DISTRIBUTION AND QUANTIFICATION OF PESTICIDES IN PROCESSED WHEAT GRAIN FRACTIONS

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Abstract. Food safety is an area of growing worldwide concern on account of its direct bearing on human health. The presence of harmful pesticide residues in cereals has caused a great concern among the consumers. For investigating the carryover of pyretroids, organochlorine and organophosphorus pesticide residues in the cereal food chain from grain to consumer, a study was set up on seven varieties of Romanian wheat. Over each variety of grain it was added a mix of pesticides. The residue levels of pesticides were determined in processed wheat grain fractions: bran, semolina and flour. The goal was to assess the absorption quantity of pesticide mixtures and their distribution in wheat fractions. The pesticides concentrations were below the maximum residue limits (MRLs) for wheat. The highest amounts of pesticides were present in bran and the least in flour.

Keywords: bran, semolina, flour, pesticides, GC-ECD, GC-NPD

1. Introduction

Cereal grains are raw materials for the main foods at the basis of all of the regional diets in the world. Wheat processing is represented by milling of wheat into bran, semolina and flour manufacturing.

Studies on grain following the effect of storage, milling and cookie processing on the residues of pesticides were investigated by many researchers (Sharma et al., 2005; Uygun et al., 2005; Uygun et al., 2009; Kolberg et al.,

L.Simeonov, F. Macaev and B. Simeonova (eds.), *Environmental Security Assessment and Management of Obsolete Pesticides in Southeast Europe,*

2011; Daba et al., 2011). Despite the considerable amount of research that has been carried out on the application of pesticides to wheat, there are limited investigations on pyretroids.

The objective of the present study was to determine the distribution of pesticides residues in processed wheat grain fractions. In this purpose the residue content in the seven varieties of wheat grain (before milling) was quantitatively determined by gas chromatography with nitrogen phosphorus detection (GC-NPD), respectively electron capture detection (GC-ECD). The seven varieties of Romanian wheat analyzed were: Dropia, Delabrad 2, Izvor, Faur F, Gruia, Boema and Glosa. Over each variety of grain it was added a mix of pesticides (organophosphorus pesticides, organochlorine pesticides and pyretroides). Then it was analyzed the contamination level of each fraction resulting after grinders: bran, semolina and flour in order to assess the absorption quantity of pesticide mixtures and their distribution in wheat fractions.

2. Experimental

2.1. SAMPLE COLLECTION

In this study, 7 different types of wheat samples have been investigated: Dropia, Delabrad 2, Izvor, Faur F, Gruia, Boema and Glosa. These samples were collected from the state reserve existing in custody of certain companies to ensure quality and quantity of existing stocks. All samples have been obtained in 2012, transported to the laboratory and stored at 4^{o}C until being analyzed.

2.2. APPLICATION OF THE PESTICIDES

In a small-scale model of a commercial storage vessel with the inner surfaces of stores covered with thin metal sheet, were introduced 100g wheat samples. Then mixes of organochlorine pesticides, pyretroids respectively organo phosphorus pesticides were prepared. The 50g mix of each pesticide was sprayed directly onto the samples. These mixes were used to obtain better accuracy in the determination of very low residue contents that were expected in some milling streams with very low extraction rates. Immediately after the treatment, the batches of treated grain per variety were thoroughly mixed to provide a homogenous distribution of pesticide on grain. For each variety, the batch was delivered to the milling plant to be processed 24 hours after treatment.

2.3. EXTRACTION

The wheat samples processed in the milling plant (8 ± 0,001g) were homogenized with 34 mL acetone/methylene chloride (50:50 v/v) and left overnight for the static extraction. The extract was filtered and centrifuged at 4000 rev/min for 10 min. Then 10 mL of extract was decanted and evaporate almost to dry using a rotary evaporator. The obtained residue was dissolved in 3 mL mixture isooctan/toluene (9:1 v/v) containing internal standard and then centrifuged 2 min at 4000 r/min. The samples were applied onto GC-ECD, GC-NPD without clean up (Uygun et al., 2008).

