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Characterization of the Fatty Acid and Mineral Compositions of Selected Cereal Cultivars from Turkey

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Abstract: In this present study, crude oil, fatty acid and mineral compositions of wheat (*Triticum* sp. L.), barley (*Hordeum vulgare* L.), triticale (*Triticosecale* Wittm. ex A. Camus.), rye (*Secale cereale* L.), and oat (*Avena sativa* L.) cultivars, respectively, from Turkey were investigated. Both the distribution of saturated fatty acids (SFA) and unsaturated fatty acids (UFA), and the mineral contents of evaluated cereals were reported. Fatty acid compositions and mineral contents were determined by gas chromatography/mass spectroscopy (GC/MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) techniques, respectively. The highest crude oil content was found in oat [cv. Seydisehir; 5.35%], whereas the lowest crude oil was in triticale [cv. Aslım-95; 1.19 %]. The results showed that the contents of total UFA in the different cultivars varied between 77.1 - 81.5 %. The major components of the cereal oils were determined as oleic and linoleic acid, respectively. The total macro-, micro- element, and heavy metal contents varied between 8638 - 16108 ppm, 113-180 ppm and 1.8 - 6.9 ppm, respectively. As a conclusion, there were significant ($p < 0.01$) differences between the cereal cultivars in view of their crude oil contents, fatty acid and mineral compositions of the investigated samples from Turkey.

Keywords: Cereal; wheat; barley; oat; triticale; rye; fatty acid; mineral; crude oil; GC/MS; ICP-OES.

1. Introduction

Cereals and their products are among the major dietary sources of essential elements and fatty acids for humans as well as for animals. The contribution of cereal products to the estimated dietary intake of several minerals and nutritionally beneficial trace elements is about 20–30% of the total, in modern societies [1]. Several unsaturated fatty acids (UFAs) are defined as 'essential fatty acids' in the normal diet for preventing nutrition-related pathologies [2]. Whole grains are well known to be the rich sources of fiber, vitamins, minerals, and phytochemicals including phenolic compounds, carotenoids, vitamins, lignans, β-glucan, inulin, resistant starches, sterols, stannols, phytates, *etc*. Plant-based foods such as fruits, vegetables, and cereals, which contain relatively high amounts of bioactive phytochemicals, may provide health benefits beyond basic nutrition to reduce the risk of several chronic diseases [3].

Wheat is the main cereal crop used for human and animal feed consumption worldwide. Common wheat (*Triticum aestivum* L.) is widely used for bread making, whereas durum wheat (*Triticum durum* Desf.) is mainly utilized in the production of other food items such pasta. The wheat grain structure and the composition of storage proteins, starch, lipids, vitamins, and micronutrients is essential for producing high quality grain [4]. Barley (*Hordeum vulgare* L.) is also one of the most

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consumed cereals. Barley was one of the very first agricultural domesticated crops together with wheat, pea, and lentils dating from about 10.000 years ago. Interestingly, barley has not been allocated as such an important grain in human diet. Barley is more associated with the beer industry, malting, and animal feed; 80–90% of barley production is used for malting and animal feedstocks [5]. Rye grain, like other cereal grains, contributes significant quantities of energy, protein, selected micronutrients and non-nutrients to a human diet. Rye (*Secale cereale*) is an excellent raw material for healthy and tasty foods and it has a high fibre content [6]. Triticale (*Triticosecale*) is a hybrid crop developed by crossing wheat (*Triticum*) and rye (*Secale*). The nutritional value of triticale is close to that of wheat and rye. In recent years, the use of triticale in the brewing industry has gained much attention. It produces beer of a quality comparable to that obtained using wheat, but at a lower cost. It can also be used as a renewable crop for more sustainable energy production [7, 8]. Owing to the chemical composition and nutritive and physiological values, oat (*Avena sativa* L.) grain is investigated popularly. Oat grain is has a good taste with dietetic properties and an activity stimulating metabolic changes. Thus the nutritive value is relatively high for both people and animals. Compared to other cereals, oat grain contains a larger amount of total protein and crude fat and a smaller amount of crude fibre. The characteristic feature of its protein is a good amino acid composition with a relatively high nutritive value. A relatively high level of its oil is considered to be a good source of essential unsaturated fatty acids [9].

