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Article

Yield, Quality, Antioxidants and Elemental Composition of New Leek Cultivars under Organic or Conventional Systems in a Greenhouse

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Abstract: Leek (*Allium porrum*) is known for its high antioxidant activity and the ability to accumulate significant amounts of potassium and iron. We assessed yield, quality indicators, antioxidants and elemental composition of nine leek cultivars grown in greenhouses under organic or conventional systems in the Moscow region. The management system did not affect yield, which attained the highest value with the cultivar Giraffe and the lowest with Premier and Cazimir. Pseudo-stem dry matter and sugars were higher with organic management, whereas nitrate concentration was higher with conventional management. The cultivars Vesta and Summer Breeze showed the highest dry matter and total sugar content, whereas Goliath had the highest antioxidant, selenium and potassium concentrations. Among the antioxidants, ascorbic acid attained higher values with organic management. The antioxidant system of leek was characterized by highly significant positive correlations between: Se and polyphenols, Se and ascorbic acid, Se and K, ascorbic acid and polyphenols, ascorbic acid and K, polyphenols and K (r = 0.94, 0.94, 0.95, 0.94, 0.95, 0.96, respectively, at $P \leq 0.001$). Negative correlations were recorded between leaf and pseudo-stem Se and between leaf and pseudo-stem polyphenols (r = −0.922 and −0.976, respectively, at $P \leq 0.001$). Among the mineral elements, only K was significantly affected by the management system, showing a higher content in organically grown pseudo-stems. Varietal differences in pseudo-stem element composition showed strong positive correlations of: Al with As, Co, Li, Pb and V; Cr with I, Mg, Si, Ca; V with As, Co and Fe; negative correlations of Se with Cr and I. Compared to related species such as garlic (A. sativum), leek accumulated levels equal to garlic of K, Mg, P, Cd, Cu, Mn, Se, Zn, lower levels of Si and significantly higher amounts of Ca, Na, Al, As, Cr, Ni, Pb, Sr, V, Sn, B, Co, Fe, I, Li. The strong relationships between quality, antioxidant and mineral components in leek plants may give wide possibilities in breeding programs for both conventional and organic management systems in greenhouses.

Keywords: *Allium porrum*; organic management; production; sugars; selenium; antioxidants; minerals

1. Introduction

Among *Allium* species, leek (*A. porrum*), garlic (*A. sativum*) and onion (*A. cepa*) are the most widely used for human consumption. The greatest production of leek is in Indonesia and Turkey, with France and Belgium being major producers in Europe.

Popularity of leek is connected not only with its high nutritional value but also with its wide spectrum of biological activities, primarily due to a high antioxidants content [1–5]. Leek shows antimicrobial, cardio-protective, hypocholesteremic, hypoglycemic and anticancer activities [6,7]. Leek consumption is known to improve liver and gastro-intestinal tract functioning, quicken metabolic processes, to be useful in rheumatism treatment, to decrease blood pressure, to protect against anemia, to enhance brain activity, to inhibit platelet aggregation and to prevent neural tube defects [3]. Moreover, consumption of *A. porrum* edible parts reportedly decreases the risk of prostate, colon, stomach and breast cancers [8,9]. Antimicrobial effects of leek have been recorded both against gram-positive (*Bacillus subtilis*, *Streptococcus pneumonia*, *Staphylococcus aureus*) and gram-negative bacteria (*Escherichia coli*, *Proteus vulgaris*, *Pseudomonasaeruginosa*) [10]; and, antifungal activity has also been reported [11,12].

The most important biologically active compounds contained in leek are polyphenols [5,13], glucosinolates, S-alkenyl-L-cysteine sulfoxides, and pectic polysaccharides, each showing immune stimulating activity [1,14,15]. Polyphenol content in *A. porrum* is comparable with the *A. ascalonicum* (shallot) and significantly exceeds that of *A. sativum*, *A. cepa* [16], *A. schoenoprasum* (chive) and *A. tuberosum* (garlic chive) [13]. The nutritional value of leek is also correlated with the high content of potassium and iron [17].

Protected cultivation is reportedly preferred for organic horticulture [18], as the latter is more susceptible to the environmental unbalances caused by less intensive management and, in addition, organic vegetables have higher market prices than the conventional ones, which results in a higher income for farmers.

The evaluation of varietal differences in accumulation of biologically active compounds as well as macro- and micro-elements by leek plants is of interest, both for identifying the characteristic interrelations between the components and for carrying out breeding for high concentrations of biologically active compounds. Despite several studies devoted to assessing leek biochemical characteristics and their role in disease treatment, there is some variation among studies concerning varietal differences in biologically active compounds [19] and their elemental composition [17].

Due to research lacking on the aforementioned topics, we have carried out a study to assess the effect of both cultivar and conventional versus organic management on leek yield, quality, antioxidant content and elemental composition of leek grown in greenhouses.

2. Materials and Methods

2.1. Plant Material and Growth Conditions

Leek was grown in a greenhouse at the experimental fields of the Federal Scientific Center of Vegetable Production, in Odintsovo (Moscow, Russia, 55°39.51′ N, 37°12.23′ E) in 2015 and 2016 on a clay-loam soil, with a pH 6.8, 2.1% organic matter, 108 mg kg^{-1} N, 450 mg kg^{-1} P_2O_5, 357 mg kg^{-1} K_2O, and exchangeable bases sum ≤95.2%. Monthly mean temperature and relative humidity values from May to October were 13.0, 16.1, 19.8, 18.6, 12.3, 6.4 °C and 59.1, 63.8, 69.7, 72.4, 79.1, 81.0% respectively. The experimental protocol was based on a factorial combination of two management systems (organic, conventional) and nine cultivars (Goliath, Summer Breeze, Premier, Casimir, Kalambus, Camus, Vesta, Giraffe, Bandit), using a split-plot design with three replicates of each cultivar by management system.

Seed was sown on 5 December in 8 × 8 cm trays and the plantlets were transplanted to the field on 14 May, spaced 15 cm within rows, with rows 40 cm apart. Leek crops were preceded by organically-grown vegetables in the previous four years, including carrot, bean, rape and pea. Prior to planting, the soil was ploughed to a 30 cm depth, hoed to 15 cm, and fertilized with 180 kg ha^{-1} N, 80 kg ha^{-1} P_2O_5 and 120 kg ha^{-1} K_2O. During plant production, 40 kg ha^{-1} N were supplied three times at two-week intervals and, in the last N application, 7 kg ha^{-1} of P_2O_5 and of K_2O were also provided. Half of each fertilizer dose was applied just before transplanting and the remaining 50% by sidedressing at two week intervals. Drip irrigation was started at 80% soil available water. The organic management practices complied with EC Regulations 834/2007 and 889/2008. Plant protection was achieved by applying copper oxychloride against rust, and deltamethrin or azadirachtin in the conventional or organic systems, respectively, against aphids.

