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Content and Distribution of Macroelements, Microelements, and Rare-Earth Elements in Different Tomato Varieties as a Promising Tool for Monitoring the Distinction between the Integral and Organic Systems of Production in *Zeleni hit*—Official Enza and Vitalis Trial and Breeding Station

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Abstract: The identification of agricultural food production systems has gained importance in order to protect both human health and the environment. The importance of organic production system of agriculture which involves the application of natural processes and substances, and limits or completely eliminates the use of synthesized means is emphasized. Knowledge of the mineral composition in tomato samples can be used as a potent tool in the identification of chemical markers as potential indicators of the farming system. A set of tomato samples taken from two factorial randomized trials were comprehended eight different varieties, belonging to four tomato types: large—BEEF and CLUSTER, and mini and midi—CHERRY and PLUM tomatoes, cultivated under two different farming systems: integral (IPM) and organic (O) were characterized based on the composition of the minerals. A total of 44 elements were quantified. To establish criteria for the classification of the samples and confirm a unique set of parameters of variation among the types of production, sophisticated chemometric techniques were used. The results indicate that the accumulation of elements varies between 8 tomato varieties and 2 different growing systems. The contents of Al, Mn, As, Pb, and some of the rare-earth elements (REEs) are able to distinguish between production types. Examination of different hybrids, which belong to different types in two production systems: organic and integral within Zeleni hit (official Enza and Vitalis trial and breeding station), was done with the aim of reaching a methodology of diversification, ie complete traceability of organic production, and to contribute to distinguishing types of agricultural systems and enhancing the possibility of acquiring a valuable authenticity factor about the type of agricultural production system employed for the cultivation of tomatoes.

Keywords: tomato; ICP-OES; ICP-MS; rare-earth elements; macroelements; microelements and potentially toxic elements; organic and integral type of production

1. Introduction

Tomato (*Lycopersicon esculentum* L.) is one of the most widely grown vegetables in the world [1]. It is cultivated for consumption as fresh products and for processing into finished products including tomato pureed, ketchup and flour [2]. Tomato contains many nutrients and secondary metabolites that are important for human health, including minerals, vitamins, lycopene, flavonoids, organic acids, phenolics, and chlorophyll [3]. Due to the importance of minerals for human metabolism, their analysis is an important part of public health studies. The presence of nutritive and toxic minerals in tomato samples depends on the growing conditions and the utilization of pesticides and fertilizers. In addition, the accumulation of metals varies greatly between examined tomato types and cultivars [4,5]. Because of its high sensitivity, wide dynamic range, and relatively low possibility of interferences as well as its multi-elemental characteristics, inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) have been chosen as one of the most commonly used analytical techniques for the analysis of the complex food matrices [6].

Minerals are micronutrients necessary for the growth, maintenance, and proper functioning of the human body [7,8]. An adequate micronutrient intake is essential for improved human health, primarily prevention or treatment of various diseases, such as bone demineralization and arterial hypertension, and for maintaining overall cardiovascular health [9]. Also, an adequate micronutrient intake is essential for the prevention of "hidden hunger"—a state which occurs due to mineral deficiency and manifests itself as insidious effects on immune system functioning which are connected to an increased risk for many girded and debilitating health conditions and diseases [10]. As humans cannot synthesize essential and trace elements, they must be introduced as part of the diet in regular quantities [7,11]. No less than 22 mineral elements are necessary for normal functioning of humans [7,12], and tomato is an excellent source of these minerals. The mineral elements are not synthesized in the plant but are absorbed from the soil by the root of the plant. The content of minerals in tomato tissues is changed during the plant's growth wherein the most significant changes occur in the days after the fruit initiation [13]. However, the concentration of minerals remains unchanged during the final stages of crop development [7]. The content of mineral elements in tomato is influenced by the availability of minerals in the soil and it is strongly dependent on local geological setting and agronomic practice, such as conventional, integral, or organic farming system [14]. Given the growing concern for human health and the environment due to the increased use of pesticides in agriculture, the identification of agricultural food production systems is gaining importance, and therefore organic production is recommended [15]. Compared to integral production, organic production involves the application of natural processes and substances while respecting environmental principles, the use of renewable energy sources, conservation of natural diversity and environmental protection, and limits or completely eliminate the use of synthetic materials [5,16]. It should also be kept in mind that despite the lack of reliable data that support claims that the quality of organically produced food is superior to the quality of foods produced in the conditions of integral production, there is an increasing consumer demand for foods cultivated under organic system of farming. Therefore, in this paper, the mineral content of tomato samples produced in organic and integral cultivation systems will be compared with the aim of investigating whether comprehensive mineral content could be used as indicators of tomato cultivation systems in order to provide sufficient information to consumers when choosing food.

Only a small number of studies reported the connection between the metal content in tomato and the farming systems used in its production [17–19]. In addition, it is assumed that the metal content in tomato crops is influenced by different factors such as type of soil, climatic conditions, crop type, and variety choices [18]. However, many so far performed comparative studies have been criticized for not controlling these factors and consequently showing contradictory results [7,20]. Therefore, the main objective of this paper was to identify which elements can be used as specific chemical markers, i.e., indicators of the type of tomato production. Also, the objective of this work was to establish criteria for element-based classification in order to define the mineral composition of tomato which is important for both the assessment of its authenticity and the assessment and fortification of the type of agricultural system, which is a current issue for both consumers and producers. Therefore, in order to find reliable chemical markers of particular varieties and to distinguish farming systems of tomato production, a set of tomato samples from two factorial randomized trials which comprehended eight different varieties, four types and grown in two growing systems, integral (IPM) and organic (O), was analyzed and characterized based on the composition of the elements. Seven macroelements (Ca, Fe, K, Mg, Na, P, S), sixteen microelements and potentially toxic elements (Li, Al, V, Cr, Mn, Co, Ni, Cu, Zn, Mo, Cd, W, Bi, As, Hg, Pb), and twenty-one rare-earth elements (Sc, Ga, Se, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Tl, Th, U), were quantified using ICP-OES and ICP-MS. The obtained results were processed in Matlab (Principal component analysis), and in NCSS statistical software package (Mann–Whitney U-test). The used statistical procedures confirm a unique set of parameters that could be used as potential phytochemical biomarkers to differentiate tomato samples belonging to different cultivars produced in different systems of production. This kind of investigation contributes to distinguishing types of agricultural systems, integral and organic, and consequently contributes to increasing the possibility of assessing and obtaining main factors for validating the authenticity of the tomato variety and the type of its production. This further raises awareness of the significance of product authenticity due to the importance of food quality data, which are necessary to protect both consumers and producers.

