Fe, K, Mg, Mn, Na and Zn concentrations using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

Materials and Methods

Study area

The experiment was designed for collecting table type tomatoes from the field and greenhouse and observing the differences between macro and micronutrient contents. For this purpose, a total of 180 samples were collected from 10 different cities of Türkiye: Antalya, Bilecik, Bursa, Canakkale, Eskisehir, Izmir, Kutahya, Mersin and Sanlıurfa (Figure 1A). Each one of these cities corresponds to the greenhouse-field cultivation hot spots of Türkiye and climatic data are given in Figure 1B. A total of 20 samples were collected from each city with 10 of the samples grown in the greenhouse and the remainder under field conditions. In each city, greenhouse and field samples were collected from the same county to preserve the homogeneity (Table 1).

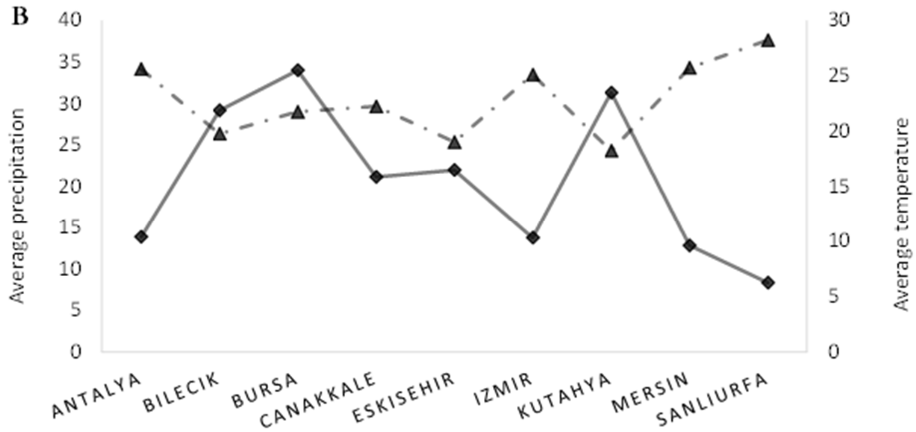


Figure 1. A. Detailed information and collection site of tomato samples in Türkiye (Picture was adapted from Google Earth Program) B. Climatic condition throughout growing season (each points represent average values from May to September) in Türkiye.

Table 1. Detail information of tomato sample collection sites and abbreviation used in text

Number	City	County	X coordinate	Y coordinate	Field sample abbreviations	Greenhouse sample abbreviations
1	Kutahya	Simav	28.943736	39.11797	FARM1	GH1
2	Eskisehir	Sandikli	30.544178	39.638478	FARM2	GH2
3	Bursa	Iznik	29.72644	40.444081	FARM3	GH3
4	Antalya	Merkez	30.606615	36.882898	FARM4	GH4
5	Izmir	Bergama	27.206506	39.114331	FARM5	GH5
6	Bilecik	Sogut	30.166227	40.016067	FARM6	GH6
7	Canakkale	Biga	27.251209	40.219648	FARM7	GH7
8	Antalya	Kumluca	30.28758	36.35964	FARM8	GH8
9	Sanliurfa	Harran	36.859691	39.012621	FARM9	GH9
10	Mersin	Silifke	33.949802	36.37695	FARM10	GH10

Measurement of element concentrations

The tomato samples were put into labelled transparent plastic bags and transferred to the laboratory. Then, samples were washed with tap-water and ultra-pure water several times. The washed samples were left to dry under room conditions and then were cut into pieces. The pieces were oven-dried at 80 °C for approximately 48 h until no water was left inside. The dried samples were ground by using a micro-hammer cutter and fed through a 1.5 mm sieve. The grinder was cleaned with 96% alcohol after each attempt. Finally, the samples were weighed to 0.2 g, transferred into Teflon vessels and 10 mL of 65% HNO_3 (by weight) was added to each vessel. Following weighing, all samples were mineralized in a microwave oven (Berghof-MWS2) programmed to 145 °C for 5 min, 165 °C for 5 min and 175 °C for 20 min respectively. After cooling, each sample was filtered using Whattman filter paper and the volumetric flasks were topped up to a volume of 50 mL with the addition of a sufficient amount of ultra-pure water. Macro and microelement (B, Ca, Cu, Fe, K, Mg, Mn, Na, and Zn) measurements were conducted by Inductively Coupled Plasma Optical Emission Spectroscopy (Perkin Elmer-Optima 7000 DV) (Karahan *et al.*, 2019; Ozyigit *et al.*, 2019).

Quality control and assurance

Eight different concentrations were prepared for each element by using 1000 ppm multi-element stock solutions (Merck) and calibration curves were generated based on 8 different concentration scales for each elemental concentration. Sample readings were performed only when the coefficient of determination, R^2, value of the calibration curve was higher than 0.999. From the first calibration, until the analysis of 5 samples was completed, the standards were read again and the deviation values were checked. The Relative Standard Deviation values above 3% were discarded during the analysis process and recalibration was performed under these circumstances (Table 2) (EPA 2007).