Harvests of mature plants were performed from 5 to 10 October, when the pseudo-stems had reached their maximum growth, and the leaf blades were trimmed to a 15 cm length for obtaining a marketable product. In each plot, determinations were made of the weight of the marketable product (pseudo-stems with 15 cm long leaf blades) and the mean pseudo-stem (with 15 cm long leaf blades) weight from twenty-plant samples. Further plant samples were collected, gently washed with water to remove surface contaminants and dried with filter paper. Pseudo-stems and leaves were separated, cut with a plastic knife, dried to a constant weight and homogenized. The resulting powders were subjected to laboratory analyses.

2.2. Dry Matter

The dry matter content in leaves and pseudo-stems of *A. porrum* was assessed after drying the fresh samples in an oven at 70 °C, until they reached constant weight.

2.3. Total Soluble Solids (TSS) and Sugars

Determination of total soluble solids was performed in filtered water extracts of leek leaves and pseudo-stems (1 g of dry sample per 100 mL) using a TDS-3 conductometer (HM Digital, Inc., Seoul, Korea).

Monosaccharides were determined using the ferricyanide colorimetric method, based on the reaction of monosaccharides with potassium ferrycianide [20]. Total sugars were determined after acidic hydrolysis of 50 mL of filtered water extracts with 5 mL of 20% hydrochloric acid. Fructose was used as an external standard.

2.4. Polyphenols

The concentrations of total phenolics in each sample of leaves and pseudo-stems were determined in filtered 70% ethanol extract (0.5 g of dry sample in 25 mL; 1 h at 80 °C) using the Folin-Ciocalteu colorimetric method, according to Golubkina et al. [21] using a Unico 2804 UV (Unico Inc., Wixom, MI, USA) spectrophotometer. The phenolic contents were calculated by using a calibration curve of gallic acid constructed with five concentrations of this compound (0–90 µg/mL). Phenolic contents were expressed as milligrams of gallic acid equivalents per 100 g of dry weight (mg GAE/100 g d.w.).

2.5. Ascorbic Acid

Ascorbic acid content of leek leaves and pseudo-stems was assessed by visual titration of fresh plant extracts in 6% trichloracetic acid with Tillmans reagent [22]. Five grams of fresh leek leaves were homogenized in porcelain mortar with 5 mL of 6% trichloracetic acid and quantitatively transferred to measuring cylinder. The volume was brought to 80 mL using trichloracetic acid, and the mixture was filtered through filter paper 15 min later. The ascorbic acid concentration was determined from the volume of Tillmans reagent which went into titration of the sample.

2.6. Antioxidant Activity

The antioxidant activity of leek leaves and pseudo-stems was assessed using a redox titration method [23], via titration of 0.01 N $KMnO_4$ solution with ethanolic extracts of leaves and pseudo-stems used for polyphenol determination (see Section 2.4). Reduction of $KMnO_4$ to colorless Mn^{+2} in this process reflects the concentration of antioxidants dissolvable in 70% ethanol. The values were expressed in mg GAE/100 g d.w. The use of $KMnO_4$ acidic solution is known to be successfully used for the determination of *Ocimum basilicum* antioxidant potential [24] and antioxidant capacity of serum [25].

2.7. Nitrates

Nitrate was assessed in fresh pseudo-stems using an ion selective electrode using a ionomer Expert-001 (Econix, Moscow, Russia). Five grams of fresh homogenized leek pseudo-stems were mixed with 50 mL of distilled water. Forty-five mL of filtered extract were mixed with 5 mL of 0.5 M potassium sulfate background solution (necessary for ionic strength regulation) and analyzed through the ionomer for nitrate determination.

2.8. Elemental Composition

Al, As, B, Ca, Cd, Co, Cr, Cu, Fe, Hg, I, K, Li, Mg, Mn, Na, Ni, P, Pb, Si, Sn, Sr, V and Zn contents of leek pseudo-stems were assessed using an ICP-MS on quadruple mass-spectrometer Nexion 300D (Perkin Elmer Inc., Shelton, CT 06484, USA) equipped with the 7-port FAST valve and ESI SC DX4 autosampler (Elemental Scientific Inc., Omaha, NE 68122, USA) in the Biotic Medicine Center (Moscow, Russia). Rhodium ^{103}Rh was used as an internal standard to eliminate instability during measurements. Quantitation was performed using external standard (Merck IV, multi-element standard solution), potassium iodide for iodine calibration and Perkin-Elmer standard solutions for P, Si and V. All the standard curves were obtained at 5 different concentrations.

For quality control purposes, internal controls and reference materials were tested together with the samples on a daily basis. Microwave digestion of samples was achieved according to the standard method [26] with sub-boiled HNO_3 diluted 1:150 with distilled deionized water (Fluka No. 02650 Sigma-Aldrich, Co., Saint Louis, MO, USA) in the Berghof SW-4 DAP-40 microwave system (Berghof Products + Instruments GmbH, 72800 Eningen, Germany). Trace levels of Hg in samples were not taken into account and, accordingly, they were excluded from the Tables below.

The instrument conditions and acquisition parameters were: plasma power and argon flow, 1500 and 18 L min^{-1} respectively; aux argon flow, 1.6 L min^{-1}; nebulizer argon flow, 0.98 L min^{-1}; sample introduction system, ESI ST PFA concentric nebulizer and ESI PFA cyclonic spray chamber (Elemental Scientific Inc., Omaha, NE 68122, USA); sampler and slimmer cone material, platinum; injector, ESI Quartz 2.0 mm I.D/; sample flow, 637 µL/min; internal standard flow, 84 µL/min; dwell time and acquisition mode, 10–100 ms and peak hopping for all analytes; sweeps per reading, 1; reading per replicate, 10; replicate number, 3; DRC mode, 0.55 L min^{-1} ammonia (294993-Aldrich Sigma-Aldrich, Co., St. Louis, MO 63103, USA) for Ca, K, Na, Fe, Cr, V, optimized individually for RPa and RPq; STD mode, for the rest of analytes at RPa = 0 and RPq = 0.25.

Se content of leek leaves and pseudo-stems was analyzed using the fluorimetric method previously described for tissues and biological fluids [27]. The method includes digestion of dried homogenized samples via heating with a mixture of nitric-chloral acids, subsequent reduction of Se^{+6} to Se^{+4} with a solution of 6 N HCl, and formation of a complex between Se^{+4} and 2,3-diaminonaphtalene. The Se concentration was assessed in triplicate by recording piazoselenol fluorescence values in hexane at 519 nm λ emission and 376 nm λ excitation. The results precision was checked using a reference standard-lyophilized cabbage at each determination with 150 µg/Kg Se concentration (Institute of Nutrition, Moscow, Russia).

2.9. Statistical Analysis

Data were processed by analysis of variance and mean separations were performed using the Duncan multiple range test, $\alpha = 0.05$, using SPSS software version 21. The data expressed as a percentage were subjected to angular transformation before processing.

3. Results and Discussion

As the year of research had no significant effect on yield, quality and antioxidant variables examined, both as main factor or in interaction with the experimental factors management system or cultivar, the results are reported as average values of the two years of investigation.

