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DOI: https://doi.org./10.52091/EVIK-2022/3-3-ENG

Received: March 2022 – Accepted: June 2022

Evolution of the mineral content of winter wheat in Hungary based on 30 years of measurement results

Keywords: grain, winter wheat, years of cultivation, mineral content, phosphorus, potassium, magnesium, calcium, manganese, zinc, copper, changes in composition by year, boxplot diagram

1. SUMMARY

Nowadays, research related to food science and nutrition places more and more emphasis on the examination of the chemical, feeding and nutrition-physiology quality of various products of plant origin and the evolution of the changes. The attention of many researchers is focused on these quality issues related to nutritional values, and on how these characteristics have changed over the past few decades, thanks to the intensive agrotechniques applied and the available varieties.

In terms of our eating habits, cereals have been playing a central role in our everyday lives for thousands of years. In addition to providing energy thanks to their carbohydrate content, cereals can also be seen as a source of proteins, fibers, vitamins and, last but not least, minerals, as there are traditions of making and eating bread made from cereals both worldwide and in Hungary. Grain-based food production is part of a nation's culture. By preparing our manuscript, our goal was to analyze the large number of samples available from different growing areas to obtain an answer to a question that arises in many people, how the mineral content of winter wheat, which is a staple food in our diet, has changed over the past decades. Thus, by demonstrating the combined effect of changing ecological conditions, the applied agrotechniques and biological foundations, we intend to provide an accurate picture of the evolution of the mineral content of cereals.

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2. Introduction

Overall, wheat grain is a significant source of nutrients for mankind **[1]**. A significant part of the mineral intake of humans comes from cereals **[2]**. At the same time, it is also worth considering during utilization that the distribution of minerals in the wheat grain is not uniform, minerals are mostly contained in the husk parts (bran), but in many countries, only the endosperm, which is much poorer in mineral elements, is utilized **[3, 4]**. Accordingly, even though whole-grain flours and products made from them have a higher mineral content, in this case, the possibility of mycotoxins entering the food chain also has to be considered. That is why a balanced and varied diet, as with all other food groups, is extremely important when consuming cereal-based products.

Reviewing literature data, a rather diverse picture is obtained regarding the mineral composition of cereals, data range in a wide interval, as evidenced by the literature data collected in ***Table 1***.

Table 1. Evolution of the mineral content of winter wheat, taking into account of different literature sources [1, 3, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14]

Mineral element	Mineral content of wheat grain (mg/kg)
P	2279 - 4704
K	1524 - 4500
Mg	700 - 2410
Ca	237 - 1000
Mn	19.7 - 88
Zn	12.0 - 74
Cu	3.0 - 10

In connection with this, several researchers **[15, 16]** have pointed out in the last few decades that the lack of certain micronutrients is a real problem worldwide, and as a result, the proportion of those suffering from some kind of nutrient deficiency within the population is getting higher and higher. At the same time, other researchers **[17, 18]** report that the amount of certain minerals in food also decreased. According to them, iron, iodine and zinc are the mineral elements that are most lacking in our daily diet. This is also confirmed by the 1996 and 2002 WHO surveys **[19, 20]**, according to which about half of the world's population may be affected by a lack of iron and zinc. According to some literature sources **[21]**, supplementing wheat flour with minerals may be a solution to this problem.

Starting from the 1960s, during cultivation, the emphasis was on the use of varieties that could really contribute to overcoming global food shortage by ensuring adequate yields, but in the meantime, the evolution of the amount of minerals, which are also of outstanding importance from a nutrition physiology point of view, received much less attention **[22]**. Increasing yields can be accompanied by a decrease in the mineral content of the wheat grain **[23]**, but this is not easy to judge, since as we know, the quality of plant products, including the mineral content, is evolves as a result of the combined effect of many factors. The composition of the crops may also depend on the biological characteristics of the plant, the applied agrotechnical factors and the existing ecological conditions **[24, 25]**.

Taking into consideration all this knowledge and performing a comparative analysis with literature data, element content data collected over 30 years were processed and statistically analyzed, in order to provide researchers and those interested in the profession with a realistic picture of the mineral composition of cereals, including winter wheat, and its evolution over time.

3. Materials and methods

The winter wheat samples that form the basis of our study come from the period between 1974 and 2004. The size of the sample set differs by year, but overall thousands of samples were analyzed in the above-mentioned time range. The test samples were primarily taken from agrotechnical experiments, in which the effects of various crop areas were examined under different ecological conditions, and the yield results were evaluated.

