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Mehmet DÜZGÜN*[1]*,
Enver KENDAL*[2]*, M. Zahir DÜZ*[3]*, Abdülkerim HATİPOĞLU*[4]*,

IDENTIFY OF MACRO AND TRACE ELEMENTS IN GRAIN OF SOME BARLEY VARIETIES AND INTERPRETATION WITH BIPLOT TECHNIQUE

SUMMARY

The purpose of this study was to determine the content of some macro and trace elements in grain of spring barley cultivars, and to state the relationships between those elements. In this study macro and trace elements (Ca, K, Mg, Fe, Zn, Mn, Si, Sn, Cu, Cr, Cd, Ni, V, Pb, As and Se) of barley cultivars were determined by inductively coupled plasma optic emission spektometry (ICP-OES) using grain. The grain samples were digested by microwave system, as well as. As and Se were determined by hydride system. The result of study showed that the content Si of barley cultivars are quite high, however, the concentrations toxic heavy metals of Cd, Pb and as were determined to be below the limit values.

The biplot indicated that three group occurred among macro and trace element and the correlation of Zn with Sn, Cr with Ca and Fe, Ca with Fe and Pb was significant and positively, while V with Si was significant and negatively. On the other hand, the study showed that Samyeli is the best cultivar based on macro and trace element concentrations and this variety can be used in animal husbandry.

Keywords: Cultivar, food, macro, ICP-OES, Heavy metal

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[1]Mehmet Düzgün, GAP International Agricultural Research and Training Center, Diyarbakır, (e_mail: mehmetdzgn@ymail.com; mehmet.duzgun@tarimorman.gov.tr); TURKEY

[2]Enver Kendal, Mardin Artuklu University, Kızıltepe VTHS, Department of Crops and Animal Production, Mardin, (corresponding author: enver21_1@hotmail.com), TURKEY

[3]M. Zahir Düz, Dicle University, Faculty of Science, Department of Chemistry, Diyarbakır, TURKEY

[4]Abdülkerim Hatipoğlu, Mardin Artuklu University, Faculty of Health Sciences, Department of Nutrition and Dietetics, Mardin, TURKEY

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INTRODUCTION

Barley is the most important food source for animal con-sumption, and historically has been an important food source in many parts of the World, as well as Turkey (Jākobsone *et al*., 2018; Kendal *et al*., 2019). Transfer of macro and trace elements to the feeding chain of animals are significantly affected by the geological origin of the soils and the ground water basin as well as the environmental conditions and genetic difference of Barley varieties (Markova Ruzdik *et al*., 2015). Since heavy metals are mobile and easily absorbed by plants in the environment, they are transmitted to the animal body through nourishment.

The studies on the transfer of chemical contaminants through the food chain provide useful information for the development of surveillance programs aimed at ensuring the safety of the food supply and minimising human exposure to toxic agents (Cubadda and Raggi, 2005). It is well known that foods take up trace metals from soils, fertilizers, air, and industrial process, transportation, and package materials. Heavy metals are mobile and easily taken up by plants in the environment (Khairiah *et al*., 2004; Chojnacka *et al*., 2005; Demirel *et al*., 2008) When considering different kinds of soil pollutants, heavy metals represent a special hazard because of their persistence and toxicity (Adriano, 2001). For the human body, certain heavy metals are essential for the biological systems as structural and catalytic components of proteins and enzymes like zinc (Zn) and copper (Cu), and others are contaminants such as cadmium (Cd), arsenic (As), lead (Pb), chromium (Cr), nickel (Ni) and so on (Rana,2008; McLaughlin, 1999). Soil behaves as a sink for heavy metals arriving by the aerial deposition of particles emitted by urban and industrial activities (Bermudez *et al*., 2010; Schuhmacher *et al*., 2009) as well as from agricultural practices (Chen *et al*., 2008; Mico *et al*., 2006). High pollution levels in soils can lead to phytotoxicity and result in the transfer of heavy metals to the human diet from crop uptake or soil ingestion by grazing livestock (Abrahams, 2002; Kabata-Pendias and Mukherjee 2007). Food and Agriculture Organization (FAO) and World Health Organization (WHO), European Commission (EC) and other regulatory bodies of other countries strictly regulate the allowable concentrations or maximum permitted concentrations of toxic heavy metals in foodstuffs (FAO/WHO 1984, EC, 1989). Reference daily intakes for 9 significant elements have been established: calcium (1000 mg), chromium (120 μg), copper (2 mg), iron (18 mg), potassium (3500 mg), magnesium (400 mg), manganese (2 mg), selenium (70 μg) and zinc (15 mg) (Mindel, 2000, Cernohorsky *et al*., 2008). However, heavy metal levels in the soil for lead (300 mg/kg), cadmium (3 mg/kg), chromium (100 mg/kg), Copper (140 mg/kg), nicel (75 mg/kg), zinc (300 mg/kg) were established (Anonymus 1). The impact of heavy metals on the environment is greatly dependent on their speciation in soil solution and solid phase which determine their environmental availability, toxicity, migration – accumulation phenomena, geochemical transfer and mobility pathways (Druteikienė *et al*., 2002; Pinto at al., 2004). Uptake and bioaccumulation of heavy metals by plants is of importance because of an impact on soils by anthropogenic emissions and its consequence for human uptake (Bradl, 2005).