3.1. Yield, Dry Matter, Sugars and Nitrates of Pseudo-Stems

The management system showed no significant effects on leek pseudo-stem yield and mean weight (Table 1). The experimental factor cultivar significantly affected the mean pseudo-stem weight and, accordingly, yield which ranged from 23.8×10^3 to 40.2×10^3 kg ha^{-1} , as an average management across systems; the variety Giraffe showed the highest yield, Premier and Kalambus the lowest. The coefficient of variation was rather low and reached 18.3%, which suggests a low genetic effect on this variable (Table 1).

Table 1. Yield, mean pseudo-stem weight, and content of dry matter, sugars and nitrates in leek.

Treatment	Yield 10^3 kg ha^{-1}	Mean Pseudo-Stem Weight g	Dry Matter %	Sugars g/100 g d.w.		Nitrates mg/kg f.w.
				Mono-	Total	
Crop management						
Organic	30.9	185.5	19.7	3.6	11.7	76
Conventional	31.2	187.0	17.8	3.2	10.4	102
	n.s.^{z}	n.s.	*	*	*	*
Cultivar						
Goliath	31.1 ^{d,e,y}	188.0 ^{d,e}	12.4 ± 0.4 ^{e}	4.8 ± 0.3 ^{a}	7.3 ± 0.5 ^{e}	77 ± 3 ^{d}
Premier	23.8 ^{g}	142.4 ^{g}	15.2 ± 0.5 ^{d}	4.4 ± 0.3 ^{a,b}	10.5 ± 0.7 ^{c}	74 ± 3 ^{d}
Bandit	35.0 ^{bc}	209.8 ^{b,c}	15.3 ± 0.6 ^{d}	3.5 ± 0.2 ^{c}	8.6 ± 0.5 ^{d}	103 ± 4 ^{a}
Kalambus	24.0 ^{g}	143.6 ^{g}	17.6 ± 0.6 ^{c}	3.9 ± 0.2 ^{b,c}	10.3 ± 0.7 ^{c}	70 ± 3 ^{d}
Cazimir	26.9 ^{f}	160.9 ^{f}	18.9 ± 0.6 ^{c}	2.8 ± 0.2 ^{d}	10.7 ± 0.7 ^{b,c}	90 ± 4 ^{b,c}
Giraffe	40.2 ^{a}	242.5 ^{a}	20.5 ± 0.8 ^{b}	3.4 ± 0.2 ^{c}	11.0 ± 0.7 ^{bc}	86 ± 3 ^{c}
Camus	33.3 ^{c,d}	201.7 ^{c,d}	21.4 ± 0.7 ^{b}	2.5 ± 0.2 ^{d}	12.2 ± 0.8 ^{b}	105 ± 5 ^{a}
Vesta	29.0 ^{e,f}	175.0 ^{e,f}	23.4 ± 0.8 ^{a}	2.6 ± 0.2 ^{d}	14.3 ± 0.8 ^{a}	98 ± 4 ^{ab}
Summer Breeze	36.7 ^{b}	221.3 ^{b}	24.3 ± 0.9 ^{a}	2.8 ± 0.2 ^{d}	15.1 ± 0.9 ^{a}	98 ± 4 ^{ab}
M	31.1	187.2	18.8	3.86	11.11	89
SD	5.7	34.8	3.2	1.23	1.84	11
CV (%)	18.3	18.6	17.3	31.9	16.8	12.4
Concentration range	23.8–40.2	142.4–242.5	12.4–24.3	2.5–8.4	7.3–15.1	70–105

^{z} n.s. not significant; * significant at $P \leq 0.05$. ^{y} Within each column, means followed by different letters are significantly different according to Duncan's Multiple Range Test at $P \leq 0.05$.

Organic management resulted in a higher dry matter and carbohydrate content in pseudo-stems, compared to the conventional managementsystem (Table 1). These results may be due to the enhancement of microbial biomass and activity leading to organic compound synthesis and, in this respect, similar trends were recorded in previous research carried out in greenhouses [28]. Moreover, dry matter content of the nine leek cultivars ranged from 12 to 24% (Table 1) which was much wider than leek grown in the Czech Republic (9–11%) [14]. These results identified varieties with high dry matter content (Summer Breeze and Vesta), which show a long shelf-life and areuseful for dry spice production, and genotypes with low dry matter content (Goliath, Premier and Bandit) more suitable for salad production, though dry matter is also dependent on water regime [29].

Cultivar differences in total sugar content were 2-fold lower than the coefficient of variation for monosaccharide content (Table 1). Therefore, the existence of a multidirectional nature of mono- and disaccharide accumulation in leek pseudo-stems may exist.

A significant positive correlation was observed between dry matter and disaccharides (r = 0.98 at $P < 0.01$), but there was a negative correlation (r = −0.86 at $P < 0.05$) between dry matter and monosaccharides (Figure 1). Indeed, the negative correlation between monosaccharides and dry matter content shown in Figure 1 is consistent with that previously found in onion [30]. Interestingly, total sugar content in onion did not differ among cultivars with low versus high dry matter content [31], in contrast to leek where the maximum value was twice the minimum. As observed in Figure 1, the highest concentrations of mono- and total saccharides in leek were associated with cultivars with high dry matter content. However, contrasting carbohydrate trends were found with the two varieties: Goliath had low dry matter content and a significantly higher concentration of monosaccharides compared to disaccharides; in Summer Breeze, the disaccharide content exceeded the monosaccharide content by 4.4-fold , with the ratio between the related total sugar contents at 2.1 (Figure 1).

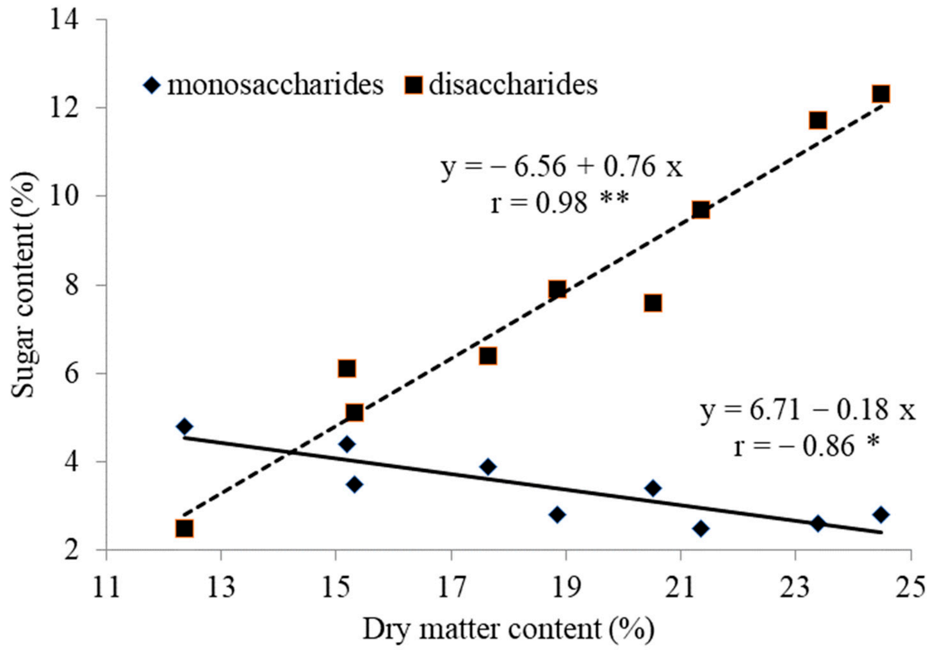

Figure 1. Correlations between dry matter and sugar content in leek pseudo-stems.

