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Evaluation of the mineral content of winter wheat in light of/as a result of the new studies

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1. Summary

Today, more and more emphasis is placed by food and nutrition research and practice on the chemical composition of winter wheat, which is considered a staple food, both in terms of organic and inorganic macro- and microcomponents. This attention is the result of several factors, of which should be highlighted the expansion of the possibilities in instrumental analysis (HPLC, HPLC-MS, ICP-OES, ICP-MS), as well as the often changing factors closely related to cultivation technology (varieties, hybrid, plant protection, fertilization, frequency of weather extremes). As a result, over the past two decades, researchers have been focusing more and more on the question whether the chemical, as well as the feedstock and nutritional physiology quality of crops, including wheat, changed because of intensive agrotechnics and the genetic capabilities of the new varieties. My intention was to provide satisfying answers, based on the analytical data of the large number of samples coming from different experiments (long-term experiments), to the questions that had been raised, one of the most important of which is the question how the mineral content of winter wheat, a staple food, had changed over the last hundred years. To this end, I used samples that had been archived at different locations of Hungary and analyzed using state-of-the-art measurement methods.

Mineral content is the quality indicator that can be used reliably to estimate and interpret long-term effects (fertilization, plant protection, SO2 emission, atmospheric nuclear explosions, accompanying elements of fertilizers, climate change, switching varieties), because it changes very little in archived samples. Phosphorus, potassium, calcium, magnesium, iron, manganese, zinc, copper and strontium were included in the analyses.

The results obtained can help researchers and practical experts of nutritional science interested in the topic to form a realistic picture about the effect of environmental factors and agrotechnics on the composition of cereals.

2. Introduction

In Hungary, research intended to follow the changes in the mineral contents of the cultivated plants started already in the late 1950s. The first results related to our topic were published by the then recognized researchers of the discipline **[1] [2] [3]**. In the early 1970s, with the advent of the use of intensive agrotechnics, such research was launched in Debrecen as well **[4]**. Noteworthy is Sarkadi's remark on the communication of the results. *„It should be noted that some of the literature – primarily publications on basic research, but recently some practical publications abroad as well – expresses nutrients not as oxides but as the elements (P: P2O5 = 2.29; K: K2O=1.2). Unfortunately, this duality can lead to misunderstandings"* **[5]**. This observation is important, because the first compilation of the mineral elements of wheat

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was published in Hungary in 1942, and in this, results were expressed not as the elemental quantities, but as the oxides by the author **[6]**. At that time, no further data were published for the grain yield itself, and little data from Germany was reported about the mineral content of different flours (wheat, corn) **[7]**.

With the expansion of research opportunities in Hungary, significant research began at the Institute for Soil Sciences and Agricultural Chemistry of the Hungarian Academy of Sciences (MTA TAKI) and at the Agricultural University of Debrecen (DATE) to investigate the mineral contents of cereals. As a result, researchers found that there had been no significant change in the mineral content **[8], [9], [10]**. Expansion of the Hungarian database was indicated by the fact that variety comparison results were published by Martonvásár researchers **[11], [12]**. At the same time, newer data on changes in the mineral content were published by foreign researchers who had at their disposal field research experimental and sample archiving capabilities, as well as analytical testing capabilities.

Of these, publication of the results of the processing samples of the Rothamsted experimental site, established in 1843, stands out, according to which there had been no change in the mineral content of the samples up to 1965, and then, with the spread of short-stemmed wheat varieties, the amount of certain elements (Cu, Mg, Zn) decreased by 15-25% by today **[13]**. When comparing crops obtained via organic and intensive farming, it was found that the mineral content of wheat grown using organic technology was higher, especially when growing ancient varieties and species **[14]**.

According to data published about varieties grown in different ecological environments, there was a significant difference between the iron and zinc contents of different bread wheat genotypes, but no such difference was observed in the case of selenium **[15]**. According to the data of long-term experiments in Sweden, a decrease in air pollution resulted in a significant decrease of the lead and cadmium contents of wheat samples, while the copper and iron contents decreased as the effect of NPK fertilization **[16]**, however, as the effect of nitrogen fertilization, an increase in the iron, zinc and copper contents were reported **[17]**. Comparison of domestic and international data is shown in ***Table 1***, in which relevant results are presented with uniform units of measurement.

