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**Study on the effect of grain storage and processing on chlorpyrifos-methyl and pirimiphos-methyl residues in post-harvest treated wheat with regard to baby food safety requirements**

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Additives/Contaminants:	Pesticide residues
Food Types:	Baby food

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Table 1. Recoveries and standard deviations of fortified pesticides from wheat versus matrix-matched standard calibration (n=5)

Pesticide	Fortification level, mg.kg <sup>-1</sup>	Mean recovery ±SD, %
Pirimiphos-methyl	0.005	106±4.2
	0.01	98.5±2.2
	0.02	102±4.0
Chlorpyriphos-methyl	0.005	122±12.5
	0.01	123±6.0
	0.02	120±9.4

Table 2. Decline of chlorpyrifos-methyl residues in whole grain and processed products with time (n=3)

Matrix	Mean residue, mg kg <sup>-1</sup> ± SD					
	Days after treatment					
	0	7	30	90	180	270
Whole grain	7.8±0.6	5.4±0.4	3.4±0.6	3.0±0.2	3.1±0.05	3.3±0.04
Bran		19.4±0.0	10.1±0.03	13.4±0.3	13.6±0.0	11.6±0.2
Semolina		19.6±0.7	8.0± 0.02	6.1±0.1	6.80±0.6	8.0±0.1
Groats 1 <sup>st</sup> fraction		1.5±0.1	1.0±0.02	1.1±0.02	1.01±0.06	1.1±0.0
Groats 2 <sup>d</sup> fraction		3.0±0.1	1.3±0.1	1.1±0.001	1.3±0.06	1.1±0.0
Groats 3 <sup>d</sup> fraction		4.7±0.4	1.6±0.1	1.4±0.001	0.9±0.03	1.3±0.03
Flour 1 <sup>st</sup> fraction		3.7±0.3	0.9±0.003	0.7±0.03	1.2±0.06	0.8±0.01
Flour 2 <sup>d</sup> fraction		5.1±0.04	0.6±0.03	0.9±0.01	1.1±0.0	1.2±0.0
Flour 3 <sup>d</sup> fraction		4.7±0.4	1.0±0.001	1.4±0.01	1.5±0.0	2.1±0.1

Table 3. Decline of pirimiphos-methyl residues in whole grain and processed products with time (n=3)

Matrix	Mean residue, mg.kg <sup>-1</sup> ± SD					
	Days after treatment					
	0	7	30	90	180	270
Whole grain	9.7±0.7	6.8±0.6	7.2±0.1	6.9±0.3	6.5±0.2	5.2±0.1
Bran		31.9±0.4	24.4±3.3	29.0±0.5	10.4±0.1	15.4±0.2
Semolina		21.7±1.0	18.8±1.1	21.6±0.4	8.3±0.4	13.9±0.5
Groats 1 <sup>st</sup> fraction		1.6±0.02	2.5±0.2	3.3±0.1	2.8±0.1	1.9±0.02
Groats 2 <sup>d</sup> fraction		2.8±0.1	3.1±0.2	3.7±0.1	3.5±0.2	1.8±0.01
Groats 3 <sup>d</sup> fraction		4.8±0.2	4.2±1.0	3.7±0.1	3.5±0.0	2.2±0.04
Flour 1 <sup>st</sup> fraction		3.7±0.1	1.9±0.1	2.8±0.1	2.8±0.03	0.6±0.01
Flour 2 <sup>d</sup> fraction		4.1±0.1	2.6±0.1	3.8±0.2	1.5±0.3	1.9±0.05
Flour 3 <sup>d</sup> fraction		5.9±0.2	3.6±0.2	3.9±0.1	1.3±0.2	3.7±0.1

Table 4. Residue balance of insecticides in processed products after 270 days of storage

Product	Chlorpyrifos-methyl		Pirimiphos-methyl	
	Amount (mean),mg	%	Amount (mean),mg	%
Bran	5.0	50.5	6.8	43.6
Semolina	2.7	27.3	5.2	33.4
Groats 1 <sup>st</sup> fraction	0.1	1.0	0.2	1.3
Groats 2 <sup>d</sup> fraction	0.2	2.0	0.3	1.8
Groats 3 <sup>d</sup> fraction	0.1	1.0	0.2	1.2
Flour 1 <sup>st</sup> fraction	1.0	10.1	0.07	0.4
Flour 2 <sup>d</sup> fraction	0.5	5.1	0.8	5.3
Flour 3 <sup>d</sup> fraction	0.2	2.0	0.3	2.1
<b>Total</b>	<b>9.8</b>	<b>99.0</b>	<b>13.9</b>	<b>89.1</b>
<b>Whole grain</b>	<b>9.9</b>	<b>100</b>	<b>15.6</b>	<b>100</b>