Zinc (Zn) and iron (Fe) deficiencies are the most common micronutrient deficiencies in human populations affecting health of over three billion people worldwide. According to a report published by the World Health Organization (WHO) in 2002, deficiencies of Zn and Fe, rank fifth and sixth in terms of leading causes of disease in developing high-mortality countries [10]. Cereals are the major staple food crop, contributing most of the human daily calorie intake in many cultures, as well as relevant quantities of minerals. However, it is well known that cereals are poor in concentration and bioavailability of some of these compounds, and therefore, when not consumed in a varied diet, they fail to satisfy the human daily requirements. As a consequence, about half the world population suffers from micronutrient deficiencies. Even in Europe, iron deficiency anaemia is frequent among preschool-age children (21.7%) and non-pregnant women (19%) (WHO et al., 2008), while 4.8% middle-aged Europeans and 5.6% older subjects show Zn deficiency [11].

The chemical characterization of a cereal cultivar is important due to the high consumption in the daily human diet. Cereal grains are grown in relatively high quantities. The nutritional relevance of cereals, and especially wheat has been considered as a characteristic of the Mediterranean diet. Diets including enriched cereal products are encouraged and generally supported in order to improve its nutritional contribution. Recent publications using data from food composition sources, indicate a downward fashion in the mineral content of foods, and it has been associated with intensive farming practices which may result in depletion of soil minerals [11-15]. The *Triticum aestivum* species had higher mean P, Mg, Fe, Cu, Zn and Mn concentrations, and a lower mean Se concentration, than *Triticum turgidum* species. The environment and agronomic practices could affect the genetic information of the seeds determining changes in the mineral and trace element composition [12]. The major factors influencing mineral levels were year and genotype, as well as their interaction. Einkorn varieties exhibited higher Zn (71.8 ppm), Fe (52.3 ppm), Mn (46.5), Cu (9.0), Mg (151.2 ppm) and P (5411 ppm) concentration than bread wheat. Mg concentration correlated positively with that of other bivalent cations (Zn and Ca) [13]. Germ constitutes about 2–3% of the wheat grain and can be separated in a fairly pure form from the grain during the milling process. Wheat germ contains about 11 % oil and wheat germ processing presents challenges due to its high content of polyunsaturated fatty acids and bioactive compounds [14]. The major fatty acids (FA) in spring and winter wheat cultivars are linoleic (C18:2), palmitic (C16:0), and oleic (C18:1) acids, whereas α-linolenic (C18:3) and stearic acids (C18:0) are minor components [15]. A previous report has indicated that total unsaturated fatty acids in the investigated wheat cultivars of *T. durum*, *T. aestivum* varied from 77.34 % to 75.31 %, respectively [16].

Information regarding the nutritional composition of cereals is still limited, especially in cultivars commonly consumed in Turkey. The present study was conducted to determine the composition of the fatty acids and mineral contents in wheat, barley, rye, triticale and oat cultivars cultivated in Turkey by using state of the art analytical systems.

2. Materials and Methods

2.1. Plant Materials

The field trials were conducted at the Experimental Field, Agricultural Faculty, Selçuk University, in Konya, during the growing seasons 2010-2011. Cereal cultivars [common wheat (*T. aestivum* cv. Gerek-79; durum wheat (*T. durum* Desf. cv. Kunduru-1189; barley (*H. vulgare*. cv. Larende); rye (*S. cereale* cv. Aslım-95); triticale (*Triticale* cv. Tatlıcak-97) and oat (*A. sativa* cv. Seydişehir) selected and cultivated in Turkey were used as study material. Noteworthy in the experimental field, summer period was dry and hot, whereas winter was rainy and cold. The soil had a sand-loam characteristic. The planting of the plant material was at the beginning of October. The experiment was designed in completely randomized block design with three replications. No fertilizers, fungicidal or insecticidal treatments were applied. The harvesting period was in July. Samples were taken randomly from each plot for analyses.

2.2. Extraction of the Oils

The oil extraction of the dried and powdered cereal seeds (5 g) was carried out at 40 °C for 6 h by Soxhlet extractor using diethyl ether. The solvent was removed by rotary evaporator. The obtained oil was esterified to determine the fatty acid composition. Methylation of the fatty acids was carried out according to the AACC Official Method [17].