For the concentrations of the different elements, specific values are given by certain authors, while other indicate fairly wide ranges. The first reliable domestic data come from the early 1960s, unfortunately, analytical results are only available for four elements (P, K, Ca, Mg), but they are in good agreement with data from other sources, published among international research results. As a result of the work of Imre Kádár, there are analytical results available for 8 elements from the late 1990s, and these results show good agreement with international literature data **[8]**. From the book of Imre Rodler, nutrition physiological data can be obtained, but both the results for potassium content and magnesium content are low in his work. There were no manganese content measurement results published **[31]**. Data on the zinc contents of winter wheat samples from different regions of the world ranged from 21.9 to 38.5 mg/kg: 26.3-38.5 mg/kg in Germany, 28.0 mg/kg in Denmark and Sweden, 32.6 mg/kg in Finland, 21.9-27 mg/kg in the USA, 22.0 mg/kg in Turkey and 26.0 mg/kg in India **[18]**. These quantities indicate significantly smaller differences than the ones published by Piironan et al. in Table 1 **[27]**. One of the major problems of today is the effect of climate change and, in particular, the increasing carbon dioxide content of the atmosphere on the zinc and iron contents of C3 and pulse crops **[19]**, since this decrease results in the change (decrease) of the element content of the staple foods of billions of people, thus increasing malnutrition. In Hungary, data on the decrease in the element contents of several plants from 1942 to 2005 were published in 2013 **[20]**. In this work, a 50% decrease in the mineral content of winter wheat is reported, but the source is only referred to as a figure from a Gödöllő source **[21]**.

Because of the occasionally contradictory results and because of the stressing of the accompanying dramatic decrease in the media, taking into consideration mainly nutrition physiological aspects, we decided to perform analyses partly by the uniform testing (instrument, method) of the sample material available in Hungary, and to evaluate the measurement results obtained by comparing them to the data of the thousands of samples analyzed earlier. This was decided because we had all the conditions available to us which were essential for the determination of element content. These are as follows: reliable sample material going back for decades (archiving), evaluation and interpretation element by element, taking into account of several factors, preferably a uniform method, measurements carried out at the same time.

3. Materials and methods

The samples included in the study came from several experimental sites and collections, which are shown in ***Table 2***.

These grain samples either came from agrotechnical experiments, where the effect of fertilization on different soil types was mainly investigated, or the crop yields of different varieties in different growing areas were evaluated. In the case of the „old sample material" (1839-1936) there was no such background information available. To characterize the samples, only a simple designation („aestivum") or – as for the 1965-68 samples – the sampling location (regional varieties?) was known.

From the experiments after 1974, several thousands of grain samples have been analyzed, while the number of samples several decades old – from before 1974 – was limited. In the case of small sample quantities, usually micro-digestion had to be used. Cutting and homogenization of the samples were performed using Retsch Sk-1 and Sk-3 instruments. For the analysis of minerals, an incineration digestion method was used initially **[24]**, while later a wet digestion procedure was applied (using a mixture of nitric acid and hydrogen peroxide) **[25]**. For the determination of element content, between 1974 and 1988, an atomic absorption spectrophotometer (SP 90; PYE UNICAM Ltd., UK) was used, then inductively coupled plasma optical emission spectrometers (LABTAM 8440; LABTAM Ltd., Australia, and, from 1998, OPTIMA 3300 DV; Perkin-Elmer Ltd., USA), as well as an ICP-MS instrument (XSeries I; ThermoFisher Scientific Inc., Waltham, MA USA). It should be noted that until 1998, the phosphorus content was measured not by using large instrument techniques, but by the molybdovanadate spectrophotometric method **[26]**.

Measurements were performed at the instrument center of DATE and its successor. The data published are on a dry matter basis. To check the accuracy of the measurements, certified wheat sample BCR CRM 189 (International Atomic Energy Agency) was used (whole meal), and we also participated in domestic and international (MTA TAKI, WESSLING Hungary Kft.) proficiency testing schemes. Statistical evaluations were performed using the program SPSS 22.0.

4. Results

When measurement results for the 1974-2004 period are grouped by the varieties, the data in ***Table 3*** were obtained.