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3 **Study on the effect of grain storage and processing on chlorpyrifos-**  
4 **methyl and pirimiphos-methyl residues in post-harvest treated**  
5 **wheat with regard to baby food safety requirements**  
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15 A. Balinova, R. Mladenova and D. Obretenchev  
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29 **Abstract**  
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33 A study was undertaken to assess the effects of storage intervals and of milling  
34 procedures on dissipation of chlorpyrifos-methyl and pirimiphos-methyl residues in  
35 post-harvest treated wheat grain with the aim to obtain scientific data on compliance  
36 of the processed products with the safety requirements concerning baby foods. The  
37 insecticide formulations were applied on stored wheat at recommended rates (20  
38 ml.t<sup>-1</sup>). The initial concentration levels in whole grain were determined in samples  
39 taken 1 h after treatment. The dissipation of residues and their distribution in different  
40 fractions of the milled grain were studied after various storage intervals, from 7 to 270  
41 days after treatment. Samples of treated grain were milled in a fractionating  
42 laboratory mill and 8 fractions - bran, semolina, 3 types of groats and 3 types of flour  
43 were collected and analysed for pesticide residues. The residues were determined by  
44 an analytical method based on acetone extraction, graphitized carbon clean-up and  
45 GC-ECD, respectively GC-NPD determination of residues. The limits of determination  
46 of both pesticides were 0.005 mg.kg<sup>-1</sup> - high enough for enforcement of the European  
47 Commission (EC) Directive that established a maximum residue level (MRL) of 0.01  
48 mg.kg<sup>-1</sup> for any pesticide in cereal-based baby food.  
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3 The results showed that the pesticides chlorpyrifos-methyl and pirimiphos-methyl  
4 applied post-harvest on wheat as grain protectants were distinguished by relatively  
5 low rates of degradation in the grain under practical storage conditions. Milling did not  
6 significantly reduce the bulk of the chemicals but resulted in distribution of residues in  
7 various processed products. The main part of the insecticides deposited on the grain  
8 remained in the bran and partly in semolina fractions. 270 days after treatment the  
9 residues of chlorpyrifos-methyl were within the range of 0.8 – 2.1 mg.kg<sup>-1</sup> and of  
10 pirimiphos-methyl - between 0.6 and 3.7 mg.kg<sup>-1</sup> in the various types of flour.  
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19 **Keywords:** chlorpyrifos-methyl, pirimiphos-methyl, post-harvest treatment, wheat  
20 grain, processing products, residues, baby food  
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## 24 Introduction

25  
26 Production of safe and healthy food is a key priority in EU and world-wide. Special  
27 attention has been paid to the health protection of infants and young children as they  
28 represent the most vulnerable group of population. Infants and young children have  
29 been shown to be very sensitive to certain toxic effects (Matsumura 2004, National  
30 Research Council 1993). Furthermore babies and young children are exposed to  
31 relatively higher doses of toxicants per body weight unit, compared to adults because  
32 of their proportionally higher consumption of food. Cereal-based products represent a  
33 substantive part of human's diet and particularly of baby's diet. Based on FDA data  
34 children receive 3 - 5 times more cereals than adults per body weight. For better  
35 protection of the health of infants and young children a general MRL of 0.01 mg.kg<sup>-1</sup>  
36 for any individual pesticide in processed cereal-based foods and baby foods has  
37 been established by EC (European Commission 2003a, b).  
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49 Post-harvest treatment for protection of raw grain against stored-product pests has  
50 been reported as a source of contamination of cereals (Joint Meeting on Pesticide  
51 Residues 1991, 1992). A summary of residue monitoring data sorted by frequency of  
52 incidents showed that grain protectants used on cereals accounted for most of the  
53 positive findings (Hamilton et al. 1997). The results of pesticide residues monitoring  
54 program of Portugal showed that wheat was found to contain frequently multiple  
55 residues, especially with those recommended as grain protectants - chlorpyrifos-  
56 methyl, pirimiphos-methyl and malathion (Pesticide residues monitoring in foodstuffs  
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3 of vegetable origin, Portugal, 1999). Studies on the effect of storage on insecticide  
4 residues following post-harvest treatments have generally shown that residues  
5 decline rather slowly (Holland et al. 1994). Typically concentrations showed little  
6 decrease over 32 weeks at 20<sup>0</sup>C and 50-70% relative humidity. Chlorpyrifos-methyl  
7 and pirimiphos-methyl were reported more persistent than malathion (Holland et al.  
8 1994). For refining of dietary intake estimates of pesticide residues a generation of  
9 food processing studies data has been required. Milling is one of the 10 processing  
10 methods identified as deserving main attention (World Health Organisation 1997).  
11 Studies on the fate of pesticide residues on grain subjected to milling and processing  
12 showed that the bulk of the insecticides deposited on the grain remained in the  
13 epidermis and was removed from the bran during milling. Most residues were found  
14 in the outer portion of grains (Hajslova 2000). The residues in bran have been  
15 reported to be consistently higher than in whole grain. The concentration on the bran  
16 was from 2 to 3.2 times the concentration on the whole wheat (Desmarchelier  
17 1979a,b). Bran/grain concentration factors in the range of 2 to 6 were reported in  
18 many studies (Joint Meeting on Pesticide Residues 1988, 1989, 1991, 1992).  
19 Generally the amount of insecticide in flour was 10% or less of the concentration on  
20 the whole wheat. Yet the reduction of fenitrothion concentrations in flour was not  
21 found sufficient enough to comply with some MRLs particularly when wheat available  
22 had been treated within the previous two to three months at the recommended levels  
23 (Murray and Snelson 1978, Snelson 1979).  
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42 Chlorpyrifos-methyl and pirimiphos-methyl are registered as grain protectants and  
43 have been used as such for more than 30 years. The MRLs established for wheat  
44 grain intended for general nutritional uses are 3 mg.kg<sup>-1</sup> and 5 mg.kg<sup>-1</sup> respectively  
45 for both insecticides (European Commission 2002) The general MRLs are set on the  
46 basis of supervised trials in which Good Agricultural Practice is observed, on results,  
47 obtained under national and international monitoring programs etc. and must not  
48 pose an unacceptable risk to human health. These levels are subject to the  
49 requirements of international trade and as a rule are not violated.  
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58 The enforcement of the very stringent European Directive on residues in processed  
59 cereal-based baby food imposes the necessity of careful tuning of all technological  
60 parameters in order to select procedures that enable production of baby food in