During sample preparation, the samples were ground with a Retsch Sk-1 or Sk-3 mill. To determine the amount of minerals, initially an ashing digestion method was used **[26]**, while later a wet digestion procedure was used **[27]**. According to the latter method, 1 g of the sample was measured into a digestion tube, after which the digestion was carried out with nitric acid and hydrogen peroxide at the appropriate temperature.

The wet digestion procedure carried out in a closed space allows the digestion of the total element content of the sample. Following digestion, an SP 90 PYE UNICAM atomic absorption spectrophotometer was used to determine the element content until 1998, and in the subsequent period until 1998, a LABTAM 8440 (LABTAM Ltd., Australia) and then an OPTIMA 3300 DV (Perkin-Elmer Ltd, USA) inductively coupled plasma optical emission spectrometer (ICP-OES) was used. The measurements were carried out at the Debrecen University of Agriculture (DATE), and then at its legal successor, the University of Debrecen, in the Instrument Center of the Institute of Food Science of the Faculty of Agricultural and Food Sciences and Environmental Management. In order to check our test methods, we took part in domestic and international proficiency tests using certified reference materials, and in the case of both flour quality and mineral content analyses, we used a BCR CRM 189 (European Reference Material) certified whole grain wheat sample. Data are reported on a dry matter basis.

To evaluate the results obtained, the SPSS 22.0 statistical program package was used, and the mean, standard deviation and relative standard deviation values were determined. To represent our measurement results, a boxplot was used, which is a graphical analysis method in which the location of the interquartile range provides information about the distribution of the analytical data, and this type of diagram also informs us about the evolution of outlying values. With the help of the boxplot diagram, we have an opportunity to separate the extreme outliers within the data set, which is important because during the processing of such a large number of measurement data, the appearance of such values among the measurement results is inevitable, and they are omitted from the evaluation during statistical processing.

4. Results

Our measurements covered a sample set of 30 years. The measurement results of about 4,200 samples were processed. The phosphorus content of the samples ranged from 1.5 to 5.6 g/kg, the potassium content from 1.6 to 5.8 g/kg, the calcium content from 200 to 780 mg/kg, the magnesium content from 600 to 2,000 mg/kg, the zinc content from 6.00 to 79.0 mg/kg, the copper content from 1.7 to 10.4 mg/kg, and the manganese content from 13.0 to 69.1 mg/kg. These data (***Table 2***) fit well into the ranges of the indicated literature data, the values in the table show the extreme values and the interquartile ranges, with the latter data expressing the range in which the middle 50% of the measured values fluctuate.

Table 2. Measurement results of winter wheat samples by tested element, processing 30 years of data

Mineral element	Wheat grain mineral element content, extreme values (mg/kg)	Wheat grain mineral element content, interquartile range (mg/kg)
P	2,279 - 4,704	2,900 - 3,400
K	1,524 - 4,500	3,300 - 3,900
Mg	700 - 2,410	1,029 - 1,213
Ca	237 - 1,000	336 - 395
Mn	19.7 - 88	33.0 - 42.9
Zn	12.0 - 74	19.9 - 28.5
Cu	3.0 - 10	3.7 - 4.9

Examining the available data element by element, the results of the statistical processing are illustrated in the form of a boxplot diagram in ***Figure 1***.

In the case of phosphorus and potassium, the deviation values covered a relatively wide range, but examining the interquartile values, it can be concluded that our results typically fall in the range of 2.9 to 4.0 g/kg. In terms of the average of the years studied, the range is between 2.9 and 3.4 g/kg for phosphorus and between 3.3 and 3.9 g/kg for potassium. These values are already in good agreement with the data reported in the literature. With regard to the concentration of these two macroelements, no decrease was found over the 30 years examined.

The values of the calcium content of the test samples also fall within a wide interval in terms of the 30-year period. By summarizing our measurement results, values between 200 and 780 mg/kg were determined. In the average of 30 years, the interquartile range of the data obtained during the statistical analysis covers a much narrower range. The middle 50% of the analytical values lies between 336 and 395 mg/kg. In the case of the lower quartile, the lowest value was measured in 1977. The average of the samples analyzed this year showed a Ca content of 252 mg/kg. The highest upper quartile was measured in 2003. In that year, an average Ca content of 530 mg/kg was detected.