2.4. GAS CHROMATOGRAPHY

Gas chromatography was performed using a Varian 520 gas chromatograph equipped with a nitrogen phosphorus detector, electron capture detector and a capillary column (HP–5 fused–silica - 29.6m×0.32mm×0.25μm) using helium carrier gas at a flow rate of 1.5mL/min. The oven temperature programmed was: initial temperature isothermal, at 170^{o}C, for 5 min, then from 170 to 200^{o}C at 10^{o}C/min, then from 200 to 210^{o}C at 1^{o}C/min, for 3 min, finally held for 3 min at 260^{o}C. Injector and detector temperatures were 250^{o}C, respectively 300^{o}C. The injection was carried out splitless and the injection volume was 1 μl. Quantification of the pesticides was performed by comparing the peak areas to that of a calibration curve of standards. Correlation coefficients were found to be above 0.98 in all cases, indicating a good linearity.

3. Results and Discussion

Determined levels of pesticides in each fraction of wheat samples resulting after grinders: bran, semolina and flour are presented in Figures 1-7.

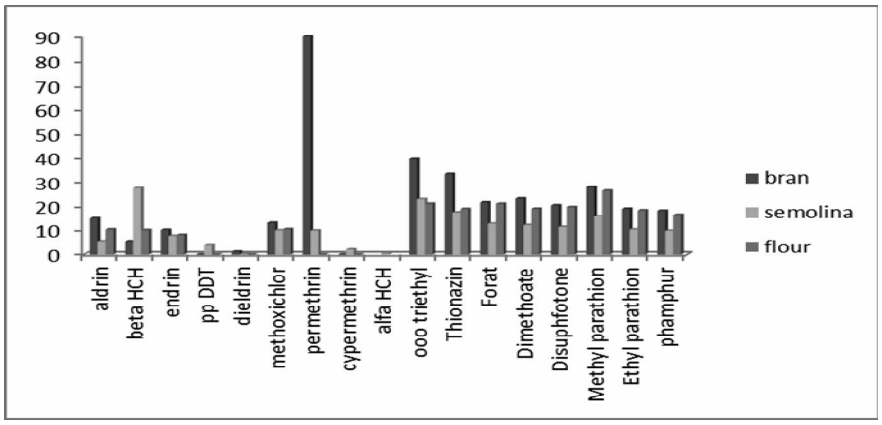

Figure 1. Distribution of pesticides residues in the three processed Delabrad 2 wheat fractions.

From the obtained data it was observed that the pesticides concentrations were below the MRL (CE Regulation, 2005; CE Regulation 2006; SR EN ISO, 2011) and furthermore, most of them are below the detection limit.

Only cypermethrin (0.2376 ppm) was detected in wheat variety Delabrad 2 and two organochlorine pesticides: folpet at a concentration of 0.1016 ppm and metoxychlor at 0.0247 ppm. After contamination with pyretroids mix and organochlorine pesticide mix was observed that: deltamethrin, fenvalerate, iprodione, endosulfan-sulphate, bifenthrin, β endosulfan, op DDT, captan, op DDE, lindan and α endosulfan have not been absorbed into the grain. These pesticides were not found into any of the three fractions (bran, semolina or flour). α HCH and cypermethrin were found only in semolina and heptachlor only in flour with a concentration of 0.0122 ppm. Folpet and DDT pesticides were detected only in bran. Aldrin, chlorothalonil, β HCH, endrin and metoxiclor were found in all three partitions in concentrations ranging from 0.0155 ppm and 0.284 ppm. In Delabrad 2 only methyl-parathion was found (0.0026 ppm) between organophosporus pesticides. After the application of organophosphorus pesticides mix was observed that sulfotep was not found in any of the three partitions and in bran were distributed in the highest amount all organophosphorus pesticides: famfur (0.1966 ppm), ethyl-parathion (0.1223 ppm), methyl-parathion (0.3557 ppm), disulfoton (0.1179 ppm), dimethoate (0.148 ppm), thionazin (0.3426 ppm), ooo triethyl (0.3743 ppm) and forat (0.104 ppm).

