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Radionuclide contamination and nutritional evaluation of the wheat mostly used in the Republic of North Macedonia

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Abstract

Wheat is one of the world's most commonly consumed cereal grains. It originates from a type of grass (Triticum) that is grown in countless varieties worldwide. Bread wheat or common wheat is a primary species. Several other closely related species include durum, spelt, emmer, einkorn, and Khorasan wheat. In addition to being a major source of starch and energy, wheat also provides substantial amounts of a number of components which are essential or beneficial for health, notably proteins, vitamins (notably B vitamins), dietary fibres, and phytochemicals. Wheat is a basic food product of Macedonian population. This study is mainly focused on measuring the concentration of radioactivity due to natural radioactive nuclides (^{226}Ra, ^{232}Th, ^{40}K) in wheat grain samples, as well as on determining the quality of wheat used in daily diet. In addition, in this study we calculated radiation hazard indices (radium equivalent activity and internal hazard index) in the wheat sample. Average activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in the wheat samples were 0.57±0.14; 0.39±0.11; 96.55±0.86 ($Bq \cdot kg^{-1}$), respectively. The radiation hazard indices were calculated for all samples in this study where mean values did not exceed safety limits, pointing out to negligible radiation hazard arising from terrestrial radionuclides that are naturally present in wheat. In terms of quality, we confirmed that all tested samples meet the requirements regarding quality in accordance with the laws in our country.

Key words: radioactivity in wheat, radionuclides, gamma spectrometer, quality control

Introduction

Although originating from Levant, a region in the Middle East, wheat (*Triticum* spp.) is a cereal plant now grown all over the world. This cereal plant grows on more land than any other commercial food. World trade in wheat is larger than the trade of all other crops combined. Globally, wheat is a leading source of plant protein in human food, which has higher protein content than other major cereals, corn, or rice. In terms of total production in tonnes of crop that are being used for food, wheat is currently in the second place, following rice as the main crop in human nutrition and before corn, allowing for more widespread use of corn in animal nutrition. Daily consumption of wheat as a basic cereal crop in the nutrition of the population of this area was the basis for this research. High content of proteins, fibre, vitamins, and minerals, and excellent benefits of its use, such as prevention of type 2 diabetes, calming of inflammatory processes, and prevention of metabolic disorders, make this crop one of the most used cereals in the region (Kumar et al., 2011). Another very important component is the detection of radioactive materials in wheat, considering that through its consumption, it is the most common route of transmission of radionuclides in the human organism (Anas et al., 2017). The growth of the world population leads to the need for large quantities of food and this has encouraged many countries to widely use phosphate fertilizers in crop production in order to increase their annual yields. The presence of anthropogenic radionuclides in food is a significant problem, which includes contamination of the food chain and damage to public health (Caridi et al., 2019). Natural radionuclides migrate from soil to crops and contribute to the total radiation load in the population. Radioactivity levels can be used to estimate public dose rates and radioactive contamination and to predict changes in environmental radioactivity caused by nuclear accidents, industrial activities, and other human activities. Radionuclides found in soil can easily accumulate in the food chain through plants (Radhakrishna et al., 1993). There are several factors that affect the absorption of radionuclides in plants, i.e., in wheat, primarily soil characteristics, physiochemical properties of the soil, and the type of plant being studied (Asaduzzaman et al., 2014). Radionuclides that are present in fertilizers used in agricultural fields are series of decay of uranium and thorium, as well as potassium, and their decay products are important natural elements that contribute to a large part of the radiation dose that is further received by humans. Numerous studies have been conducted with the aim to research and assess natural radioactivity in food consumed worldwide, including wheat (Alrefae, 2015).

Therefore, the focus of this study was to assess the radioactivity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in wheat consumed in the Republic of North Macedonia, as well as to determine its chemical composition that is the basis for the quality of wheat used in this country.

