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Analysis of macro- and Microminerals Content in the Einkorn (*Triticum monococcum* L.) Samples Cultivated in Kastamonu, Turkey

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ABSTRACT

Wheat is an important cereal product because of its nutritional value, economy, culture, and history. Einkorn (*Triticum monococcum* L.) assumed as the oldest wheat. Einkorn locally called "siyez" has recently become popular as a super grain with the thought of being very nutritious in Turkey. In this study, the contents of macrominerals (Na, Mg, Ca, and K) and microminerals (Cr, Cu, Fe, Mn and Zn) in twenty-one einkorn samples collected from different cultivation areas in Kastamonu were determined by using an inductively coupled plasma-optical emission spectrometry following microwave-assisted acid digestion. The results were compared with those analyzed in einkorn and other wheat types in the literature. Average concentrations of K, Ca, Mg, Na, Fe, Zn, Mn, Cr and Cu analyzed in einkorn samples were found as 3712, 1303, 656, 53, 167, 34, 29, 0,7 and 0,6 mg kg^{-1}, respectively. The literature comparison revealed that the investigated einkorn samples were richer in terms of Ca and Fe contents compared to einkorn, emmer, spelt, buckwheat, and durum wheat samples grown in our country and different countries.

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Introduction

Cereals are known as edible grains or seeds that are the grass (Gramineae) family members (McKevith, 2004). Cereals and grain-based foods contain protein and minerals that are indispensable for the world population. Some cereals are essential foods both for direct human consumption and indirectly through animal feed since the beginning of civilization. The production of cereals is generally cheap. Grains are easily stored, transported, and do not spoil easily if kept dry. Cereals and derivatives (food products obtained from cereals) are an important food group in both developed/developing countries. Cereals and their products are a series of essential elements sources such as carbohydrates, protein, fiber, lipids, vitamins (E vitamin, some B vitamins) and sodium, potassium, calcium, magnesium, iron, zinc, selenium, etc. The increased interest in cereals and derivatives is due to their bioactive components and the potential benefits of regular consumption of cereals and cereal products (McKevith, 2004).

Wheat, rice, and corn are the most produced and consumed cereal products worldwide. Wheat and rice are the most important crops with more than fifty percent of world grain revenue (McKevith, 2004). Wheat, which constitutes 30% of the grain production in the world, is the oldest known grain product that can be grown as both spring and winter food and therefore can be harvested at any time of the year (McKevith, 2004; Şenoğlu, 2019). Wheat, which has thousands of species, belongs to the *Triticum* family. Due to many wheat species and varieties and their easy adaptations, it is grown in many countries worldwide (more than 120 countries), under different climatic conditions and different environments, using different agricultural technologies or traditionally (Şenoğlu, 2019). Large parts of the wheat produced in Turkey as well as all over the world are used for human consumption. Due to its unique properties, a wide variety of ingredients and foods are produced from wheat, including wheat germ, couscous, shredded wheat, bulgur or cracked wheat, flour, and wheat starch. Wheat type *Triticum Aestivum* subspecies Vulgare and hard wheat *Triticum durum* is the most commercially important wheat type (McKevith, 2004).

Einkorn means "single grain" or "one seed" in German. Einkorn is the known oldest wheat type and its production date extends to approximately 12 thousand years (Sultan et

al., 2020). Einkorn is among the diploid species of hulled wheat with 2n chromosome structure and its grains are tightly covered with their hard hulls (Emeksizoğlu, 2016). Einkorn wheat is known as *Triticum boeoticum* (wild wheat) or *Triticum monococcum* (domestic species) in taxonomy. Native and wild wheat forms can be considered as separate species or subspecies of *Triticum monococcum*. Einkorn (*Triticum monococcum* L.) is known with various names such as "siyez" and "kabulca" in Anatolia. Einkorn is accepted to be resistant to pests and diseases, as an extremely competitive species in poor soils and arid conditions since it has a single grain in its ears and its tight hull (Sultan et al., 2020). While einkorn cultivation was done more than a thousand years ago in Anatolia, today it is limited to only a few regions. A large part of einkorn (siyez) cultivation is done in İhsangazi districts of Kastamonu. The production of siyez wheat in Kastamonu province has increased linearly in the last five years. Siyez production (9110 tons) in 2018 increased by 6.2 times compared to 2014 siyez production (1472 tons). In the same way, the planting area of siyez in Kastamonu was 6690 decares in 2014 and reached 41409 decares in 2018 (Dalal et al., 2020). Siyez wheat boiled in hot water is dried under natural conditions and separated from its shells in water-operated mills in Kastamonu and its vicinity (Atak, 2017). Local people make use of siyez wheat as a "bulgur". Wheat stems are also a source of food for animals.