Table 2. Parameters of the analytical method applied for the determination of elements by ICP-OES

Elements	Spectral lines (nm)	LoD (mg kg^{-1})	LoQ (mg kg^{-1})	RSD (%)	R^2
B	249.677	0.043	0.143	0.62	.999943
Ca	317.933	0.585	1.950	2.15	.999791
Cu	327.393	0.038	0.127	1.93	.999848
Fe	238.204	0.472	1.573	1.26	.999862
K	766.490	0.531	1.770	1.65	.999778
Mg	285.213	0.287	0.957	0.93	.999913
Mn	257.610	0.194	0.647	1.04	.999819
Na	589.592	0.235	0.783	2.48	.999452
Zn	213.857	0.204	0.680	1.21	.999795

LoD: limit of detection; LoQ: limit of quantification;
RSD: relative standard deviation; R^2: coefficient of determination

Statistical analyses

Statistical analyses such as Hierarchical Cluster and ANOVA analysis were executed using IBM SPSS Statistics 22 software. Levels of statistical significance were expressed as $^{**}P<0.01$ and $^{*}P<0.05$ level (2-tailed). The hierarchical clustering analysis and Principle component analysis (Minitab 19 software) both revealed the similarity/dissimilarity relationships on the field and greenhouse-grown tomato samples. In addition to hierarchical clustering and PCA analysis, daily dietary consumption of related minerals were calculated by using mineral element concentrations in dry weighted tomatoes according to the Recommended dietary allowance (RDA).

Results and Discussion

Macro and microelement concentrations of greenhouse and field-grown tomatoes from 10 different locations in Turkey are given in Table 3. According to the elemental analysis of collected samples, a narrow diversity was observed among some metal and mineral nutrient element concentrations. The highest and lowest elemental concentration readings (in mg kg^{-1} dry) were detected as follows; the highest reading for B was 28.303 in a greenhouse sample from Mersin and the lowest was 18.127 in a field sample from Kutahya; the highest reading for Ca was 1835.886 in a greenhouse sample from Mersin and the lowest was 1276.535 in a field sample from Kutahya; the highest reading for Cu was 9.448 in a greenhouse sample from Mersin and the lowest was 4.608 in a field sample from Kutahya; the highest reading for Na was 209.106 in a greenhouse sample from Mersin and the lowest was 119.653 in a field sample from Kutahya; finally for Zn, the highest was 25.411 in a greenhouse sample from Mersin and the lowest was 15.545 in a field sample from Kutahya. It is seen that the element contents of tomato samples gradually increase from location 1 to location 10 (Table 3). Another case related to these elemental readings is that the concentrations of field-grown tomatoes appeared to be lower than that of the greenhouse-grown tomatoes in all locations except for Mn. The Mn concentration was observed to be higher in field tomatoes when compared with all greenhouse location samples. The highest reading for Fe was 27.333 belonging to a sample from a greenhouse in Mersin and the lowest was 18.858 in a field sample from Kutahya; for K, the highest reading was 22304.75 in a greenhouse sample from Mersin and the lowest was 20383.74 in a field sample from Kutahya. For Mg, the highest reading was 2106.979 in a greenhouse sample from Mersin and the lowest was 1870.182 from a field sample grown in Kutahya. For Mn, the highest reading was 23.271 in a field sample from Mersin and the lowest was 10.117 in a greenhouse sample from Kutahya.

Table 3. Mineral nutrient concentrations in tomato fruits

		Locations									
Element	Sample Origin	Kutahya (Simav)	Eskisehir (Sandikli)	Bursa (Iznik)	Antalya (Merkez)	Izmir (Bergama)	Bilecik (Sogut)	Canakkale (Biga)	Antalya (Kumluca)	Sanliurfa (Harran)	Mersin (Silifke)
B	F	18.127± 0.058	18.719± 0.122	20.920± 0.128	21.643± 0.123	22.118± 0.108	21.346± 0.361	24.588± 0.314	25.232± 0.153	24.987± 0.117	25.972± 0.354
	G	19.273± 0.082	19.693± 0.277	21.758± 0.156	22.614± 0.044	22.769± 0.076	23.500± 0.126	25.731± 0.192	25.847± 0.293	26.665± 0.320	28.303± 0.112
Ca	F	1276.535± 15.092	1454.202± 15.354	1445.429± 18.445	1418.112± 12.199	1444.253± 10.687	1463.411± 6.159	1590.577± 7.103	1534.70± 7.621	1605.566± 24.486	1677.300± 4.855
	G	1408.085± 7.264	1478.607± 16.004	1488.274± 15.552	1540.080± 13.575	1555.833± 16.093	1595.751± 27.651	1627.374± 21.438	1668.61± 10.935	1770.996± 7.559	1835.886± 4.522
Cu	F	4.608± 0.024	5.307± 0.065	5.097± 0.074	5.781± 0.037	6.159± 0.049	6.706± 0.100	7.425± 0.167	7.781± 0.051	8.381± 0.067	8.759± 0.065
	G	5.477± 0.063	5.756± 0.066	6.312± 0.014	6.627± 0.046	6.854± 0.058	7.170± 0.051	7.916± 0.131	8.251± 0.125	8.932± 0.070	9.448± 0.050
Fe	F	18.858± 0.089	20.356± 0.029	20.589± 0.080	20.801± 0.050	21.084± 0.080	21.651± 0.116	22.086± 0.308	21.947± 0.081	22.294± 0.091	23.616± 0.328
	G	20.851± 0.091	21.600± 0.077	22.009± 0.194	23.236± 0.117	22.737± 0.105	24.020± 0.198	25.377± 0.208	25.374± 0.310	26.185± 0.297	27.333± 0.277
K	F	20383.74± 6.837	20509.220± 12.378	20578.925± 12.733	20647.427± 11.887	20748.238± 40.313	20869.276± 27.345	21105.395± 30.727	21377.128± 22.689	21597.05± 39.825	21798.04± 59.618
	G	20874.72± 23.58	20976.212± 40.730	21064.333± 40.231	21342.663± 20.380	21357.485± 28.042	21469.566± 42.493	21716.560± 52.192	21865.089± 57.812	22051.71± 59.143	22304.75± 67.086
Mg	F	1870.182± 14.501	1936.784± 8.023	1984.359± 1.404	1993.811± 0.645	2007.491± 1.076	2017.023± 0.982	2026.900± 0.696	2074.096± 2.373	2053.010± 2.436	2078.262± 2.607
	G	2003.633± 3.599	2015.325± 1.454	2023.016± 1.287	2037.799± 1.170	2045.388± 1.707	2056.117± 1.325	2068.187± 2.327	2035.971± 0.575	2094.220± 2.520	2106.979± 2.712
Mn	F	10.911± 0.182	11.598± 0.184	14.566± 0.212	14.682± 0.204	15.205± 0.311	17.429± 0.279	19.478± 0.200	19.990± 0.138	22.903± 0.509	23.271± 0.272
	G	10.117± 0.034	10.654± 0.077	13.096± 0.224	13.384± 0.090	14.352± 0.117	16.599± 0.198	17.234± 0.242	17.999± 0.355	20.757± 0.206	22.243± 0.149
Na	F	119.653± 0.675	139.927± 0.863	148.990± 0.934	154.492± 0.626	163.308± 0.909	165.096± 3.861	169.408± 1.749	180.080±0 .979	194.660± 2.079	193.440± 0.820
	G	133.823± 2.751	148.357± 0.973	157.920± 1.103	165.573± 0.350	170.762± 1.907	178.039± 2.454	182.840± 2.470	192.329± 1.909	205.875± 1.674	209.106± 0.679
Zn	F	15.545±0.1 42	16.306± 0.110	16.625± 0.102	16.712± 0.060	17.314± 0.123	17.771± 0.366	19.669± 0.291	21.038± 0.121	21.799± 0.236	23.496± 0.190
	G	16.391± 0.085	16.921± 0.163	17.138± 0.147	17.364± 0.215	17.601± 0.151	18.193± 0.139	20.299± 0.100	22.194± 0.287	23.767± 0.316	25.411± 0.269

