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ENVIRONMENTAL ANALYSIS

Trace Elemental Analysis of *Allium* Species by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) with Multivariate Chemometrics

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ABSTRACT
Aerial parts and roots of the 12 *Allium* species collected from five localities of Turkey were studied for trace elements (Ag, As, Cd, Co, Cr, Cu, Ni, Pb, Se, Tl, V, and Zn) using inductively coupled plasma mass spectrometry (ICP-MS). A tomato leaves certified reference material was used to characterize the accuracy and precision of the analysis. Each *Allium* species contained Se (315–2740 µg/kg), Tl (2.75–71 µg/kg), V (77–6790 µg/kg), and Zn (3.73–26.6 mg/kg) which can meet the necessary daily intake of these minerals. In addition, chemometric analyses were performed using correlation analysis, principal component analysis, and hierarchical cluster analysis to determine the association of 12 trace elements in the *Allium* species. Using chemometrics, the distribution of elements between aerial parts and roots, and geographic collection localities of *Allium* species were also examined. This study is important the consumers because of the wide consumption of *Allium* species. This report is the first detailed characterization of the metal content of *Allium* species.

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Allium species; hierarchical cluster analysis; inductively coupled plasma mass spectrometry; principal component analysis; trace elements

Introduction

The *Allium* genus belonging to Amaryllidaceae family is represented by more than 800 species around the world, 179 of which grow naturally in Turkey (Guner et al. 2012). Garlic (*A. sativum*), leek (*A.ampeloprasum*), and onion (*A. cepa*) are well-known *Allium* species. Generally, *Allium* genus is native to the Northern Hemisphere. Most of the garlic smelling *Allium* species are in the Eastern Europe and Western Asia (Guner et al. 2012). Various types of onion and garlic have been used medicinally and also consumed as food since ancient times.

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In general, the leaves and bulbs of some of the *Allium* species are cultured for consumption (Özçelik 1992; Ozyurt et al. 2013; Devi et al. 2014). The whole parts of *Allium* species are used for the preparation of cheese (Özçelik 1992), and the leaves and roots are used in meals, pilaf, and soups (Baytop 1999; Devi et al. 2014; Fırat 2015a, 2015b). Due to the edibility, scientists have been interested in search *Allium* species for years. These scientific studies revealed that onion and garlic possessed various biological and pharmacological activities. Therefore, the extracts obtained from different *Allium* species are used in modern medicine (Shirshova et al. 2013). In particular, onions and garlic have potential health benefits against many diseases (Fırat 2015a, 2015b). To the best of our knowledge, *Allium* species minimize or stop the progress of cancer, respiratory tract, gastroenterological, asthma, joint pains, rheumatism, liver failure diseases due to their antibiotic, and antiseptic and antioxidant properties (Corzo-Martinez et al. 2007).

Trace elements are necessary for the human diet. The medicinal plants are valuable sources of the elements which have different roles in biological systems (Basgel and Erdemoglu 2006; Negi et al. 2012). They play important roles in the formation of bioactive pharmaceuticals in the living organisms. The elemental composition of medicinal plants and foods should be well defined since medicinal plants can be contaminated easily during cultivation (Wesolowski and Konieczynski 2003; Basgel and Erdemoglu 2006). The connection of trace elements and living organisms is mainly plants. Therefore, the level of these elements in medicinal plants is very important and affected by the geochemical conditions of the soil and the accumulation ability of plant for these elements.

Bioavailability of the trace elements depends on their form of accumulation in plant such as ionic or non-ionic form and this term is important for metal toxicity in living organisms (Basgel and Erdemoglu 2006). Excessive concentrations of elements such as chromium, copper, cobalt, iron, and zinc lead to metal toxicity (Abugassa et al. 2008). Heavy metals such as cadmium, lead, and mercury are toxic even at low concentrations (Tokalioglu 2012). There are various reasons for the heavy metal accumulation in plants. The cadmium and lead concentrations in plants growing near industrialized cities are high due to the environmental pollution. Accordingly, high levels of arsenic and other heavy metals may be related to the over-application of fertilizers and pesticides (Matos-Reyes et al. 2010; Giacomino et al. 2015). Macro- and micro-environmental variables of soil and climate may change the elemental compositions of the same species (Wesolowski and Konieczynski 2003). Considering these facts, it is important to examine the trace element composition of medicinal plants and foods (Nookabkaew et al. 2006; Abugassa et al. 2008).

To determine the trace element composition in plants, many techniques have been used such as graphite furnace atomic absorption spectrometry (Kalicanin and Velimirovic, 2013), flame atomic absorptions spectrometry (Shen et al. 2015; Basgel and Erdemoglu 2006; Choudhury and Garg 2007; Tokalioglu 2012; Pereira and Dantas 2016; Yildiz et al. 2016), inductively coupled plasma optical emission spectrometry, (Basgel and Erdemoglu 2006; Pytlakowska et al. 2012; Szymczycha-Madeja et al. 2013; Froes et al. 2014; Szymczycha-Madeja et al. 2015) and inductively coupled plasma mass spectrometry (ICP-MS) (Filipiak-Szok et al. 2015; Tokalioglu 2012; Bora et al. 2015; Milani et al. 2015; Hwang et al. 2016; Nho et al. 2017; Voica et al. 2017) and X-ray fluorescence spectrometry (Vassileva and Hoenig 2001; Sun et al. 2004). Among the techniques, ICP-MS is effective and widely used due to its excellent precision, accuracy and wide dynamic range in determining multiple elements at trace levels.

The aim of the present study is to determine silver (Ag), arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), selenium (Se), thallium (Tl), vanadium (V), and zinc (Zn) by ICP-MS technique in different tissues of 12 *Allium* species, which were collected from Hakkari, Van, Şırnak, Malatya, and Adıyaman, Turkey technique. Chemometric analyses were performed using principal component analyses (PCA) and hierarchical cluster analyses (HCA) to evaluate the relationship between the selected metals and the different parts of *Allium* species with the collection locations. The results of this study provide a better understanding of the trace element content of *Allium* species and facilitate the identification of plants for further investigations.