2.3. Fatty Acid Analysis by GC/MS

GC analysis was performed on an Agilent 6890N system. The column was HP Innowax Capillary; 60 m × 0.25 mm, 0.25 µm. The column temperature was held initially at 60 °C for 3 min after the injection, then increased to 185 °C with 10 °C min^{-1} heating ramp, and increased to 200 °C with 5 °C min^{-1} heating ramp for 10 min. Then, the final temperature was increased to 220 °C with 5 °C min^{-1} heating ramp for 20 min. The injector temperature was 250 °C; detector (FID) temperature was 275 °C. The carrier gas was He with an inlet pressure of 40.65 psi. The linear gas velocity was at 39 cm s^{-1} where the column flow rate was 2.7 mL min^{-1}. The splitless mode was used with an injection volume of 1 µL. Agilent 6890N system was used for the GC/MS analyses combined with Agilent 5973 MS Selective Detector. The GC conditions were; as column HP Innowax Capillary (60 m × 0.25 mm, 0.25 µm). The oven temperature program was set so that the column was held initially at 60 °C for 3 min after injection, then increased to 185 °C with 10 °C min^{-1} heating ramp and increased to 200 °C with 5 °C min^{-1} heating ramp for 10 min. Then the final temperature was increased to 220 °C with 5 °C min^{-1} heating ramp for 20 min. The injector temperature was set to 250 °C. The carrier gas was helium with an inlet pressure of 40.65 psi. The linear gas velocity was 44 cm s^{-1} at a column flow of 2.9 mL min^{-1} in splitless mode. The MS conditions were; ionization energy was 70 eV, the ion source temperature was 280 °C, the interface temperature was 250 °C where the MS range was set to 35–450 atomic mass units. Determination of the components in the cereal fatty oils was performed by comparison of their MS with commercial libraries such as Wiley and NIST GC/MS Libraries and their retention indices, relative to *n*-alkanes (C6-26 series) as well as corresponding data from relevant literature [17]. The relative percentages (%) of the components were calculated from the GC peak areas using the normalization method.

2.4. Determination of Minerals

The analyses of mineral compositions in the cereal cultivars studied herein were performed using macro element (P, K, Ca, Mg, Na) and micro trace elements (Fe, B, Mn, Zn, Cu) and heavy metal (Pb, Ni, Cr, Co) content was determined on a Varian Vista-MPX simultaneous ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) with CCD detection [18]. It was used to analyze the elements in cereal samples. All experiments were performed qualitatively and quantitatively with statistical data comparison to a certified reference plant material, respectively.

2.8. Statistical Analysis

Each parameter was tested in triplicate samples with three replications. Conventional statistical methods were used to calculate means. Collected data were subjected to statistical analyses using JMP statistical package software (Version 5.0.1.a, SAS Institute. Inc. Cary, NC). One way ANOVA was used to evaluate the effect of cereal varieties on the parameters studied. When significant ($p < 0.01$) main effect was found, the mean values were further analyzed using the t-test.

3. Results and Discussion

3.1. Crude oil Content of the Cereal Cultivars

Table 1 indicates that there were significant (p <0.01) differences between the cereal cultivars with respect to their crude oil contents and fatty acids (saturated and unsaturated) compositions. The oil yields of the cereal cultivars ranged from 1.19 to 5.35 %. This results revealed that the highest crude oil content was determined in oat (*A. sativa* cv. Seydişehir; 6.43 %) cultivar, followed by durum wheat (*T. durum* cv. Kunduru-1189; 1.76 %), common wheat (*T. aestivum*. cv. Gerek-79; 1.44 %), rye (*S. cereale* cv. Aslım-95; 1.37%), barley (*H. vulgare* cv. Larende 1.27 %) and triticale (*Triticosecale* cv. Tatlıcak-97; 1.19 %) cultivars.

Interactions between cereal cultivar and fat content may vary considerably depending on the plant species, genotype and cultivated conditions, as also observed within these experiments.

3.2. The Fatty Acid Compositions of the Cereal Cultivars

Table 1. summarizes the results of fatty acids composition from cereal oils. In the course of the present study, 8 main components amounting to 99.35 % of the cereals oils were identified in the samples. Regarding the fatty acid compositions of the cereal cultivars, according to this results for comparison of the unsaturated fatty acid (palmitoleic (16:1), oleic (18:1), linoleic(18:2) and linolenic (18:3) acid), and saturated fatty acids [myristic (14:0), palmitic (16:0), stearic acid (18:0), and arachidic (20:0)] compositions with respect to the cultivars were also presented in Figure 1. Total saturated fatty acid contents ranged from 17.07 to 22.26 whereas total unsaturated fatty contents acids ranged from 77.09 to 81.46. The content of total unsaturated fatty acids content was higher in rye cultivar (81.46 %) than in oat (80.12 %), triticale (79.51 %), durum wheat (78.14 %), and common wheat (77.97 %) and in barley (77.09 %). The major constituents of cereal cultivars oils are oleic acids (=omega 3), linoleic acid (= omega 6) and linolenic acid (= omega 9). The environmental and genotype factors may have a great influence on oil content and fatty acids composition [16]. Thirteen fatty acids were detected with oleic, linoleic and palmitic acids comprising more than 95% of the total fatty acids in Australian oats grown in several locations [20].