F: Field grown tomatoes, G: Greenhouse grown tomatoes, B: Boron, Ca: Calcium, Cu: Copper, Fe: Iron, K: Potassium, Mg: Magnesium, Mn: Manganese, Na: Sodium, Zn: Zinc, each data point expressed as mg kg^{-1}, data points represent the mean of ten different samples

The quality of the tomato fruit is simply characterized by two parameters; the amount of minerals, pigments, vitamins, protein, lipids, fat, and the amount of phytochemical substances with antioxidant properties (Higashide, 2013; Li *et al.*, 2011). The presence of adequate mineral nutrition engenders a relationship between the above-mentioned two parameters, namely; the quality of marketable fruits and the amount of healthful phytochemicals (Groher *et al.*, 2018). This study is predominantly focused on the mineral nutrient contents of tomato samples of various origins and the classification of these samples. The mineral elements that should be present in tomato leaves for healthy growth are as follows; B 35 mg kg^{-1}, Ca 25000 mg kg^{-1}, Cu 15 mg kg^{-1}, Fe 90 mg kg^{-1}, K 55000 mg kg^{-1}, Mg 5000 mg kg^{-1}, Mn 350 mg kg^{-1}, Zn 80 mg kg^{-1} (Winsor, 1973). Another study listed the recommended amount of mineral elements that should be present in the tomato plant for healthy growth as; B 40-60 mg kg^{-1}, Ca 12500 mg kg^{-1}, K 60000 mg kg^{-1}, Mg 5000 mg kg^{-1} and Mn 30 mg kg^{-1} (Gallagher, 1972). The results of this study revealed that all mineral nutrients determined in tomato fruits are within acceptable limits. A comparison of previous studies on nutrient contents of tomato fruits and the aforementioned nutrient contents of this study were given in Table 4.

Table 4. Tomato nutrient contents of some selected studies and comparison with the current study

Elements	References					Current study
	1	2	3	4	5	
B	-	-	-	-	10-21.6	18-27
Ca	1600-2000	1000	1788- 3017	1380	1900-2300	1276-1835
Cu	15.99-18.88	8.5	7- 8.8	7	10.5-12	4.6-9.4
Fe	26.74-30.98	24.7	39.3- 41.3	54.36	72-109	18.8-27.3
K	34700-37700	28600	31938.4-22540.8	33280	39500-43300	20383-22304
Mg	1100	1100	1072.3-774.6	1950	1700-2200	1870-2106
Mn	32.04-33.50	22.6	11.2- 10.6	8.9	10.2-19.4	10.1-23.2
Na	950-880	-	402.9- 345.1	-	400	119-209
Zn	40.43-47.58	16.2	24.6 - 33.7	27.71	10.2-19.4	15.5-25.4

1; Roosta and Hamidpour (2013), 2; Schmautz *et al.* (2016), 3; Capel *et al.* (2017), 4; Ambrosano *et al.* (2018), 5; Barker *et al.* (2019)

Although tomatoes are cultivated in open field conditions all over the world, greenhouse production has become widespread in the Mediterranean and Middle East regions, Latin America, Australia and China in recent years (Costa and Heuvelink, 2018). In Turkey, 82% of the greenhouse tomato production is located mainly in the Mediterranean basin followed by the Aegean and Marmara regions (Keskin *et al.*, 2010). The monoculture production activities in the greenhouses reveal various problems, such as productivity and quality failures due to soil-borne diseases and pests, low organic content, pH increase, salinization and reduction in soil microbial flora owing to intensive fertilization (Chen *et al.*, 2004; She *et al.*, 2017; Shi *et al.*, 2009). The majority of those problems are directly or indirectly related to soil. The health/balance of the soil is disturbed by long-term high-yield tomato or any other crop cultivation in a certain place. Among all these components, mineral nutrition along with fertilization is the second crucial parameter affecting the yield and quality, following water availability. Plants are generally either not fertilized or rarely fertilized according to their requirements during their development period (Quesada-Roldán and Bertsch-Hernández, 2013). Although it is essential to provide the necessary mineral nutrients related to the various developmental phases of the plant, there are still problems in applying fertilizer dosage (Bugarín-Montoya *et al.*, 2002).