MATERIAL AND METHODS

In the study, four barley cultivars (Altıkat, Samyeli, Şahin-91, Sur-93) used and the samples of grain of these cultivars was taken from the Department of field crops department of GAP International Agricultural Research and Training Center.

Table 1. Sample digestion program for barley and soil

Step(barley)	Time(min)	T (^{o}C)	Power(W)
1	20:00	180	1200
2	20:00	180	1200
Step(soil)			
1	20:00	180	500
2	15:00	180	500

Table 2. Instrumental Operating Conditions Using Thermo ICAP 6300 ICP-OES

Parameter	**Normal**	**Hydride System**
Power	1150 W	1350 W
Pomp speed	50 rpm	30 rpm
Purge gas	Argon	Argon
Coolant Gas		
Flow	12 L/min.	16 L /min.
Auxiliary gas		
Flow	0.5 L/min.	0.5 L/min.
Torch	Axial, Radial	Axial
Auto sampler	Cetac ASX-260	

The nearly 0.25 g dried and ground sample of grain barley was put into burning cup and 8 ml % 65 HNO_3 and 2 ml % 30 H_2O_2 added on this grain samples. The samples were dissolved in a Milestone Smart D microwave oven according to program showing at Table 2. Soil sample was weighed 0.25 g in TFM containers and 6 ml % 65 HNO_3, 1 ml % 30 H_2O_2 and 3 ml % 40 HF added (Table 1). After dissolving of soil sample 1,2 g H_3BO_3 added in burning cup and dissolved.

Samples dissolved and diluted a certain volume with ultra-pure water (Elga ultra-Pure water system). The Concentrations were determined by ICP-OES (Thermo ICAP, 6300).

Total element concentration of soil was determined and showed in Table 3.

According to determined data in the soil Se content found below dedection limit. On the other hand, macro elements in the soil were showed normal concentration but micro element content such as Fe was found higher than other elements.

Table 3. Micro and trace element content in soil sample (n=3, mean±standart deviation, (mg/kg) dry weight)

Elements	Soil	Elements	Soil
Ca	9550±33	Cr	119±6
K	4083±44	Cu	23.8±2.3
Si	1971±32	Sn	10.8±0.7
Fe	16594±102	Pb	10.2±0.1
Zn	44.5±1	V	70.6±6.8
Mn	520±10	As	8.92±0.32
Ni	64.6±0.8	Se	<0.0045
Cd	0.56±0.01		

Statistical analysis (GT)

The GT biblot analeyses were carried out using GT biplot software to assess micro and macro element content (Yan and Rajcan, 2002; Kendal *et al*., 2019). In multi-traits (MT) for cultivars, biplots were constructed by plotting the first two principal components (PC1 and PC2) derived from centered micro and macro element content data to singular value separation. Also, with the GT biplot analysis graphs in the study: It was aimed at revealing relation among examined micro and macro elements content and cultivars means by scatter plot (Fig. 1), and grouped micro and macro elements content and performance of each cultivars at each trait (Fig. 2), the stable and high performance of gcultivars micro and macro elements content by ranking model (Fig. 3), compare the desirable cultivars to ideal center based on micro and macro elements content by comparison model (Fig. 4).