Materials and methods

Collection and preparation of plant samples

The trace elemental composition (Ag, As, Cd, Co, Cr, Cu, Ni, Pb, Se, Tl, V, and Zn) of aerial parts and roots of the 12 *Allium* species collected from five regions of Turkey (Hakkari, Van, Şırnak, Malatya, and Adıyaman) were studied by ICP-MS.

The samples were washed with tap water, then ultrapure deionized water and dried at 70°C for 48 h. The dried samples were powdered using a blender (Basgel and Erdemoglu 2006; Tokalioglu 2012; Pereira and Dantas 2016).

The species, notations, and provenance of the *Allium* species are given in Table 1. The aerial parts and roots were coded as A (*Allium* sp.), ap (aerial parts) and r (roots), respectively.

Table 1. List of species, abbreviations, collection locations, and herbarium numbers of the *Allium* species.

Allium species	Abbreviations	Collection localities	Herbarium numbers
Allium subakaka	AAHap[a]	Hakkari	M Fırat 31017
Allium subakaka	AAHr	Hakkari	M Fırat 31017
Allium subakaka	AAVap[a]	Van	VANF 164090
Allium atroviolaceum	AAap[a]	Van	M Fırat 31039
Allium atroviolaceum	AAr	Van	M Fırat 31039
Allium chrysantherum	ACr	Şırnak	M Fırat 30188
Allium kharputense	AKap[a]	Malatya	VANF 164091
Allium kharputense	AKr	Malatya	VANF 164091
Allium rhetoreanum	ARap[a]	Hakkari	VANF 164084
Allium scabriscapum	ASap[a]	Van	M Fırat 31171
Allium scabriscapum	ASr	Van	M Fırat 31171
Allium scorodoprasum subsp. *roturdum*	ASRap[a]	Van	VANF 164093
Allium scorodoprasum subsp. *roturdum*	ASRr	Van	VANF 164093
Allium shatakiense	ASHap[a]	Van	VANF 164086
Allium shatakiense	ASHr	Van	VANF 164086
Allium shirnakiense	ASlap[a]	Şırnak	VANF 164085
Allium shirnakiense	ASlr	Şırnak	VANF 164085
Allium tripedale	ATap[a]	Hakkari	M Fırat 30835
Allium vineale	AVap[a]	Van	VANF 164089
Allium vineale	AVlr	Malatya	VANF 164087
Allium ssp.	ASSap[a]	Adıyaman	VANF 164088
Allium ssp.	ASSr	Adıyaman	VANF 164088

[a]ap: aerial parts and r: roots.

Reagents

Ultrapure deionized water (18.2 MΩ cm^{-1}) was used in all experiments. Nitric acid (Merck, Darmstadt, Germany) and hydrogen peroxide (Merck, Darmstadt, Germany) with analytical purity were used in the digestion process. Internal and calibration standards were obtained from Agilent Technologies (USA).

In the ICP-MS measurements, high purity solutions of ^{45}Sc for Co, Cr, Cu, Ni and V; ^{72}Ge for As, Se and Zn; ^{115}In for Ag; and ^{209}Bi for Cd, Pb and Tl were used as the mixed internal standards (200 µg/L). The calibration standard solutions (0–100 µg/L) were prepared by appropriate dilution of the stock mixed standards (10 mg/L).

Digestion of the samples

The powdered samples (200 mg) were digested with concentrated HNO_3 (6 mL) and H_2O_2 (2 mL) using a microwave system. After completion of the process, the cooled and digested samples were transferred from polytetrafluorethylene tubes to volumetric flasks and diluted to 25 mL with ultrapure deionized water. During the experiments, all glassware and equipment were carefully cleaned starting with 2–4% HNO_3 and ending with repeated rinsing with ultrapure deionized water to prevent contamination (Basgel and Erdemoglu 2006). Three blank solutions were also prepared. The same digestion process was applied to the CRM NIST1573a tomato leaves in order to determine the accuracy and precision of the method.

Instrumentation

An Agilent 7700X ICP-MS (Tokyo, Japan) was used for the determination of Ag, As, Cd, Co, Cr, Cu, Ni, Pb, Se, Tl, V, and Zn in the samples. The operating conditions for the ICP-MS are shown in Table 2. High purity argon was used as a carrier, makeup, and plasma gas. Helium was used to eliminate interferences. Digestion procedure of the samples prior to analysis was carried out in a Milestone Start D microwave digestion system (Denmark). The operation conditions of the microwave digestion system are given in Table 3.

Table 2. Optimum ICP-MS operating conditions for the analysis of *Allium* species (Bora et al. 2015).

Instrument parameter	Condition
Radio frequency power	1550 W
Radio frequency	27.12 MHz
Radio frequency matching	1.80 V
Carrier gas (inner)	1.1 L/min
Makeup gas	0.9 L/min
Plasma gas	Ar X50S 5.0
Plasma gas flow (Ar)	15 L/min
Nebulizer pump	0.1 rps
Sample intake	0.5 mL/min
Spray chamber temperature	2°C
Resolution *m/z*	244 amu
Background	<5 cps (9 amu)
Short-term stability	<3% RSD
Long-term stability	<4% RSD/2 h
Isotopes measured	^{51}V, ^{52}Cr, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{75}As, ^{78}Se, ^{107}Ag, ^{111}Cd, ^{205}Tl, ^{208}Pb

Table 3. Microwave operating conditions for the digestion of *Allium* species (Bora et al. 2015).

Step	Time (min)	T1 (°C)	T2 (°C)	*P* (bar)	Power (W)
1	15	200	110	45	1200
2	15	200	110	45	1200

Performance parameters

The linear range, regression correlation coefficient (r^2), limits of quantification (LOQ) and limits of detection (LOD) values, which belong to the calibration curve drawn under the optimum operating conditions for 12 elements, are given in Table 4. The linearity was evaluated to be acceptable for r^2 values that were higher than 0.99. The limits of detection and quantification for the metals were calculated using standard deviation (σ_{blank}) of 12 independent blank solutions and the slope (m) of the calibration graph to obtain

$$\text{LOD or LOQ} = a \times \frac{\sigma_{\text{blank}}}{m} \quad (1)$$

where a is equal to 3 for the LOD and 10 for the LOQ. The accuracy and precision of the method were evaluated using certified reference material CRM NIST1573a tomato leaves (National Institute of Standards and Technology, NIST, Gaithersburg, MD, USA). The analytical results for CRM NIST1573a tomato leaves are given in Table 5.