Boron

To be useful for plants, boron has a very narrow range between its deficiency and toxicity (Siddiqui *et al.*, 2013). Turkish soils (especially in Central Anatolia) widely suffer from B deficiency and toxicity is also observed in a narrow area (Gezgin *et al.*, 2002). Davis *et al.* (2003) reported that 0.56 kg h^{-1} B fertilization in B deficient soil (0.1 mg kg^{-1}) improves almost all kinds of quality parameters (fruit firmness, fruit set, yield, marketable yield, shelf life, and concentration of N, K, Na, B contents in plant tissue) in tomatoes and fruit B concentrations were found as 17.1-28.8 mg kg^{-1} under this fertilization regime (Davis *et al.*, 2003). The results of Davis *et al.* (2003) exactly matched with the results of our study (varying between 18-28 mg kg^{-1}), nonetheless, there are contradictory results reported from various researchers such as Islam *et al.* (2016) who reported much lower B contents in cherry tomatoes (approximately 5-6 mg kg^{-1}) compared to our results (Islam *et al.*, 2016). Another study conducted in two separate seasons by Barker et al. showed that the B concentrations in the first season (approximately 10 mg kg^{-1}) were found to be lower than those of the current study, while the second season values (approximately 21 mg kg^{-1}) were found to commensurate with the results of the current study (Barker *et al.*, 2019). Consequently, the results of the current study manifest that a balanced B fertilization regime should be applied in major tomato-producing fields and greenhouses in Turkey. In the forthcoming years, intensive fertilization in greenhouses will possibly increase the B contents in tomato fruits whereas field-grown tomatoes may not experience a significant change.

According to a publication by the Institute of Medicine Panel on Micronutrients (2001), the safe upper and lower intake level of B was recommended as 17-20 mg kg^{-1} for humans (Supplementary Table 1). In this study, DDI values for B ranged between 1.812-2.830 mg kg^{-1} per day in analyzed tomato samples. Therefore, a daily tomato consumption of 100 g will provide approximately 10-16% B of the safe upper limit values.

Calcium

Blossom end rot and fruit cracking are also two physiological disorders that have been strongly associated with low-level Ca and observed under deficiency conditions (Hagassou *et al.*, 2019). Also, Ca has numerous functions in the human body and important nutrient source of the human diet. Therefore, EFSA (2017) recommended (RDA) a consumption level of 950-1150 (depends on body weight, gender and age) mg kg^{-1} per day along with a diet for a healthy life. In this study, 100 g of daily tomato consumption provides Ca, ranged between 127.6-187.0 mg kg^{-1} in analysed tomatoes samples and supplies approximately 11-19% of the recommended values (RDA) (Supplementary Table 1) Considering that Ca is taken along with many dietary components, the amount of Ca supplied by the analysed tomato samples is found to be quite adequate.

In terms of plant nutrition, the most frequent symptom encountered in calcium deficiency is blossom end rot problem in tomatoes, whereas symptoms of excessive Ca, which is rarely observed in tomato production, are decreasing availability of P, Fe and Mn elements (Ismail *et al.*, 1996; Sainju *et al.*, 2003). A study analysed Ca concentrations of tomato samples grown in the aquaponics and hydroponics respectively and found Ca concentrations as 1600 mg kg^{-1} in aquaponics and 2000 mg kg^{-1} in hydroponics (Roosta and Hamidpour, 2013). Another aquaponic study reported Ca concentration in tomato samples to be 1000 mg kg^{-1} (Schmautz *et al.*, 2016). Tomatoes grown in aquaponics or hydroponics were thought to have the ideal Ca contents since the rate of mineral nutrients can be easily adjusted in these types of growth environments. Ca contents of field-grown tomatoes were recorded between 1000-1900 mg kg^{-1} without any fertilization (Demir *et al.*, 2010; Ekinci *et al.*, 2015). Different fertilization applications were reported to have varying effects on Ca contents of tomato fruits such as Ca humate application increasing the Ca contents (Ekinci *et al.*, 2015) while poultry manure has just the opposite effect, decreasing the Ca contents of tomatoes (Demir *et al.*, 2010). Consequently, Ca values obtained from our study (1276-1835 mg kg^{-1}) are in agreement with the aforementioned data, suggesting that our tomato samples may have been grown under ideal pH conditions and in soils with adequate Ca for tomato plants both in the fields and greenhouses.