Minerals are essential for good health and growth. Certain amounts of minerals are needed to keep our bodies functioning properly. Minerals are defined as vital elements for the normal structure and functions of the body, except for H, C, O, N and S which constitute the body's basic structure. Minerals with a daily requirement of more than 100 mg are named as macrominerals (Na, K, Ca, Mg, etc.) and minerals less than 100 mg are named as microminerals or trace elements (Al, Ba, Fe, Zn, Mn, Sr, etc.) because their concentration in the body is very low. When not sufficiently taken, the elements that cause a dysfunction in the body and provide the correction of the related disorder as a result of physiological intake are known as essential elements. So far, several studies were published in the literature on the determination of elemental contents of wheat species (Abdel-Aal et al., 1995; Çakmak et al., 2000; Bâlint et al., 2001; Gabrovská et al., 2002; Løje et al., 2003; Özkan et al., 2007; Brandolini et al., 2008; Zhao et al., 2009; Erba et al., 2011; Suchowilska et al., 2012; Mutlu et. al., 2013; Mutlu and Uncumusaoğlu 2016; Kurnaz et. al., 2016; Mutlu et. al., 2016; Khan et al., 2017; Mutlu and Kurnaz, 2017; Zhang et al., 2018; Ertop and Atasoy, 2019; Mutlu, 2019). However, these studies are generally related to the human consumption and food preparation potential and there is no detailed study in the literature for determining the macro- and microminerals content of einkorn (siyez) samples. The purpose of this study is to complete the information missing in the literature by determining the levels of macrominerals (Na, Mg, Ca, and K) and microminerals (Cr, Cu, Fe, Mn and Zn) in twenty-one einkorn (siyez) samples collected from different cultivation areas in Kastamonu were determined by using an inductively coupled plasma-optical emission spectrometry (ICP-OES) and compare those obtained in the literature.

Material and Methods

Collection and Preparation of Sample

Einkorn (siyez) samples were collected from twenty-one different cultivation areas from the Ihsangazi district of Kastamonu province (Figure 1). Each siyez sample was extracted from their shells and coded to include information about the locations where they were collected. All samples were washed with water and then dried. The samples were homogenized by grinding in a sterile environment using a grinder (Isolab). Then, approximately 250 mg of each siyez sample was inserted directly into a high-pressure laboratory microwave oven (Milestone Ethos 1600). Ten milliliters of HNO_3 (67% v/v) solution were added to each vessel. The heating program was carried out in two consecutive steps. Firstly, the temperature was linearly increased to 200°C in 15 min. Secondly, the temperature was held at 200°C for 15 min. After the digestion procedure the solutions were cooled to room temperature. Every digested sample was diluted with ultra-pure water. Also, blanks were prepared in each lot of siyez samples. All reagents used for analyses were of analytical grade.