The major component of cereal oils were linoleic acid (52.16 %) for durum wheat, (59.10 %) for common wheat, (55.20 %) for barley, (55.01 %) for rye, (59.26 %) for triticale, while oleic acid (40.55%) for oat cultivar grain was major component. The compositions of polyunsaturated fat oil observed in cereal cultivars were in agreement with previous results [16,19-21].

3.3. Mineral Composition of the Cereal Cultivars

Table 2 shows the mean value of the tested macro elements (K, P, Ca, Na and Mg) in cereal cultivars. The highest K content was detected in common wheat cv. (6490 ppm), whereas the lowest content was determined in triticale cv. (4510 ppm). Furthermore, the highest and lowest P contents were found in common wheat cv. (5503 ppm) and in triticale cv. (2933 ppm), respectively. Ca and Mg contents were varied from 1133, 2766 to 184,1011 respectively. On the other hand, it observed that the Na was the lowest macro element of cereal cultivars analyzed (Figure 2). The most abundant macro elements in cereal cultivars were potassium (K) phosphorus (P). It is reported that macro elements P (5411 ppm), K (3221 ppm), Ca (3876 ppm) and Mg (1512 ppm) concentrations were determined in bread wheat cultivar [13].

Table 1. Fatty acid composition of selected cereals cultivated in Turkey

Cereals	Crude oil (%)	Saturated Fatty Acids (SFA) (%) Myristic acid RI	C14:0	Palmitic acid RI	C16:0	Stearic acid RI	C18:0	Arachidic acid RI	C20:0	ΣSAFA (%)	Unsaturated fatty acids (UFA) Palmitoleic acid RI	C16: 1	Oleic acid RI	C18:1	Linoleic acid RI	C18:2	Linolenic acid RI	C18:3	ΣUFA (%)
***T. durum* cv. Kunduru 1149**	1.76^{b}	1224	0.12^{b}	1286	18.79^{a}	1565	1.52^{a}	1844	**0.15^{c}**	20.59^{a}	1296	0.24^{a}	1597	23.40^{b}	1654	52.16^{a}	1739	2.35^{c}	78.14^{b}
***T. aestivum* cv. Gerek 79**	1.44^{b}	1224	0.12^{b}	1286	18.26^{a}	1566	1.20^{a}	1844	0.17^{c}	19.75^{a}	1296	0.21^{a}	1597	**14.86^{c}**	1657	59.10^{a}	1741	3.81^{b}	77.97^{b}
***H. vulgare* cv. Larende**	1.27^{b}	1224	0.30^{a}	1286	**20.41^{a}**	1566	1.25^{a}	1843	**0.30^{a}**	**22.26^{a}**	1296	**0.13^{b}**	1598	17.08^{c}	1658	55.20^{a}	1742	4.69^{b}	**77.09^{b}**
***S. cereale* cv. Aslım 95**	1.37^{b}	1224	**0.11^{b}**	1286	**15.92^{b}**	1565	0.87^{b}	1844	0.18^{c}	**17.08^{b}**	1296	**0.30^{a}**	1598	19.42^{c}	1656	55.01^{a}	1741	**6.73^{a}**	**81.46^{a}**
***T. Wittmack* cv. Tatlıcak 97**	**1.19^{b}**	1224	0.14^{b}	1286	19.03^{a}	1565	**0.31^{c}**	1844	0.17^{c}	19.65^{a}	1296	0.23^{a}	1598	15.39^{c}	1656	**59.26^{a}**	1741	4.63^{b}	79.51^{a}
***A. sativa* cv. Seydişehir**	**5.35^{a}**	1224	**0.30^{a}**	1286	16.76^{b}	1566	**1.79^{a}**	1844	0.21^{b}	19.05^{a}	1296	0.16^{b}	1599	**40.55^{a}**	1654	**38.54^{b}**	1739	**0.87^{d}**	80.12^{a}
min:	**1.19**		**0.11**		**15.92**		**0.31**		**0.15**	**17.08**		**0.13**		**14.86**		**38.54**		**0,87**	**77,09**
max:	**5.35**		**0.30**		**20.41**		**1.79**		**0.30**	**22.26**		**0.30**		**40.55**		**59.26**		**6,73**	**81,4**

ΣSFA; total saturated fatty acid content, **ΣUFA**; total unsaturated fatty acid content.