Copper

In Mediterranean regions (particularly Antalya and Mersin), calcareous soils and high pH values cause either very low or no Cu content in the soil. Consequently, excessive Cu fertilization in combination with the use of Cu-containing fungicides increased the Cu levels in Mediterranean region soils up to the toxic level (validated in the field by Kaplan (Kaplan, 1999) and experimentally by (Sonmez *et al.*, 2006)). Non-toxic level of Cu (46.7 mg kg^{-1}) was reported in greenhouse and field samples from Canakkale region (Sungur *et al.*, 2016). The results for Cu in this study (varying between 4.6-9.4 mg kg^{-1}), were very much alike with the results of similar studies (Schmautz *et al.*, 2016); Capel *et al.*, 2017; Ambrosano *et al.*, 2018) attained 7.7-8.8 and 8.5 respectively) (Table 4). Demir et al. reported that the use of poultry manure increases Cu contents of tomatoes from 13.5 mg kg^{-1} up to 18.53 mg kg^{-1} in Ankara region (Demir *et al.*, 2010). On the other hand, Barker and Roosta published higher Cu values for tomato samples when compared to the results of this study (Barker *et al.*, 2019; Roosta and Hamidpour, 2013) whereas Taharn et al. (2014) reported relatively lower Cu values (varying between 2.9 and 6.2 mg kg^{-1}) (Taharn *et al.*, 2014). Osma et al. (2012) also studied the Cu content of tomato samples from 6 different stations of Istanbul which were brook coast, suburban, industrial, inner-city, roadside, and control regions (Osma *et al.*, 2012). Due to the ecological differences of locations, the Cu content of some tomatoes was similar to our study while others presented higher values than ours (12.54, 8.07, 11.25, 8.10, 13.38 and 7.67 mg kg^{-1}). It can be inferred that there is no Cu accumulation in the soils of studied regions since the Cu concentrations of tomatoes in our study were found to be in the moderate levels. Above mentioned Cu contaminated soils are most probably the result of changing greenhouse soils with fresh soil which is a frequent practice in greenhouse cultivation.

The recommended RDA value for Cu is 0.9 mg per day for adults, and 1.0-1.6 mg per day of average Cu consumption were reported from North America (Pierson *et al.*, 2019; Trumbo *et al.*, 2001). In order to get enough Cu, EFSA (2017) advocates a daily consumption of 1.3-1.6 (RDA) mg Cu with the diet. According to the results of this study, daily tomato consumption of 100 g will supply somewhere between 28-72 % of the daily Cu requirement which suggests that tomato consumption (72 %) can solely be able to provide a considerable portion of the daily Cu requirement (Supplementary Table 1).

Iron

High soil pH values and calcareous soil types decrease the availability and solubility of iron, making it another scarce micronutrient of Turkish soils without extra fertilization. Findings in the current study exhibit that tomato samples have 18-27 mg kg^{-1} of Fe content depending on their locations. Some relevant studies reported somewhat similar Fe contents (26.74-30.98, 24.76, 31.76 mg kg^{-1} respectively) compared to our results from greenhouses whereas our field results were found to be lower than the values of these studies (Roosta and Hamidpour, 2013; Schmautz *et al.*, 2016; Taharn *et al.*, 2014). The lower Fe contents are most probably associated with the K contents of fruits. This idea is supported by Daoud et al. and the increased K fertilization dosages on greenhouse soil cause the increased Fe levels (39.7-62.4 mg kg^{-1}) in fruits (Daoud *et al.*, 2020). Low Fe contents of tomato in our study are not surprising and may be a result of the fruits having low K (20.383-22.304 mg kg^{-1}) contents. Some studies also reported higher Fe and K contents (72-109, 54.36 and 39.3- 41.3 mg kg^{-1} respectively) in tomatoes when compared to our results (Ambrosano *et al.*, 2018; Barker *et al.*, 2019; Capel *et al.*, 2017). Data from similar studies infer that reduced Fe concentrations in tomato samples might be due to a lack of potassium fertilization in the region, increased P fertilization, or elevated pH levels in soils. Consequently, the outstanding reasons for Fe deficiency in tomatoes produced by Turkish farmers can be defined as lack of adequate potassium fertilization, excessive P fertilization and high soil pH values.

To provide the daily Fe requirement of a human, EFSA (2017) recommends taking 11-16 mg Fe (RDA) per day from dietary resources. In this regard, 100 g of daily tomato consumption may supply 11-24 % of the daily Fe requirement (Supplementary Table 1).

Potassium

As mentioned above, the major problem of producers in Turkey both for tomato and other vegetables is generally excessive mineral fertilization (N and P) in either greenhouses or fields. From the plant nutrition aspect, an increased level of K fertilization causes a decrease in K uptake of tomato fruits under field conditions (Zhu *et al.*, 2017). In the present study, the K content of tomato samples was found to be 20.383-22.304 mg kg^{-1} depending on the locations they were collected from. Some studies reported higher levels of K (39500-43300, 33280, 31938-22540, 28600 and 34700-37700 mg kg^{-1} respectively) in comparison to the current study (Ambrosano *et al.*, 2018; Barker *et al.*, 2019; Capel *et al.*, 2017; Roosta and Hamidpour, 2013; Schmautz *et al.*, 2016). Hernandez et al. (2014) reported that the K contents of tomato fruits under ideal fertilization should be within the range of 33.800-34.500 mg kg^{-1} in field conditions (Hernández *et al.*, 2014). An average of 40000 mg kg^{-1} K was discovered in control groups of tomato samples in our study and other similar studies (Tavallali *et al.*, 2018). In another study about field fertilization, Khan et al. investigated various NPK applications and analyzed mineral contents of tomato fruits (Khan *et al.*, 2019). They found the K content is fluctuating between 22700-49700 mg kg^{-1} with the fertilizer application of N and P at 250 and 100 kg ha−1 respectively, and our findings are in similarity with the lower portion of these values. In Turkey, poultry manure application was found to decrease fruit K contents from 53070 to 46220 mg kg^{-1} in Ankara region (Demir *et al.*, 2010). It can be inferred from these results that nearly all relevant studies including Turkish ones reported the K contents of tomato fruits ranging between 35000-40000 mg kg^{-1}. When compared with these results, the average K content of tomato fruits in our study was discerned to be lower. Since there is an antagonism between K and Ca/Mg, the excess amount of K fertilization decreases the Ca content in tomato fruits (Malvi, 2011). As previously mentioned, excessive N and P fertilization is causing N leaching and decreased soil pH (Sungur *et al.*, 2016; Zhou *et al.*, 2014). Consequently, low pH value in the soil affects K solubility and availability together with insufficient potassium fertilization. Under these circumstances, even starting a sufficient K fertilization may not restore the balance since K, by its nature, can be easily leached from the soil when excessive irrigation application habits were taken into consideration. Thusly, the inadequate amounts of K found in tomatoes in our study can be explained by the reasons mentioned above. Aydınsakir *et al.* (2019) published similar results from Turkish greenhouses, backing our findings that excessive N fertilization decreases K contents (Aydinsakir *et al.*, 2019).