2. Materials and Methods

2.1. Chemicals and Materials

Hydrogen peroxide and nitric acid, both of analytical grade of purity, were purchased from Merck (Darmstadt, Germany). Standard solutions and blanks were prepared with ultra-pure water obtained by the Milli-Q system (Millipore Simplicity 185 System incorporating dual UV filters, 185 nm and 254 nm). A semi-quantitative stock solution containing 0.0100 g L^{-1} of major and trace elements (Alfa Aesar—Ward Hill, MA, USA) and a stock solution containing 0.5000 g L^{-1} of major elements (VHG Labs, Manchester, NH 03103, USA, United States of America) were used to prepare intermediate multi-element standard solutions for determination on ICP-MS (iCAP Q, Thermo Scientific X series 2, Loughborough, UK, United Kingdom) and ICP-OES (Thermo Fisher Scientific, Waltham, Massachusetts USA). Commercial calibration stock standards, used in this study, were Multi–Element Plasma Standard Solution 4, Specture®, Alfa Aesar, John Mutthey Company; Vanadium Plasma Standard Solution, Specture®, Alfa Aesar, John Mutthey Company; Tungsten, Specture®, Alfa Aesar, John Mutthey Company; Major Elements Stock, EPA Method Standard, VHG Labs; 6020A ICS Stock, EPA Method Standard, VHG Labs; Multi–Element Aqueous CRM, Comprehensive Mix A, VHG Labs; Selenium Standard for AAS, Fluka; Mercury Standard, Merck; Arsen Standard, Merck.

2.2. Sample Preparation—Cultivation Experiments

This study included eight varieties, belonging to four tomato types: large—BEEF and CLUSTER, and mini and midi—CHERRY and PLUM tomatoes, grown in two types of farming systems, integral and organic (Table 1). In a two factorial greenhouse trial, eight tomato hybrids were observed in two cultivation systems in three replicates. The total size of the heated greenhouse was 320 m^2 and individual plots have considered 12 to 16 plants, depending on recommended density for different tomato hybrids. Young plants were produced according to the certified procedure for the organic and integral growing systems, using Vitalis (organic) and Enza (conventional) seeds of 8 different varieties. All samples were properly taken at the same time of harvest and stored in the refrigerator for later preparation of samples and analysis, with adequate size, which excludes errors related to uniformity in quality and chemical composition of the fruit. For each tomato variety, there were three replicates, each of which had an average weight of 500–600 g, i.e., it contained 2 to 20 fruits, depending on the type of tomato to which the variety belongs (depending on whether it is large—BEEF and CLUSTER, or mini and midi—CHERRY and PLUM tomatoes). Tomato samples were thoroughly washed with lukewarm water and sliced to the thickness of 1–2 cm to enhance the drying process. In order to obtain a representative sample, all replicates were dried separately. The samples were oven dried on glass plates for 24 h at 105 °C, after which the temperature in oven was reduced to 55 °C and the samples were dried to constant weight. Then, the replicates of the same variety were ground together, pulverized in a blend, and thus homogenized. The obtained powder was kept in plastic containers in a dark place at 4 °C until the analysis was performed.

Table 1. Tomato types and varieties in two production systems, integral (IPM) and organic (O).

No. of Sample (Type of Production)	Large Varieties		No. of Sample (Type of Production)	Finer Varieties	
1a (IPM) 1b (O)	VELOCITY	Beef	5a (IPM) 5b (O)	VESPOLINO	Plum
2a (IPM) 2b (O)	RALLY	Beef	6a (IPM) 6b (O)	ARDILES	Plum
3a (IPM) 3b (O)	AVALAVTINO	Cluster	7a (IPM) 7b (O)	TOMAGINO	Cherry
4a (IPM) 4b (O)	DIRK	Cluster	8a (IPM) 8b (O)	SAKURA	Cherry

The soil was prepared according to standard technology using both organic and conventional mineral fertilizers for an integral production system, and only organic certified and mineral fertilizers for an organic one. The long trellising crop was planted at the beginning of March and grown until the end of the season end of October. The assimilation and growth differences as well yield and fruit quality were regularly analyzed and compared between tomato varieties and different growing systems.

In the integral production system the use of fertilizers and pesticides is reduced in comparison to the conventional production, whereas various biological components (sometimes even predators) are used for plant protection [21]. The use of mineral fertilizers, growth regulators and pesticides is not allowed in what is called organic farming. This system is based on minimal use of non-agricultural substances and the natural ecological balance in management practices [21]. In this case, for integral production system adequate Integrated Pest Management system was used combining both, some fungicides and biological protection systems, whole for an organic system of production only certified biopesticides and predators, massive pheromone traps and other plant protection methods being considered organically certified.

Weed suppression accordingly was achieved by covering raised beds with polyethylene mulch with silver color in Integral tomato growing system and with organic peat moss mulch layer 7–10 cm of thickness, providing also high thermic stability and soil water and nutrients conservation.

