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Distribution of some toxic contaminants in the milling products, during the milling process

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Abstract

We processed a batch from the Romanian wheat of the 2008 harvest in the mill, obtaining flour type 550, flour type 800 and bran. Both for the initial batch of wheat, and for each product obtained after its processing, we analyzed: moisture, ash content, total content of aflatoxins, ochratoxin A content and the content of heavy metals (cadmium and lead). We identified total amounts of aflatoxins from 3.74 ppb in flour type, 550 to 87.71 ppb in bran, while the content of ochratoxin A and heavy metals was situated below the limits set by the European health legislation. We also noted that the distribution of the concentration of contaminants was correlated with the extraction degree, namely: higher concentrations of contaminants were identified in the products of higher extraction.

Keywords: wheat flour, toxic contaminants, aflatoxins, ochratoxin A, heavy metals

Introduction

Research conducted by *Schollenberger et al.* (2002) on 60 samples of wheat flour from a mill in South-West Germany, showed that the degree of contamination with mycotoxins such as **deoxynivalenol (DON), nivalenol (NIV), 3 - and 15-acetyldeoxynivalenol, HT-2 toxin (HT -2), T-2 toxin (T-2), fusarenona X (FUS-X), zearalenona (ZEA), α- and β-zearalenol (α-and β-ZOL),** decreases as the ash content decreases. This fact suggests that most of the investigated contaminants are in the areas situated outside the grain **[11]**. *Oh-Kyung Kwon et al.* (2004) have shown that there is a **dynamic of the content of mycotoxins in cereals** such as barley and wheat, characterized by decreasing the amount of mycotoxins in the flour, compared with bran. Researches have also shown that different technological treatments applied in order to reduce the content of mycotoxins are not so effective. Thus, the alcoholic fermentation of the cereal products causes a significant further decrease of the content of mycotoxins, than the operations of simple washing with water, or boiling. The content of mycotoxin also decreases with increasing number of washing of grain products with water **[9].** Various studies on wheat flours showed that, although the level of contamination by mycotoxins varies from one agricultural area to another, or even from one harvest to another, the impact on human health is extremely important.

Abdullah et al. (1998) tested 83 samples of wheat flour in Malaysia and determined average amounts of **aflatoxin B_1** up to 25.6 ppb, **aflatoxin B_2** amounts between 25.0-289.4 ppb and **aflatoxin G_2** in concentrations ranging from 16.3 to 436.3 ppb **[1]**. *Halt* (1994) reported an average content of 16.3 ppb **aflatoxin B_1** for a total of 475 samples of wheat from Croatia, and *Aydin et al*. (2008) determined for 100 samples of wheat flour derived from 7 areas in Turkey, a content of **total aflatoxins** ranging between 0.05 and14.01 ppb total aflatoxin **[7, 4]**.

A study made by *Gyrai et al.* (2007) regarding 41 samples of Turkish wheat, showed that 59% of them were contaminated with aflatoxins, most of the contaminants being **aflatoxin B_1** and **aflatoxin G_2** **[6]**. *Ayalew et al* .(2006), who studied more than 350 samples of different cereals (wheat, barley, sorghum, etc.), found that nearly 9% of them were contaminated with total aflatoxins in quantities up to 26 ppb **[4]**.

In most areas within Eastern Europe, the contaminant with the highest exposure is considered to be **Ochratoxin A**. Correlation studies of ochratoxin A with the Balkan endemic nephropathy have shown significantly higher quantities of ochratoxin A in the cereal products from endemic areas within the compared products grain from not endemic areas **[4]**. *Aydin et al.*(2008) determined quantities of **ochratoxin A** ranging from 0.025 to 10 ppb in the samples of wheat flour obtained from Turkish wheat, and *Zinedine et al*.(2006) have identified a contamination rate of 40% with a maximum level of 1.73 ppb in samples of wheat from Morocco **[5, 13]**. *Araguas et al.* (2005) reported a degree of contamination with **ochratoxin A** of 23.4% for 107 samples of Ethiopian wheat, with a maximum level of contamination ppb µg / kg **[3]**. *Araguas et al.* have identified 58 wheat samples contaminated with **ochratoxin A**, from a total of 115, in a medium level of contamination of 0.219 ppb **[3]**. Finally, *Muscarella et al.* (2004) identified in Italian grains a degree of contamination of 15.8% and limits of variation in the level of contamination with **ochratoxin A** between 0.2 and 3.9 ppb **[8]**.