To meet the daily requirement of K, the most prevalent mineral in the human body, EFSA (2017) suggested an intake of K to be 2700-4000 mg kg^{-1} when dietary sources are consumed. Analysed tomato samples in this study supply various amounts of daily K content varying between 50-82% (Supplementary Table 1). Consequently, 100 g of daily tomato consumption can supply at least 50% of daily average human K demand.

Magnesium

Deficiency of Mg is generally observed in calcareous soils and this deficiency significantly reduces the yield and quality of tomatoes in solar energy based greenhouses (Yan *et al.*, 2016). In plant nutrition aspect, Mg deficiency, rather than its toxicity, is considered a common challenge in vegetable farming. The deficiency of Mg reveals itself under unbalanced fertilization practices with cationic nutrients such as K, NH4 and Ca (Gransee and Führs, 2013). Various chemical fertilizers (MAP, Ammonium sulfate, Triple superphosphate, Calcium sulfate, and Magnesium oxide) had no considerable differences in Mg contents (1530-1820 mg kg^{-1}) of tomato fruits (Cole *et al.*, 2016). A greenhouse from the Ankara region also validates these results and reported similar Mg contents from tomato fruits under poultry manure application (Demir *et al.*, 2010). Our results related to tomato samples were found to be within the range of 1870-2106 mg kg^{-1} based on their locations. While concentrations of Mg were found to be higher than ours in some studies (1100, 1100, and 1072.3-774.6 mg kg^{-1}) (Capel *et al.*, 2017; Roosta and Hamidpour, 2013; Schmautz *et al.*, 2016), the results of Baker and Ambrosano are in agreement with ours (Ambrosano *et al.*, 2018; Barker *et al.*, 2019). Based on these researches, our results can be classified as being within the acceptable limits concerning Mg contents.

From a dietary perspective, EFSA (2017) verified that the RDA values of Mg should be 300-350 mg kg^{-1} when dietary sources are consumed. Tomato samples in this study could supply 53-70% of the predetermined RDA values (Supplementary Table 1). Therefore, 100 g of tomato consumption can provide at least half the amount of daily Mg requirements.

Manganese

Cases of excess Mn nutrition in plants are associated with significantly reduced photosynthetic activity, high H_2O_2 accumulation, lipid peroxidation and disrupted Fe, Zn, or Cu nutrition (Kleiber, 2015; Kleiber *et al.*, 2014). Our results regarding Mn contents exhibit perfect resemblance with results of the similar following studies (Ambrosano *et al.*, 2018; Barker *et al.*, 2019; Capel *et al.*, 2017; Schmautz *et al.*, 2016) however, the results of one study yielded slightly higher results (Roosta and Hamidpour, 2013). Our Mn results also validated some other studies such as a study on Thailand tomatoes, a study on Italian cherry tomatoes and a study on Turkish tomatoes (Bressy *et al.*, 2013; Demir *et al.*, 2010; Taharn *et al.*, 2014). Based on these findings and the Fe, Cu, and Zn contents of our tomato fruits, there appears to be no problem regarding the nutrition and fertilization in terms of Mn values in Turkish production sites.

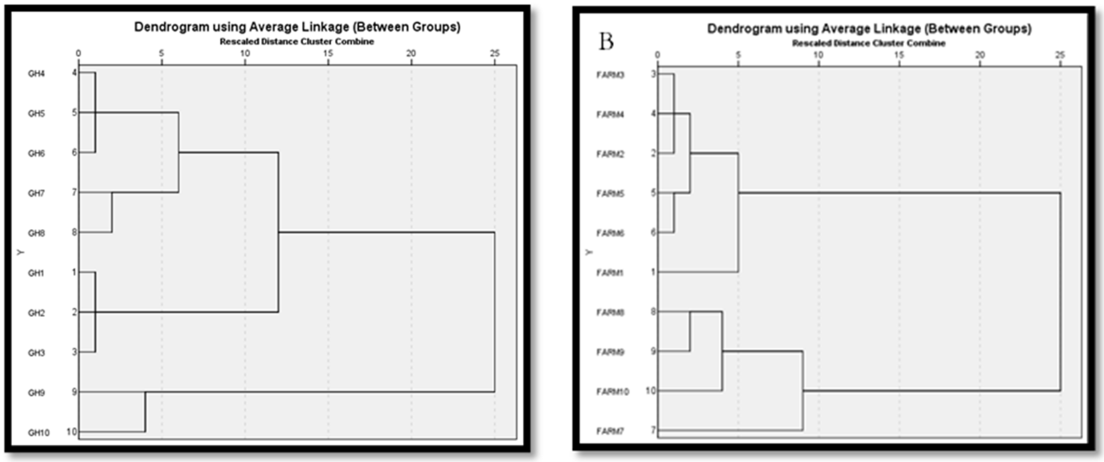
From a dietary perspective, EFSA (2017) recommended the RDA values of Mn to be 2-3 mg kg^{-1} when dietary sources are consumed. Tomato samples utilized in this study could supply 33-116% of the predetermined RDA values (Supplementary Table 1). Therefore, a daily tomato consumption of 100 g may provide Mn requirements at varying rates some of which may even surpass the daily consumption requirements. Interestingly, when greenhouse-type tomatoes were compared to those from the fields, it can be seen that the Mn contents in greenhouse types are lower. Higher levels of Mn in field samples can be attributed to significant amounts of Mn from traffic emissions since Mn has replaced Pb in fuels after the prohibition of Pb usage in fuels (Union, 2009). It is believed that the greenhouse medium is not influenced by these emissions since its environment is sheltered and controlled. On the other hand, concentrations of elements other than Mn are lower in field tomatoes. This is possibly due to the negative influence of Mn on the uptake of other elements.