No significant decrease in the calcium content can be reported during this period either in the case of the samples analyzed by us.

The magnesium content results fell in a wide range of 600 to 2,000 mg/kg, in accordance with the literature data. The interquartile range gives values between 1,029 and 1,213 mg/kg in the average of the years of the study, with significant differences between the year in this case as well, as the 25% percentile value was the lowest in 1978 at 622 mg/kg, while the 75% percentile value was outstanding in 1980 at 1,703 mg/kg.

When examining our data, a relative standard deviation of nearly 20% was determined for the evolution of the manganese content. The standard deviation values are well illustrated in the boxplot diagram. Our results ranged from 13.0 to 69.1 mg/kg, but the range between the 25 and 75% percentiles is only 33.0 to 42.9 mg/kg, i.e., 50% of the analytical data is located in this narrow range. However, statistical analysis also indicates several outliers in the diagram.

In the case of microelements, such as zinc and copper, relative standard deviation values even higher than those found for manganese were encountered. In the average of the study years, a relative standard deviation of 25.8% was calculated for zinc and the result was 22.8% for copper. The boxplot diagram clearly shows that the measurement data range widely, there is a large standard deviation, and there are many outliers among the individual results. Looking at the results of the boxplot diagram, the values of the 25 and 75% percentile range for zinc are between 19.9 and 28.5 mg/kg, while in the case of copper the values of this range are between 3.7 and 4.9 mg/kg.