Statistical analysis

Common chemometric techniques include PCA and the HCA. PCA is a multivariate data analysis method that provides the relationship between the samples and the interaction between the variables. This technique reveals new relationships and is used to make predictions which cannot be characterized as ordinary results (Diraman and Dibeklioglu 2009). Based on a large number of variables on a given sample system, PCA-based methods can cluster and classify the mentioned samples into various groups. Principal component analysis was applied to clear classification of the analyzed trace elements of plant samples belonging to same species.

Table 4. Analytical parameters of the ICP-MS method (Bora et al. 2015).

Element	Linear range (μg/kg)	Regression	Correlation coefficient (*r*)	Limit of detection (μg/kg)	Limit of quantification (μg/kg)
Ag	0–100	$y = 0.4810\ x - 2.5400$	0.9818	0.2356	0.7068
As	0–100	$y = 0.0773\ x + 0.1801$	0.9963	0.1607	0.5328
Cd	0–100	$y = 0.0344\ x + 0.0280$	0.9993	0.0132	0.0396
Co	0–100	$y = 0.1221\ x + 0.0811$	0.9977	0.2202	0.6606
Cr	0–100	$y = 0.1026\ x + 0.3012$	0.9969	0.2175	0.6525
Cu	0–100	$y = 0.0662\ x + 0.1028$	0.9999	1.0200	3.0600
Ni	0–100	$y = 0.0282\ x + 0.0370$	0.9999	0.3108	0.9324
Pb	0–100	$y = 0.1861\ x + 0.2314$	0.9996	0.0832	0.2777
Se	0–100	$y = 0.0024\ x + 0.0075$	0.9920	0.4321	1.2963
Tl	0–100	$y = 0.1388\ x - 0.1225$	0.9994	0.9151	2.7453
V	0–100	$y = 0.1178\ x + 0.0854$	0.9999	0.2236	0.7446
Zn	0–100	$y = 0.0837\ x + 0.1766$	0.9996	0.3685	1.2270

Values expressed are means ± standard deviation of three parallel measurements ($p < 0.05$).

Table 5. Accuracy assessment by the analysis of the tomato leaves certified reference material (CRM NIST1573a) (Bora et al. 2015).

Elements	Certified (mg/kg)	Found (mg/kg)	Fortified recovery (%)
As	0.122 ± 0.004	0.127 ± 0.005	104
Cr	1.99 ± 0.06	2.01 ± 0.08	101
Cd	1.52 ± 0.04	1.49 ± 0.04	98
Co	0.57 ± 0.02	0.56 ± 0.06	98
Cu	4.70 ± 0.14	4.76 ± 0.08	101
Ni	1.59 ± 0.07	1.57 ± 0.11	99
Se	0.054 ± 0.003	0.051 ± 0.003	94
V	0.835 ± 0.010	0.826 ± 0.008	99
Zn	30.9 ± 0.7	31.3 ± 0.2	101

Values expressed are means ± standard deviation of three parallel measurements ($p < 0.05$).

Cluster (CA) technique gives information about the classification of the samples. HCA is a method which classifies the samples in a given sample set and the variables defining those samples by their similarities.

Minitab 16.2.1. statistical software (MINITAB Inc., 2010) was used for statistical analysis of the data. Among the methods of multivariate data analysis, PCA and HCA were used on experimental measurements of the trace element components of the *Allium* species. The chemometric analysis was applied to discriminate and classify parts and geographic origins of 12 *Allium* species according to trace element concentrations. The main goal while performing PCA and HA methods to the entire data set was to examine similarities between the *Allium* species and trace element concentrations.

Results and discussion

The trace elements concentrations of *Allium* species are presented in Table 6. The results exhibited that the concentrations of studied metals (Ag, As, Cd, Co, Cr, Cu, Ni, Pb, Se, Tl, V, and Zn) varied depending on the parts of *Allium* species (aerial parts or root), and the collection localities. Cu and Zn concentrations were relatively high in all species while Tl existed at the lowest concentrations.

The concentrations of Ag and Se metals in aerial parts and roots of *A. kharputense* (AKap, AKr) and *A. shatakiense* (ASHap, ASHr) were at the same level. Moreover, the levels of Se and Tl were same in the aerial parts and roots of *A. shirnakiense* (ASIap, ASIr). The Ag, Cd and Tl levels were similar in *A. scorodoprasum* subsp. *roturdum* samples (ASRap, ASRr). The levels of other elements differed from part to part.

Arsenic can be commonly found in food. Medicinal plants, vegetables, pulses, and cereals generally represent the source of arsenic intake. The level of human exposure is considered part of the health protection programs because of its toxicity (d'Amato et al. 2004; Sanz et al. 2005; Matos-Reyes et al. 2007). Therefore, it is important to monitor arsenic available in foods (Matos-Reyes et al. 2010). As can be seen from Table 6, the concentration of arsenic was between 13 and 325 µg/kg in the *Allium* species. Matos-Reyes et al. (2010) found 39 and 83 µg/kg of arsenic in onion and garlic, respectively. Choudhury and Garg (2007) determined arsenic to be in the ranges of 55.1–111.0 µg/kg in the medicinal plant *Murraya koenigii*, which is grown in different cities of India.