[a,b,c] Means with no common superscripts within each row are significantly different ($p < 0.01$).

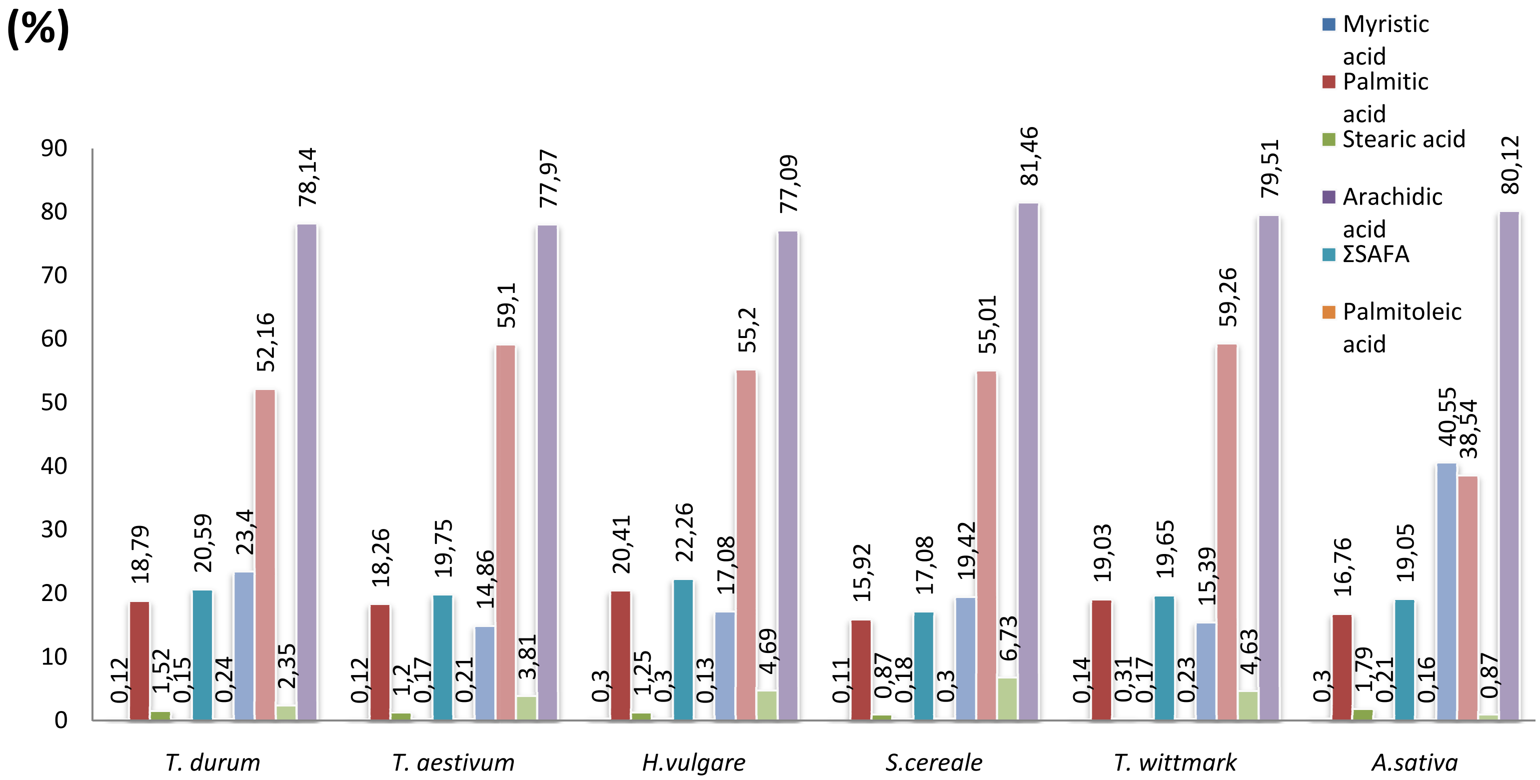

Figure 1. Fatty acid composition of selected cereals cultivated in Turkey

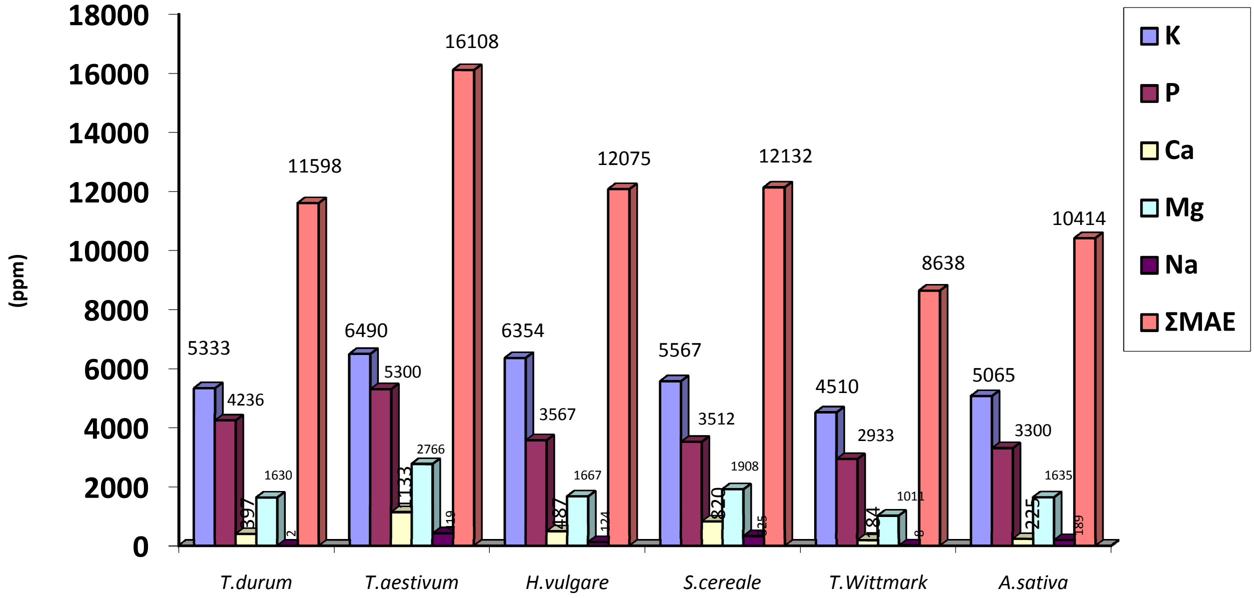

Figure 2. Macro elements contents of selected cereals cultivated in Turkey

On the other hand, total micro element composition (MIEs) of cereal cultivars varied from 113 to 180 ppm. It was observed that the highest iron (Fe) were to be in oat cv. (92 ppm). The lowest iron content was determined rye cv. (32 ppm). The highest zinc (Zn) content was detected in rye cv. (28 ppm), whereas the lowest content was determined in durum wheat cv. (20 ppm). The results of trace elements are presented in Table 2~~.~~, and Figure 3. Significant differences were also found in content of trace elements among cereal cultivars. Manganese (Mn) content ranged from 17 to 40 ppm and Boron (B) content was varied 13 to 47. In present study, Cupper (2-8 ppm) in cereal cultivars was the lowest quantity. It was reported that significant differences were found in total content of iron and zinc among cereal cultivars and results also showed that iron content ranged from 46 to 10 ppm and zinc content from 22 to 62 ppm for nine different cereal cultivars.

In another study, the zinc (Zn) and iron (Fe) contents of wheat were found to be 28.5 - 46.3 for Zn and from 33.6-65.6 for Fe, respectively. The results were much lower than that of our investigated samples [18]. Noteworthy, several factors may affect the elemental contents of plants such as the variety, harvesting time, soil type, soil conditions, fertilization, irrigation and weather etc. [22, 23].