The average phosphorus content of the varieties presented were between 2.8 and 4.0 g/kg, while the potassium content varied between 2.8 and 4.4 g/kg during the period investigated. In the case of calcium, values were between 334 and 433 mg/kg, for magnesium, they were between 887 and 1423 mg/kg, for zinc, between 16.7 and 25.8 mg/kg, and for manganese, between 31.6 and 43.3 mg/kg. Copper contents varied between 3.0 and 5.4 mg/kg, while for iron, values in the range of 36.5-45.9 mg/kg were obtained. It is noteworthy that the Mv23 variety, having only a medium flour quality **[34]** had the highest values for the elements of phosphorus, potassium, magnesium, manganese, zinc and copper. The changes from year to year in the composition of a given variety are well illustrated by the macroelement (P, K) content of the Jubilejnaja 50 variety, which has been studied for a long time. Phosphorus, potassium, calcium and magnesium data of a given variety (Mv Csárdás), measured at different growing sites, are summarized in ***Figures 1 and 2***, where the results of the same variety are shown. This way, the effect of the growing site on a certain year's crop can be evaluated. As a summary of the above it can be concluded that there no extreme values were found among the measurement results.

Data from the analysis of samples from a period spanning nearly 170 years are summarized in ***Table 4***, where the sulfur content was also included, together with the standard deviation of the results. A clear change, i.e., a decrease can be observed in the case of the zinc, magnesium and iron contents. The calcium content increased, and with it the strontium content increased as well. The observed tendencies can be illustrated well by using the so-called trend line representation, which is shown in ***Figure 3*** for zinc and iron. These data show the same trend which was reported by Fan et al., based on the test results of the Rothamsted long-term experiments **[13]**.

According to my results, a slight decrease could be observed in the case of the manganese content, which is opposite to the trend of the results measured earlier in Hungary **[33]**.

Figure 4 shows that an increase can be observed in the calcium content values, suggesting that our soils have sufficient calcium stocks for the cultivated varieties. At the same time, it should be pointed out that, due to the close calcium-strontium interaction **[34]**, the strontium contents of the samples increased as well, as shown by ***Figure 5***. This could be noteworthy in cases where meat consumption is much greater than what is recommended by nutrition scientists, because here the calcium to strontium ratio is low in the bones of humans **[35]**.

To refine the evaluation, we managed to take into account the analytical results of further samples. The special nature of these results originates from the fact that the 12 wheat samples, obtained from the Museum of Hungarian Agriculture, are from those years (1965-1968) when intensive agrotechnics were not yet used. Thus, these represent the classical varieties, and not the short-stemmed varieties. At the same time, post-cultivated samples of the same varieties from 2015 were obtained from the Nyíregyháza Research Institute of the University of Debrecen. This way, the comparative analysis became almost complete, although, of course, identical microecological conditions could not be ensured. Measurement results are shown in ***Table 5***. From the data, the following trends can be identified for the last fifty years: the amounts of calcium, manganese, iron, sodium, sulfur and zinc increased by 6%, 9.5%, 26%, 17%, 19% and 12%, respectively. Magnesium, phosphorus and copper contents remained practically the same.

The increase in the sulfur content is due to the significant increase in the nitrogen content, i.e., the amount of proteins. This phenomenon is not surprising, in view of the close nitrogen-sulfur relationship **[36]**.

Domestic old and new wheat breeds (Bánkúti 1201, GK Tiszatáj, Mv Suba, among others), provided by the Martonvásár researchers participating in the European Union project titled Healthgrain, were also included in the series of tests performed and published by Zhao et al. in 2009 **[15]**. By comparing the results to the data presented by me, no significant difference could be found in the iron and zinc contents of varieties of different intensities.

When comparing our results with those of Dworak, published in 1942, regarding phosphorus, potassium and calcium, three elements that are analyzed often (P 3,49 g/kg^{-1}, K 4,25 g/kg^{-1}, Ca 355 mg/kg^{-1}), allegations that the mineral contents in the grains of winter wheat had halved could not be substantiated.

It is recommended that data for potassium, magnesium and manganese are corrected in the book titled “Új tápanyagtáblázat“ (New Nutrition Table) **[38]**, based on today's experimental and test results.

5. Conclusions

By carrying out the analyses and publishing the data, I intended to answer the question that has become more and more common these days: to what extent did the mineral content of the grain of winter wheat (aestivum) change over the last 150 plus years, due to all of the factors impacting the grain of this staple food raw material over this period. According to the analysis, performed mainly using ICP-OES and ICP-MS techniques, the mineral content of the grain of winter wheat has not changed significantly.