The cadmium concentrations of samples varied between 17 and 703 µg/kg. The World Health Organization (WHO) reported the permissible level for Cd in edible plants to be

Table 6. Trace element concentrations of *Allium* species by ICP-MS.[a]

Allium species	Abbreviations	^{51}V (μg/kg)	^{52}Cr (μg/kg)	^{59}Co (μg/kg)	^{60}Ni (μg/kg)	^{63}Cu (μg/kg)	^{66}Zn (μg/kg)	^{75}As (μg/kg)	^{78}Se (μg/kg)	^{107}Ag (μg/kg)	^{111}Cd (μg/kg)	^{205}Tl (μg/kg)	^{208}Pb (μg/kg)
A. subakaka	AAHap	77 ± 3	485 ± 10	37.12 ± 1.48	340 ± 10	1642 ± 30	3734 ± 17	13.05 ± 0.04	315 ± 6	7.08 ± 0.06	17.08 ± 0.10	<LOQ	132 ± 4
A. subakaka	AAHr	123 ± 4	507 ± 12	87 ± 2	899 ± 13	2940 ± 40	13422 ± 40	27.75 ± 012	1241 ± 11	11.64 ± 0.08	49.69 ± 1.10	5.75 ± 0.02	80 ± 2
A. subakaka	AAVap	1405 ± 35	2415 ± 10	291 ± 8	1904 ± 60	7601 ± 23	20793 ± 60	209 ± 6	2391 ± 50	449 ± 10	184 ± 8	15.32 ± 0.10	799 ± 24
A. atroviolaceum	AAap	949 ± 20	1218 ± 30	189 ± 6	1019 ± 31	5989 ± 13	25036 ± 75	214 ± 6	2416 ± 30	127 ± 4	84 ± 3	13.21 ± 0.10	1028 ± 30
A. atroviolaceum	AAr	305 ± 90	375 ± 9	50 ± 2	386 ± 12	5968 ± 11	26656 ± 78	58 ± 2	1973 ± 20	76 ± 2	43.54 ± 2.01	<LOQ	131 ± 4
A. chrysantherum	ACr	162 ± 7	322 ± 8	58 ± 2	575 ± 18	2676 ± 26	24523 ± 75	73 ± 3	2005 ± 40	111 ± 3	703 ± 10	71 ± 2	1736 ± 52
A. kharputense	AKap	2333 ± 33	1644 ± 55	575 ± 15	3626 ± 10	4001 ± 12	18003 ± 54	225 ± 7	1168 ± 35	119 ± 4	59 ± 2	15.87 ± 0.13	493 ± 15
A. kharputense	AKr	6790 ± 22	331 ± 4	1482 ± 47	6934 ± 21	5984 ± 18	16885 ± 48	842 ± 9	1117 ± 35	183 ± 5	200 ± 6	50 ± 2	1911 ± 30
A. rhetoreanum	ARap	684 ± 21	1055 ± 40	151 ± 5	1128 ± 33	2970 ± 60	12386 ± 37	89 ± 4	1088 ± 30	13.77 ± 0.09	378 ± 11	7.98 ± 0.01	416 ± 12
A. scabriscapum	ASap	944 ± 14	1230 ± 28	217 ± 7	903 ± 27	3175 ± 10	9703 ± 29	101 ± 5	1747 ± 55	55 ± 2	43.23 ± 1.10	10.45 ± 0.02	282 ± 6
A. scabriscapum	ASr	4359 ± 13	4041 ± 16	847 ± 9	2702 ± 81	3975 ± 11	10178 ± 30	325 ± 8	2370 ± 70	117 ± 5	59 ± 2	24.43 ± 1.07	867 ± 25
A. scorodoprasum subsp. *roturdum*	ASRap	302 ± 9	1048 ± 30	70 ± 2	767 ± 23	3740 ± 41	8922 ± 27	57 ± 2	1266 ± 40	21.43 ± 0.10	138 ± 4	5.09 ± 0.01	478 ± 15
A. scorodoprasum subsp. *roturdum*	ASRr	947 ± 7	1515 ± 20	230 ± 7	1227 ± 36	3109 ± 50	4225 ± 12	167 ± 5	1006 ± 30	14.34 ± 0.03	174 ± 5	7.09 ± 0.02	626 ± 19
A. shatakiense	ASHap	811 ± 7	1242 ± 15	175 ± 5	1306 ± 39	3568 ± 10	9241 ± 21	238 ± 6	1154 ± 35	9.19 ± 0.05	88 ± 3	11.90 ± 0.05	479 ± 15
A. shatakiense	ASHr	381 ± 9	758 ± 21	107 ± 3	977 ± 28	5639 ± 17	10654 ± 30	107 ± 4	986 ± 30	10.98 ± 0.10	46.32 ± 1.20	5.09 ± 0.02	317 ± 10
A. shirnakiense	ASIap	2592 ± 64	3436 ± 14	603 ± 18	3582 ± 11	6316 ± 18	20071 ± 60	319 ± 90	2740 ± 55	501 ± 10	181 ± 5	26.76 ± 1.05	1373 ± 45
A. shirnakiense	ASIr	1277 ± 33	1759 ± 75	288 ± 11	1977 ± 60	3102 ± 10	10575 ± 30	162 ± 50	2622 ± 55	221 ± 7	88 ± 5	15.56 ± 0.10	813 ± 24
A. tripedale	ATap	637 ± 21	1273 ± 50	135 ± 40	1285 ± 40	3153 ± 10	14292 ± 45	97 ± 30	1388 ± 45	14.32 ± 0.10	368 ± 11	7.88 ± 0.02	303 ± 10
A. vineale	AVap	479 ± 15	1487 ± 55	114 ± 30	1581 ± 45	8686 ± 24	18447 ± 55	52 ± 20	1297 ± 40	17.94 ± 0.05	106 ± 34	25.93 ± 1.08	668 ± 23
A. vineale	AVIr	627 ± 21	872 ± 27	231 ± 60	2021 ± 60	4816 ± 14	14341 ± 45	63 ± 20	1281 ± 40	10.21 ± 0.10	63 ± 2	12.89 ± 0.05	344 ± 8
Allium sp.	ASSap	3400 ± 11	3311 ± 14	853 ± 26	2513 ± 75	4563 ± 14	8486 ± 25	170 ± 50	2231 ± 70	167 ± 5	71 ± 3	16.09 ± 0.05	384 ± 9
Allium sp.	ASSr	1433 ± 28	1534 ± 55	515 ± 16	1977 ± 58	2966 ± 87	10605 ± 30	54 ± 20	1974 ± 60	64 ± 2	59 ± 2	5.90 ± 0.01	80 ± 2

[a]Values expressed are means ± standard deviation of three parallel measurements ($p < 0.05$).

