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## Evaluation of cadmium, lead, zinc and copper levels in selected ecological cereal food products and their non-ecological counterparts

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### ABSTRACT

In the everyday human diet, cereal products are considered to be basics. Such food should have healthy properties and not contain harmful additives, especially heavy metals as exposure to low doses of such xenobiotics can adversely affect human health. Ecological farming is the answer to consumer expectations regarding food safety, and ecological products are recommended as a basis for proper nutrition, despite the higher cost of their purchase. The present study was carried out to evaluate the content of heavy metals in ecological cereal products and their non-ecological analogues.

### INTRODUCTION

According to the Polish Food Pyramid, the share of cereal products in the daily diet is significant and thus forms the basis of healthy human nutrition [1]. What is more, such cereal products should be of the minimum degree of processing, e.g. cereal grains, meal grains, grits, flour, bran and embryos. In the Polish diet, cereal products are the main source of carbohydrates (about 70%), as well as protein (about 10%) and they contain low fat (about 2%). Products made from whole grain flour especially provide essential vitamins and minerals. Indeed, consumption of whole grains ensures the intake of minerals such as iron, magnesium, zinc, copper and phytochemicals, especially phosphorus and potassium, as well as B-group vitamins. Furthermore, whole meal products have lower caloric content because they contain a lot of indigestible fiber. The disadvantage of fiber rich foods, however, is that the contained mineral compounds are present in the form of complexes with fiber and phytic acid.

Still, cereal products can be hazardous because they can also deliver harmful substances, including heavy metals. Heavy metals are those elements which have density higher than 5 g/cm<sup>3</sup> [2]. Harmful elements are defined as those that harm in any quantity, e.g. lead, cadmium, mercury, arsenic. On the other hand, elements classified as micronutrients

(copper, zinc, cobalt, iron, manganese, selenium, molybdenum) act harmlessly after exceeding certain amounts specified in the standards [3]. Contamination of food with heavy metals comes from pollution of soil, water and air, mainly from industry, transportation and agricultural chemistry [4-6]. Food is the main source of lead, cadmium and mercury introduced into the body. The occurrence of bioaccumulation of toxic compounds in living organisms forming food chains is also noted [5,7].

The recognition of the need for availability of safe products has led to the development of ecological farming. Ecological products should have better pro-health properties, as many consumers are looking for ecological products which consumption is recommended as healthy. Moreover, they are often willing to pay the higher costs of buying ecological products by deciding to adopt the principles of good nutrition. This behavior is related to a greater awareness of society in the topic of the health effects of nutrition on the body. However, sometimes, the products identified as safe have minimal or no health benefits. Ecological food is widely regarded as a high quality food, because ecological farming requires a specific method of production and a suitable location for the farm. In the European Union, ecological food is properly labeled and its production is controlled by certification bodies [8]. In recent years, there has been observed an increase in the number of ecological farms in Poland [9].

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## MATERIAL AND METHODS

Cereal products such as flour, flakes and bran (ecological and non-ecological) originating from different producers and different regions of Poland were selected for the study. The list of the tested products is presented in Table 1 and Table 2.

Tabela 1. Ecological cereal products

No.	Sample	Research material
1.	A	Oatmeal
2.	B	Barley flakes
3.	C	Rye flakes
4.	D	Wheat bran
5.	E	Rye bran
6.	F	Oat bran
7.	G	Wheat flour type 2000
8.	H	Spelt flour type 2000
9.	I	Rye flour type 2000
10.	J	Buckwheat flour

Tabela 2. Non-ecological cereal products

No.	Sample	Research material
1.	a	Oatmeal
2.	b	Barley flakes
3.	c	Rye flakes
4.	d	Wheat bran
5.	e	Rye bran
6.	f	Oat bran
7.	g	Wheat flour type 2000
8.	h	Spelt flour type 2000
9.	i	Rye flour type 2000
10.	j	Buckwheat flour

Determination of the content of Pb, Cd, Zn, and Cu was performed by atomic absorption spectrometry. Preparation of samples for analysis included their mineralization. For this purpose, 0.5 g of each product was weighed to an accuracy of 0.001 g and then placed in a plastic vessel for mineralization. Subsequently, 3 ml of 65% nitric acid (V) (Merck, Germany) was added. The closed vessels were inserted into the MARS 5 Corporation microwave oven and mineralized at 200°C for 20 minutes. The mineralized samples were cooled and transferred quantitatively to 50 ml volumetric flasks. The flasks were then filled with deionized water to a volume of 50 ml. The heavy metal content in the samples was determined by atomic absorption spectrometry using the FAAS flame technique, in a VARIAN AA-280 FS apparatus.