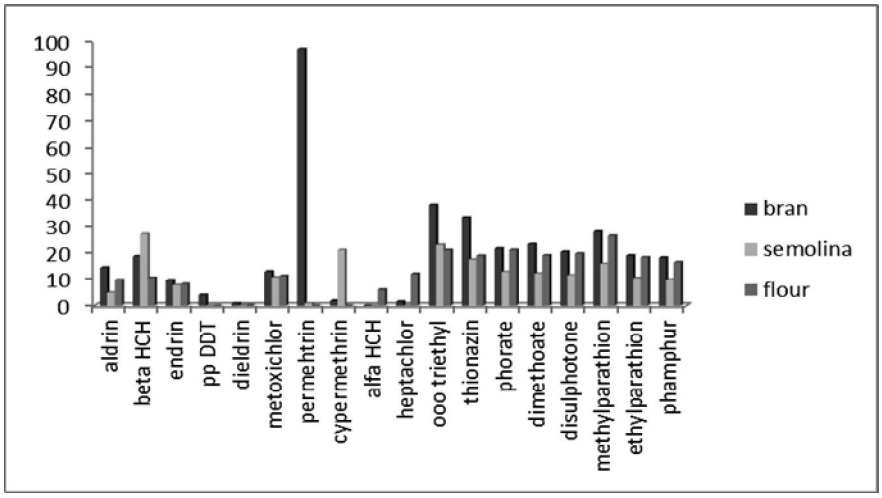

Figure 2. Distribution of pesticides residues in the three processed Dropia wheat fractions.

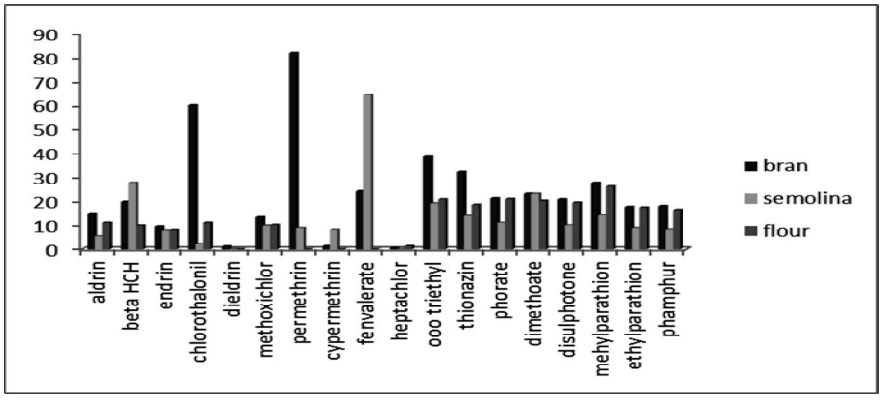

Figure 3. Distribution of pesticides residues in the three processed Glosa wheat fractions.

After analyzing the varieties Dropia and Glosa it was found that no organophosphorus pesticide was detected and only two pyretroids and organochlorine pesticides were detected: cypermethrin and metoxychlor. After contamination is observed a much better absorption of pesticide mix, only unabsorbed pesticide has been sulfotep (it was not found into any of the three fractions).