Table 1. The operating parameters of the ICP-OES (Spectro Blue II)

Wavelength	nm
Replicates	3
Spray chamber	Cyclonic
Nebulizer flow (L min^{-1})	0.8
Plasma torc	Quartz
Coolant flow (L min^{-1})	13
Auxiliary gas flow (L min^{-1})	0.8
Sample pump speed (rpm)	30
Plasma power (W)	1200

Figure 1. Location of İhsangazi district (Kastamonu, Turkey)

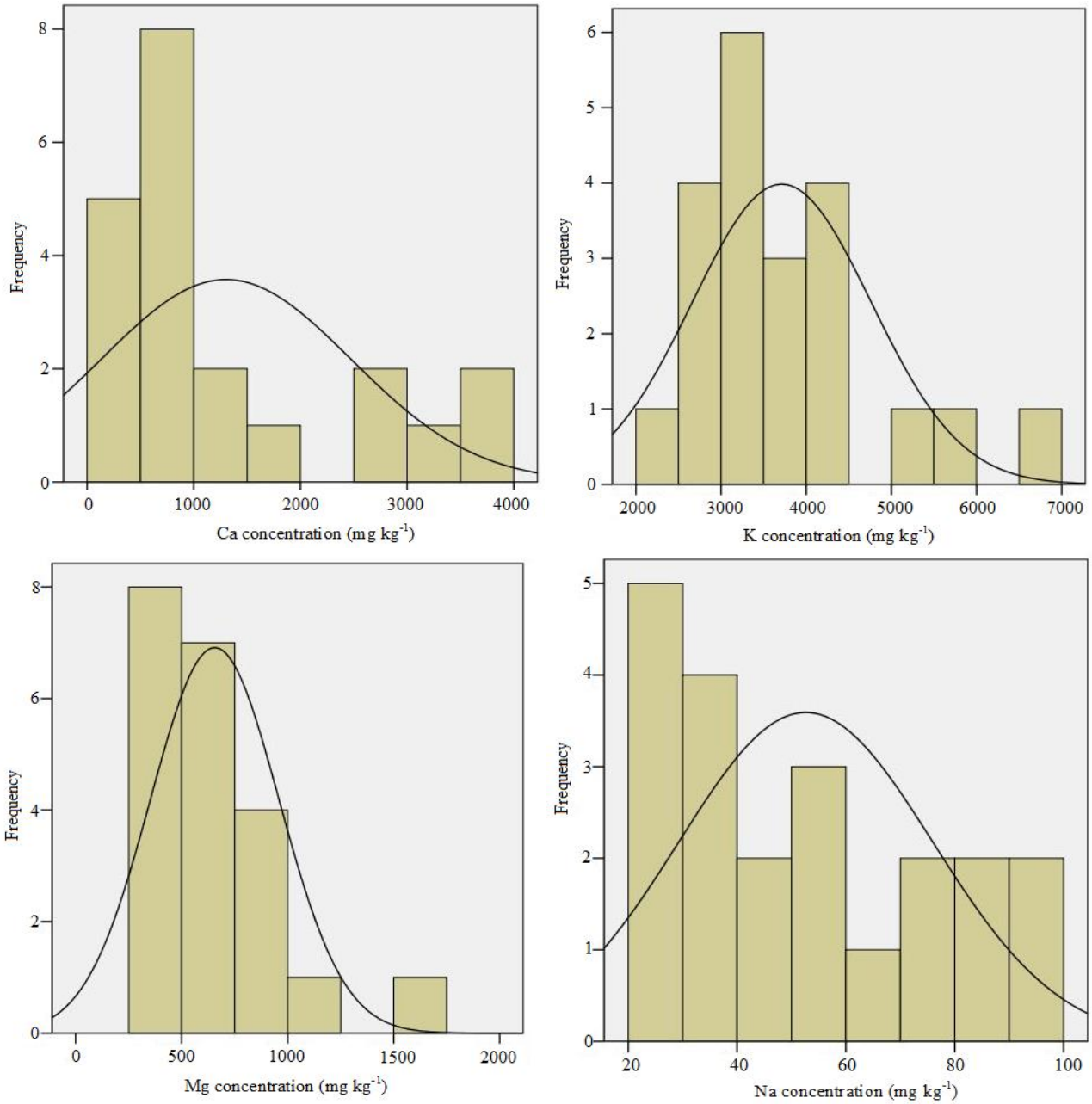

Figure 2. Concentration distribution of the macrominerals in siyez samples

Analysis Procedure

The analysis of macro-and microminerals were performed using an inductively coupled plasma-optical emission spectrometer (ICP-OES) with an axially viewed configuration (SPECTROBLUE II) equipped with Spectro's proprietary ICP Analyzer Pro software making it easy to take full advantage of the instrument's simplified operation and analytical capabilities. The operating conditions of the ICP-OES are given in Table 1. Calibration solutions were prepared by diluting the certified standard ICP multi-element standard solution IV of 1000 mg L^{-1} (23 elements in diluted nitric acid) purchased from Merck (Darmstadt, Germany). Calibration of the ICP–OES system was carried out at the beginning of the measurements and the correlation coefficients were equal to 0.999 for all analytes. The reading was made in triplicate.

Results and Discussion

The concentrations of macrominerals and microminerals analyzed in each siyez sample are given in Tables 2 and 3, respectively. The frequency distributions of macrominerals and microminerals are shown in Fig. 2. The comparisons of average concentrations of macrominerals and microminerals analyzed in the siyez samples with those analyzed in wheat species (einkorn, spelt, durum, emmer, and buckwheat) grown in some countries and Turkey are given in Tables 4 and 5, respectively.

As can be seen form Table 2, macrominerals are ranked as potassium (K) > calcium (Ca) > magnesium (Mg) > sodium (Na) according to their average concentration values. K is essential element in in protein synthesis and activation of enzymes (Soetan et al., 2010). K helps in the proper function of brain and nerves and regulates acid-base

and water balance in the blood and tissues (Adamu et al., 2016). The concentrations of K analyzed in the siyez samples varied from 2493 to 6571 mg kg^{-1} with an average of 3712 mg kg^{-1}. The highest concentration of K is analyzed in the Einkorn-4 while the lowest activity concentration is analyzed in the Einkorn-1. The concentration distribution of K exhibits log-normal distribution as shown in Fig. 2. 