Zinc

Similar to some other micronutrients, pH is the main reason for Zn deficiency in calcareous soils (solubility decrease with high pH). High P application and some metal cations also (Cu2+ and Fe2+) decrease Zn availability in plants (Mousavi, 2011). Zn can contribute to the increase of tomato yield by increasing the number of fruits per plant and also can prevent flower and fruit abscission (Ruby *et al.*, 2001; Shnain *et al.*, 2014). Zn content of our field and greenhouse-grown tomato samples were varied between 15.5-25.4 mg kg^{-1}. These results are similar with some other studies (Ambrosano *et al.*, 2018; Barker *et al.*, 2019; Capel *et al.*, 2017; Schmautz *et al.*, 2016) (10.2-19.4, 27.71, 24.6 - 33.7 and 16.2 mg kg^{-1} respectively). Cole et al. reported that the Zn contents of tomato fruits grown with different chemical fertilizer applications ranged between 22-29 mg kg^{-1} and the MAP fertilizer application in this study resulted in similar Zn concentrations in tomato fruits (22 mg kg^{-1}) which is in agreement with our results since our samples were also largely collected from MAP fertilization sites (Cole *et al.*, 2016). Poultry fertilization in Turkey seems to make a significant effect on the Zn contents of tomatoes, which shows an increasing pattern with increasing poultry manure, whereas the control group showed identical results with our samples. According to Osma's research, the Zn contents of suburban and control samples were comparable/similar to that of our results (Osma *et al.*, 2012). Taharn *et al.* (2014) and Bressy *et al.* (2013) reported similar Zn content in tomatoes (27.18 and 22.3, 29.5, 19.7 mg kg^{-1} respectively) (Bressy *et al.*, 2013; Taharn *et al.*, 2014). It is observed that the Zn amounts that we determined in this study are compatible with the results of similar published studies, which can be interpreted that there is no excessive Zn fertilization in Turkish tomato production sites except for Osma *et al.* (2012)'s study where the high Zn readings of brook coast, industrial, inner-city and roadside grown tomatoes were most probably observed as a result of intense anthropogenic activity. From a dietary perspective, EFSA (2017) proposed the RDA values of Zn to be 7.5-16.5 mg kg^{-1} when dietary sources are consumed. Tomato samples utilized in this study could supply 9-33% of predetermined RDA values (Supplementary Table 1). Therefore, 100 g of tomato consumption can provide up to 33% of the daily Zn requirement.

Hierarchical cluster analysis

Using quantified elemental readings from greenhouse-grown tomato samples, a dendrogram was constructed and two main groups clustered at this dendrogram based on Average Linkage cluster analysis (Figure 2A). One of those main groups consists of tomato samples from two locations (Sanliurfa and Mersin) which are geographically very close and represent hotspots of greenhouse tomato production. Another set of samples (from Kutahya, Eskisehir, and Bursa) again from geographically close locations constitute the second main group and these were found to have a close relationship. Regions like Canakkale, Mersin, and Antalya are places where greenhouse activities are performed very intensely. Due to intense fertilization activity in those soils, getting high elemental readings in tomato samples collected from these regions is not surprising.



(A) (B)

Figure 2. The dendrogram constructed for field and greenhouse tomato samples based on their mineral nutrient status

By using quantified elemental readings from field-grown tomato samples, another dendrogram was constructed and two main groups were also clustered at this dendrogram based on Average Linkage cluster analysis (Figure 2B). As a result of field cultivation activity, tomato samples from Canakkale, Antalya, Mersin, and Sanliurfa regions were found to have close relationships based on the elemental readings. Under field conditions, due to the fertilization of large areas, essential macro and microelement accumulations were expected to be lower than those of greenhouse samples. Regions like Canakkale, Antalya, Sanliurfa and Mersin are also primary production centres of tomatoes in Turkey. Even if intensive fertilization is performed in these field production centres, fertilization in large areas does not increase the nutrient content as it does in greenhouses. Tomato samples, from Izmir and Bilecik regions, were also found to be close conforming to their geographically close locations.

Principle component analysis

The performed study determined the similarities of 20 tomato samples, collected from various fields and greenhouse sites in Turkey, using 9 quantitative elemental readings. The variations between field and greenhouse-grown tomato fruits explained by PCA were determined as % 95.95 using two following components; for component 1; % 90.24 and for component 2; %5.70 respectively. Principal component analysis results showed considerable similarities with the results of cluster analysis and classified the tomato fruits as field-grown and greenhouse-grown. According to the PCA analysis results of the tomato samples collected from the greenhouse (Figure 3, blue rectangle); Sanliurfa (GH9) and Mersin (GH10) samples were found to be closer, while Kutahya (GH1), Eskisehir (GH2), and Bursa (GH3) were clustered together (figure 3). Antalya (GH4), Izmir (GH5), and Bilecik (GH6) are other groups located close to each other in terms of elemental compositions. It is seen from PCA analysis that tomato samples of Canakkale (GH7) and Antalya (GH8) exhibit a close relationship with each other. In terms of greenhouse tomato samples, PCA results validated the above-given cluster analysis results (Figure 3, within the blue rectangle).