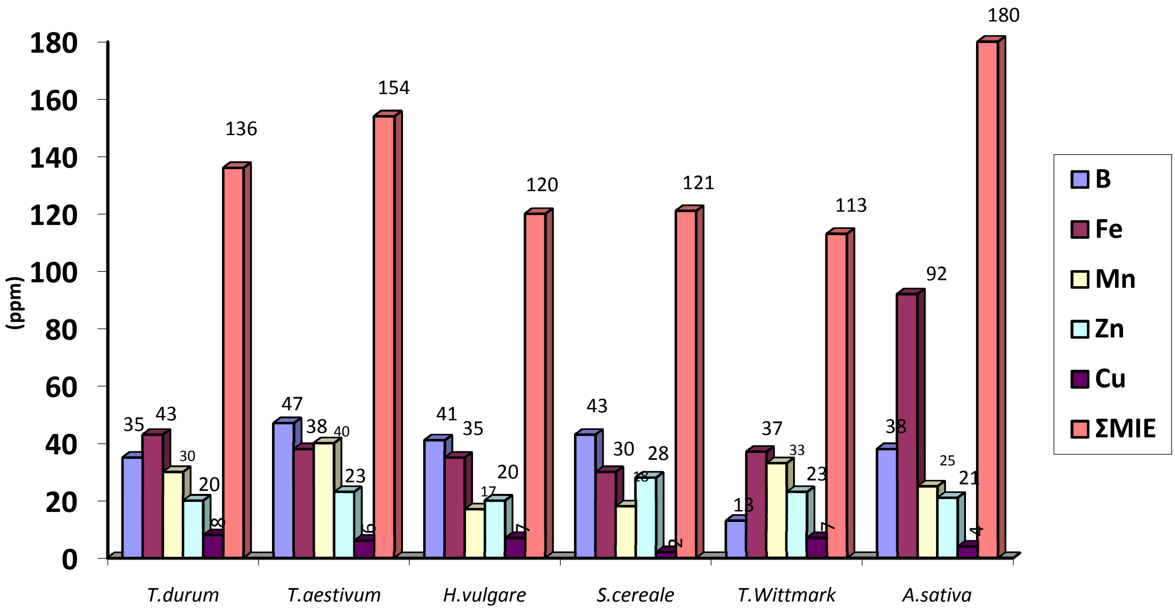

Figure 3. Micro elements contents of selected cereals cultivated in Turkey

Furthermore, as it can be seen in Table 2. the composition of heavy metals such as lead (Pb), nickel (Ni), chrome (Cr) and cobalt (Co) of the cereal cultivars ranged from 1.8 to 6.9 (comparative Figure 4.). The highest heavy metal lead (Pb) content varied between 1 ppm and 5.4 ppm. The lowest heavy metal cobalt (Co) content ranged from 0.3 ppm to 0.2 ppm. It was indicated that the concentration of heavy elements in cereal cultivars are affected by various agricultural practices, type of soil, type of fertilizer and chemicals used type of pesticides and herbicides sprayed. The values obtained from this study are in agreement to the Zn and Fe values reported previously for the cereals [22, 24].