67% and 33% of K concentrations are between 2400 and 4000 mg kg^{-1} and 4200 and 6600 mg kg^{-1}, respectively. From Table 3, the average K content of the siyez samples investigated is higher than the K content analyzed in emmer (Turkey) and spelt (Czech) while it is lower than the K content analyzed in einkorn (Poland, Czech, Canada and Belgium), emmer (Czech and Belgium), spelt (Canada), buckwheat, (Czech), durum (Turkey) and wheat (Belgium). Ca is the most abundant and important essential element in the human body. Ca plays important role in bones, teeth and muscles system and has key metabolic functions (Adamu et al., 2016). The concentrations of Ca analyzed in the siyez samples varied from 343 to 3669 mg kg^{-1} with an average of 1303 mg kg^{-1}. The highest concentration of Ca is analyzed in the Einkorn-20 while the lowest activity concentration is analyzed in the Einkorn-2. The frequency distribution of Ca concentration exhibits a log-normal distribution. Approximately 71% of Ca concentrations are in the range of 340 to 1100 mg kg^{-1}. The average Ca content of the siyez samples investigated is significantly higher than the Ca content analyzed in einkorn, emmer, spelt, buckwheat, durum and other wheat samples grown in different countries. Mg is an important essential element for all the cells in human body and present in many enzymes involved in lipids, proteins, and carbohydrate metabolism (Adamu et al., 2016). It activates more than 300 enzymes in the body (Abugoufa et al., 2020). The concentrations of Mg analyzed in the siyez samples varied from 369 to 1706 mg kg^{-1} with an average of 656 mg kg^{-1}. The highest concentration of Mg is analyzed in the Einkorn-4 while the lowest activity concentration is analyzed in the Einkorn-18. The frequency distribution of Mg concentration exhibits a log-normal distribution. Approximately 91% of Mg concentrations are in the range of 350 to 950 mg kg^{-1}. The average Mg content of the siyez samples investigated is higher than the Mg content analyzed in emmer (Turkey) while it is lower than those analyzed in einkorn, emmer, spelt, buckwheat, durum and other wheat samples grown in different countries. Na is an essential element for all living organisms (Adamu et al., 2016). Especially it is of great important for maintaining the balance of the fluid system and the work of nerves and muscles in the human body (Adamu et al., 2016). The concentrations of Na analyzed in the siyez samples varied from 28 to 97 mg kg^{-1} with an average of 53 mg kg^{-1}. The highest concentration of Na is analyzed in the Einkorn-14 while the lowest activity concentration is analyzed in the Einkorn-2. The frequency distribution of Na concentration exhibits a non-normal distribution. Approximately 86% of Na concentrations are in the range of 25 to 85 mg kg^{-1}. The average Na content of the siyez samples investigated is higher than the Na content analyzed in einkorn (Poland and Czech), spelt and buckwheat (Czech), durum (Turkey) and wheat (Belgium) while it is lower than the Na content analyzed in emmer (Czech and Belgium) and einkorn (Belgium).