Materials and methods

Sampling. The wheat samples for analysis were collected in 2020 from different locations in areas located in the city of Skopje. All samples were thoroughly cleaned, grounded to a predetermined particle size according to the analytical requirements, and finally passed through a sieve. The homogenized samples were packed in plastic containers (Marinelli) of 0.5 l which were fully filled, sealed, and stored in order to establish a secular balance (Nasim et al., 2012). In order to determine the nutritional quality of the samples, accredited methods were applied in accordance with the MKC EN ISO/IEC 17025:2018 standard, as follows: determination of the presence of total protein, total fat, moisture, minerals (ash), and cellulose. Before the analysis, verification on each method was performed by determining accuracy, precision (repeatability and reproducibility) by using standard reference material and proficiency testing. The results for the extended measurement uncertainty for each method were as follows: total protein content ± 1.17%, total fat content ± 8.59%, moisture content ± 4.32%, ash content ± 2.97%, and cellulose ± 28.40%. To determine the total protein content, the Kjeldahl method was used by automatic incineration and titration with 0.1M HCl. Total fat content was determined by using the Sohxlet equipment, with diethyl ether as solvent. The content of total moisture and mineral substances was determined by drying, i.e., burning using a dryer at 104ºC and an oven at 550ºC, respectively. The determination of cellulose was gravimetric (Šramkováa et al., 2009).

In regard to radioactivity, the gamma ray spectrometry technique was used for radioactivity determination of the samples tested. The spectrometer consisted of an HPGe detector, model 3020 (Canberra Packard, Meriden, CT, USA), with active volume of 180 cm2, relative efficiency of 30 %, 3000 V operating voltage, and resolution of 2 keV at 1332.5 keV. The detector was enclosed in a massive 12 cm thick lead shielding and internal lining of 2 mm high purity copper. Data acquisition and analysis were performed with 8192 channel digital analyzer; duration of acquisition interval for each sample was 65 ks. The activity of 226Ra was determined from the gamma lines associated with low half-live time daughters of 214Bi (609.31, 1120.29, and 1794.49 keV) and 214Pb (351.93 keV). The 232Th activity was determined by 338.4, 911.2 and 969.1 keV gamma lines form 228Ac and its decay products. The gamma line at 1460.8 keV was used to determine the activity of 40K. Efficiency calibration was performed with mixed calibration standard sources MBSS2, supplied from the Czech Metrological Institute, Inspectorate for Ionizing Radiation. In order to determine the background distribution in the detector environment, an empty sealed Marinelli beaker with the same geometry was measured at equal counts as the soil samples. The analysis procedure included the subtraction of the background spectrum (Alshahri, 2016).

- *Calculation of activity*

The specific activity (A) was determined according the equation

$$A = \frac{\frac{N}{t} - \frac{N_0}{t_0}}{\varepsilon \cdot \gamma \cdot m} \quad (Bq \cdot kg^{-1})$$

Where, N is a clean surface of the peak accumulated from a specific radionuclide in the analysis of a specific sample (number of readings), N_0 is a clean surface of the peak accumulated from the spot of a specific radionuclide without an analysis of the sample (number of readings), t is live time of accumulation of the sample spectrum (s), t_0 is live time of accumulation of the phone spectrum (s), ε is detector efficiency for a given energy (for a specific peak), γ is intensity of gamma transition in radioactive decay for a respective radionuclide (%), and m is sample mass (kg).

- *Calculation of radium equivalent activity*

Radium equivalent activity (Ra_{eq}) is used to assess hazards associated with materials that contain ^{238}U, ^{232}Th and ^{40}K in $Bq \cdot kg^{-1}$ which is determined by assuming that 370 $Bq \cdot kg^{-1}$ of ^{226}Ra or 260 Bq/kg of ^{232}Th or 4810 $Bq \cdot kg^{-1}$ of ^{40}K produce the same γ dose rate. The Ra_{eq} of a sample in $Bq \cdot kg^{-1}$ can be achieved using the following relation (Singh et al., 2005; Yu et al., 1992)

$$Ra_{eq}(Bq \cdot kg^{-1}) = A_{Ra} + 1.43A_{Th} + 0.07A_k$$

- *Calculation of the external hazard index*

This hazard can be quantified by the internal hazard index (H_{in}) (El-Arabi, 2007). This is obtained by the following equation:

$$H_{eks} = A_{Ra}/370 + A_{Th}/259 + A_k/4810 \leq 1$$

The internal hazard index should also be less than one to provide safe levels of radon and its short-lived daughters for the respiratory organs of individuals living in the dwellings.