200 μg/kg (Dubale et al. 2015; WHO 2007). The Cd levels of all the samples, except ATap, ARap, and ACta, were below the WHO limits. The Cd content was also detected to be 200 μg/kg in *Allium cepa* grown in two places in Africa (Bvenura and Afolayan 2012).

Another essential element, chromium serves as a cofactor in insulin synthesis and cholesterol. In this study, the concentration of Cr was found in the ranges of 322–4044 μg/kg in the *Allium* species. Between the *Allium* groups, the concentration of Cr was the highest in ASr (4044 μg/kg) and the concentration of the Cr was lowest in ACr (322 μg/kg) samples. Camargo et al. (2010), determined Cr to be 15.3–39.4 mg/kg in 10 *Allium sativum* L. species grown in Argentina.

In the raw herbal plant materials, the toxicity limits for lead, arsenic, chromium, and cadmium were reported to be 10.0, 5.0, 2.0, and 0.3 ppm, respectively (WHO 2007; Pereira and Dantas 2016).

Plants require nutrients including trace elements that are found in the soil (Taha et al. 2013). Zinc is one of the basic elements necessary for plant growth. Among the *Allium* species, the Zn concentrations were comparatively high. Similar result was obtained in the study of Razic et al. 2003 for the purple coneflower (*Echinacea purpurea*). Zinc in the *Allium* species was in the range of 3.73–26.66 mg/kg. The highest Zn concentration was encountered in AAr (26.66 mg/kg), while the lowest was in AAHap (3.73 mg/kg). The WHO has established the permissible level for Zn in edible plants as 27.40 mg/kg (WHO 2007). The Zn concentrations of the studied *Allium* species were below the permissible level. In recent studies, the Zn levels were in the range of 46.34–89.88 mg/kg in onions growing in South Africa (Bvenura and Afolayan 2012), 439–957 mg/kg in *Allium sativum* L. growing in Argentina (Camargo et al. 2010), and 0.92–1.53 mg/kg in *A. cepa* L. from Tenerife (Galdon et al. 2008).

Hitherto, there has been no cobalt level criteria established in medicinal plants (Dubale et al. 2015). The concentration of Co varied from 37 to 853 μg/kg in *Allium* species. The highest concentration was determined in ASSap (853 μg/kg), while the lowest in AAHap (37 μg/kg). Camargo et al. (2010) determined Co to be 0.216–2.490 mg/kg in *Allium sativum* L. from Argentina.

Copper is a micronutrient element for plants. Excessive concentrations are toxic (Tarakci and Temiz 2009; Brun et al. 2001) and harmful to human health. Furthermore, it can decrease hypertension and enhance the infertility effects of lead (Vitali et al. 2008). The Cu concentration of the tested *Allium* species were 1.64–8.69 mg/kg. The highest concentration of Cu was in AVap (8.69 mg/kg) and the lowest in AAHap (1.64 mg/kg). Bvenura and Afolayan (2012) found Cu to be 7.56–9.24 mg/kg in onions (*A. cepa*) from South Africa. Galdon et al. (2008) determined Cu to be 0.25–0.41 mg/kg in the *A. cepa*. The WHO established the permissible level for Cu in edible plants to be 3 mg/kg (WHO 2007). The Cu concentration of the *Allium* species, except AAHap, AHHr, ACr and Arap, exceeded these limits.

The cadmium concentrations of *Allium* species ranged from 17 to 703 μg/kg. The WHO has assigned the permissible level for Cd in edible plants to be 200 μg/kg (Dubale et al. 2015; WHO 2007). The Cd levels of all samples, except ATap, ARap, and ACta, were below the WHO limit. Bvenura and Afolayan (2012) determined Cd to be 0.20 mg/kg in *A. cepa* from two African locations (Bvenura and Afolayan 2012; Tokalioglu 2012).

Lead is a highly toxic heavy metal which causes various health problems including anemia, chills, diarrhea, headache, behavior disorders, and mental retardation (Singh et al. 2008; Oymak et al. 2009; Liu et al. 2010; Terzioglu et al. 2017). The Pb concentrations of samples varied between 0.08 and 1.74 mg/kg. The Pb concentrations of all *Allium* species, except ASIap and AAap, were below the WHO limit (10 mg/kg) for Pb (Dubale et al. 2015; WHO 2007).

The WHO has provided reported the permissible level for Ni in edible plants to be 1.63 mg/kg (WHO 2007). However, there are not any established WHO limits for Ni in medicinal plants. Nickel-induced toxicity in humans is rare since the Ni absorption in the body is very low. The Ni concentrations of studied *Allium* species varied between 0.34 and 3.63 mg/kg.

Selenium is essential trace element necessary for people and animals. It has antioxidant, anti-inflammatory, and immunological properties and also protective effects against toxic elements, cancer, and heart problems (Al-Saleh 2000; Chope et al. 2016). The Se concentrations of *Allium* species varied between 0.32 and 2.74 mg/kg.

Thallium is more toxic than mercury, lead, and cadmium. It can be harmful to living organisms even at very low levels (Leonard and Gerber 1997; Nriagu 1998). The intake of 20–60 mg of thallium per kilogram human body weight can be fatal. In this study, the samples had low thallium concentrations (2–71 µg/kg).

Vanadium has both positive and negative health effects. Its compounds lead to hypoglycemia by lowering blood sugar for people, while they can be evaluated as an antineoplastic agent against human cancer (Evangelou 2002). There is not any study in the literature conducted on the determination of V and Ag elements in garlic species. V and Ag have been examined in the *Allium* species for the first time. The V and Ag concentrations of samples were 0.77–4.36 mg/kg and 7–501 µg/kg, respectively.