The results of the tests were analyzed statistically, and average values and standard deviations were determined. A statistical verification of differences between groups was performed using the t-Student test, with significance level  $p = 0.05$ . Statistica software version 13.1 was used for statistical calculations.

## RESULTS

The present studies conducted on the heavy metals content in selected ecological and non-ecological cereal products allowed to evaluate their quality and determine

whether the level of pollutants found meets the standards for this type of impurities occurring in this kind of food products. The study showed that ecological flours contained higher amount of cadmium (mean 12.28 mg/kg) than conventional ones (average 0.12 mg/kg) (Fig. 1). The presence of cadmium was also found in non-ecological flours: wheat type 2000 and rye type 2000. Other tested non-ecological flours (spelt and buckwheat) were free from cadmium contamination. In contrast, the content of cadmium in rye flour exceeded the permissible values. The average lead content in ecological flours was 2.07 mg/kg. Its concentration in this kind of cereal products ranged from 1.28 mg/kg (spelt flour), to 2.88 mg/kg (rye flour) (Fig. 1). A significantly higher level of lead contamination, ranging from 0.26 mg/kg (buckwheat flour), to 30.10 (spelt flour), was determined for non-ecological flour (Fig. 1). The average concentration of this element was 8.73 mg/kg. The concentration of lead in both tested ecological and conventional products exceeded the specified standards of permissible levels. On average, the content of copper in ecological flour (23.98 mg/kg) was higher than that in non-ecological (14.55 mg/kg) (Fig. 1). Of note, determination of copper content in wheat flour was not possible due to exceeding the detection limit of the measuring device. Likewise, it was not possible to determine the content of zinc in non-ecological wheat flour. The average concentration of zinc in ecological flours was 48.2 mg/kg and was in commercial flours – 38.46 mg/kg. The highest concentration of this metal was found in non-ecological spelt flour (73.3 mg/kg) and in ecological wheat flour (55.69 mg/kg) (Fig. 1).

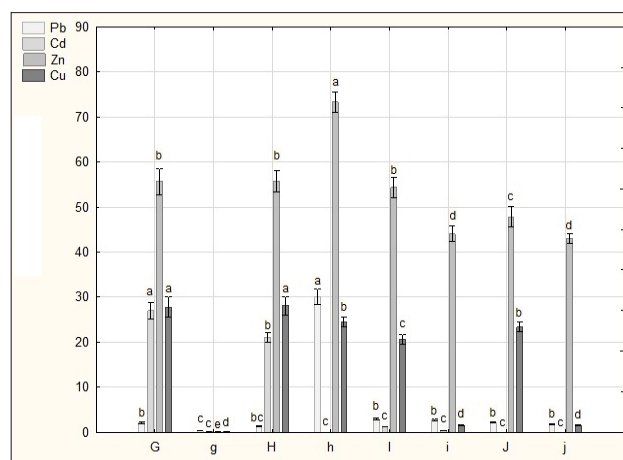
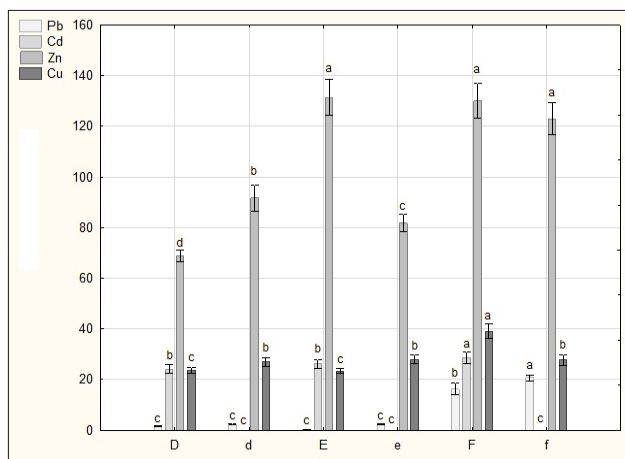