Results and Discussion

Wheat has a higher protein content than other cereals and is therefore often used in human nutrition. When it comes to the chemical composition of wheat, determining its nutritional value is the basis for determining the quality of the product. Regarding the obtained results, we can notice that there are no significant differences in terms of total protein content in all examined samples. The concentration ranges from 11.96 ± 0.14% to 14.18 ± 0.17%. Wheat fats are found in significantly lower concentrations ranging from 1.03 ± 0.09% up to 2.50 ± 0.21%. According to the Rulebook on the minimum conditions for quality, properties, and classification of cereals and rice, no. 104/2011, the moisture content in wheat must not exceed 14%. Therefore, according to the results obtained we can confirm that all samples are within allowable moisture values. When it comes to cellulose, its content is quite high and ranges up to 12.10 ± 3.43% (Table 1).

Tab. 1. Quality parameters in wheat samples

Sampling sites	*Total protein content (%)*	*Total fat content (%)*	*Moisture content (%)*	*Ash content (%)*	*Cellulose content (%)*
B1	13.50±0.16	1.15±0.10	8.70±0.37	2.10±0.06	10.50±2.98
B2	14.10±0.16	1.28±0.11	9.20±0.40	2.15±0.06	9.80±2.78
B3	12.86±0.15	2.10±0.18	10.15±0.87	2.18±0.06	10.22±2.90
B4	13.45±0.16	1.15±0.10	6.50±0.28	1.95±0.06	11.10±3.15
B5	14.18±0.17	1.30±0.11	8.80±0.38	2.18±0.06	9.90±2.81
B6	12.75±0.15	1.03±0.09	10.15±0.87	2.13±0.06	9.95±2.82
B7	11.96±0.14	1.95±0.17	3.45±0.30	2.25±0.07	10.36±2.94
B8	12.75±0.15	2.22±0.19	8.88±0.76	1.89±0.06	10.45±2.96
B9	13.00±0.15	2.50±0.21	9.36±0.80	1.97±0.06	11.60±3.29
B10	13.50±0.16	1.80±0.15	10.18±0.87	2.09±0.06	12.10±3.43
Average value	13.20±0.15	1.65±0.14	8.54±0.37	2.09±0.06	10.60±3.00

In Table 2 the average radionuclide concentrations for ^{226}Ra, ^{232}Th and ^{40}K obtained from three measurements of individual wheat samples are presented, associated with the respective standard deviations (SD).

Tab. 2. Mean values of specific activities (A) of values of ^{226}Ra, ^{232}Th, and ^{40}K in wheat

Sampling sites	A±SD (Bq·kg^{-1}) ^{226}Ra	A±SD (Bq·kg^{-1}) ^{232}Th	A±SD (Bq·kg^{1}) ^{40}K
B1	0.70±0.1.0	0.58±0.05	118.15±2.00
B2	0.52±0.05	0.18±0.03	99.00±1.00
B3	0.34±0.10	0.22±0.12	79.70±1.00
B4	0.65±0.60	0.41±0.50	85.15±1.50
B5	0.88±0.15	0.42±0.08	99.86±1.54
B6	0.25±0.10	0.76±0.03	115.04±1.40
B7	0.41±0.15	0.17±0.05	87.00±0.05
B8	0.82±0.05	0.65±0.07	82.50±0.05
B9	0.44±0.05	0.29±0.10	114.22±0.05
B10	0.72±0.05	0.25±0.05	84.90±0.05
Average value	0.57±0.14	0.39±0.11	96.55±0.86

The specific activity due to ^{226}Ra, ^{232}Th and ^{40}K in different types of wheat samples was measured as presented in Table 2. The specific activity of ^{226}Ra was found to be within the range of (0.25±0.10) Bq·kg^{-1} to (0.88±0.15) Bq·kg^{-1} with an average of (0.57±0.14) Bq·kg^{-1}, the specific activity of ^{232}Th was within the range of (0.17±0.05) Bq·kg^{-1}to (0.76±0.03) Bq·kg^{-1} with an average of (0.39±0.11), and ^{40}K had a specific activity within the range of (79.70±1.00) Bq·kg^{-1}to (118.15±2.00) Bq·kg^{-1}with an average of (96.55±0.86) Bq·kg^{-1}.