2.3. Mineral Analysis—Microwave Digestion

Microwave digestion was performed in the SpeedWave XPERT instrument, manufactured by Berghof. About 0.3 g of dehydrated tomato was measured in teflon cuvettes individually and 6 mL of purified nitric acid, HNO_3, and 2 mL of 30% hydrogen peroxide, H_2O_2 were added. Purified nitric acid was made by purification of 65% HNO_3 in a 2000 W microwave oven Berghof-purification apparatus-BSB-939-IR. Degradation was performed according to Microwave Digestion of Fruit, Application Note Food & Feed, Digestion, Berghof [22] by setting it to reach a temperature of 180 °C in 15 min, maintaining the same temperature for 10 min. Then, the temperature was set to 200 °C in 10 min, which was maintained for 15 min. After completion of the program and cooling of the cuvettes, the samples were quantitatively transferred and diluted with ultra-pure water in normal flasks of 50 mL. Two blank digestions were performed using the same procedure as for the samples. All samples were measured the same day on both instruments. For quality control and method validation, standard reference material BCR–679 was used with recovery between 93% and 104%. The standard material went through the same preparation procedure as the samples themselves. It was digested with the same volume of nitric acid and hydrogen peroxide, diluted with ultra-pure water, and analyzed for ICP-OES and ICP-MS.

2.4. Measuring Settings of ICP-OES and ICP-MS

Operating conditions for the ICP-OES and ICP-MS were set by the manufacturer. For ICP-OES ICP RF power was set at 1150 W, nebulizer gas flow at 0.5 L min^{-1}, coolant gas flow at 12 L min^{-1}, and pump rate was set to work at 50 rpm. In the case of ICP-MS, operating conditions were slightly different. ICP RF power was set at 1050 W, nebulizer gas flow at 0.75 L min^{-1}, lens voltage at 7 V, pulse stage voltage at 950 V, and sample uptake rate was set at 25 rpm.

2.5. Statistical Analysis

The PLS ToolBox, v.6.2.1, for MATLAB 7.12.0 (R2011a) was used to conduct the principal component analysis (PCA). PCA was carried out as an exploratory data analysis by using a singular value decomposition algorithm (SVD) and a 0.95 confidence level for Q and T2 Hotelling limits for outliers. The PCA grouped the parameters based on their similarity and resulted in a less number of principal components that, in turn, reduced the dimensionality of the retention data space, thus further simplifying the analysis [23].

In order to verify the existence of statistically significant differences between samples, and types of agricultural systems, the Mann–Whitney U-test was applied using a demo version of NCSS statistical software [24], as well as descriptive statistics.

3. Results

3.1. Multielemental Composition Assessment

In the 16 different types of tomato samples (Table 1), 44 elements were quantified, including 7 macro (major) elements (Na, Ca, K, Mg, Fe, P and S) which were analyzed on ICP-OES, 16 micro (trace) elements and potentially toxic elements (Li, Al, V, Cr, Mn, Co, Ni, Cu, Zn, Mo, Cd, W, Bi, As, Hg, Pb) and 21 REEs (Sc, Ga, Se, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Tl, Th, U) which were analyzed on ICP-MS (Table S1). Standard series were made from internal standards (500 mg L^{-1} for macroelements, 1000 µg L^{-1} for microelements and REEs). Internal standards were made by diluting the commercial calibration stock standards. The data are given in the form of an Excel datasheet (Table S1), and represent the average value of three repeated measurements. Also, the contents of macroelements, microelements and potentially toxic elements, and rare-earth elements in the samples of 8 different tomato varieties in two different systems of tomato production expressed as mg kg^{-1} dw (dry weight), are presented in Figure 1 for integral and in Figure 2 for organic production. Vertical bars denote 0.95 confidence intervals.

3.2. Data Analysis

In order to understand the data structure and determine similarities and particular grouping patterns, PCA was conducted on quantified mineral elements (Table S1) in tomato samples. Before application of the statistical operations, all data were mean-centered and scaled to the unit standard deviation in order to reduce the possibility of predominant components significantly influencing the final result at the expense of those less present. Since the values for the content of elements are below the limit of detection only in the case of element V in sample 2a, element Hg in samples 5a–8a and 5b–8b, and element Se in sample 6a, and in all other samples the concentrations of these elements as well as everyone else elements were above the limit of detection (Table S1), no element was excluded when processing the results by PCA test.