My analyses confirmed those similar foreign results, according to which zinc, iron and magnesium contents have decreased by 15 to 25% over more than a century. This is especially true for the composition of cereals harvested after the inclusion in public cultivation of shorter stem intensive varieties. On the other hand, the calcium content is significantly higher today, than it was in the case of the cultivation of traditional varieties, and at the same time, the strontium content is higher as well. The major decrease (50%) in phosphorus and potassium content, an idea mainly propagated in Hungary, was not confirmed by the analyses performed. Based on my results, it is justified to correct the data for potassium, magnesium and manganese for wheat in the book titled “Új tápanyagtáblázat“ (New Nutrition Table) **[38]**, to correct the data in the sources required to perform nutrition science education, research and consulting activities.

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7. References

[1] Sarkadi J., 1960. Kísérletek különféle foszfát műtrágyákkal. Növénytermelés 9. (2) 159–170.

[2] Krámer M., 1967. A műtrágyák és az istállótrágya hatásának illetve kölcsönhatásának vizsgálata a Martonvásári tartamkísérletekben In: Trágyázási Kísérletek 1955–1964. (Ed.: Sarkadi J.) 131–144. Akadémiai Kiadó. Budapest

[3] Kuthy S., 1961. Az őszi búza és az őszi árpa permetező trágyázásának problémái és eddigi eredményei. OMMI évkönyve. 5. 131–154.

[4] Bocz E. & Győri Z., 1978. Az öntözés és trágyázás hatásának vizsgálata a különböző növények minőségére. OMFB Tanulmány. p. 49 Budapest

[5] Sarkadi J., 1975. A műtrágyaigény becslésének módszerei. Mezőgazdasági Kiadó. Budapest.

[6] Dworak L., 1942. A talajból felvett tápláló-anyagok mennyisége a fontosabb gazdasági növényekben. In: KÖZTELEK Zsebnaptár (Ed.: Szilassy Z. & Budai B.) 389. OMGE. Budapest.

[7] Sós J., 1940. Néptáplálkozási vizsgálat kalóriát adó anyagokra, vitaminokra és ásványi elemekre nézve, IV. Vizsgálatok ásványi anyagcserére nézve. Népegészségügy. 6. 373–386.

[8] Kádár I. 1997. Mikroelemterhelés hatása a búzára 1997-ben. In: A főbb szennyező mikroelemek környezeti hatása. (Ed.: KÁDÁR I.) 359. MTA ATK TAKI. Akaprint. Budapest.

[9] Lásztity B., 2006. Az ásványi tápelemek felhalmozása gabonafélékben. Műegyetemi Kiadó, Budapest.

[10] Lásztity B., 2004. A nem esszenciális elemek forgalma a hazai gabonafélékben. MTA ATK TAKI. Budapest.

[11] Szira, F., Monostori, I., Galiba, G., Rakszegi, M. & Bálint, A. F., 2014. Micronu-trient contents and nutritional values of commercial wheat fluors and fluors of field – grown wheat varieties – A survey in Hungary. Cereal Research Communications. 42. (2) 293–302.

[12] Bálint, A. F., Kovács, G., Erdei, L. & Sutka, J., 2001. Comparison of the Cu, Zn, Fe, Ca and Mg contents of the grains of wild, ancient and cultivated wheat species. Cereal Research Communications. 29. (3–4) 375–382.

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[13] Fan, M. S., Zhao, F. J., Fairweather-Tait, S. J., Poulton, P. R., Dunham, S. J. & Mcgrath, S. P., 2008. Evidence of decreasing mineral density in wheat grain over the last 160 years. Journal of Trace Elements in Medicine and Biology. 22. (4) 315–24.

[14] Hussain, A., Larsson, H., Kuktaite, R. & Johansson, E., 2010. Mineral composition of organically grown wheat genotypes: Contribution to daily minerals intake. Int. J. Environ. Res. Public. Health. 7. (9) 3442–3456.

[15] Zhao, F. J., Su, Y. H., Dunham, S. J., Rakszegi, M., Bedo, Z., Mcgrath, S. P. & Shewry, P. R., 2009. Variation in mineral micronutrient concentrations in grain of wheat lines of diverse origin. Journal of Cereal Science. 49. (2) 290–295.

[16] Kirchmann, H., Mattson, L. & Eriksson, J., 2009. Trace element concentration in wheat grain: Results from the Swedish long-term soil fertility experiments and na-tional monitoring program. Eviron. Geochem. Health. 21. (5) 561–571.

[17] Shi, R., Zhang, Y., Chen, X., Sun, Q., Zhang, F., Römheld, V., Zou, C. (2010): Influence of long-term nitrogen fertilization on micronutrient density in grain of winter wheat (Triticum aestivum, L.). Journal of Cereal Science. 51. 165-170.