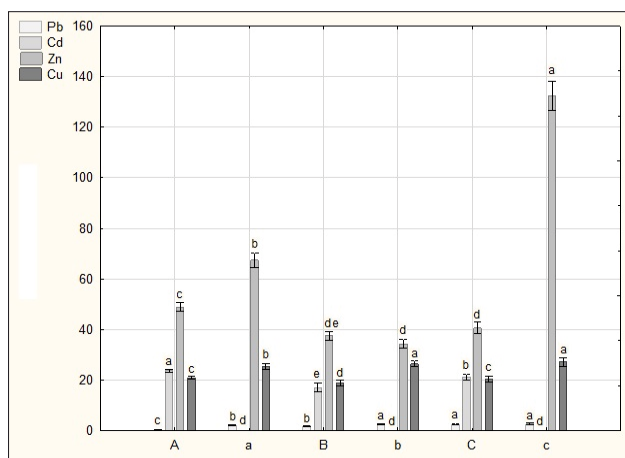
Figure 1. Contents of lead, cadmium, zinc and copper in ecological flours and their non-ecological counterparts. Means calculated for each of element followed by same letter (a-e) do not significantly differ ( $p=0.05$ )

In the case of bran, cadmium content in ecological samples was, on average, 26.3 mg/kg. On the other hand, non-ecological samples did not contain cadmium. The average lead content was significantly higher in ecological bran (6.07 mg/kg) than in conventional bran (2.24 mg/kg) (Figure 2). Such concentrations exceeded the lead content deemed acceptable by the standards. It was found that lead concentration in ecological bran ranged from 0.28 mg/kg (rye), to 16.25 mg/kg (oat), while in non-ecological samples, this was from 2.07 mg/kg (oat), to 2.44 mg/kg

(rye). A slightly higher mean content of copper was found in ecological bran samples – 28.93 mg/kg (from 23.56 mg/kg in wheat bran, to 38.39 mg/kg in oat bran) than in the non-ecological – 27.40 mg/kg (from 26.93 mg/kg in wheat bran, to 27.93 mg/kg in rye bran). Zinc content determined in ecological and non-ecological bran samples was, on average, respectively, 110.10 mg/kg and 98.79 mg/kg. In ecological products, the lowest zinc content was found in wheat bran (68.91 mg/kg) and the highest in rye bran (131.42 mg/kg). In the case of non-ecological products, the lowest concentration of zinc ions was determined in rye bran (81.70 mg/kg) and the highest in oat bran (123 mg/kg) (Fig. 2).



**Figure 2.** Contents of lead, cadmium, zinc and copper in ecological bran and their non-ecological counterparts. Means calculated for each of element followed by same letter (a-e) do not significantly differ ( $p=0.05$ )



**Figure 3.** Contents of lead, cadmium, zinc and copper in ecological flakes and their non-ecological counterparts. Means calculated for each of element followed by same letter (a-e) do not significantly differ ( $p=0.05$ )

The content of heavy metals in flaked products is presented in Figure 3. The concentration of cadmium in conventional flakes was given as zero because it was below the determination limit of the measuring device. Cadmium content in ecological flakes was, on average 20.70 mg/kg (from 16.90 in barley flakes, to 23.75 mg/kg in oat flakes), whereas the mean lead content was 1.58 mg/kg (from 0.39 mg/kg in oat flakes, up to 2.44 mg/kg in rye flakes). Non-ecological products contained lead of average concentration

of 2.43 mg/kg (from 2.12 mg/kg in oat flakes, to 2.61 mg/kg in rye flakes). The concentration of copper ions in ecological flakes was 19.98 mg/kg on average, and it was lower than in non-ecological samples, with an average concentration of 26.26 mg/kg. The lowest content of copper in ecological products was found in barley flakes (18.91 mg/kg), and the highest in oats flakes (20.77 mg/kg). In the conventional products, copper concentration ranged from 25.22 mg/kg (oat flakes) to 27.16 mg/kg (rye flakes). The average content of zinc was also lower in ecological products (48.95 mg/kg) than in the non-ecological (77.88 mg/kg). Concentration of this metal in ecological samples ranged from 37.55 mg/kg in barley flakes, to 48.81 mg/kg in oat flakes – and in conventional samples, from 34.30 mg/kg in barley flakes, to 132.00 mg/kg in rye flakes (Fig. 3).