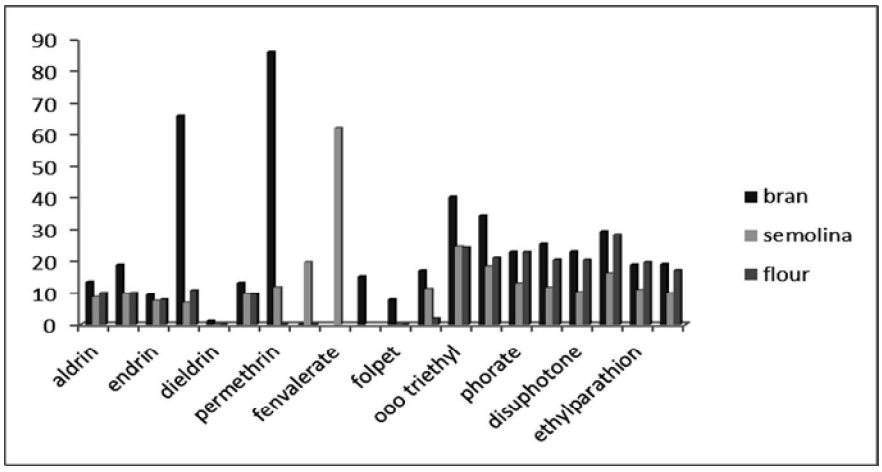

Figure 4. Distribution of pesticides residues in the three processed Faur F wheat fractions.

Thus in bran it was assigned the highest amount of all other eight pesticides in varying concentrations from 0.106 ppm to 0.3654 ppm. In semolina were encountered pesticide amounts ranging between 0.0529 ppm (forat) and 0.2163 ppm (ooo triethyl). α HCH and cypermethrin were found in Dropia semolina and α HCH and fenvalerat were found in Dropia flour. In Dropia bran were detected in very low concentrations folpet (0.094 ppm) and pp DDT (0.021 ppm). In Glosa variety were detected in all three fractions the organochlorine pesticides: aldrin, endrin, metoxiclor, β HCH and chlorothalonil.

Sulfotep was not detected in the other wheat samples Gruia, Boema, Izvor and Faur F as in previous varieties.

In Gruia type of grain was detected methylparathion, folpet, metoxychlor and cypermethrin before the mix treatment and in Izvor type was detected thionazin, ooo triethyl and methylparathion. So in Gruia bran was distributed in higer concentration famfur, methylparathion, disulfoton, dimethoate, thionazin, ooo triethyl and folpet. Pesticide forat is the only exception (has a higher concentration in semolina). The same distribution was registered for Izvor wheat sample, with the exception of disulfoton pesticide, which was encountered in higher concentration in flour.

In Boema variety it was not detected any organophosphorus pesticide, but in Faur F variety was detected tionazin and methylparathion (the lowest detected concentrations). In bran were distributed all other pesticides in concentrations ranging from 0.1048 ppm to 0.3808 ppm. As in Gruia variety pesticide forat is the only exception (has a higher concentration in semolina).

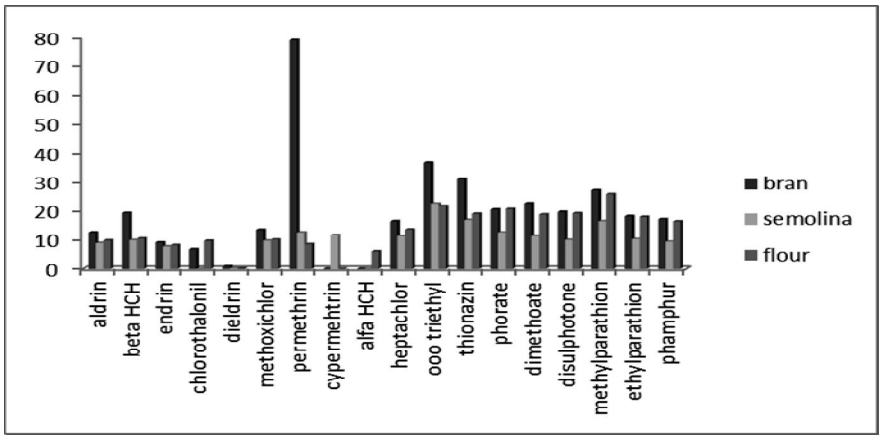

Figure 5. Distribution of pesticides residues in the three processed Gruia wheat fractions.