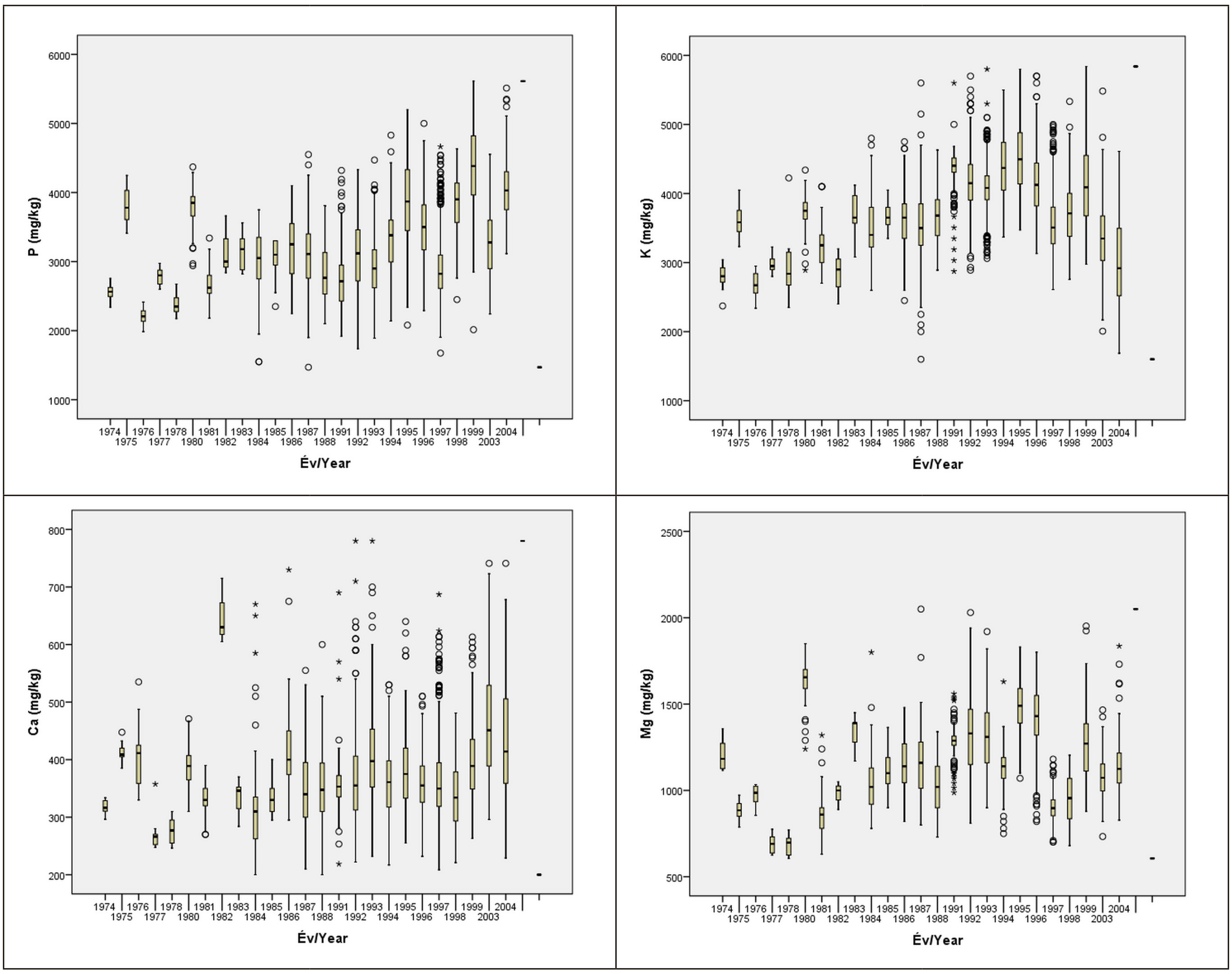

Figure 1. Evolution and distribution of mineral content in winter wheat test samples

(The figure is continued in the next page)

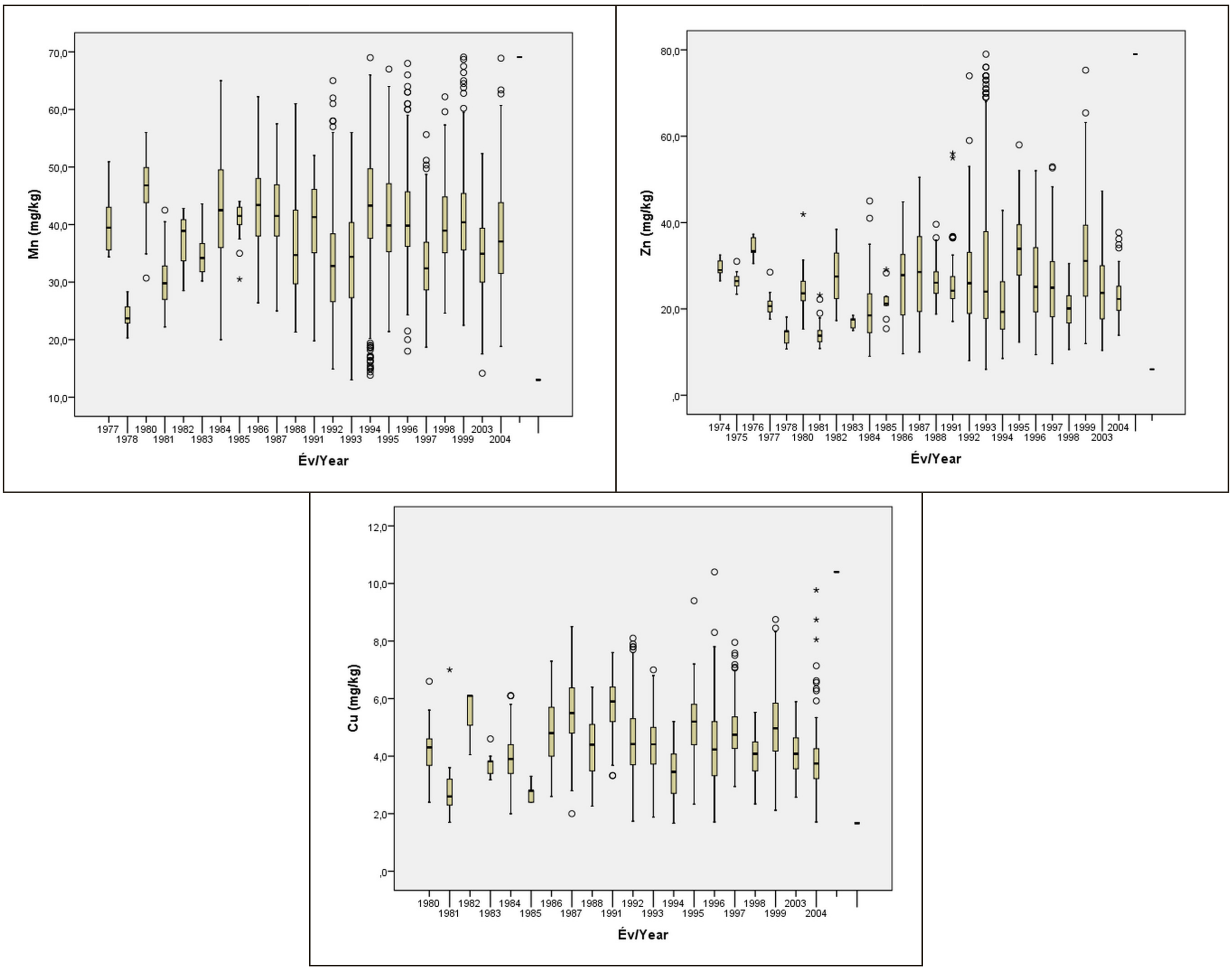

Figure 1. Evolution and distribution of mineral content in winter wheat test samples (continued)