In terms of **heavy metal** content, the results highlighted in literature vary significantly both from one area to another, and from one harvest to another. Thus, investigations carried out on a large number of samples of wheat flour in Japan by *Shimbo et al*.(2001) showed a geometric average of **Cd** content of 0.0019 ppm, respectively values of **Pb** content between 0.002-0.003 ppm **[12]**. Previously, a similar study conducted in China, highlighted for the wheat flour samples an average value of the **Pb** content of 0.0288 ppm **[14]**. In a study regarding the content of heavy metals in grain produced and imported in Yemen, *Al-Gahri et al*. (2008) determined the average amounts of **Pb** between 0.257 and 0.367 ppm for native wheat, respectively 0.346 ppm for the wheat imported from the U.S.A. In terms of **Cd**, the results ranged between 0.246 and 0.296 ppm for the wheat produced in Yemen and 0.117 ppm for wheat from the U.S.A. **[2]**. In the Middle East, *Salama et al.* (2005) determined an average content of 0.131 ± 0.02 **Pb** and 0.398 ± 0.180 ppm **Cd** for the the grains sold on the Egyptian market **[10]**. Studies made so far suggest that the level of contaminants decreases in the processed agricultural products against the raw material source, but the dynamics of this phenomenon is shaped by factors relating to the nature and complexity of each technological process.

Material and Method

The analyzed material consisted of a batch of Romanian wheat from the harvest of the year 2008. The wheat has been processed in the mill of S.C. FARINSAN S.A., obtaining a flour type 550, a flour type 800, and bran. Both for the wheat as raw material and for each of the products obtained from it, were determined: the **moisture content [15]**, the **ash content [16**], the **Cd** and **Pb content** (by atomic absorption spectrophotometry, using a flame spectrometer model AI - 1200 with graphite furnace) **[17**], respectively the content of **total aflatoxins** and **ochratoxin A** (Elisa method)**.**

Results and discussion

Table 1 presents the results obtained from determining the level of contamination with **total aflatoxins** and **ochratoxin A**, in raw wheat and in the milling products derived from it.

We have also analyzed the moisture content (%) and the ash content (%) of the samples, which are important factors in the distribution of contaminants, along the processing technological chain in the mill.

Table 1. The total aflatoxin and ochratoxin A content in the samples

Sample	Moisture content %	Ashes Content %	Content of mycotoxins (ppb)	
			Total Aflatoxins (max. lim. adm. = 4 ppb)	Ochratoxina A (max. lim. adm.= 3-5 ppb)
Wheat	12.12	1.80	28.13	1.11
Wheat bran	14.85	4.08	87.71	2.19
Flour type 800	13.91	0.77	8.92	1.20
Flour type 550	14.56	0.54	3.75	ND

As the table shows, the maximum permissible limit for **total aflatoxins** in wheat was **exceeded by 7 times**, but we did not detect ochratoxin A amounts above the permissible limit (max. limit for wheat = 5 ppb). The **total aflatoxin** contamination for bran has increased dramatically, exceeding almost **22 times** the maximum permissible limit. The level of **ochratoxin A** doubled for bran, compared to wheat, but has not exceeded the permissible limit. The **total aflatoxin A** detected for flour type 800 exceeded the permissible limit about **2 times**.

The titre of total aflatoxins was placed under the permissible limit of detection, only at the extraction appropriate to flour type 550. For the two flours, type 800 and type 550, the concentration of ochratoxin was situated below the allowed limit, even undetectable, for flour type 550 (max. lim. for flour = 3 ppb).

Recalculation of the concentration of mycotoxins in dry matter results in higher values for total aflatoxins (32 ppb for wheat, 103 ppb for bran, 10.36 ppb for flour 800, 4.33 ppb for flour type 550 - all these values over the allowed limit) and for ochratoxin (2.57 ppb for bran).

The distribution of the content of aflatoxins in wheat and milling products, depending on the degree of processing, i.e. the extraction performed in the mill, is highlighted in Figure 1.

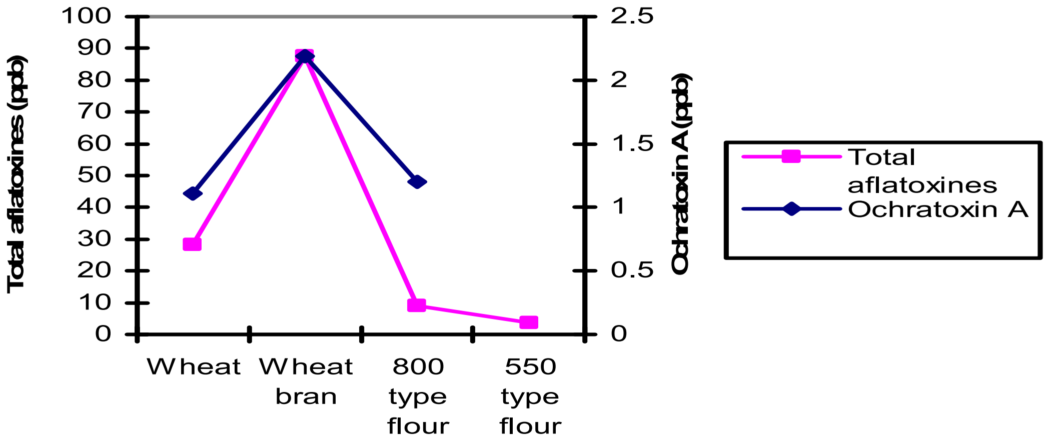

Figure 1. Distribution of the content of mycotoxins according to the degree of processing of raw material in the mill

A significant decrease of the total aflatoxin and ochratoxin A levels was noticed, with the massive accumulation in the by-product (bran), as the process forwards and extractions fall.