RESULTS AND DISCUSSION

The result of element concentrations of barley cultivars showed in Table 4. According to these data, the concentrations of macro and trace elements were very variable in barley cultivars.

The consentration of Ca, Mg, K, Fe, Cr, V and Pb were changed from 471-521 mg·kg-1, 637-846 mg·kg-1, 2611-3116 mg·kg-1, 36.6-68.7 mg·kg-1,0.55-0.97 mg·kg-1,0.010-0110 mg·kg-1, 0.034-0140 mg·kg-1 respectivelly. The concentrations of these elements in Samyeli cultivar were higher than other three cultivars, while the concentration of Si (134 mg/kg 1) in Samyeli cultivar were quite lower. On the other hand, the concentration of Si (239 mg·kg-1) and Cu (5.83 mg·kg-1) in Sur 93 were quite higher than other three cultivars, while the concentration of Vanadium content (0.010 mg·kg-1) in Sur-93 quite lower than other cultvars. Moreover, the concentration of Se was changed from 0.210-0.380 mg·kg 1, and the consentration of this element was higher in Altıkat than other cultivars. Meanwhile Arsenic concentration of all cultivars found below, compare with dedection limits. The elements of Pb benefical for nutrition animal and human food. When the results of this study compare to other literature results, some elements concentration of barley taked from this study were higher and some of them were lower than other results and some of them were like some results of other studies. This differencies is normal, because these differences are estimated to be caused by climatic factors, varieties, genotypes, and soil factors (Ereifej *et al.*, 2001 Salama and Radwan, 2005). On the other hand, Jâkobsone *et al.* (2018) reported that barley products can provide necessary macro and trace elements, especially of Mn, Mg, Fe, and Zn (7.8–16.1; 1024–1249; 29.2–52.9, and 20.5–33.7 mg·kg-1, respectively). Jakobsone *et al.* (2015) reported that the obtained data from trace and macro elements will expand the opportunity for food and nutrition scientists to evaluate content of the examined elements in grain products, and dietary consumption (bioavailability) of the examined macro-elements and trace elements.

Table 4. Concentrations of macro and trace elements in barley cultivars (n=3, mean±standart deviation, (mg/kg), dry weight)

Elements($mg.kg^{-}$)	Cultivars			
	Altıkat	Samyeli	Şahin-91	Sur-93
Ca	471±12	521±15	480±13	488±8
Na	449±39	415±9.4	415±8.5	489±16
Mg	637±14	846±11	720±90	844±23
K	2837±172	3116±78	2611±153	2547±143
Si	160±35	134±11	171±12	239±3
Fe	36.6±5.6	68.7±1.8	38.3±2.4	47.7±0.6
Zn	19.4±0.2	23.4±1	28.4±0.25	21.3±0.08
Mn	13.7±0.07	15.1±0.37	14.2±1.3	21.4±0.3
Ni	0.53±0.07	0.54±0.04	0.44±0.01	0.52±0.02
Cd	0.041±0.004	0.023±0.006	0.029±0.006	0.032±0.002
Cr	0.55±0.02	0.97±0.05	0.55±0.004	0.61±0.008
Cu	3.90±0.3	4.81±0.2	4.47±0.45	5.83±0.02
Sn	16.6±0.7	17.3±1.1	18.3±1.8	16.8±0.2
Pb	0.090±0.02	0.140±0.01	0.121±0.08	0.034±0.01
V	0.090±0.005	0.110±0.02	0.063±0.006	0.010±0.001
As	<0.002	<0.002	<0.002	<0.002
Se	0.380±0.24	0.210±0.2	0.311±0.1	0.312±0.12

Graphically the performance of cultivars based on macro and trace elements and correlation among macro and trace elements

Principal component analysis was used to show the distribution of cultivars based on macro and trace elements. The two-dimensional PCA score plot, derived from macro and trace elements and accounted for 78.37% (45.32% and 33.05% for PC1 and PC2, respectively) of the total variation (Figs. 1-4).

The relationship each cultivar by each macro and trace element showed by cultivar vectors and macro and trace element vectors are drawn in Fig. 1, so that the specific interactions between a cultivar and a trait can be seen.