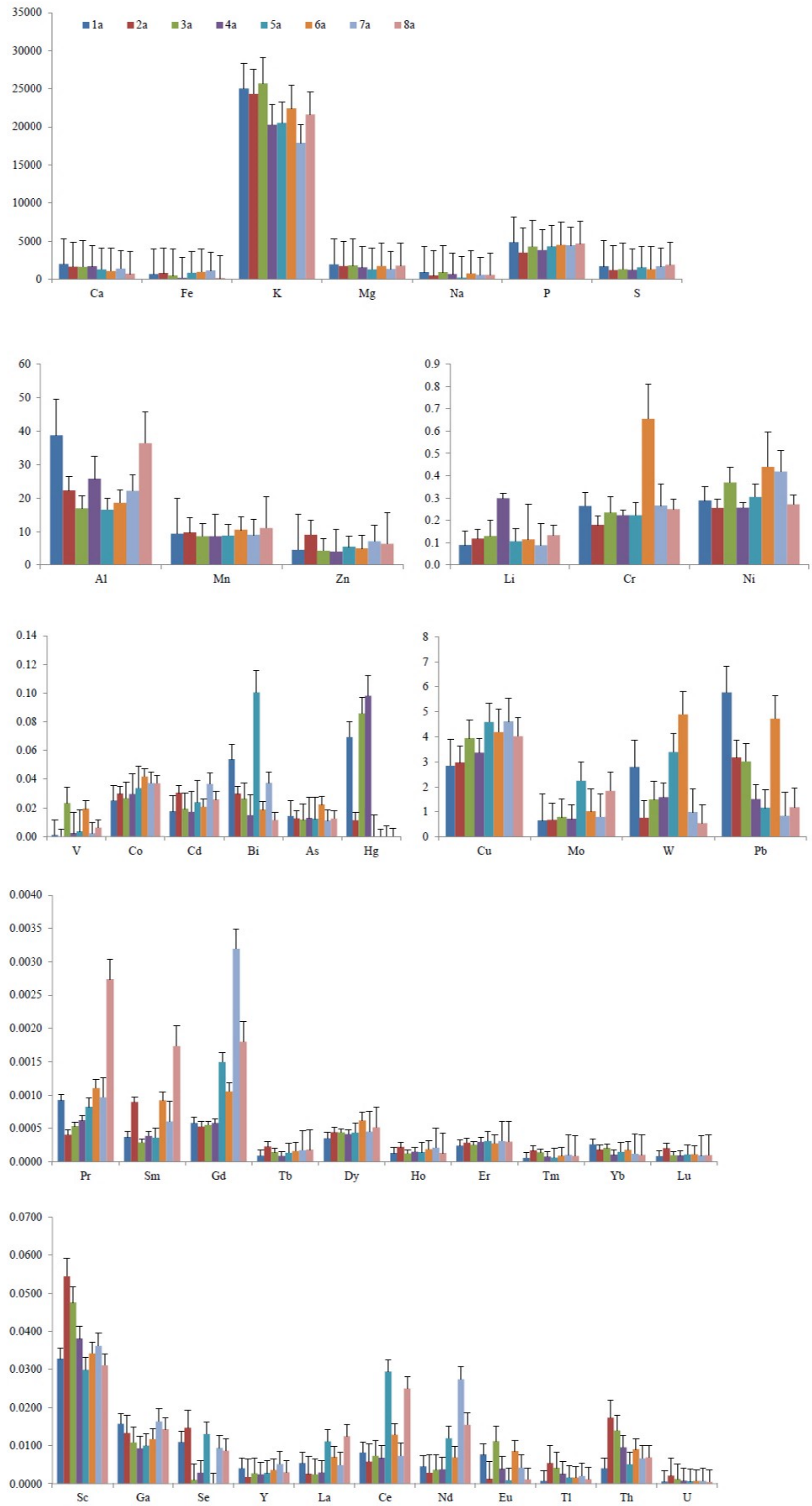

Figure 1. Contents of macroelements, microelements and potentially toxic elements, and rare-earth elements in the set of 8 different varieties of tomato (Table 1) grown in integral (IPM) agricultural system expressed as mg kg^{-1} dw. Vertical bars denote 0.95 confidence intervals. The concentrations of elements (mg kg^{-1}) were plotted on the y-axis; the symbols of elements were plotted on the x-axis.

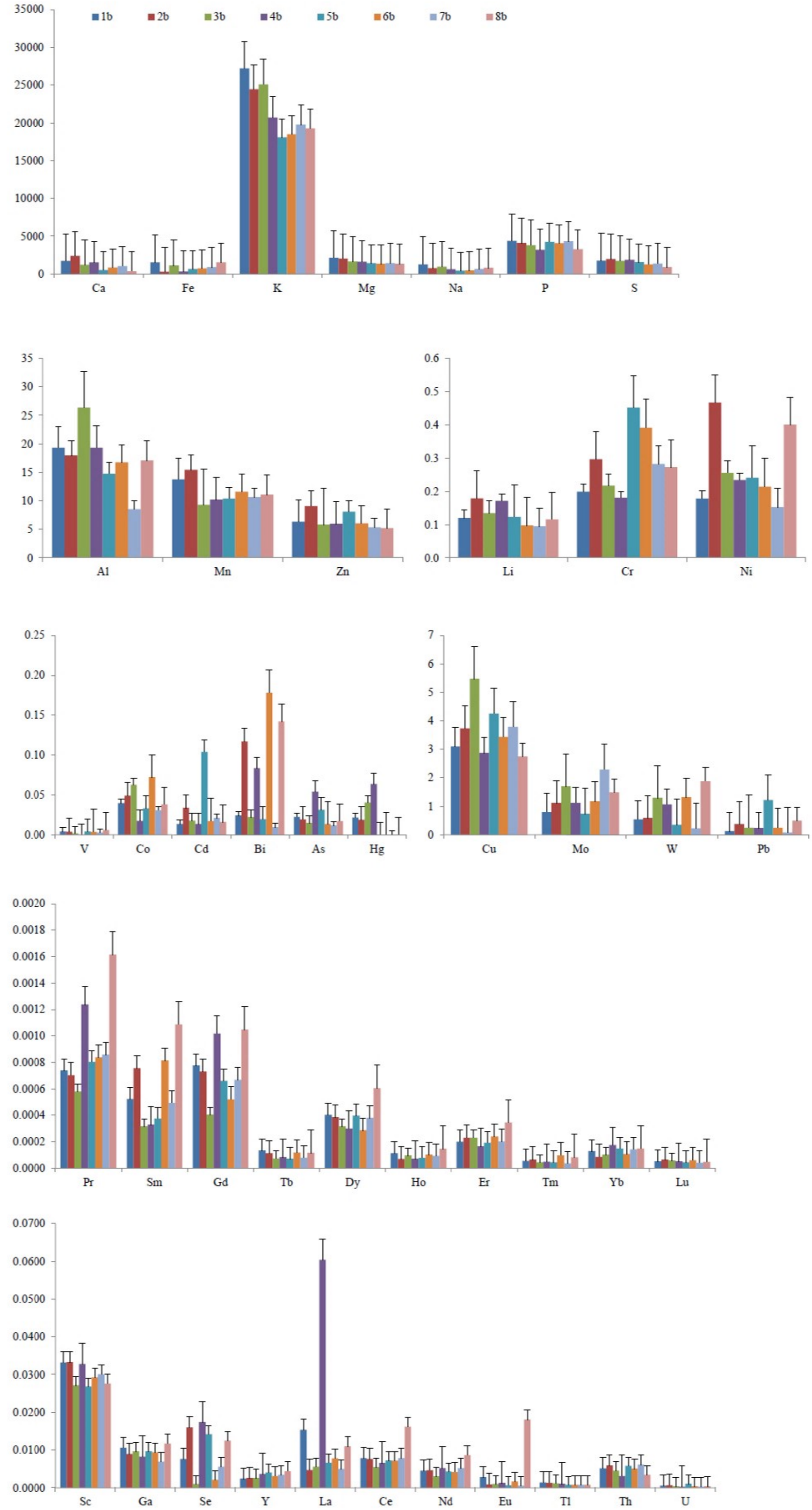

Figure 2. Contents of macroelements, microelements and potentially toxic elements, and rare-earth elements in the set of 8 different varieties of tomato (Table 1) grown in organic (O) agricultural system expressed as mg kg^{-1} dw. Vertical bars denote 0.95 confidence intervals. The concentrations of elements (mg kg^{-1}) were plotted on the y-axis; the symbols of elements were plotted on the x-axis.