The radiation hazard indices (radium equivalent activity and internal hazard indices) were calculated for all samples in this study where the mean value for (Raeq) was 7.87, which is lower than the international recommended value (370 Bq·kg^{-1}) (UNSCEAR, 2000), while for (Hex), an average value of 0.02 was calculated. The mean values of the radiation risk index Heks and Raeq show that there is no significant radiation risk to the population.

The measured activity concentrations for radionuclides have been compared with the data reported by other countries and presented in Table 3.

Tab. 3. Comparison between the natural radioactivity levels in wheat samples in this study and some other studies

Country/ Region	A±SD (Bq·kg^{-1}) ^{226}Ra	A±SD (Bq·kg^{-1}) ^{232}Th	A±SD (Bq·kg^{-1}) ^{40}K	References
Egypt	1.352	1.142	111.98	(AL-harbiI and ElTaher, 2013)
Iran	1.67	0.5	91.73	(Changizi, et al., 2013)
France	0.57±0.057	<0.035	146.3±7.3	(Akhtar et al., 2006)
Belgium	0.1±0.05	0.15±0.05	115±22	(Lindahl et al., 2011)
India	0.7±0.09	0.7 ± 0.01	88.7±7.8	(Pulhani et al., 2005)
Republic of North Macedonia	0.57±0.14	0.39±0.11	96.55±0.86	

Conclusions

This study presented the specific activity of the radionuclides ^{226}Ra, ^{232}Th and ^{40}K using a gamma ray spectroscope in wheat that is regularly used in the Republic of North Macedonia. Specific activity concentrations of these radionuclides in the samples were lower than reported by UNSCEAR. In addition, the obtained values of radium equivalent activity and the internal hazard indices, in comparison with the world permitted values, were found to be below the standard limit which is safe in terms of radiological risk. Regarding the chemical composition of the products, we can conclude that all samples that have been the subject of this research meet the requirements according to the Rulebook on the minimum conditions for quality, properties, and classification of cereals and rice, No. 104/2011 in the Republic of North Macedonia.

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Контаминација радионуклидима и нутритивна евалуација најчешће коришћене пшенице у Републици Сјеверној Македонији

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Сажетак

Пшеница је једна од житарица које се најчешће конзумира у свијету. Потиче од врсте траве (Triticum) која се узгаја у безброј варијанти широм свијета. Хљебна пшеница или обична пшеница је примарна врста. Неколико других блиско сродних врста укључују durum, spelltu, emmer, einkori и khorasan пшеницу. Осим што је главни извор скроба и енергије, пшеница такође обезбјеђује значајне количине бројних компоненти које су есенцијалне или корисне за здравље, посебно протеине, витамине (посебно витамине Б), дијетална влакна и фитохемикалије. Пшеница је основни прехрамбени производ македонског становништва. Ова студија је углавном усмјерена на мјерење концентрације радиоактивности усљед природних радиоактивних нуклида (^{226}Ra, ^{232}Th, ^{40}K) у узорцима зрна пшенице, као и на одређивање квалитета пшенице која се користи у свакодневној исхрани. Поред тога, у овој студији смо израчунали индексе опасности од зрачења (еквивалентну активност радијума и интерни индекс опасности) у узорку пшенице. У узорку пшенице, просјечне концентрације активности ^{226}Ra, ^{232}Th и ^{40}K биле су 0,57±0,14; 0,39±0,11; 96,55±0,86 (Bq/kg^{-1}), респективно. Индекси опасности од зрачења израчунати су за све узорке у овој студији гдје средње вриједности нису прелазиле границе безбједности, што указује на занемарљиву опасност од зрачења која произилази из земаљских радионуклида који су природно присутни у пшеници. У погледу квалитета, потврдили смо да сви испитани узорци испуњавају услове у погледу квалитета у складу са законима о квалитету у нашој земљи.

Кључне ријечи: радиоактивност у пшеници, радионуклиди, гама спектрометар, контрола квалитета

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