## DISCUSSION

Consumers of ecological foods are hoping to avoid substances harmful to their health. However, assessment of quality of such products may raise some reservations, especially their pollution with heavy metals, pesticides or nitrates. Numerous studies did not find a lower content of these xenobiotics in ecological products, yet, the results of the studies on heavy metal levels sometimes are contradictory. The quality of food declared as ecological, thus, often does not meet safety requirements. Perhaps the reason for this is the location of ecological farms which can be exposed to pollution from industrial, transport and municipal sources. Ecological and conventional farms located in the same area are equally exposed to these factors [10,11].

The content of heavy metals in cereal products indicates the safety of consuming of this type of food. Permissible levels of heavy metal ions are given in EN 14084: 2004P [12]. The specified safe level of cadmium and lead in flour is 0.20 mg/kg, zinc – 73.5 mg/kg, copper – 10.3 mg/kg.

Determination of heavy metals content in rye and wheat flours of various types has been studied intensively. Kot *et al.* [13-18] investigated lead and cadmium content in wheat flour of types: 450, 500, 720, 850, 1400, and 1850. Herein, all results of heavy metal concentrations obtained were in accordance with the applicable standards. Zajac *et al.* [19] determined the content of lead, cadmium and copper in wheat and rye flour. In addition, they note that many organizations routinely carry out investigations to monitor the content of these xenobiotics [19].

Our research revealed that ecological crops had higher zinc and copper contents. This situation could have come about due to the use of phosphorus fertilizers in conventional agriculture. These fertilizers limit the growth of mycorrhizal bacteria and thus reduce zinc intake. Staniek and Krejpcio [20] also investigated the content of lead and cadmium in ecological and conventional products. They found that ecological products contained higher level of cadmium, but its concentration met the permissible levels of pollutants. Some other reports indicate an increase in copper and zinc content in ecological barley grains [21].

Soil, atmosphere, water and the use of phosphorous and natural fertilizers and sewage can be sources of cadmium in ecological production. For example, one known reason

why more cadmium can be found in ecological products is fertilization with pig manure, which contains higher amounts of this element than does artificial fertilizers [22].

The studies on heavy metal content in plants of the same species grown under greenhouse conditions and on the field indicates that heavy metals can be absorbed from the atmosphere. Higher concentration of pollutants was found in field crops, therefore, atmospheric pollution directly affects the amount of xenobiotics in plants [23]. A factor that can affect heavy metals removal from soil by plants is pH and content of dissolved organic carbon. The studies of soil samples from ecological farms demonstrate that they had much lower pH and higher organic matter content than conventional crop land soil [24].

## CONCLUSION

Ecological products were not distinguished by a lower content of heavy metals, compared to non-ecological products. This situation may be due to the accumulation of these elements from the atmosphere, water and soil. Contamination with heavy metals by fertilization is of no importance in this case.

All cereal products tested, except conventional flours and ecological buckwheat flour, exceeded cadmium levels permitted by the standard. The greatest content of cadmium (and other heavy metals) was found in the cereals' bran because of the higher exposure of this part of grain to the heavy metals present in the environment.

All products contained higher lead concentration than allowed by the standard. Ecological products had a higher copper content than conventional products, which can be considered as an advantage from the point of view of nutrition and the importance of copper for the body. The concentration of this metal in all ecological products exceeded the average content set by the PN-EN 14084: 2004P standard, whereas conventional rye flour and wheat flour met the standard.

Ecological and non-ecological products contained similar levels of zinc. Concentrations of this metal in ecological products such as rye and oat bran and non-ecological rye flakes, wheat, rye and oats bran were exceeded according to EN 14084: 2004P.

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