PCA was performed in order to establish the differences between two different production systems as well as between tomato types and varieties. Principal component analysis based on the content of 44 minerals in tomato samples resulted in a twelve-component model that explained 95.45% of the total variability among the data. Statistical parameters (the number of principal components and the percentage of variance they explain) are shown in Table 2.

Table 2. The number of principal components and the percentage of variance they explain.

Principal Component Number	Eigenvalue of Cov(X)	% Variance Captured	% Variance Captured Total
1	8.47×10^3	19.24	19.24
2	7.59×10^3	17.26	36.50
3	4.92×10^3	11.17	47.68
4	3.54×10^3	8.05	55.73
5	3.41×10^3	7.76	63.48
6	3.37×10^3	7.67	71.15
7	2.33×10^3	5.29	76.45
8	2.26×10^3	5.13	81.58
9	2.11×10^3	4.80	86.37
10	1.60×10^3	3.64	90.02
11	1.30×10^3	2.96	92.98
12	1.09×10^3	2.47	95.45

Mutual projections of factor scores and their loading for the first two PCs for 44 minerals are shown in Figure 3.

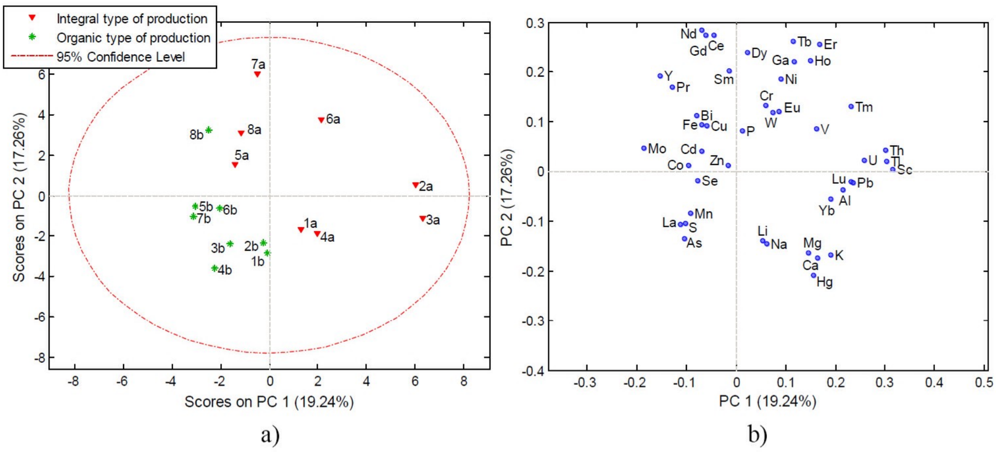

Figure 3. Principal component analysis based on the content of 44 minerals in tomato samples (Table 1) produced under two different production systems, integral (IPM) (samples 1a–8a) and organic (O) (samples 1b–8b): (**a**) Score plot and (**b**) Loading plot.

Since principal component analysis based on the content of all 44 minerals showed that REEs can serve as a potential factor for distinguishing types of production (Figure 3), PCA based only on the content of macroelements as well as PCA based only on the content of microelements and potentially toxic elements were also carried out. Principal component analysis based on the content of macroelements resulted in a two-component model that explained 68.45% of the total variability among the data, while PCA based on the content of microelements and potentially toxic elementsresulted in a six-component model that explained 80.66% of the total data variance (Table 3).

Table 3. The number of principal components for macroelements (A) and microelements and potentially toxic elements (B), and the percentage of variance they explain.

(A) Principal Component Number	Eigenvalue of Cov(X)	% Variance Captured	% Variance Captured Total
1	3.24×10^3	46.33	46.33
2	1.55×10^3	22.12	68.45
(B) Principal component number	**Eigenvalue of Cov(X)**	**% Variance captured**	**% Variance captured total**
1	3.89×10^3	24.30	24.30
2	2.70×10^3	16.85	41.16
3	1.89×10^3	11.82	52.98
4	1.81×10^3	11.32	64.30
5	1.44×10^3	9.00	73.30
6	1.18×10^3	7.36	80.66

Mutual projections of factor scores and their loadings for the first two PCs for macroelements (A), and microelements and potentially toxic elements (B) are shown in Figure 4.

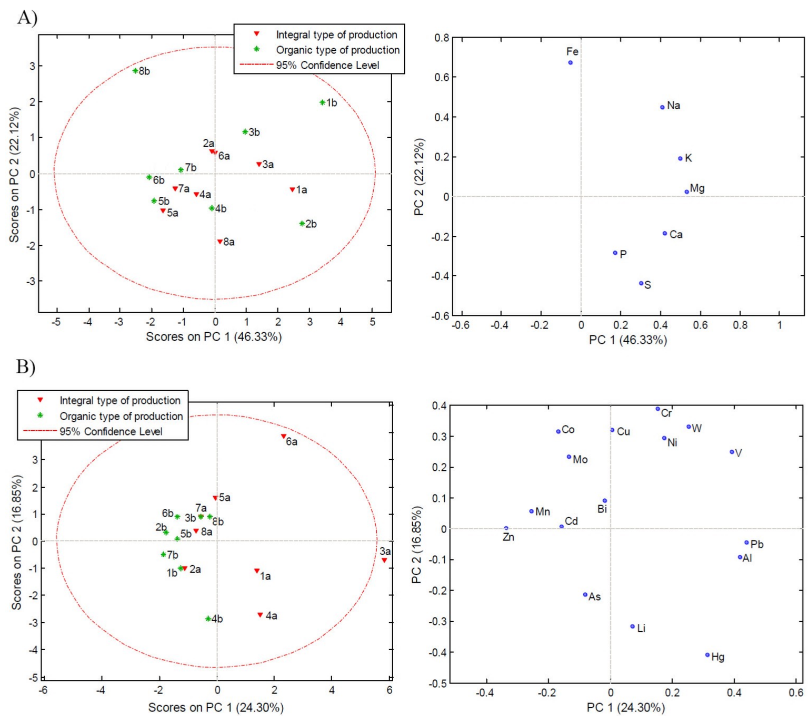

Figure 4. Principal component analysis—mutual projections of factor scores and their loadings for the first two PCs for macroelements (**A**), and microelements and potentially toxic elements (**B**) in the samples of tomato (Table 1) produced in two types of the agricultural system, integral (IPM) (samples 1a–8a) and organic (O) (samples 1b–8b).