With regard to nitrate concentration in pseudo-stems (Table 1), lower values were recorded the organic management system compared to conventional management, consistent with previous reports [28]. Indeed, a slow nitrate release from organic fertilizers does not elicit abundant uptake of this anion in a short time period, which prevents its accumulation in plant parts [32].

Leek is characterized by a relatively high plant nitrate content [33], though it is much lower than in the top-accumulating species [32]. However, in our research the cultivars investigated had less than 105 mg nitrate per kg fresh weight (f.w.) and, moreover, the ascorbic acid content was sufficient to make the product safe and healthy, as ascorbic acid participates in producing essential nitrogen oxide for humans thus preventing nitrosamine formation [33]. Notably, low varietal differences in nitrate accumulation make this quality parameter the most stable among the cultivars grown in similar conditions.

3.2. Antioxidants

Polyphenols and vitamin C significantly affect plant antioxidant activity [34]. In our research, organic management resulted in higher vitamin C in leek pseudo-stems compared to conventional management, consistent with some previous investigations [35], but differently from others where no significant differences were observed between the two management systems [28]. The management system did not affect either polyphenol or selenium concentration in leek pseudo-stems and leaves.

There were significant varietal differences in ascorbic acid accumulation, in contrast to polyphenol content which was characterized by higher stability in both stems and especially in leaves (Table 2). Among the cultivars, Goliath showed the highest ascorbic acid content; notably, all of the cultivars from domestic selection had lower levels of polyphenols compared to prior reports, which may be related to different crop cycles and harvest times [36]. Similar findings have been reported from an investigation in Belgium on thirty leek cultivars [19], where the ascorbic acid concentration range was 90 to 350 mg/100 g d.w. and the polyphenol ranged from 7.3 to 11.3 mg GA/g d.w., whereas the domestic cultivars showed lower polyphenol values, i.e., 3.0 to 5.5 mg GA/g d.w. (Table 2).

Table 2. Concentrations of ascorbic acid, polyphenols and selenium in leek.

Treatment	Ascorbic Acid in Pseudo-Stems mg/100 g f.w.	Polyphenols mg GAE/100 g d.w.		Selenium μg/kg d.w.	
		Pseudo-Stems	Leaves	Pseudo-Stems	Leaves
Crop management					
Organic	47.2	375.4	696.7	76.3	64.4
Conventional	37.0	356.2	674.9	73.1	60.8
	* ^{z}	n.s.	n.s.	n.s.	n.s.
Cultivar					
Goliath	136.8 ± 8.1 ^{a,y}	555 ± 52 ^{a}	711 ± 19 ^{a}	107 ± 7 ^{a}	14 ± 1 ^{e}
Premier	58.6 ± 3.3 ^{b}	432 ± 34 ^{b}	650 ± 21 ^{b}	80 ± 5 ^{b}	65 ± 3 ^{c}
Bandit	40.5 ± 2.6 ^{c}	394 ± 26 ^{b,c}	647 ± 26 ^{b}	75 ± 5 ^{b,c}	48 ± 2 ^{d}
Kalambus	25.5 ± 2.3 ^{d,e}	319 ± 19 ^{d,e}	731 ± 46 ^{a}	72 ± 4 ^{b,c}	74 ± 3 ^{b}
Cazimir	30.2 ± 2.6 ^{d}	284 ± 20 ^{e}	728 ± 53 ^{a}	60 ± 3 ^{e}	76 ± 4 ^{a,b}
Giraffe	24.9 ± 2.0 ^{e,f}	331 ± 19 ^{d}	665 ± 41 ^{a,b}	73 ± 4 ^{b,c}	49 ± 2 ^{d}
Camus	21.1 ± 1.4 ^{f,g}	347 ± 21 ^{c,d}	684 ± 43 ^{a,b}	64 ± 3 ^{d,e}	81 ± 5 ^{a,b}
Vesta	19.2 ± 1.3 ^{g}	301 ± 19 ^{d,e}	740 ± 55 ^{a}	69 ± 3 ^{c,d}	84 ± 5 ^{a}
Summer Breeze	22.2 ± 1.9 ^{f,g}	329 ± 20 ^{d,e}	616 ± 42 ^{b}	72 ± 3 ^{b,c}	72 ± 4 ^{b,c}
M	42.1	317	686	74.7	62.5
SD	24.7	71	37	8.4	17
CV, %	58.7	22.4	5.4	11.2	27.2
Concentration range	19.2–136.8	284–555	616–740	60–107	14–84

^{z} n.s. not significant; * significant at $P \leq 0.05$. ^{y} Within each column, means followed by different letters are significantly different according to Duncan's Multiple Range Test at $P \leq 0.05$.

A significant positive correlation between ascorbic acid and polyphenol concentration in leek stems is of particular interest (r = 0.94 at $P < 0.01$). The lack of a similar correlation in a study using thirty leek cultivars conducted in Belgium [19] was presumably related to the heterogeneity of the cultivars, which were selected on the basis of morphological types (light-green summer type, dark-green winter type and intermediate autumn type). Indeed, the autumn-grown Belgium varieties resulted in a similar correlation to ours between ascorbic acid and polyphenol content (r = 0.71 at $P < 0.05$).

The ratio between leaf and stem polyphenol concentration in leek plants was of interest. In the nine cultivars in our research polyphenol content was always higher in leaves compared to stems, with a negative correlation between the tissues (Figure 2). Otherwise, as found by Ben Arfa et al. [5], polyphenol levels in *A. porrum* leaves may be both higher or lower than those in stems. In this respect, the total polyphenol content per plant should be more stable that polyphenol concentrations recorded in stems or leaves.

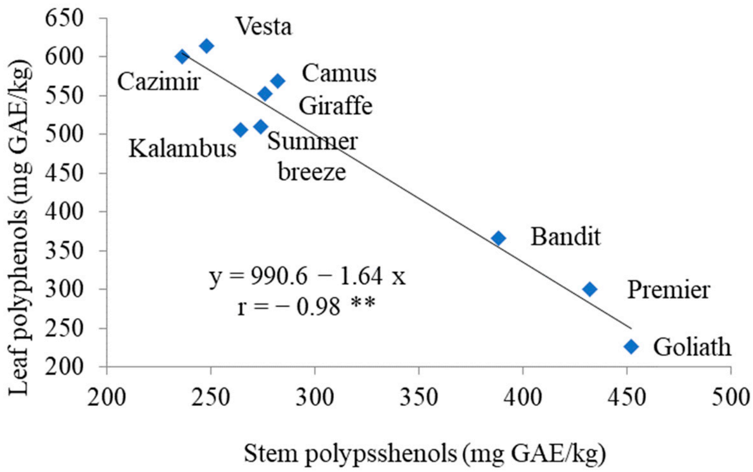

Figure 2. Correlation between leaf and stem polyphenol content.