Table 2. Concentrations of macrominerals in the einkorn (siyez)

Sample code	Concentration of macrominerals (mg kg^{-1})			
	Na	Mg	Ca	K
Einkorn-1	57.1	520.0	2806.7	2493.0
Einkorn-2	27.7	538.7	343.1	3113.3
Einkorn-3	86.3	1009.1	590.9	5286.3
Einkorn-4	77.0	1706.1	3548.1	6571.2
Einkorn-5	52.6	581.7	373.3	3315.1
Einkorn-6	41.8	739.8	724.5	4139.4
Einkorn-7	38.2	603.9	542.5	3664.7
Einkorn-8	36.8	375.3	1063.2	2701.2
Einkorn-9	50.5	456.3	2809.9	3210.1
Einkorn-10	29.5	700.9	1537.2	4151.8
Einkorn-11	31.2	597.1	516.2	3578.7
Einkorn-12	29.8	835.3	449.9	4317.0
Einkorn-13	40.4	440.6	462.9	2721.9
Einkorn-14	96.5	895.5	3482.1	5625.2
Einkorn-15	29.7	382.5	942.5	3003.7
Einkorn-16	28.2	491.0	453.8	2954.3
Einkorn-17	64.7	818.1	638.4	4134.7
Einkorn-18	83.9	369.1	706.5	2769.3
Einkorn-19	72.8	431.9	645.9	3097.1
Einkorn-20	38.9	498.9	3669.1	3239.1
Einkorn-21	91.4	780.6	1045.3	3871.4
Average	52.6	655.8	1302.5	3712.3
Standard error	5.1	66.1	255.6	229.4
Median	41.8	581.7	706.5	3315.1
Standard deviation	23.3	303.0	1171.3	1051.2
Kurtosis	-1.1	6.6	-0.1	1.6
Skewness	0.6	2.2	1.2	1.4
Min	27.7	369.1	343.1	2493.0
Max	96.5	1706.1	3669.1	6571.2

Table 3. Concentrations of microminerals in the einkorn (siyez)

Sample code	Concentration of microminerals (mg kg-1)				
	Fe	Zn	Mn	Cr	Cu
Einkorn-1	712.40	28.05	30.01	0.70	0.58
Einkorn-2	37.70	34.89	22.02	0.30	3.49
Einkorn-3	93.30	49.77	39.64	0.37	0.97
Einkorn-4	1834.90	50.86	62.83	5.46	2.53
Einkorn-5	35.90	39.59	24.06	0.33	0.15
Einkorn-6	140.10	32.82	29.90	1.76	0.30
Einkorn-7	36.70	25.76	22.99	0.67	0.14
Einkorn-8	35.40	16.45	20.22	0.11	0.47
Einkorn-9	37.50	33.66	24.23	0.52	0.30
Einkorn-10	36.80	23.50	28.49	0.30	0.09
Einkorn-11	37.20	23.95	23.34	0.27	0.17
Einkorn-12	36.20	30.14	29.79	0.22	0.20
Einkorn-13	35.50	43.50	24.68	0.28	0.08
Einkorn-14	37.90	42.03	40.51	0.52	0.81
Einkorn-15	38.10	26.39	22.43	0.27	0.61
Einkorn-16	39.02	30.86	24.29	0.18	0.08
Einkorn-17	40.70	50.18	29.47	0.48	0.12
Einkorn-18	38.90	30.12	20.29	0.15	0.45
Einkorn-19	39.70	45.81	27.02	0.20	0.07
Einkorn-20	38.30	28.92	25.02	0.50	0.42
Einkorn-21	126.80	34.68	29.55	1.10	0.20
Average	167.10	34.38	28.61	0.70	0.58
Standard error	89.38	2.11	2.08	0.25	0.19
Median	38.10	32.82	25.02	0.33	0.30
Standard deviation	409.58	9.66	9.52	1.15	0.86
Kurtosis	15.28	-0.70	8.21	16.16	7.25
Skewness	3.83	0.30	2.61	3.89	2.71
Min	35.40	16.45	20.22	0.11	0.07
Max	1834.90	50.86	62.83	5.46	3.49