In order to determine the existence of a statistically significant difference between the systems of production used for the different tomato variety cultivation, the Mann–Whitney U-test was performed. This test was used to discover if the two populations (organic and integral type of production) had the same distribution of metal content or not (Table 4, Figures 1 and 2). Due to the significant deviation from the normal distribution of each of the studied variables a nonparametric test was used. The Mann–Whitney U-test was performed to clearly see which minerals were responsible for the existence of a statistically significant difference between the production systems, i.e., which elements could serve as potential indicators for distinguishing organic from the integral production systems (Table 5).

Table 4. Parameters of descriptive statistics obtained from macroelements (A), microelements and potentially toxic elements (B), and rare-earth elements (C) content analysis (mg kg^{-1} dw) of different tomato varieties in two production systems. Elements below the limit of detection are marked with BLOD.

(A)		**Ca**	**Fe**	**K**	**Mg**	**Na**	**P**	**S**	
Integral system of production	mean	1410	643	22,300	1640	625	4300	1470	
	median	1490	737	22,100	1720	608	4380	1430	
	stdev	401	358	2680	239	241	458	265	
	min	704	143	17,900	1280	192	3470	1180	
	max	1990	1130	25,700	1950	918	4870	1900	
Organic system of production	mean	1210	894	21,700	1630	760	3930	1580	
	median	1120	828	20,300	1520	733	4080	1660	
	stdev	667	484	3450	317	279	457	355	
	min	389	296	18,100	1340	440	3220	916	
	max	2400	1550	27,300	2160	1300	4360	2000	
(B)		**Li**	**Al**	**V**	**Cr**	**Mn**	**Co**	**Ni**	**Cu**
Integral system of production	mean	0.14	24.7	0.0074	0.29	9.47	0.033	0.33	3.82
	median	0.12	22.2	0.0031	0.25	9.18	0.032	0.30	3.98
	stdev	0.07	8.55	0.0089	0.16	0.93	0.006	0.08	0.69
	min	0.09	16.6	BLOD	0.18	8.60	0.025	0.26	2.85
	max	0.30	38.8	0.0234	0.66	11.1	0.042	0.44	4.62
Organic system of production	mean	0.13	17.6	0.0034	0.29	11.6	0.043	0.27	3.68
	median	0.13	17.6	0.0038	0.28	10.9	0.039	0.24	3.59
	stdev	0.03	4.99	0.0018	0.10	2.06	0.018	0.11	0.89
	min	0.10	8.52	BLOD	0.18	9.27	0.018	0.16	2.76
	max	0.18	26.4	0.0060	0.46	15.5	0.072	0.47	5.48
(B)-continued		**Zn**	**Mo**	**Cd**	**W**	**Bi**	**As**	**Hg**	**Pb**
Integral system of production	mean	5.73	1.09	0.024	2.06	0.037	0.014	0.033	2.67
	median	5.22	0.79	0.022	1.54	0.028	0.013	0.006	2.26
	stdev	1.72	0.60	0.007	1.51	0.029	0.004	0.043	1.83
	min	4.01	0.65	0.017	0.54	0.012	0.011	BLOD	0.83
	max	9.07	2.24	0.037	4.90	0.100	0.022	0.098	5.78
Organic system of production	mean	6.49	1.31	0.030	0.91	0.075	0.023	0.018	0.38
	median	6.01	1.15	0.018	0.83	0.054	0.018	0.010	0.25
	stdev	1.39	0.51	0.031	0.57	0.065	0.014	0.024	0.36
	min	5.16	0.74	0.013	0.23	0.010	0.012	BLOD	0.08
	max	9.11	2.29	0.104	1.89	0.178	0.054	0.064	1.22

Table 4. *Cont.*

(C)		Sc	Ga	Se	Y	La	Ce	Pr	Nd	Sm	Eu
Integral system of production	mean	0.0381	0.0127	0.0076	0.0032	0.0061	0.0128	0.0010	0.0096	0.0007	0.0049
	median	0.0352	0.0125	0.0090	0.0029	0.0052	0.0077	BLOD	0.0057	0.0005	0.0041
	stdev	0.0086	0.0026	0.0056	0.0011	0.0039	0.0092	0.0007	0.0085	0.0005	0.0039
	min	0.0299	0.0093	BLOD	0.0018	0.0024	0.0058	BLOD	0.0029	0.0003	BLOD
	max	0.0545	0.0163	0.0147	0.0052	0.0125	0.0295	0.0027	0.0274	0.0017	0.0112
Organic system of production	mean	0.0300	0.0094	0.0096	0.0033	0.0146	0.0083	0.0009	0.0050	0.0006	0.0034
	median	0.0297	0.0095	0.0101	0.0033	0.0072	0.0074	0.0008	0.0046	0.0005	0.0011
	stdev	0.0028	0.0015	0.0063	0.0007	0.0189	0.0033	0.0003	0.0016	0.0003	0.0060
	min	0.0268	0.0069	BLOD	0.0024	0.0047	0.0055	0.0006	0.0030	0.0003	0.0005
	max	0.0332	0.0117	0.0174	0.0044	0.0604	0.0162	0.0016	0.0086	0.0011	0.0180