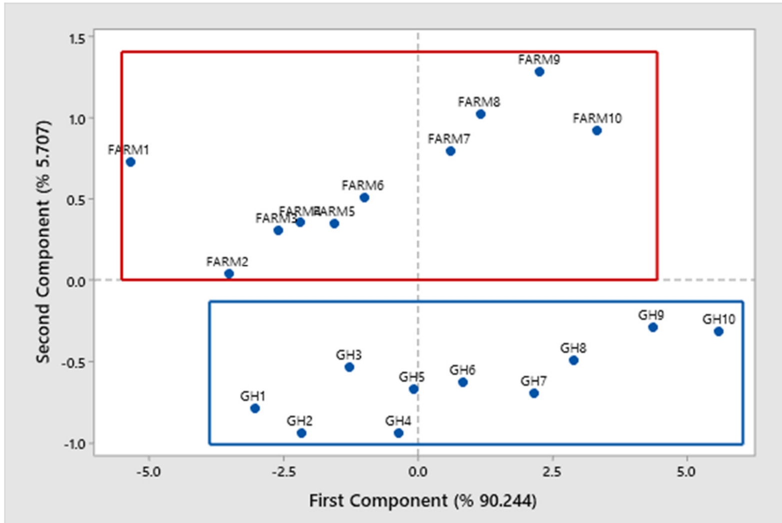


Figure 3. Principle Component Analysis of overall collected tomato samples based on their mineral nutrient status (Kaiser-Meyer-Olkin measure of sampling Adequacy. is 0.902 and Bartlett's test of sphericity is at 0.001 statistically significant level)

Considering the field-grown samples (Figure 3, red rectangle), two main groups and FARM1 are selected specifically from PCA analysis. Eskisehir (FARM2), Bursa (FARM3), Antalya (FARM4), Izmir (FARM5), and Bilecik (FARM6) constitute one of the major group as seen in the dendrogram (Figure 3), whereas Canakkale (FARM7), Antalya (FARM8), Sanliurfa (FARM9) and Mersin (FARM10) constitute the other major group. Similar elemental contents were observed either by using cluster analysis or by using PCA analysis in the tomato fruits grown at geographically close sites.

Watanabe *et al*. (2015) explained 88% of the variance in the first two components concerning pesticide, chemical and organic fertilizer effects on the mineral nutrient status of tomato fruits (Watanabe *et al.*, 2015). Wang and Xing (2017) successfully evaluated fruit-quality parameters of tomatoes under different irrigation regimes and suggested that drip irrigation together with higher fertilization is a good choice in having high-quality tomato fruit cultivation within greenhouse conditions (Wang and Xing, 2017). PCA analysis is a strong predictor for the classification in nutritional values of tomatoes by using various characteristics and used for metabolic profiling data of tomato fruits, for classification of tomato fruit quality via colorimetric and physical-chemical variables (explained variance with PCA is %97.01) and for evaluating some tomato collections in previous studies (Dimova and Krasteva, 2007; Abou Chehade *et al.*, 2018; Bello *et al.*, 2020). In this study, cluster and PCA analysis results were in support of each other. It was also seen that the results obtained from the PCA analysis are compatible/comparable with previous studies, and also the relationship between tomato samples is revealed at the end of the study.

Conclusions

The order of locations with respect to the element concentrations from the highest to the lowest is Mersin, Sanliurfa, Antalya, Canakkale, Izmir, and Eskisehir. Statistically significant differences were obtained in mineral nutrients from greenhouse and field samples except for Mg, Mn, and Zn due to the fact that intensive regimes of production and fertilization were practiced in greenhouses. K content was detected to be low in comparison with previous results. Generally, it would not be wrong to say that either MAP-weighted fertilization might have lowered the K uptake/availability or inadequate K fertilization might have caused the low amounts of K contents in tomato fruits. Due to relatively dense traffic emission and intense industrial activity in open field production sites, the atmosphere in these places has a higher density of particulate matter, causing an increase of the Mn concentration in tomato fruits when compared to the greenhouse samples. In this study, it was seen that greenhouse and open-field grown tomatoes can provide significant portions of daily Cu, K, Mg, and Mn requirement by being included in the daily dietary program (Based RDA values). From a dietary perspective, tomatoes from Sanliurfa and Mersin are more mineral nutritive and therefore need less external dietary mineral nutrients than those from Izmir and Eskisehir. Based on elemental concentration, no excessive accumulation of any element was observed in the studied tomatoes. Based on production areas, it was ascertained that the tomatoes grown in the greenhouse had higher mineral nutrient content than field-grown ones. On the other hand, due to the intensive fertilization during the growing season or out-season within the same production area of greenhouse, it would be normal for the greenhouse-grown tomatoes to acquire a higher amount of nutrients than those of field-grown ones. As a result of this study, it can be stated that both domestically consumed tomatoes grown in various production areas of Türkiye seem to be a rich nutritional source for Cu, K, Mg, Mg and Mn when other relevant studies were also taken into consideration.

Authors' Contributions

Data curation and Formal analysis: IEY and OLU; Supervision: IIO; Validation, Visualization, Writing - original draft: HC; Writing - review and editing: GD.

All authors read and approved the final manuscript.

Ethical approval (for researches involving animals or humans)

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Conflict of Interests

The authors declare that there are no conflicts of interest related to this article.

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