Table 4. Comparison of the average concentration of macrominerals with the literature values

Wheat type/Origin	Concentration (mg kg^{-1})				Reference
	Ca	K	Mg	Na	
Einkorn/Czech	290	3940	1310	18	Gabrovská et al. 2002
Einkorn/Poland	420	4290	1630	7	Suchowilska et al. 2012
Einkorn/Canada	-	3900	-	-	Abdel-Aal et al. 1995
Einkorn/Poland	690	4890	1490	-	Rachoń et al. 2014
Einkorn/ Belgium	570	5715	1516	106	Daelemans et al. 2019
Einkorn/Hungary	540	-	1434	-	Bâlint et al. 2001
Emmer/Belgium	423	5308	1671	143	Daelemans et al. 2019
Emmer/(Turkey)	-	1630	380	-	Zengin, 2015
Emmer/Czech	260	3730	1300	71	Gabrovská et al. 2002
Buckwheat/Czech	200	4550	2060	28	Gabrovská et al. 2002
Spelt/Czech	280	2810	1170	29	Gabrovská et al. 2002
Spelt/Canada	-	3750	-	-	Abdel-Aal et al. 1995
Durum/Turkey	479	4770	1119	26	Ertop and Atasoy (2019)
Durum/Poland	600	4390	1170	-	Rachoń et al. 2014
Wheat/Belgium	371	4448	1300	26	Daelemans et al. 2019
Einkorn (siyez)/Turkey	1303	3712	656	53	This study

As can be seen form Table 3, microminerals are ranked as iron (Fe) > zinc (Zn) > manganese (Mn) > chromium (Cr) > copper (Cu) according to their average concentration values. The concentrations of Fe analyzed in the siyez samples varied from 35.4 to 1834.9 mg kg^{-1} with an average of 167.1 mg kg^{-1}. The highest concentration of Fe is analyzed in the Einkorn-4 while the lowest activity concentration is analyzed in the Einkorn-8. The average Fe content of the siyez samples investigated is significantly higher than the Fe content analyzed in einkorn, emmer, spelt, buckwheat, durum and other wheat samples grown in different countries. The concentrations of Zn analyzed in the siyez samples varied from 16.5 to 50.9 mg kg^{-1} with an average of 34.4 mg kg^{-1}. The highest concentration of Zn is analyzed in the Einkorn-4 while the lowest activity concentration is analyzed in the Einkorn-8.

Table 5. Comparison of the average concentration of microminerals with the literature values