(C)-continued		Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Tl	Th	U
Integral system of production	mean	0.0012	0.0001	0.0005	0.0002	0.0003	0.0001	0.0002	0.0001	0.0024	0.0091	0.0009
	median	0.0008	0.0001	0.0004	0.0001	0.0003	0.0001	0.0002	0.0001	0.0018	0.0080	0.0007
	stdev	0.0009	0.0000	0.0001	0.0000	0.0000	0.0000	0.0001	0.0000	0.0016	0.0045	0.0005
	min	0.0005	0.0001	0.0003	0.0001	0.0002	0.0001	0.0001	0.0001	BLOD	0.0041	0.0005
	max	0.0032	0.0002	0.0006	0.0002	0.0003	0.0002	0.0003	0.0002	0.0054	0.0173	0.0021
Organic system of production	mean	0.0007	0.0001	0.0004	0.0001	0.0002	0.0001	0.0001	0.0001	0.0010	0.0049	0.0005
	median	0.0007	0.0001	0.0004	0.0001	0.0002	0.0001	0.0001	0.0001	0.0009	0.0051	0.0004
	stdev	0.0002	0.0000	0.0001	0.0000	0.0001	0.0000	0.0000	0.0000	0.0003	0.0011	0.0003
	min	0.0004	0.0001	0.0003	0.0001	0.0002	BLOD	0.0001	BLOD	0.0007	0.0031	0.0003
	max	0.0010	0.0001	0.0006	0.0001	0.0003	0.0001	0.0002	0.0001	0.0014	0.0062	0.0011

Table 5. Man-Whitney U-test for organic (O) and integral (IPM) production system.

Metal	*p* *	Man-Whitney U-Test (Z-Value and *Ho* **)	
Al	**0.03569**	**2.1004**	**I (O)**
Bi	0.40081	0.8402	/
Cd	0.24800	1.1552	/
As	**0.03569**	**2.1004**	**I (O)**
Ca	0.34456	0.9452	/
Ce	0.18926	1.3147	/
Co	0.14148	1.4703	/
Cu	0.52861	0.6301	/
Dy	0.34456	1.0519	/
Cr	0.52861	0.6301	/
Er	**0.01172**	**2.9047**	**I (O)**
Eu	0.14148	1.4725	/
Ga	**0.01359**	**2.4716**	**I (O)**
Fe	0.34456	0.9452	/
Gd	0.43090	0.7935	/
Hg	0.67442	0.4487	/
Ho	0.20758	1.8605	/
K	0.67442	0.4201	/
La	0.17217	1.3653	/
Li	0.52861	0.6301	/
Mg	0.83363	0.2100	/
Lu	**0.12781**	**2.0108**	**I (O)**
Mo	0.14148	1.4703	/
Mn	**0.02086**	**2.3105**	**I (O)**
Na	0.52861	0.6301	/
Ni	0.05871	1.8904	/
Nd	0.63650	0.4729	/
P	0.09289	1.6803	/
Pb	**0.00232**	**3.0456**	**I (O)**
Pr	0.83363	0.2111	/
S	0.40081	0.8402	/
Sc	**0.01813**	**2.3665**	**I (O)**
Se	0.49484	0.6831	/
Sm	0.71319	0.3723	/
Tb	**0.09289**	**2.2361**	**I (O)**
Tl	**0.01813**	**2.3752**	**I (O)**
Th	**0.02086**	**2.3173**	**I (O)**
Tm	**0.04871**	**2.3238**	**I (O)**
U	**0.03569**	**2.1288**	**I (O)**
V	1.00000	0.0000	/
W	0.07420	1.7854	/
Y	0.79290	0.2633	/
Yb	0.18926	1.6137	/
Zn	0.24800	1.1552	/

* Differences between two sets of data are significant when *p*-value is less or equal to 0.05. ** Medians significantly different if z-value > 1.9600, and the bold values were ***Accepted Ho***, while the others were *Rejected Ho.*

4. Discussion

The results obtained by analyzing the first two main components, their mutual projections of score values, and their loading vectors, based on the content of macroelements, microelements, potentially toxic elements, and REEs in different tomato samples (Tables 1 and S1,) are shown in the score and loading plots (Figure 3). The first main component covers 19.24% of the variability, while the second covers 17.26%, and each next principal component explains less than 12% of the total variance. It is not unusual to get the low overall data variance captured by a few PCs, especially in the case when the number of samples is small, but the variability among the samples is relatively high because it is a group of natural samples and a diverse set of parameters (variables) is considered. On the score plot (Figure 3a) it can be clearly seen that two distinct groups of samples were obtained. The first one consisted of samples of tomato cultivated in the organic type of production (1b–8b) while the second encompasses the tomato samples cultivated in the integral type of production (1a–8a) (Figure 3a).

Loading plot (Figure 3b), a plot of the direction vectors that define the model, revealed that the highest positive influences on the separation of samples produced in the organic cultivation system (1b–8b) (Table 1, Figure 3a), have variables S, microelements As, Mn, Co, and Mo, and rare-earth elements Se and La (Figure 3b) which is consistent with the fact that their concentration is higher in different tomato varieties produced under organic production system (Tables 4 and S1, Figures 1 and 2). S is necessary for normal metabolic processes in plants and highly influences the biosynthesis of chlorophyll. It is an essential component of the structure of lipids, proteins and amino acids and is, as such, used to activate important vitamins and enzymes in plants [25]. The majority of S in plants is absorbed through their roots as $SO4^{2-}$ [26]. Unlike s, As is not essential for plants and, as F. Burlo et al. showed, it does not influence some metabolic reactions at lower concentrations. However, when found in higher amounts, As can hinder plant growth or even lead its death. Taking that into account, over the last few decades the inorganic arsenical pesticides were replaced by organic herbicides such as methylarsonic and dimethylarsinic acids. When used at lower concentrations these herbicides are less toxic for both animals and humans [27]. Mn supports several biochemical processes but due to its immobility, this element moves only towards the leaves through the xylem. Once there, it cannot be transferred anywhere else in the plant. Higher concentration of Mn in samples produced in the organic type of production and variations in its concentrations is caused by the arbuscular mycorrhizal fungi usually found in the soil used for organic crop production [28]. Increased availability of Co is in correlation with the content of organic matter and depends on soil properties. Co has a significant synergistic effect on tomato growth, yield, nutrients status, physical and chemical composition, especially under organic fertilization which can explain its higher concentration in samples of tomato from organic production [29]. The essential micronutrient with the least concentration in most plant tissues is Mo. The foliar fertilization by Mo can compensate the internal Mo deficiencies and that is a possible explanation for higher concentration of this element in tomato samples. The effects of Mo on plant growth are significantly higher than the amount usually found in plants [30].