Among the components of plant antioxidant systems, selenium plays a significant role. Indeed, though it is not an essential element for plants, selenium is able to provide a powerful antioxidant defense to plants against drought, salinity, frost, flooding, UV light and herbivores [37]. Notably, *Allium* species belong to the secondary selenium accumulators, which show a remarkable tolerance to high concentrations and consequent accumulation of this element due to Se ability to substitute for sulfur in natural compounds, as also reported by Turkish scientists in leek [17].

In our research, *A. porrum* grown in the Moscow region showed a Se accumulation range from 60 to 107 µg/kg d.w., which is much lower than the values recorded in Turkey [17]. This suggests the significant effect of selenium status in the environment on plant ability to concentrate the trace element. The negative correlation between selenium content in leaves and stems ($r = -0.95$ at $P < 0.01$; Figure 3), similar to that recorded for polyphenols, entails a rather stable level of selenium accumulation in the plant.

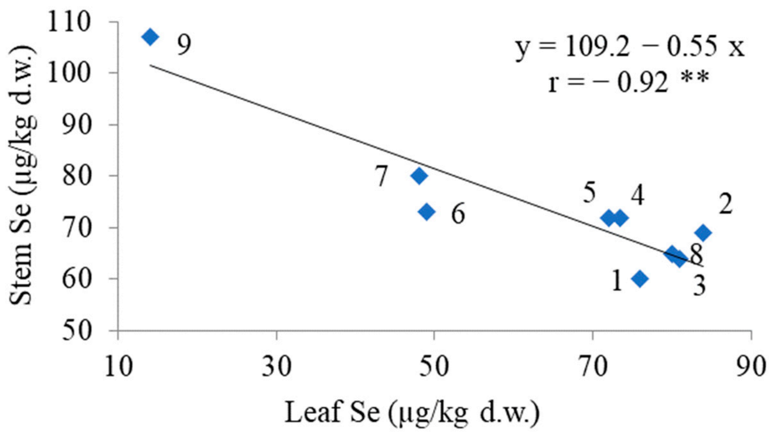

Figure 3. Correlation between leaf and stem selenium content in leek cultivars: (1) Cazimir, (2) Vesta, (3) Camus, (4) Kalambus, (5) Summer Breeze, (6) Giraffe, (7) Bandit, (8) Premier, (9) Goliath.

Reports relevant to selenium as plant secondary metabolites, as well as Se to polyphenols particularly in the absence of selenium loading are rather scarce and often controversial. In this respect, a positive correlation between selenium and polyphenol content was found in wheat [38] and an adverse correlation between quercetin and selenium was recorded in onion [30]. However, moderate doses of selenium are deemed to enhance the content of antioxidants such as polyphenols, flavonoids and carotenoids [39,40].

In our research, the leek genotypes investigated showed significant correlations between the components of the antioxidant system, i.e., selenium, ascorbic acid and polyphenols: Se and ascorbic acid ($r = 0.93$ at $P < 0.01$); Se and polyphenols ($r = 0.92$ at $P < 0.01$); ascorbic acid and polyphenols ($r = 0.94$ at $P < 0.01$). The latter correlations relevant to leek stems may be very useful for leek selection based on high antioxidant content.

3.3. Elemental Composition

The beneficial effect of many elements to human health has created unflagging interest in mineral composition of vegetable crops and in particular of leek [17,41]. Investigations of element content in leek have revealed that the plant is able to accumulate high concentrations of K and Fe. However, all investigations to date have restricted macro- and microelements (K, Ca, P, Na, Mg, Fe, Zn, Cu, Se) availability, giving no opportunity to evaluate either the leek total mineral profile or the varietal peculiarities of element accumulation.

Our research with nine leek cultivars has shown the existence of significant varietal differences in stem and leaf ash content (Figure 4). The ratio between leaf and stem ash content decreased as follows: Summer Breeze > Cazimir > Vesta > Giraffe > Bandit > Kalambus > Camus > Premier > Goliath.

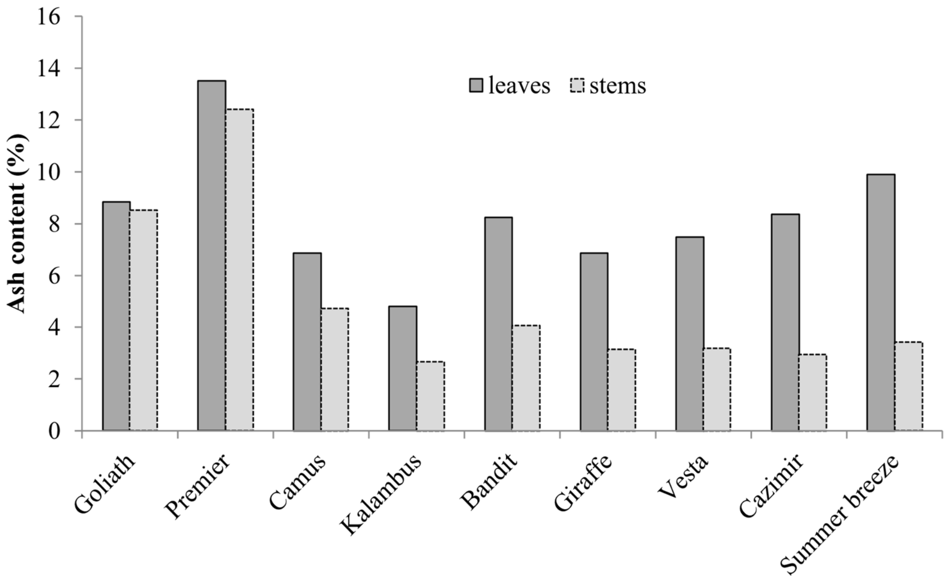

Figure 4. Varietal differences in leek leaf and stem ash content.

The ratio between leaf and stem element content was negatively correlated with stem polyphenol concentration (Figure 5), the latter being therefore related to both content and distribution of minerals in leek plants. As shown in Figure 5, the higher value of angular coefficient was associated with the water extract method, which provides higher mineral concentrations but lower polyphenol levels compared to an ethanol extract.