Therefore, this figure can be used (1) to rank the cultivar based on performance in any trait, and (2) to rank macro and trace elements on the relative performance of any cultivar. The interpretation of performance a cultivar in a trait is better than average if the angle between its vector and the element's vector is <90°; it is poorer than average if the angle is >90°; and it is near average if the angle is about 90° (Yan and Thinker, 2009; Dogan *et al*., 2016). The results of traits showed that there is high variation among cultivars based on elements. According to results, there was high correlation by Zn with Sn (r=1.00), Cr with Ca and Fe (r=098), Ca with Fe (r=0.99) and Pb (0.45) was significant and positively, while V with Si (r=-0.99) was significant and negatively (Fig.1; Table 5).

Moreover, Samyeli cultivar related with especially Cr, Ca and Fe, Sur 93 related with Mn and Cu, Altıkat with Se, Cd and Şahin 91 with Zn and Sn elements (Fig.1). On the other hand, the scatter plot indicated that three groups were occurred among macro and trace elements and cultivars showed a wide distribution on macro and trace element, and also The biplot indicated that three group occurred among macro and trace elements(Fig. 2). First group was occurred among V, Pb, Sn, Zn, K, Cr, Ca, Fe, Mg and related with Samyeli cultivar. The second group occurred among Cu, Mn, Na, Cd and related with Sur 93 cultivar. The Altıkat and Şahin 91 did not related with any group of macro and trace elements (Fig1 and Fig 2).

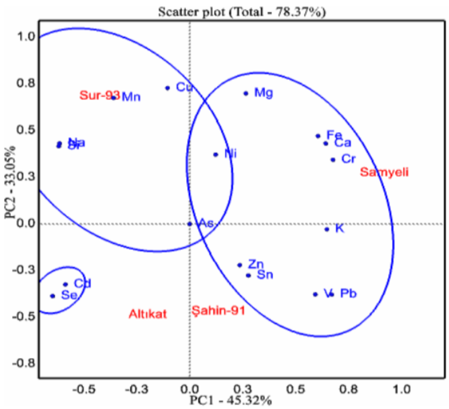

Figure 1. Relation among cultivars and macro and trace elements content.

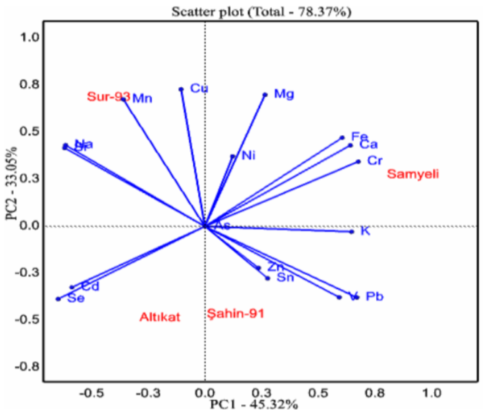

Figure 2. Groups of macro and trace elements content based on cultivars.

The third group occurred only Cd, Sa and did not related with any cultivar. The GT biplot mainly allows the visualization of any crossover GT interaction, which is very important for the breeding program (Kilic *et al*., 2018).

The ranking biplot indicate that the cultivars located close to the origin of the coordinate system of the Biplot graph (Fig. 3) are considered more stable and the opposite is equivalent, the greater the distance from the origin, the less the stability based on mean of trace and macro elements (Kendal and Dogan, 2015). The Samyeli cultivar can be considered stable based on mean of trace and macro elements, when compared other cultivars, while, Altıkat and Şahin 91 were undesirable, because these two cultivar located under mean line of trace and macro elements, and Sur 93 was favorable but unstable because it was located far from origin of the coordinate line axis. Therefore, we can be used the Samyeli cultivar based on macro and trace elements for animal food.