Variables that potentially have the highest influence on the separation of tomato samples along the PC2 axis were macroelements Mg, K, and Ca, as well as potentially toxic element Hg (Figure 3) whose concentrations in samples of organic production are lower compared to samples produced in the conditions of an integral cultivation system (Tables 4 and S1, Figures 1 and 2). The higher content of K and Ca in the samples produced in integral system can be explained with the fact that the integral farming system requires the application of fertilizers based on K and Ca salts, which secures the development and growth of tomato plants, while in the organic farming systems their use is prohibited [7,31,32]. The higher content of Mg also can be explained by the foliar applications of fertilizers which is simple and affordable. Foliar application of adequate Mg concentration plays important role in biochemical and physiological processes of plants like protein synthesis, metabolism of carbohydrates, enzymes activation, and energy transfer, just as Mg likewise proceeds as an impetus in oxidation and reduction reaction inside the tissues of the plant along and enhance the resistance against dry spell in the plant [33]. Also, higher Mg content can be correlated with increased mercury content. Shekar et al. proved that even at low concentrations of Hg (10 mg L^{-1}) there is a significant increase in the amount of chlorophyll [34], and as Mg is known to be the central chlorophyll atom [32], we can take advantage of this fact and thus explain the positive correlation of these elements.

Rare-earth elements Th, Tl, and Sc, as well as U, Tm, Lu, and microelements Al and Pb (Figure 3b) have the most positive influence along the PC1 axis on the separation of the tomato sample produced in the integral cultivation system (1a–8a) (Table 1, Figure 3a), while along the PC2 axis the greatest influence have the rare-earth elements Nd, Gd, Ce, Sm, Dy, Ga, Tb, Ho, and Er. The rare-earth elements in samples of integral production have higher concentrations than samples of organic production (Tables 4 and S1, Figures 1 and 2). The content of REEs in tomato plants was previously rarely used to determine differences between two examined production systems. Earlier studies showed the enhanced effects of organic acids on the accumulation of light REEs by plants [35,36]. Shan et al. found evidence that organic acids are responsible for the accumulation of REEs in plants by treating the soil with histidine and malic and citric acids [35]. As the result, the concentrations of light REEs increased. Additionally, the exposure to low concentrations of some REEs, in particular Ce, Nd, La, and Sm, is known to enhance crop production. They can increase photosynthesis, uptake, and utilization of nutrients and water, and enhance respiration and stress tolerance.

Since PCA based on the content of all 44 mineral elements showed that rare-earth elements can serve as a potential factor for distinguishing types of production (Figure 3), PCAs based only on the content of macroelements and on the content of microelements and potentially toxic elementswere also done (Table 3, Figure 4). A clear separation of organic production samples (1b–8b) from tomato samples grown in the integral cultivation system (1a–8a) cannot be observed based on the content of macroelements and microelements and potentially toxic elements (Figure 4). This confirms the assumption that REEs are actually the ones responsible for separating the two data sets, i.e., tomato samples produced in the integral cultivation system, from the samples of organic production system (Figure 3).

Considering that PCA was used to understand the data structure and identify similarities and particular grouping patterns, in order to determine the existence of a statistically significant difference between two different systems of tomato production, and confirmed in that way the previous interpretation of the results—whether and which minerals lead to a difference in the production systems as well as whether REEs can be used as potential indicators of the production systems, the Mann–Whitney U test was performed. Based on this test, the contents of Al, Mn, As, Pb, Sc, Ga, Tb, Er, Tm, Lu, Tl, Th, and U were identified as parameters that showed a significant difference among the organic and integral production systems ($p < 0.05$; Table 3). The assessment of the distribution pattern of REEs in the different varieties of tomatoes produced under different production systems provides information that improves the understanding of the soil uptake and plant translocation mechanisms for these elements. This allows us to estimate the possibility of using comprehensive REEs content as indicators of tomato cultivation systems, i.e., which elements could serve as potential indicators of distinguishing organic from the integral system of production on the territory of Serbia, in order to confirm products' authenticity and provide sufficient information to consumers when choosing food.

5. Conclusions

Taking into consideration all aforementioned, it may be concluded that the mineral profile is a parameter of utmost importance for assessing the productive characteristics of tomato samples taken from two factorial randomized trials. This work employed the use of eight different varieties, belonging to four tomato types: large—BEEF and CLUSTER, and mini and midi—CHERRY and PLUM tomatoes, cultivated under two different farming systems: integral (IPM) and organic (O). A total of 44 mineral elements were quantified using ICP-OES and ICP-MS analytical techniques. A clear separation of tomato samples cultivated under organic production systems from the integral type cannot be observed based on the content of macroelements and microelements and potentially toxic elements. PCA based on the content of all 44 minerals showed that rare-earth elements can serve as a potential factor for distinguishing types of production. The rare-earth elements in samples of integral production have higher concentrations than samples of organic production. In order to see whether and which elements lead to a difference in the production systems as well as whether REEs can be used as potential indicators of the production systems, the Mann–Whitney U test was performed. Based on this test, the contents of Al, Mn, As, Pb, Sc, Ga, Tb, Er, Tm, Lu, Tl, Th, and U were identified as parameters that showed a significant difference among the organic and integral production systems.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/agriculture11101009/s1, Table S1: *Excel datasheet*—Contents of macroelements, microelements and potentially toxic elements, and rare-earth elements (mg kg^{-1} dw) in samples of tomato, eight different varieties, belonging to four different tomato types: large—BEEF and CLUSTER, and mini and midi—CHERRY and PLUM tomatoes, which were cultivated in two different types of agricultural systems: integral (IPM) and organic (O).

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