However, it has been shown, and the literature abounds in the area, that the cereals are contaminated with a wide range of fungi, which mostly produce various mycotoxins in impressive quantities (mycotoxins and their toxic derivatives), when they have proper favorable conditions such as moisture, temperature, aeration, etc. Even if the technology of cultivation and storage of the wheat have followed the quality standards and the detected content of mycotoxins is low, the main problem is the **synergism of action** of some small quantities of different mycotoxins, whose physiological effect is amplified and becomes harmful, even though individually each detected mycotoxin was quantitatively placed under the permissible limit.

In this case, although ochratoxin A did not exceed the allowed limits, it could be involved into a toxic synergistic activity process with the existing aflatoxins (which far exceeded the acceptable limits).

Table 2 shows the values of contamination with heavy metals, Cd and Pb respectively, for wheat, bran, flour 800 and flour 550.

Table 2. The content of heavy metals (Cd and Pb) and ash in the samples

Sample	**Ash content %**	**Content of heavy metals (ppm)**	
		Cd	**Pb**
Wheat	1.80	0.008	0.010
Wheat bran	4.08	0.012	0.019
Flour type 800	0.77	0.005	0.005
Flour type 550	0.54	0.004	0.005

From the table we can see that in terms of heavy metals, the quantities identified in the four samples did not exceed the maximum permitted by applicable law (0.1 ppm for Cd and 0.2 ppm for Pb).

Figure 2 shows the Cd and Pb content in products obtained by milling the investigated wheat.

We noted that the trend is decreasing the content of Cd and Pb as the extraction and thus the ash content decrease. The highest amount of Cd is concentrated in the bran (which reaches a value almost three times higher than in flours) while in the two flours of different extraction, the determined quantities are almost equal.

A similar trend was observed regarding the Pb content. The largest quantity of Pb was determined in bran (0.019 ppm), while flours type 800 and type 550 contained equal amounts (0.005 ppm). We noticed that the overall quantities of Pb determined in wheat and wheat products, were higher than those of Cd.

This observation indicates that the products obtained from the outside parts of the wheat grain present a higher risk of contamination with Cd and Pb, due to the greater exposure to the environment.

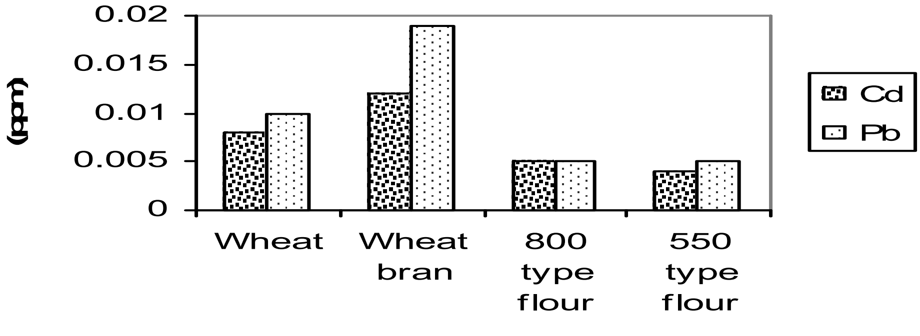

Figure 2. The content of cadmium and lead in wheat and milling products processed from it

The obtained results suggest that there is a dynamic of the content of contaminants in the milling products, depending on the of extraction degree. The meaning of this dynamic is the same, regardless of the nature of the contaminant, namely **increasing content of contaminant with increasing the extraction degree.**

As a consequence, it can be concluded that the toxic potential of cereals and products derived from them can never be exhaustively known, as detection of all existing mycotoxins (under and above allowed limits) is impossible. Also, the influence of heavy metals detected in the grains, even under acceptable limits, could represent a potential danger, taking into consideration the hypothesis that some metals increase the enzymatic activity of fungi and implicitly the production of mycotoxins, under certain conditions.

Conclusions

- For all categories of contaminants (heavy metals, total aflatoxins, ochratoxin A), the largest quantities were found in the bran, and decreased gradually to wheat flour type 800 and type 550, for wheat these values being intermediate;
- The values of total aflatoxins far exceeded the limits permitted by law, except the flour 550, for which the amount detected was slightly below the limit;
- The values detected for ochratoxin A contamination were placed under acceptable limits for all analyzed samples, but toxicity can occur and enhance, through synergism with aflatoxins;
- Decrease in moisture of wheat and wheat flours leads to amplification of toxicity, by increasing the concentration of contaminants;
- Distribution of concentration of contaminants was correlated with the dynamic of the extraction degree, namely: higher concentrations of contaminants have been identified in higher extraction products.

To minimize as much as possible the contamination of cereals, there must be established effective means of monitoring the state of sanitation and innocuity on food-specific paths. Also, promoting the expected benefits of the consumption of high extraction flours products, motivating that they contain fibers (obtained from bran, for example), must be made with caution, since for these products appears a serious danger of toxic contaminations, which means serious risks to the health of consumers.

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