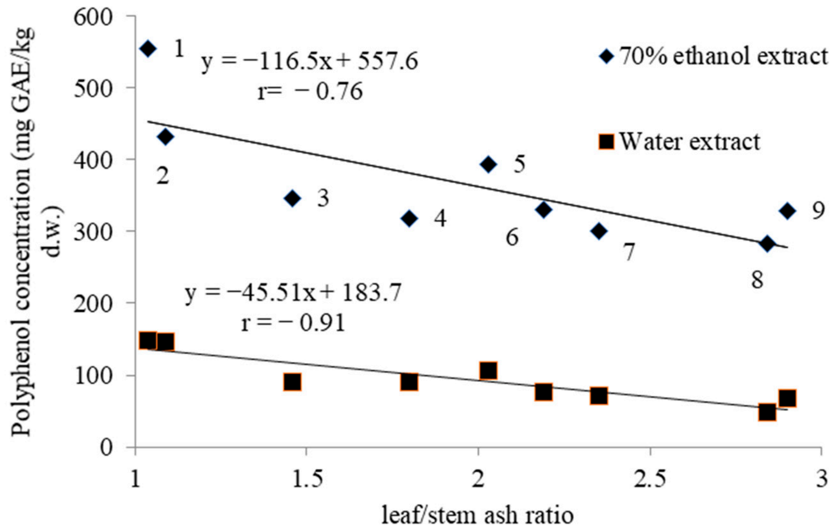

Figure 5. Correlations between leaf/stem ash content and stem polyphenol concentration: (1) Goliath; (2) Premier; (3) Camus; (4) Kalambus; (5) Bandit; (6) Giraffe; (7) Vesta; (8) Cazimir; 9) Summer Breeze.

The analysis of the content of twenty-five mineral elements in leek pseudo-stems has provided the opportunity to assess the varietal differences in elemental profile and has demonstrated that the ash content is directly connected with the concentration of K (Tables 3–5). The latter mineral showed a higher accumulation in pseudo-stems grown with organic management compared to those grown with conventional management (19.46 vs. 17.23 g/kg d.w.), whereas no significant differences were evident between the two management systems with regard to all the other elements analyzed.

Table 3. Macroelement concentration in *A. porrum* pseudo-stems (g/kg d.w.).

Element	Goliath	Cazimir	Premier	Vesta	Kalambus	Summer Breeze	Bandit	Giraffe	Camus
					Macro elements				
Ca	3.98 ^{b,c,z}	3.40 ^{c,d}	11.32 ^{a}	4.35 ^{b}	4.68 ^{b}	2.81 ^{d}	4.82 ^{b}	4.24 ^{b,c}	4.73 ^{b}
K	51.76 ^{a}	4.71 ^{e}	23.39 ^{b}	13.50 ^{c}	8.00 ^{d}	15.94 ^{c}	16.95 ^{c}	15.05 ^{c}	15.82 ^{c}
Mg	0.78 ^{c}	0.76 ^{c}	2.02 ^{a}	0.56 ^{d}	0.53 ^{d}	0.65 ^{c,d}	1.00 ^{b}	0.70 ^{c,d}	0.80 ^{c}
Na	0.34 ^{b,c}	0.39 ^{b}	0.81 ^{a}	0.16 ^{e}	0.16 ^{e}	0.12 ^{e}	0.17 ^{e}	0.19 ^{d,e}	0.28 ^{c,d}
P	2.95 ^{b}	2.61 ^{bc}	2.41 ^{c,d}	2.30 ^{c,d}	1.97 ^{d}	2.37 ^{cd}	3.85 ^{a}	2.64 ^{bc}	2.65 ^{b,c}

^{z} Within each row, means followed by different letters are significantly different according to Duncan's Multiple Range Test at $P \leq 0.05$.

Table 4. Microelements concentration in *A. porrum* pseudo-stems (mg/kg d.w.).

Element	Goliath	Cazimir	Premier	Vesta	Kalambus	Summer Breeze	Bandit	Giraffe	Camus
B	21.25 ^{a,z}	15.21 ^{b,c}	16.75 ^{b}	9.68 ^{d,e}	8.61 ^{e}	9.55 ^{d,e}	9.73 ^{d,e}	12.79 ^{c,d}	11.14 ^{d}
Co	0.070 ^{c}	0.050 ^{d}	0.091 ^{b}	0.034 ^{d}	0.290 ^{a}	0.035 ^{d}	0.035 ^{d}	0.035 ^{d}	0.099 ^{b}
Cu	4.81 ^{d,f}	4.52 ^{e,f}	3.46 ^{g}	5.90 ^{b,c}	6.66 ^{a,b}	5.15 ^{c,e}	7.18 ^{a}	4.08 ^{f,g}	5.53 ^{c,d}
Fe	221 ^{a}	116 ^{c}	178 ^{b}	101 ^{b,d}	77 ^{e}	84 ^{d,e}	98 ^{c,e}	104 ^{c,d}	235 ^{a}
I	0.060 ^{a}	0.040 ^{d}	0.353 ^{a}	0.042 ^{c,d}	0.055 ^{b,d}	0.057 ^{b,d}	0.038 ^{d}	0.071 ^{b,c}	0.073 ^{b}
Li	0.110 ^{b}	0.040 ^{c}	0.160 ^{a}	0.025 ^{c}	0.014 ^{c}	0.032 ^{c}	0.023 ^{c}	0.029 ^{c}	0.109 ^{b}
Mn	12.57 ^{c}	12.18 ^{c}	23.15 ^{a}	9.87 ^{c}	6.39 ^{d}	9.69 ^{c}	10.93 ^{c}	19.97 ^{b}	22.51 ^{a,b}
Si	14.62 ^{c}	10.74 ^{b}	28.78 ^{a}	9.50 ^{e}	13.43 ^{c,d}	13.86 ^{c,d}	11.41 ^{d,e}	20.00 ^{b}	16.17 ^{c}
Sn	0.160 ^{e}	0.240 ^{c,d}	0.023 ^{f}	0.171 ^{e}	0.519 ^{b}	0.193 ^{d,e}	0.574 ^{a}	0.245 ^{c}	0.247 ^{c}
Zn	23.97 ^{a,b}	27.27 ^{a}	11.96 ^{f}	18.45 ^{de}	16.26 ^{e}	19.58 ^{ce}	21.96 ^{b,c}	22.83 ^{b,c}	21.72 ^{b,d}

^{z} Within each row, means followed by different letters are significantly different according to Duncan's Multiple Range Test at $P \leq 0.05$.

Table 5. Heavy metal concentration in *A. porrum* pseudo-stems (mg/kg d.w.).