Wheat type/Origin	Concentration (mg kg^{-1})				Reference
	Mn	Fe	Cu	Zn	
Einkorn/Poland	28	49	4	53	Suchowilska et al. 2012
Einkorn/Czech	34	29	-	42	Gabrovská et al. 2002
Einkorn/Canada	44	-	6	-	Abdel-Aal et al. 1995
Einkorn/Poland	55	54	4	66	Rachoń et al. 2
Einkorn/Hungary	-	41	6	35	Bâlint et al. 2001
Einkorn/Belgium	-	41	6	46	Daelemans et al. 2019
Einkorn/Israel	-	48	-	56	Çakmak et al. 2000
Emmer/Czech	29	36	-	40	Gabrovská et al. 2002
Emmer/Turkey	32	46	-	34	Zengin, 2015
Emmer/Belgium	-	61	7	38	Daelemans et al. 2019
Emmer/Turkey	18	42	3	17	Tekin et al., 2018
Spelt/Czech	28	29	-	31	Gabrovská et al. 2002
Spelt/Canada	37	-	-	-	Abdel-Aal et al. 1995
Durum/Turkey	-	28	6	-	Ertop and Atasoy (2019)
Durum/Israel	-	32	-	31	Çakmak et al. 2000
Durum/Turkey	-	39	-	26	Çakmak et al. 2000
Durum/Turkey	30	37	14	3	Tekin et al., 2018
Buckwheat/Czech	17	23	-	28	Gabrovská et al. 2002
Wheat/Belgium	-	44	5	33	Daelemans et al. 2019
Einkorn (siyez)/Turkey	29	167	0.6	34	This study

Table 6. Pearson's correlation coefficient for mineral concentrations

elements	Na	Mg	Ca	K	Fe	Zn	Mn	Cr	Cu
Na	1.0								
Mg	0.4	1.0							
Ca	0.3	0.4	1.0						
K	0.5	0.9	0.4	1.0					
Fe	0.3	0.7	0.5	0.5	1.0				
Zn	0.6	0.6	0.1	0.5	0.3	1.0			
Mn	0.5	0.9	0.5	0.9	0.8	0.6	1.0		
Cr	0.3	0.8	0.5	0.7	0.9	0.4	0.8	1.0	
Cu	0.1	0.4	0.2	0.3	0.5	0.3	0.4	0.5	1.0

The average Zn content of the siyez samples investigated is higher than the Zn content analyzed in emmer (Turkey), spelt (Czech), Durum (Turley, Israel), buckwheat and wheat (Belgium) while it is lower than those analyzed in einkorn (Poland, Czech, Canada, Hungary, Israel, and Belgium), emmer (Czech, and Belgium). The concentrations of Mn analyzed in the siyez samples varied from 20.2 to 62.8 mg kg^{-1} with an average of 28.6 mg kg^{-1}. The highest concentration of Mn is analyzed in the Einkorn-4 while the lowest activity concentration is analyzed in the Einkorn-8. The average Mn content of the siyez samples investigated is higher than the Mn content analyzed in einkorn (Poland), emmer (Turkey), spelt (Czech), and buckwheat (Belgium) while it is lower than those analyzed in einkorn (Czech, Canada), spelt (Canada), and drum (Turkey). The concentrations of Cr analyzed in the siyez samples varied from 0.1 to 5.5 mg kg^{-1} with an average of 0.7 mg kg^{-1}. The highest concentration of Cr is analyzed in the Einkorn-4 while the lowest activity concentration is analyzed in the Einkorn-8. The concentrations of Cu analyzed in the siyez samples varied from 0.1 to 3.5 mg kg^{-1} with an average of 0.6 mg kg^{-1}. The highest concentration of Cu is analyzed in the Einkorn-2 while the lowest activity concentration is analyzed in the Einkorn-19. The average Cu content of the siyez samples investigated is significantly lower than the Cu content analyzed in einkorn, emmer, spelt, buckwheat, durum and other wheat samples grown in different countries.

The Pearson coefficients for the relationship between the macro- and microminerals analyzed in the einkorn (siyez) samples are given in Table 6 in which bold value indicates significant correlation at P≤0.05. It can be observed from Table 6 that strong positive correlation coefficients are obtained for the following minerals: Mg vs. K (0.9), Fe (0.7), Mn (0.9) and Cr (0.8); K vs. Mn (0.9) and Cr (0.7); Fe vs. Mn (0.8) and Cr (0.9); Mn vs. Cr (0.8).

Conclusions

The literature comparison revealed that the investigated siyez samples are richer in terms of Ca and Fe contents compared to einkorn, emmer, spelt, buckwheat, and durum wheat samples grown in different countries and Turkey.

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