In the raw herbal plant materials, the toxicity limits for lead, arsenic, chromium, and cadmium have been reported to be 10.0, 5.0, 2.0, and 0.3 ppm, respectively (Pereira and Dantas 2016; WHO 2007).

The magnitude of heavy metal accumulation determined in different tissues of *Allium* species was arranged as Zn > Cu > Cr > Pb > Cd. Our results were in agreement with those of Ali and Al-Qahtani (2012) who reported the concentration of heavy metals (Fe, Mn, Cu, Zn, Pb, Cd, and Hg) in various vegetables (turnips, carrot, onions, potatoes, parsley, jews mallow, spinach, arugula, cabbage, cucumber, tomato, wheat, rice, beans, haricot, kidney bean) collected from main cities (Damamm, Jazan, Riyadh, and Tabouk) of Kingdom of Saudi Arabia. Also, Singh et al. (2012) reported a similar arrangement for heavy metal content (Zn > Cu > Pb > Ni > Cd) of different vegetables.

The variations in concentrations of the elements are partly due to the differences in the anatomy of the specific part of the plant, as well as to the chemical composition of the soil in the different localities (Razic et al. 2003). Absorption and accumulation of trace elements in plant tissue are based on several factors (Sharma et al. 2007). Nevertheless, the uptake and transfer of trace elements may be altered depending on the properties of the element and type of plant (Chauhan and Kumar 2015).

Correlation analysis

Pearson correlation coefficients for 12 trace elements are given in Table 7. The positive and negative correlation coefficients between two metals indicate the positive and negative correlations, respectively. The positive correlation can be explained by a direct relationship of

Table 7. Correlation matrix of trace element concentrations in the *Allium* species.

	V	Cr	Co	Ni	Cu	Zn	As	Se	Ag	Cd	Tl
Cr	**0.580**[a]										
Co	0.450	0.419									
Ni	0.262	0.279	**0.925**[a]								
Cu	0.032	0.213	0.194	0.312							
Zn	−0.049	−0.121	−0.020	0.106	**0.571**[a]						
As	0.354	0.180	**0.858**[a]	**0.892**[a]	0.298	0.137					
Se	0.327	**0.612**[a]	0.222	0.125	0.301	0.453	0.123				
Ag	0.097	**0.561**[a]	0.398	0.451	0.453	0.401	0.420	**0.701**[a]			
Cd	−0.143	−0.184	−0.108	−0.055	−0.167	0.331	0.022	0.067	0.080		
Tl	0.168	−0.006	0.403	0.437	0.154	0.435	0.485	0.242	0.310	**0.651**[a]	
Pb	0.229	0.114	0.498	**0.574**[a]	0.297	0.440	**0.702**[a]	0.345	**0.525**[a]	**0.528**[a]	**0.876**[a]

[a]Values in bold have high correlations with each other.

variables in which both variables increase or decrease together. If the value of correlation coefficients of two variables is near ±1, it indicates a high level of correlation between the variables. However, a value near 0 signifies actually no correlation between two variables (Karadas and Kara 2012). Ag, As, Se, and Pb had positive correlations with all elements given in Table 7. Moreover, Tl has positive correlation with all elements except Cr. Also Ni and Cu have the positive correlation with all elements except Cd.

Correlation coefficient values higher than 0.5 were evaluated for the discussion of the results. Ni has very high positive correlation with As and Co, while a moderate positive correlation was observed with Pb. Tl has a high positive correlation with Pb and moderate positive correlation with Cd. Co was positively correlated to As. Ag has a high correlation with Se and lower correlation with Cr. Arsenic has a high correlation with Pb.

The correlation analysis can be summarized with three groups as Group 1 (Ni, As, Co, Pb, and Tl), Group 2 (Se, Ag, and Cr), and Group 3 (As, Pb, and Cd). The groups were formed according to the strongly correlated elements. The high correlation of Pb-As and Pb-Cd reflect that the *Allium* species may be affected by the industrial activities and traffic.

Principal component analysis

Table 8 shows the PCA results which were calculated using the concentrations of 12 trace elements of the *Allium* species collected from different localities. As a result of PCA calculations, four principal components were formed according to the extracted components with eigenvalues higher than 1. According to the PCA results of the *Allium* species, the first four principal components explained 85.10% of the total variation of all data. The first principal component (PC1) accounted for 40.20%, the second principal component (PC2) for 18.80%, the third principal component (PC3) for 15.50% and the fourth principal component for 10.60% of the total variation of the data. The values in bold type in Table 8 were more important than the others in explaining the principal components. The Co, Ni, As, Ag, Tl, and Pb were the dominant variables for the first principal component, Cd and Tl were dominant for the second principal component, Se, Ag, Zn, Cu, and Cr were dominant for the third principal component, and Cu was dominant for the fourth principal component.

Table 9 shows the score values of the first four principal components belonging to each sample. It can be said that among the loading values of the first principal component, Co, Ni, As, Ag, Tl, and Pb were the dominant elements. The highest concentrations of those

Table 8. Contribution of trace elements to the four main principal components.

Trace element	Principal component 1	Principal component 2	Principal component 3	Principal component 4	Principal component 5
V	0.197	−0.321	−0.000	−0.413	0.682
Cr	0.215	−0.400	**0.304**[a]	−0.319	−0.129
Co	**0.359**[a]	−0.257	−0.289	0.045	−0.070
Ni	**0.366**[a]	−0.153	−0.303	0.225	−0.150
Cu	0.218	0.019	**0.307**[a]	**0.558**[a]	0.298
Zn	0.197	0.381	**0.333**[a]	0.258	0.338
As	**0.374**[a]	−0.091	−0.328	0.169	0.010
Se	0.254	−0.045	**0.509**[a]	−0.229	−0.094
Ag	**0.331**[a]	−0.026	**0.339**[a]	0.054	−0.500
Cd	0.094	**0.525**[a]	−0.072	−0.396	−0.130
Tl	**0.313**[a]	**0.372**[a]	−0.161	−0.214	0.108
Pb	**0.382**[a]	0.277	−0.118	−0.104	0.014
Eigenvalue	4.8201	2.2581	1.8647	1.2743	0.7243
Variance (%)	40.20	18.80	15.50	10.60	6.00
Cumulative (%)	40.20	59.00	74.50	85.10	91.20

[a]Larger number indicates a more significant contribution of that trace elements to the separation along the principal component (PC) axes. The bold values are the major contributors to each principal component.

metals were in AKr, ASIap, ASr, and AAVap, while the lowest concentrations of the same metals were in AAHap and AAHr. It can be interpreted that while the concentrations of the Cd and Tl metals were the highest in the ACr for the second principal component and lowest for ASr. For AAVap, the concentrations of Se, Ag, Zn, Cu, and Cr belonging to the third principal component were the highest as indicated by the bold font.