Element	Goliath	Cazimir	Premier	Vesta	Kalambus	Summer Breeze	Bandit	Giraffe	Camus
					Heavy metals				
Al	84.0 c,z	31.3 d	137.0 a	21.9 d,f	8.0 g	25.3 d,e	12.6 f,g	20.2 e,f	96.2 b
As	0.030 b	0.020 c,d	0.066 a	0.015 c,e	0.013 d,e	0.017 c,e	0.009 e	0.023 b,c	0.066 a
Cd	0.090 c,d	0.110 b,c	0.196 a	0.110 b	0.085 d	0.073 d	0.113 b	0.182 a	0.122 b
Cr	0.130 c	0.080 g	0.524 a	0.104 d,f	0.095 e,g	0.122 c,d	0.085 f,g	0.161 b	0.111 c,e
Ni	1.100 a	0.480 c	1.000 a,b	1.010 a,b	0.578 c	0.588 c	0.875 b	0.621 c	1.140 a
Pb	0.360 b	0.290 b,c	0.894 a	0.108 e	0.096 e	0.143 d,e	0.220 c,d	0.117 e	0.878 a
Sr	29.0 a,b	25.7 c	31.3 a	25.0 c	28.7 a,b	17.8 d	29.3 a,b	26.8 b,c	29.1 a,b
V	0.230 b	0.090 c,d	0.311 a	0.079 c,d	0.043 e	0.097 c	0.066 d,e	0.073 c,d	0.299 a

z Within each row, means followed by different letters are significantly different according to Duncan's Multiple Range Test at $P \leq 0.05$.

The comparison between the nine leek cultivars, in terms of elemental composition, has indicated three cultivars with contrasting features: Premier, Goliath and Cazimir. Indeed, Premier preferably accumulated Co, I, Al, As, Cd, Ni, Pb and Sr, but low levels of Cu and Zn. Goliath was characterized by the highest content of Fe, B, Zn, Se and K, and the lowest of Cd. Cazimir showed the highest concentration of Zn and Na, but the lowest of I, Se, K, Cr and Ni.

In our research, the nine leek cultivars have shown higher concentrations of most elements, compared to twenty varieties belonging to related species such as garlic grown in the same geochemical conditions [42]: Ca, Na, As, Cr, Ni, Co, Fe, I, Li, Pg, Sr, V, B, Co, Fe, I, Li, Sn; equal amounts of K, Mg, P, Cd, Cu, Mn, Se and Zn; and lower concentrations of Si. It is worth noting that, in conditions of marginal selenium deficiency in the Moscow region, the average levels of selenium accumulation by leek and garlic did not differ from each other (Figure 6).

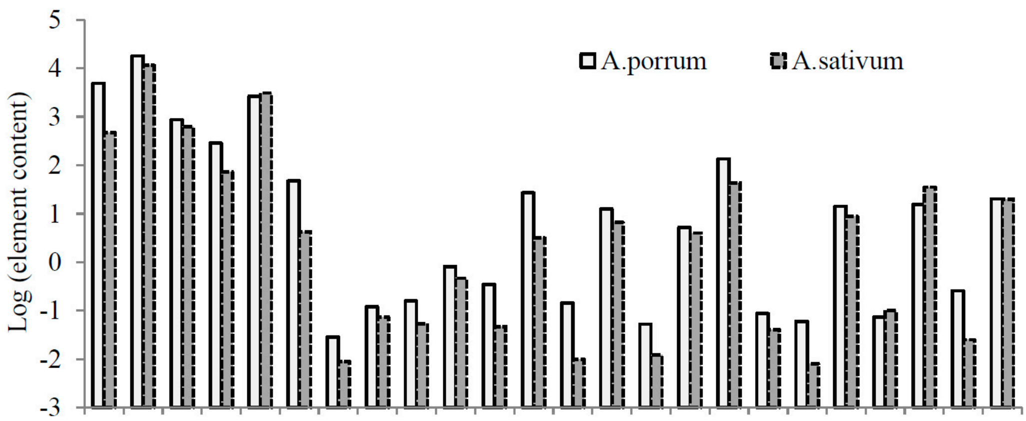

Figure 6. Comparative elemental profile of leek and winter garlic [42] grown in the same geochemical conditions of the Moscow region.

Interestingly, significant varietal differences in the content of most elements were evident (Figure 7). Though the values of the coefficient of variation (CV) relevant to macroelements were considerably lower than those of heavy metals and microelements, even among the former the CV reached 30 to 50%, with the exception of P having lower values. Among heavy metals, Al, Pb, V, As and Cr attained the highest coefficients of variation (40 to 80%), whereas among microelements Li, I, Sn, Co, Fe and Mn showed a CV > 40%.

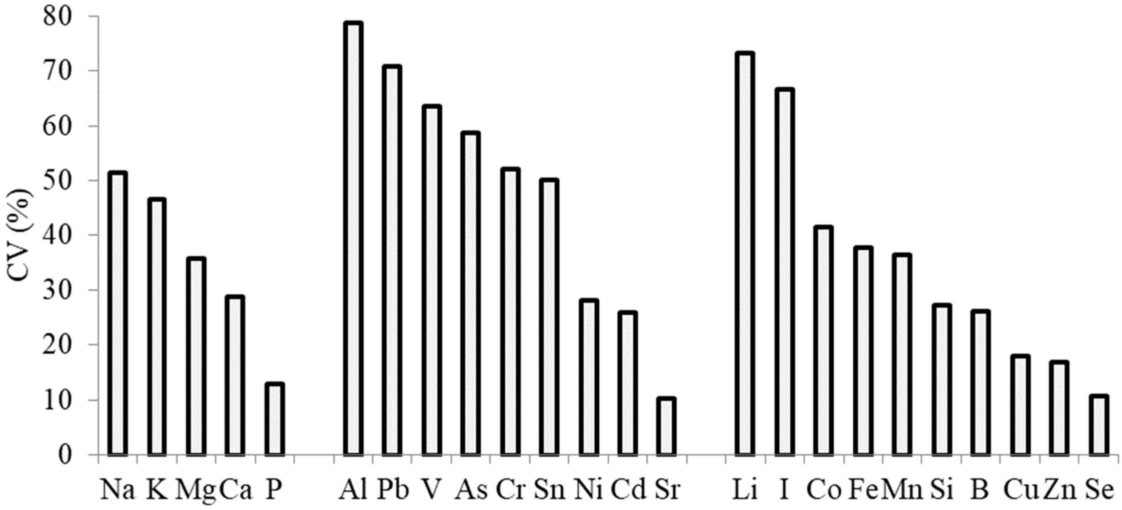

Figure 7. Coefficients of variation relevant to macro- and microelement content in *A.porrum*.

The several significant correlations recorded between the different elements revealed a higher complexity concerning the mineral dynamics in leek plants (Table 6), compared to related species such as garlic [42].

The highest number of significant correlations was recorded for Al, whose physiological role in plants has not been clearly determined so far, though this element is supposed to both activate some enzymes and control membrane permeability at low doses [43]. The significant intra- and interspecies variability in Al accumulation depends on plant tolerance thresholds to this element. The multiplicity of relationships between Al and other elements (Ca, Mg, Na, Co, Li, Fe, I, Cr, Mn, Cr, As, Pb, V) undoubtedly reflects the complex physiological functions of Al in leek. Among the minerals analyzed, the highest correlation coefficients were recorded between Al and As, Pb, V, Co and Li. As for heavy metals and As, highly significant correlations were found between V and Al, As, Co, Pb and Fe.