5. Conclusions

Among cereals, wheat is the dominant arable crop in the world, accounting for a significant part of the plant-derived products made from it, thus providing the human body with important minerals as a whole. Nowadays, many researchers raise the question of how, in the case of field crops grown for the production of various food raw materials, the amount of minerals and their relative proportions have changed over the decades, while there have been a change in the varieties available, in ecological conditions and, of course, the applied agrotechniques, i.e., all of the factors that simultaneously influence the quality of a plant product and its nutritional value.

Our test results came from cultivation years between 1974 and 2004 and from different growing areas. In the investigated production areas, the effectiveness of different agrotechnical treatments was investigated, typically under different ecological conditions, with different varieties.

Looking at the average of the years, of the elements analyzed in the samples, lower relative standard deviation data were found for phosphorus, potassium and magnesium, with values of 11.7%, 11.0% and 13.0%, respectively. The standard deviation of our measurement results was much more hectic in the case of copper and zinc. The standard deviation value was 22.8% for copper and 25.8% for zinc.

In terms of the 30 years examined, no decrease in the mineral content was experienced. At the same time, it should be emphasized that reliable conclusions and authentic timeline findings can only be drawn on the basis of simultaneous measurements of archived samples. We intend to continue our work in this spirit.

6. References

[1] Zhao, F. J., Shu,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 lives of diverse origin. *Journal of Cereal Science*. 49. 290-295. https://doi.org/10.1016/j.jcs.2008.11.007

[2] Henderson, L., Irving, K., Gregory J., Bates, C. J., Prentice, A., Perks, J. (2003): The national diet & nutrition survey: adults aged 19-64 years, vol. 3. Her Majesty's Stationery Office. London

[3] Szabó, S. A., Regiusné, M. Á., Győri, D., Szentmihályi, S. (1987): *Mikroelemek a mezőgazdaságban I. Esszenciális mikroelemek.* Mezőgazdasági Kiadó. Budapest

[4] Kutman, U. B., Yildiz, B., Cakmak, I. (2011): Improved nitrogen status enhances zinc and iron concentrations both int he whole grain and endosperm fraction of wheat. *Journal of Cereal Science.* 53. pp. 118-125. https://doi.org/10.1016/j.jcs.2010.10.006

[5] Dworak, L. (1942): *A talajból felvett táplálóanyagok mennyisége a fontosabb gazdasági növényekben.* In: Köztelek Zsebnaptár (Szerk.: Szilassy Z – Budai B.) p. 389. OMGE. Budapest

[6] Pais, I. (1980): *A mikrotápanyagok szerepe a mezőgazdaságban.* Mezőgazda Kiadó, Budapest.

[7] Győri, Z. (1983): Mezőgazdasági termékek tárolása és feldolgozása. *Egyetemi jegyzet. Debreceni Agrártudományi Egyetem.* Debrecen

[8] Győri, Z. (2002): Tápanyaggazdálkodás és minőség. In: Győri, Z., Jávor, A. (eds.): Az agrokémia időszerű kérdései. *Debreceni Egyetem ATC, MTA Talajtani és Agrokémiai Bizottsága.* Debrecen. pp. 79-89.

[9] Győri, Z. (2015): Az őszi búza ásványielem-tartalmának változása Magyarországon 1839-től napjainkig. *Agrokémia és Talajtan.* **64** (1): pp. 189-198. https://doi.org/10.1556/0088.2015.64.1.13

[10] Győri, Z. (2017): Az őszi búza ásványianyag tartalmának értékelése az új vizsgálatok tükrében/ eredményeként, Evaluation of the mineral content of winter wheat in light of/as a result of the new studies. Élelmiszervizsgálati Közlemények **63** (2) pp. 1519-1534.