The score plot of the first two principal components (PC1 and PC2) for different tissues of the *Allium* species is given in Figure 1. It was clear from the score plot of the analyzed metals in the aerial tissue and roots of the *Allium* species that the metal

Table 9. Score values of the trace elements in *Allium* species.

Samples	Principal component 1	Principal component 2	Principal component 3	Principal component 4
AAHap	*−3.37403*[b]	−0.59010	−1.44363	−0.21237
AAHr	*−2.29744*[b]	−0.05012	−0.18056	0.25518
AAVap	**2.10097**[a]	0.20903	**2.52613**[a]	0.86668
AAap	0.94406	0.59922	1.59816	0.49171
AAr	−1.20713	0.76944	1.81695	1.51705
ACr	1.40711	**5.22046**[a]	−0.18588	−2.41233
AKap	0.59613	−0.55607	−0.74044	0.81750
AKr	**5.63807**[a]	0.47374	−4.04038	1.76213
ARap	−1.51235	0.88564	−0.64365	−0.73528
ASap	−1.37394	−0.54974	0.05065	−0.24717
ASr	**2.91553**[a]	*−3.21570*[b]	0.10709	−2.72716
ASRap	−1.81890	−0.00455	−0.21770	−0.15390
ASRr	−1.36563	−0.44930	−1.15428	−0.57546
ASHap	−1.14014	−0.32525	−0.86311	0.07364
ASHr	−1.70840	−0.21764	−0.22088	1.04279
ASIap	**4.03340**[a]	−0.22378	1.92665	0.10811
ASIr	0.50009	−0.44903	0.75387	−0.71458
ATap	−1.31807	0.79188	−0.21393	−0.69492
AVap	−0.07672	0.77403	0.85428	1.52972
AVIr	−1.09498	−0.02686	−0.22403	0.77461
ASSap	1.10934	−1.93818	0.42993	−0.52022
ASSr	−0.95697	−1.12712	0.06477	−0.24575

[a]Bold numbers indicate the samples containing highest concentration of dominant trace elements shown in Table 7.
[b]Italic numbers indicate the samples containing the lowest concentration of dominant trace elements shown in Table 7.

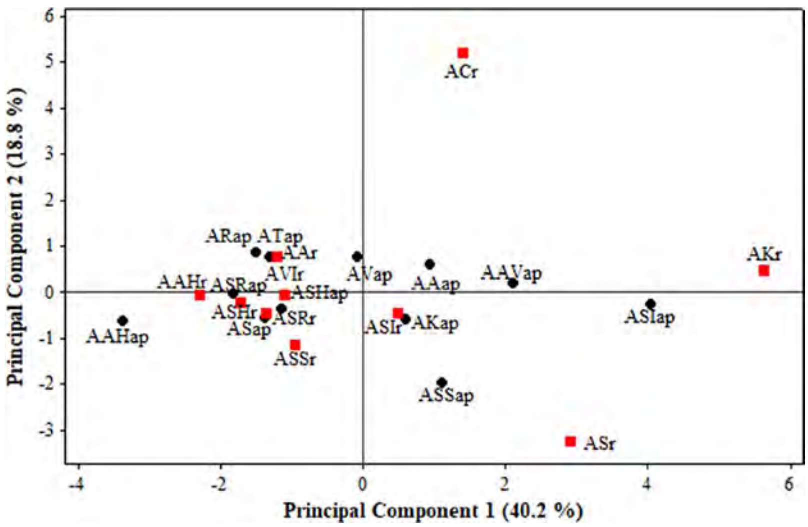

Figure 1. Score plot of the first two principal components (first principal component and second principal component) for aerial parts (•) and roots (◆) of the *Allium* species. AAHap, Arap, and ATap are aerial and AAHr roots from Hakkari; AAVap, AAap, ASap, ASRap, ASHap, and AVap are aerial and AAr, ASr, ASRr, and ASHr roots from Van; ASIap are aerial and ACr and ASIr roots from Şırnak; AKap are aerial and AKr and AVIr roots from Malatya; and ASSap are aerial and ASSr roots from Adıyaman.

concentrations in the roots showed similarities and were lower. Therefore, the aerial tissue and roots formed two groups. When the score (Figure 1) and the loading plots (Figure 2) were evaluated together, it is seen that ACr differed in terms of high Cd concentration. On the other hand, AKr was distinguished from the others because of the high concentrations of Pb, Cu, Ag, and Se. The ASr sample was separated due to high concentrations of Cr and V.