Following Al, Li showed wide varietal variation, consistent with previous reports [44]. According to the literature, leek is one of the least Li accumulating species. However, compared to Yalamanchali's [45] findings, our results suggest a wider concentration range of Li content in leek plants. The relationships between Li and other elements are in agreement with those reported, and, in particular, correlations between Li and Al, As, Ca, Co, Cr, Fe, I, Pb, Na, V, Co, Pb, V, Fe and Cr were found in five species grown both in ecological unpolluted and in oil polluted areas of Nigeria [46]. Investigations carried out in New Zealand showed correlations between Li, Fe and Ca only in ryegrass (*Lolium perenne)* [47], whereas such relationships were not recorded in lettuce (*Lactuca sativa)* and beet *(Beta vulgaris)* [48]. Positive correlations were also detected in a plant-soil system between Li and Fe, Al and Na.

Among the relationships involving Li, the interactions between this element, Al and Fe should be considered important, as the two latter minerals show similar atomic radius to lithium.

Although varietal differences in Se content in leek were rather low compared to other elements, the significant correlation between Se and K is a remarkable characteristic of this *Allium* species and it has been scarcely investigated so far.

Table 6. Correlation coefficients between mineral elements in leek.

	Al	**As**	**B**	**Ca**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**I**	**K**	**Li**	**Mg**	**Mn**	**Pb**
As	0.93 *	1	0.38												
Ca	0.71 *	0.66	0.29	1											
Cd	0.47	0.54	0.26	0.72 *	1										
Co	0.95 ***	0.95 ***	0.53	0.55	0.37	1									
Cr	0.74 *	0.66	0.40	0.94 ***	0.73	0.53	1								
Fe	0.85 **	0.80 **	0.64	0.31	0.20	0.92 ***	0.30	−0.36	1						
I	0.77 **	0.70 *	0.37	0.96 ***	0.70 *	0.58	0.99 ***	−0.60	0.33	1					
K	0.50	0.23	0.75 [e]	0.13	−0.03	0.39	0.21	−0.23	0.63	0.17	1				
Li	0.99 ***	0.90 ***	0.68	0.70 *	0.46	0.93 ***	0.73 *	−0.59	0.86 **	0.76 *	0.56	1			
Mg	0.75 *	0.65	0.41	0.94 ***	0.69	0.59	0.93 ***	−0.50	0.36	0.94 ***	0.21	0.75 *	1		
Mn	0.74 *	0.86 **	0.36	0.58	0.81 **	0.77 *	0.62	−0.65	0.64	0.62	0.14	0.72 *	0.62	1	
Na	0.83 **	0.71 *	0.64	0.85 **	0.63	0.70	0.88 **	−0.59	0.50	0.90 ***	0.25	0.83 **	0.90 ***	0.61	
Ni	0.65	0.58	0.32	0.38	0.16	0.66	0.27	0.01	0.76 *	0.29	0.60	0.65	0.34	0.42	
Pb	0.92 ***	0.97 ***	0.38	0.67	0.47	0.97 ***	0.63	−0.42	0.80 **	0.68	0.22	0.90 ***	0.71 *	0.79 **	1
Se	0.35	0.05	0.69	0.14	−0.06	0.19	−0.72 *	−0.16	0.42	−0.71 *	0.95 ***	0.42	0.18	−0.03	0.04
Si	0.72 *	0.72 *	0.39	0.83 **	0.80 **	0.57	0.91 ***	−0.70	0.37	0.90 ***	0.23	0.72 *	0.81 **	0.77 *	0.64
Sn	−0.66	−0.57	−0.57	−0.37	−0.39	−0.53	−0.58	0.844 [c]	−0.47	−0.55	0.26	−0.64	−0.42	−0.52	−0.45
V	0.98 ***	0.94 ***	0.56	0.60	0.38	0.98 ***	0.61	−0.50	0.91 ***	0.65	0.51	0.97 ***	0.64	0.75 *	0.94 ***
Zn	−0.34	−0.33	0.21	−0.74 *	−0.31	−0.15	−0.69	0.05	0.07	−0.71 *	0.05	−0.31	−0.54	−0.14	−0.29

*** $P < 0.001$; ** $P < 0.01$; * $P < 0.05$.

In spinach (*Spinacia oleracea*) plants fertilization with sodium selenate increased K content in female but not male plants [21], whereas in other research [49] garlic biofortification led to selenium antagonistic activity towards K. Taking into account that K participates in plant protection against all forms of biotic and abiotic stresses along with Se and other components of antioxidant defense systems [50], the close relationship between the two minerals in leek suggests intensive interactions of all components of the defense system. The predominance of K in leek elemental composition and the significant correlation between polyphenol concentration and ash content (Figure 5) is in good agreement with the mentioned results. The correlation coefficient relevant to ash to K in leek was 0.78 at $P < 0.01$, whereas that related to K and polyphenols reached 0.96 at $P < 0.01$. The known ability of K to decrease the activity of polyphenol oxidase in plants and enhance polyphenol accumulation [51] may be a good explanation of the positive correlation between polyphenols and K in leek plants. The active participation of K in the antioxidant defense system of this *Allium* species was also characterized by a positive correlation of the element with the ascorbic acid content ($r = 0.95$ at $P < 0.01$). In this respect, the results of the present work revealed the close relationship between the main components of leek antioxidant systems including polyphenols, ascorbic acid as well as the macro- and trace elements Se and K.

In our research, the lowest negative correlation coefficients were Se with Cr and I. Se is known as an antagonist of Cr and its protective role towards Cr has been previously reported [24,52,53]. The interaction between Se and I is more complex; neither element is essential for plants, but at low concentrations, they may improve plant growth, development and protection from biotic and abiotic stresses [54]. However, the rather scarce and contradictory data about Se and I interactions in plants do not allow clear conclusions. Separate plant fortification with Se and I showed the possibility of mutual stimulation by the two elements in some but not all cases [40]. The selective accumulation of selenium in male spinach plants and of iodine in female spinach plants suggests the participation of phytohormones in the interactions between Se and I [21]. A negative correlation between Se and I in leek plants has not yet been reported.

4. Conclusions

From research carried out in the Moscow region with the aim of evaluating the performance of nine leek (*A. porrum*) cultivars grown in greenhouses under either organic or conventional management systems, interesting clues have been drawn. The varieties showed a uniform behavior under both management systems: no yield differences were recorded between organic and conventional systems. When cultivated with organic procedures, all cultivars attained higher dry matter, sugar, ascorbic acid and potassium content but lower nitrates in the pseudo-stems than for conventional management, but with the same ranking as for conventional management. Moreover, in contrast to related species, highly significant correlations between the antioxidants and mineral elements in leek plants provide opportunities for obtaining genotypes with improved quality features.

Author Contributions: N.A.G. and G.C. designed the experimental protocol; T.M.S. and G.C.T. were concerned with the crop organic management; N.A.G., M.S.A. and O.V.K. performed analytical measurements; G.C. and N.A.G. equally performed the data statistical processing and manuscript writing.

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