The results show that Izvor, Boema and Faur F wheat samples considered in the present study contained detectable residues of various pyretroids and oranochlorine pesticides (folpet, metoxychlor, fenvalerate, cypermethrin, β HCH, permetrhrin, chlorotalonil) before the mix treatment. Similar to the results of this study, it was reported that methoxychlor has been determined in all wheat samples (Guler et al., 2010).

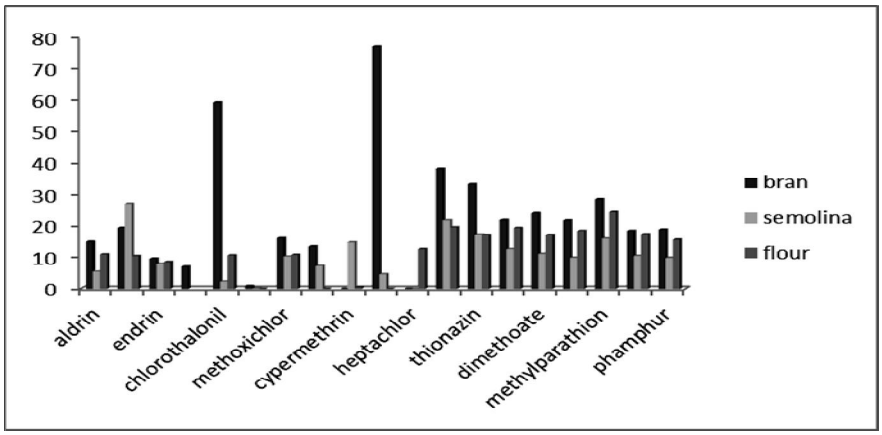

Figure 6. Distribution of pesticides residues in the three processed Boema wheat fractions.

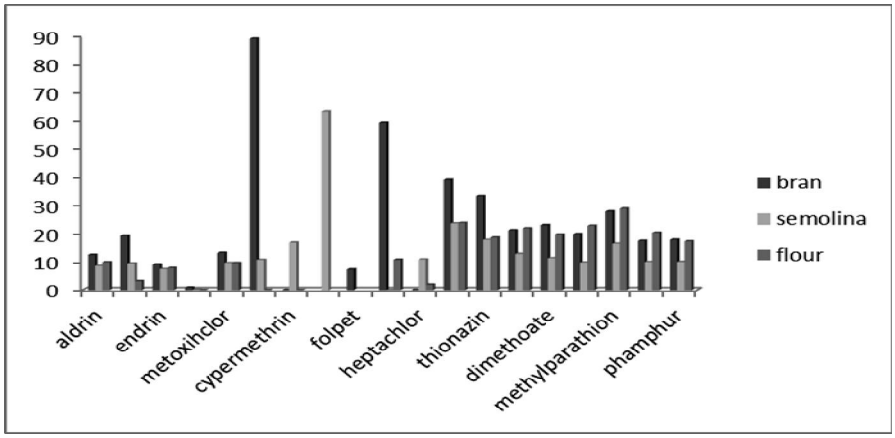

Figure 7. Distribution of pesticides residues in the three processed Izvor wheat fractions

In case of Gruia, Boema, Izvor and Faur F varieties the organochlorine pesticides were distributed in flour in lower concentrations and pesticide folpet was found only in bran. The results showed that the pesticides were distributed in the bran in highest amount and in a smaller amount in semolina. The distribution in flour was the smallest one. In application of pesticides, considerable amounts of them remain on the surface of wheat and some penetrate to internal parts of wheat. Consequently, residue levels in bran were found to be higher than in wheat (Uygun et al., 2007).

4. Conclusions

The pesticides concentrations were below the maximum residue limits (MRLs) for wheat. The highest amounts of pesticides were present in bran and the least in semolina. All fractions absorbed in large amounts endrin, methoxychlor, triethyl and thionazin. These pesticides were distributed differently in the studied fractions of wheat. Deltamethrin and sulfotepp were not detected in any samples. The lowest absorption capacity had wheat variety - Boema and the largest absorption capacity had wheat variety- Dropia.

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