[18] Scherz, H., Kirchhoff, E. 2006. Trace elements in foods: Zinc contents of raw foods—A comparison of data originating from different geographical regions of the world. Journal of Food Composition and Analysis 19. p.420–433

[19] Myers, S. S., Zanobetti, A., Kloog, I., Huybers, P., Leakey, A.d.b., Bloom, A. J., Carlisle, E., Dietterich, L. H., Fitzgerald, G., Hasegawa, T., Holbrook, N. M., Nelson, R. L., Ottman, M. J., Raboy, V., Sakai, H., Sartor, K. A., Schwartz, J., Seneweera, S., Tausz, M. & Usui, Y., 2014. Increasing CO_2 threatens human nutrition. Nature. 511. 139–142.

[20] Bardócz Zs. & Pusztai Á., 2013. Eltérő gazdálkodási rendszerekből származó élelmi-szer fogyasztásának következményei. A vegyszeres, nagyüzemi mezőgazdaság. Biokultúra. 24. (1) 31–34.

[21] http://www.agrarszektor.hu/novenytermesztes/elrettento_kutatasi_eredmenyek_60_evunk_van_hatra_a_termo_foldon.3382.html

[22] Vörös L, Zs., 1971. Pannonhalmi maggyűjtemény az 1830-as évekből. Botanikai Gyűjtemények 58.3. 179-180.

[23] Nagy Á. 2012.: A pannonhalmi maggyűjtemény. Üvegbe zárt botanika történet. Élet és tudomány, 67.12. 358-360.

[24] Varju M., 1972. Növényi anyagok hamvasztásának néhány módszertani kérdése Agro-kémiai és Talajtan 21. (1–2) 139–153.

[25] Kovács, B., Győri, Z., Prokisch, J., Loch, J. & Dániel, P., 1996. A study of plant sample preparation and inductively coupled plasma atomic emission spectrometry parameters. Comm. Soil Sci. Plant Anal. 27. (5–8) 1177–1198.

[26] Duduk V., 1973. Takarmánykémia IV. A takarmányok kémiai vizsgálatának módsze-rei. KATE MGK. Keszthely.

[27] Piironen, et al. 2009. cit.: WRIGLY, C. W., 2010. Wheat characteristics and quality requirements. In: Cereal Grains Assessing and Managing Quality. (Ed.: WRIGLY, C. W. & BATEY, I. L.) 59–103. Woodhead Publishing. Oxford, Cambridge, New Delhi.

[28] Kent, N. L. 1983. Technology of cereals. Pergamon Press. Oxford.

[29] Lockhart, H. B. & Nesheim, R. O., 1978. Nutritional qualities of cereal grains. In: Ceraals '78 Better Nutrition for Worlds Millions (Ed.: POMERANZ, Y.) 201–221. American Association of Cereal Chemists. St. Paul, MN.

[30] Láng I., 1961. Adatok néhány gazdasági növény ásványi táplálkozásáról réteges homokjavítás esetén. Kandidátusi értekezés. MTA. Budapest.

[31] Rodler I., 2006. Új tápanyagtáblázat. Medicina Könyvkiadó Zrt. Budapest.

[32] Burján Z. & Győri Z., 2013. A termőhelyek hatása a búzaszem és a liszt ásványi anyag és fehérjetartalmára. Agrokémia és Talajtan. 62. (2) 387–400.

[33] Győri Z., 2006. Effect of mineral fertilization on the Mn-Zn-Cu and Sr content of winter wheat. Cereal Research Communications. 34: (1) 461-464.

[34] Győri Z., 1999. A termesztési tényezők hatása egyes gabonafélék és maghüvelyesek minőségére. MTA Doktori értekezés. Debrecen

[35] S. Ozgur, H. Siimer, G. Kocoglu. 1996. Rickets and soil strontium. Archives of Disease in Childhood. 75:524-526.

[36] S. Haneklaus, E. Schnug. 1992. Baking quality and sulphur content of wheat II: Evaluation of the relative importance of genetics and environment including sulphur fertilization. Sulphur in Agriculture, 16: 889–892.

[37] Győri Z. 2005. Sulphur Content of Winter Wheat Grain in Long Term Field Experiments. Communications in Soil Science and Plant Analysis. 36:(1-3) 373-382.

[38] Rodler, I. (ed.) (2005): Új tápanyagtáblázat. Medicina Könyvkiadó Rt. Budapest. pp. 245