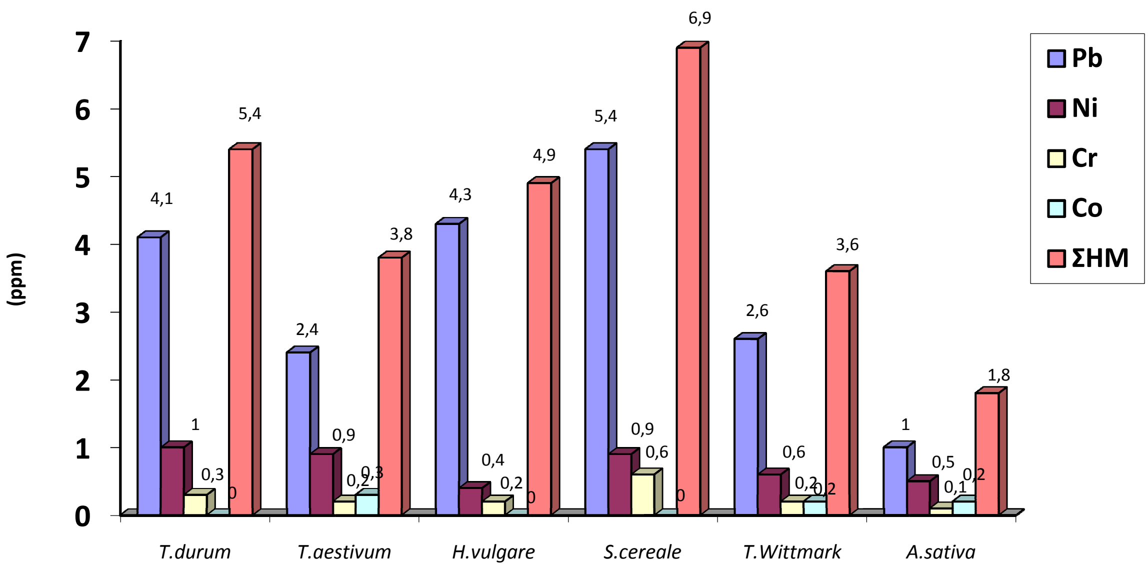

Figure 4. Heavy metals contents of selected cereals cultivated in Turkey

Table 2. Mineral contents of selected cereals cultivated in Turkey

	Macro elements (ppm)							Micro elements (ppm)					Heavy metals (ppm)				
Cereals	**K**	**P**	**Ca**	**Mg**	**Na**	**ΣMAE**	**B**	**Fe**	**Mn**	**Zn**	**Cu**	**ΣMIE**	**Pb**	**Ni**	**Cr**	**Co**	**ΣHM**
T. durum cv. Kunduru 1149	5333^{b}	4236^{b}	397^{c}	1630^{c}	**2^{c}**	11598^{b}	35^{b}	43^{b}	30^{b}	**20^{b}**	**8^{a}**	136^{c}	4.1^{a}	**1.0^{a}**	0.3^{b}	**nd**	5.4^{a}
T. aestivum cv. Gerek 79	**6490^{a}**	**5300^{a}**	**1133^{a}**	**2766^{a}**	**419^{a}**	**16108^{a}**	**47^{a}**	38^{b}	**40^{a}**	23^{b}	6^{b}	154^{b}	2.4^{b}	0.9^{a}	0.2^{c}	**0.3^{a}**	3.8^{c}
H. vulgare cv. Larende	6354^{a}	3567^{c}	487^{c}	1667^{c}	124^{b}	12075^{b}	41^{a}	35^{b}	**17^{c}**	20^{b}	7^{a}	120^{c}	4.3^{a}	**0.4^{b}**	0.2^{c}	**nd**	4.9^{b}
S. cereale cv. Aslım 95	5567^{b}	3512^{c}	820^{b}	1908^{b}	325^{a}	12132^{b}	43^{a}	**30^{b}**	18^{c}	**28^{a}**	**2^{d}**	121^{c}	**5.4^{a}**	0.9^{a}	**0.6^{a}**	**nd**	**6.9^{a}**
T. Wittmack cv. Tatlıcak 97	**4510^{c}**	**2933^{d}**	**184^{e}**	**1011^{d}**	8^{c}	**8638^{d}**	**13^{c}**	37^{b}	33^{b}	23^{b}	7^{a}	**113^{c}**	2.6^{b}	0.6^{b}	0.2^{c}	**0.2^{b}**	3.6^{c}
***A. sativa cv.* Seydişehir**	5065^{b}	3300^{c}	225^{d}	1635^{c}	189^{b}	10414^{c}	38^{b}	**92^{a}**	25^{b}	21^{b}	4^{c}	**180^{a}**	**1.0^{c}**	0.5^{b}	**0.1^{d}**	**0.2^{b}**	**1.8^{a}**
min:	**4510**	**2933**	**184**	**101**	**2**	**8638**	**13**	**30**	**17**	**20**	2	**113**	**1.0**	**0.4**	**0.1**	**0.2**	**1.8**
max:	**6490**	**5300**	**1133**	**2766**	**419**	**16108**	**47**	**92**	**40**	**28**	8	**180**	**5.4**	**1.0**	**0.6**	**0.3**	**6.9**

ΣMAE; total macro element content, **ΣMIE**; total micro element content, **ΣHM,** total heavy metal content

[a,b,c] Means with no common superscripts within each row are significantly different ($p < 0.01$).

nd; not determined

As an overall result, the differences of the applied practices study may have caused the observed increases of heavy metals (such as Pb, Ni, Cr, Co) within the cereals under cultivation conditions. In conclusion of this study, the results indicate that the investigated cereal cultivars are rich in unsaturated fatty oil and mineral content, respectively. Furthermore, it is concluded that the genetic differences of the species and cultivars significantly influenced their chemical composition of minerals and fatty acids. The finding of these outcomes may be applied to functional foods and special diets directly as part of the daily intake of the consumer.

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