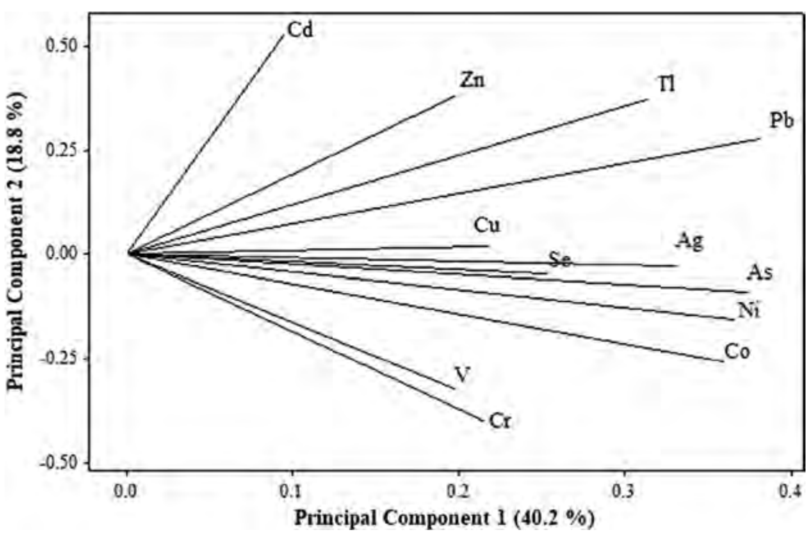

Figure 2. Principal component 1 and principal component 2 loading plot of the *Allium* species.

ACr, ASlap, and ASlr are in the right part of the score plot with higher metal concentrations. It is remarkable that the concentration of Cd was high in the ACr, while V and Cr were high in ASlr, and As and Ni were high in ASlap. The samples collected from the Hakkari and Van provinces were mainly situated in the left side of the score plot. Therefore, the metal concentrations of samples, especially roots, from those provinces were lower than for the other samples. Among the samples from Malatya, AKr, and AKap differed from the AVlr sample from Malatya. While the sample ASSr from Adıyaman was in the same region as the other root samples, the aerial tissue of this sample (ASSap) was in the right lower area of the score plot. Higher concentrations of Cr and V were determined in ASSap compared to in ASSr.

Different patterns in the trace element concentrations between different plant tissues have been reported in the earlier studies (Mestek et al. 2007; Tinkov et al. 2016; Tozser et al. 2017). These factors include the type of soil, forms of metals in the soil and growth stage of species (Tozser et al. 2017). Antagonistic and synergistic interactions between trace elements can influence their absorption and translocation (Madejon et al. 2004).

Cluster analysis

The dendogram of the cluster analysis (HCA) which was applied to the principal component score matrix is presented in Figure 3. This methodology was used in order to determine the similarities of samples belonging to the *Allium* species divided into aerial parts and roots. The cluster analysis was performed to compare the distributions of trace elements (Ag, As, Cd, Cr, Co, Cu, Ni, Pb, Se, Tl, V, and Zn) in all samples. The cluster analyses data were also compared with those of the PCA data. The data obtained for 12 trace elements in the *Allium* species were evaluated using cluster analysis. The

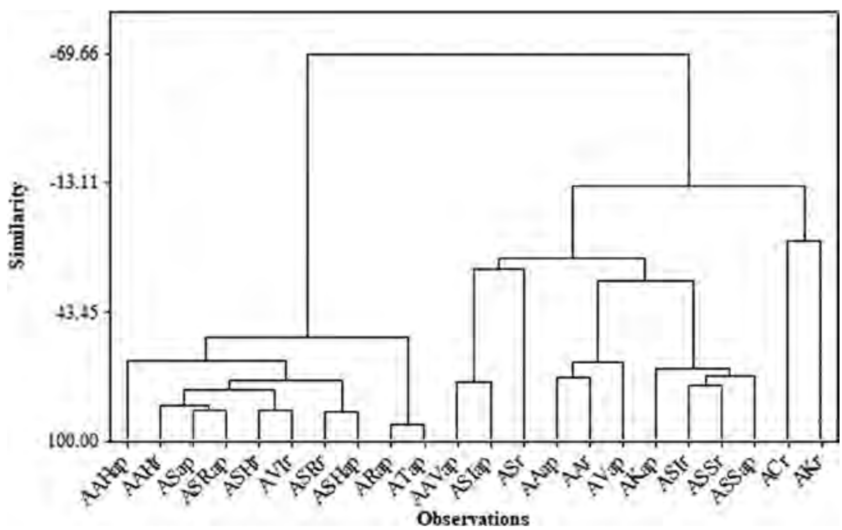

Figure 3. Dendograms obtained by the Euclidean distance and the Ward Linkage method. AAHap, Arap, and ATap are aerial and AAHr roots from Hakkari; AAVap, AAap, ASap, ASRap, ASHap, and AVap are aerial and AAr, ASr, ASRr, and ASHr roots from Van; ASlap are aerial and ACr and ASlr roots from Şırnak; AKap are aerial and AKr and AVlr roots from Malatya; and ASSap are aerial and ASSr roots from Adıyaman.

measurement and classification method were based on squared Euclidean distance and Ward method, respectively. Four groups were obtained from HCA analysis:

Group 1: AAHap, AAHr, ASap, ASRap, ASHr, AVIr, ASRr, ASHap, ARap, ATap (samples from Hakkari, Van, Malatya).

Group 2: AAVap, ASIap, ASr, AAap, AAr, AVap, AKap, ASIr, ASSr, ASSap (samples from Van, Şırnak, Malatya, Adıyaman).

Group 3: ACr (sample from Şırnak).

Group 4: AKr (sample from Malatya).

Conclusion

This study is important for consumers because the *Allium* species are widely consumed and the metal concentrations have not been studied in detail to date. The results obtained in this study provide knowledge about the relationship between the levels of metals in *Allium* species that were collected from various localities of Turkey. The evaluation of the results of ICP-MS analysis showed that all tested *Allium* species are suitable for medicinal or nutritional purposes because the toxic metal concentrations (As and Pb) of all *Allium* species found below the WHO limits for edible plants. However, the Cd concentrations of the ATap, ARap, and ACr were higher in comparison to the limit (300 µg/kg) established by the WHO. The Cr concentration of the AAVap, ASr, ASIap, and ASSap were also higher than the WHO limit (2 mg/kg). These results demonstrate the importance of the dose-controlled use of the stated *Allium* species. It should be emphasized that *Allium* species are valuable sources of nutritive elements which should be consumed for recommended daily intakes. PCA and HCA calculations using metal concentrations of the *Allium* species revealed that there is a relationship between the *Allium* species based on these parameters. The *Allium* species were classified into four groups by HCA.

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