[11] Győri, Z., Győriné, M. I. (1998): *A búza minősége és minősítése*. Mezőgazdasági Szaktudás Kiadó. Budapest

[12] Dániel, P., Győri, Z., Szabó, P., Kovács, B., Prokisch, J., Phillips, C. (1998): A sertések ásványianyag ellátottságával összefüggő vizsgálatok. 1. Közlemény: Sertéstakarmányok ásványianyag-tartalma. Állattenyésztés és takarmányozás. 47. pp. 277-286.

[13] Kincses, S.-né (2002): Az NPK-trágyázás hatása az őszi búza és kukorica szemtermésének mennyiségére és ásványianyag tartalmára. In: Győri, Z., Jávor, A. (szerk.): Az agrotechnika időszerű kérdései. *Debreceni Egyetem. Agrártudományi Centrum. Mezőgazdaságtudományi Kar. MTA Talajtani és Agrokémiai Bizottsága.* Debrecen. pp. 163-171.

[14] Oury, F. X., Leenhardt, F., Rémésy, C., Chanliaud, E., Duperrier, B., Balfourier, F., Charmet, G. (2006): Genetic variability and stability of grain magnesium, zinc and iron concentrations in bread wheat. *European Journal of Agronomy*. 25. pp. 177-185. https://doi.org/10.1016/j.eja.2006.04.011

[15] Whelch R. M., Graham R. D. (2002): Breeding crops for enhanced mivronutrient content. *Plant and Soil*. 245. pp. 205-214. https://doi.org/10.1023/A:1020668100330

[16] Graham R. D., Welch R. M., Saunders D. A., Ortiz-Monasterio I., Bouis H. E., Bonierbale, M., de Haan. S., Burgos. G., Thiele. G., Liria. R., Meisner. C. A., Bebbe S. E., Potts M. J., Kadian M., Hobbs P. R., Gupta R. K., Twomlow S. (2007): Nutritious subsistance of food systems. *Advances in Agronomy*. 92. pp. 1-74. https://doi.org/10.1016/S0065-2113(04)92001-9

[17] White P. J., Broadley M. R. (2005): Historical variation in the mineral composition of edible horticultural products. *The Journal of Horticultural Science and Biotechnology*. 80. pp. 660-667. https://doi.org/10.1080/14620316.2005.11511995

[18] White P.J., Broadley M. R. (2005) Biofortifying crops with essential mineral elements. *Trends in Plant Science*. 10. pp. 586-593. https://doi.org/10.1016/j.tplants.2005.10.001

[19] WHO (1996): Trace elements in human nutrition and health. *World Health Organization*. Geneva

[20] WHO (2002): The World Health Report 2002. Reducing Risks. Promotin Healthy Life. *World Health Organization*. Geneva

[21] Gleason G., Sharmanov T. (2002): Anemia prevention and control on four central Asian republics and Kazakhstan. *Journal of Nutrition*. 132. pp. 867-870. https://doi.org/10.1093/jn/132.4.867S

[22] Morris C. E., Sands D. C. (2006): The breeder's dilemma – yield or nutrition? *Nature Biotechnology*. **24** (9):1078-1080. https://doi.org/10.1038/nbt0906-1078

[23] Fan M. S., Zhao, F. J., Fairweather_Tait S. J., Poulton, R. P., Dunham J. S., McGrath P. S. (2008): Evidence of decreasing mineral density in wheat grain over the last 160 years. *Journal of Trace Elements in Medicine and Biology*. **22** (4) pp. 15-324. https://doi.org/10.1016/j.jtemb.2008.07.002

[24] Burján, Z., Győri, Z. (2013): A termőhelyek hatása a búzaszem és a liszt ásványi anyag és fehérjetartalmára. *Agrokémia és Talajtan*. **62** (2) pp. 387-400. https://doi.org/10.1556/agrokem.62.2013.2.15

[25] Győri, Z. (2018): Essential Mineral Element Status in Wheat and Maize Grains. *EC Nutrition* **13** (1) pp. 1-3.

[26] Varju, M. (1972): Növényi anyagok hamvasztásának néhány módszertani kérdése. *Agrokémiai és Talajtan* **21** (1-2) pp. 139–153.

[27] Kovács, B., Győri, Z., Prokisch, J., Loch J., Dániel, P. (1996): A study of plant sample preparation and inductively coupled plasma emission spectrometry parameters. *Communications in soil Science and Plant Analysis*. 27. pp. 1177-1198. https://doi.org/10.1080/00103629609369625