Table 5: The correlation among trace and macro elements content

	Ca	Na	Mg	K	Si	Fe	Zn	Mn	Ni	Cd	Cr	Cu	Sn	Pb	V
Na	-0.34														
Mg	0.79	0.17													
K	0.68	-0.55	0.12												
Si	-0.37	0.87	0.28	-0.83											
Fe	**0.99****	-0.25	0.79	0.70	-0.33										
Zn	0.08	-0.62	0.08	-0.23	-0.16	-0.05									
Mn	0.10	0.82	0.67	-0.50	0.88	0.15	-0.26								
Ni	0.41	0.35	0.27	0.59	-0.10	0.53	-0.87	0.22							
Cd	-0.86	0.49	-0.77	-0.35	0.25	-0.78	-0.57	-0.09	0.11						
Cr	**0.98***	-0.40	0.65	0.82	-0.51	0.98*	-0.04	-0.05	0.52	-0.75					
Cu	0.41	0.56	0.88	-0.32	0.70	0.43	-0.03	0.93	0.17	-0.45	0.24				
Sn	0.09	-0.69	0.02	-0.16	-0.25	-0.05	**1.00****	-0.35	-0.86	-0.55	-0.01	-0.12			
Pb	**0.45***	-0.99	-0.12	0.69	-0.93	0.37	0.49	-0.82	-0.18	-0.50	0.52	-0.55	0.57		
V	0.37	-0.78	-0.28	0.89	**-0.99***	0.36	-0.01	-0.84	0.25	-0.17	0.53	-0.69	0.09	0.86	
Se	-0.97	0.44	-0.80	-0.56	0.34	-0.93	-0.32	-0.08	-0.18	0.96	-0.91	-0.43	-0.32	-0.50	-0.30

******: Probability value is significiant at $P<0.01$ level, *****: Probability value is significiant at $P<0.05$ level.

The discriminating and representativeness of genotypes-based traits are visualizing the "ideal center" over the mean values of the environments and offers the opportunity to evaluate genotypes according to their proximity or distance to this center (Kendal, 2020). If the genotypes are located in the center, they are the most ideal, if they are located above the average vertical axis, but far from the center, it means that they are ideal, if they are located below vertical axis, it means that they are undesirable. Based on this overview the *Fig. 4* explained that the Samyeli located near center of AEA, and so, it is more desirable than other cultivars, while Altıkat and Sahin 91 are the poorest cultivars, because these two cultivars are located under mean axis. The term "ideal genotype" is meaningful only when associated with mean performance. According to *Fig. 4*, the Samyeli is highly "ideal", Sur 93 is desirable genotypes, and because of Samyeli took places in center of AEA and Sur 93 took places on above averages of macro and trace elements axis, and so it means that it is just good for macro and trace elements.

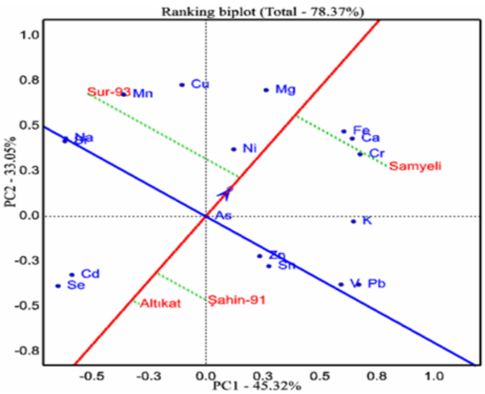

Figure 3. Ranking of cultivars based on macro and trace elements content.

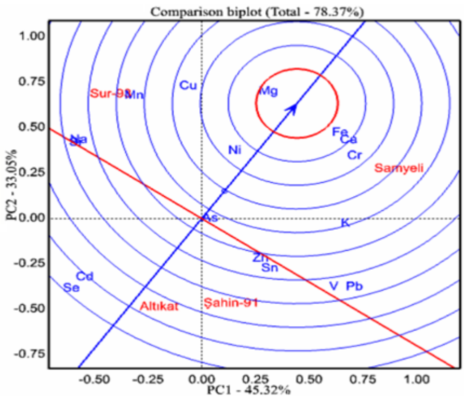

Figure 4. Comparison of cultivars based on macro and trace elements content

CONCLUSIONS

The According to result of study, there were differences among cultivars in terms of macro and trace elements. These differences are caused by climatic factors, varieties, cultivars, and soil factors. The study showed that Samyeli cultivar is the best in terms of majority macro and trace elements which examined in the study, while it was poor in terms of concentration of Si. On the other hand, Sur 93 was good based on some macro and trace elements, while Şahin 91 and Altıkat cultivars were poor based on majority macro and trace elements. The study showed that barley is importance to research and raise the quality of fattening. According to the biplot techniques indicated that there is high correlation between Zn with Sn. Also, the study showed that the biplot technique is a very suitable method for visually understanding and evaluating the relationship between varieties and macro and trace elements.

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