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3 compliance with the established MRL from potentially contaminated raw materials. A  
4 study was thus undertaken aimed at assessment of the risk of baby food MRL  
5 violation due to utilisation of contaminated wheat grain for processing and production  
6 of baby food. It was focused on the influence of storage intervals and milling  
7 processes on behaviour of chlorpyrifos-methyl and pirimiphos-methyl applied on  
8 stored wheat grain.  
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16 The established MRL for residues in baby food is tens to hundreds times below the  
17 MRLs for food of general consumption. This imposes the necessity considerable  
18 attention to be paid to the problems of assurance the high quality of analytical  
19 methods both in respect of quantitative parameters (sensitivity, trueness, precision,  
20 and range) and of qualitative assessment (identification and confirmation).  
21 Implementation of analytical methods capable to determine the pesticides studied at  
22 or below  $0.01 \text{ mg.kg}^{-1}$  was mandatory in the study.  
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30 The objectives of this work were: to study the influence of the wheat grain storage  
31 intervals and of milling on the decline and distribution of residues of the selected  
32 post-harvest applied insecticides in the processed fractions; to establish the residue  
33 balance of selected insecticides in processed products of post harvest treated wheat  
34 grain; to provide scientific data on compliance of the processed post-harvest treated  
35 wheat grain products with the safety requirements concerning baby foods.  
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## 42 **Materials and methods**

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45 All processes applied to the study for processing effects assessment were planned in  
46 a way to correspond as closely as possible to those that occur in actual practices.  
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### 49 ***Wheat treatment, sampling and processing.***

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51 High grain quality wheat (*Triticum estivum*) cultivar "Momchil" was used in the  
52 experiments. The initial grain moisture was  $14.0 \pm 0.5\%$ . The commercial insecticide  
53 formulations were Reldan 50 EC (chlorpyrifos-methyl  $500 \text{ g.l}^{-1}$  active ingredient [a.i])  
54 and Actellic 50 EC (pirimiphos-methyl  $500 \text{ g.l}^{-1}$  a.i). They were applied at  
55 recommended rate of  $20 \text{ ml.t}^{-1}$ , at working solution volume 1 l. 40 kg of wheat grain  
56 for each treatment were spread in about 1 cm thick layer and sprayed with 40 ml of  
57 working solution. The application was accomplished by means of hand-operated  
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3 spraying device. After treatment the wheat grain of each particular variant (and of  
4 untreated control) was mixed thoroughly and kept in open containers in a storehouse  
5 at conditions simulating the practical grain storage. The room temperature was  
6  $20\pm 2^{\circ}\text{C}$  and the air moisture -  $70\pm 5\%$ .  
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12 Samples of 0.5 kg grain of each variant were taken 1 hr after treatment, when the  
13 grain became dry, for determination of the initial concentrations of pesticides in the  
14 whole grain. The following samplings were made after 7, 30, 90, 180 and 270 days  
15 storage periods. 3 kg of each treated grain variant and of untreated control were  
16 taken on particular sampling dates and submitted to milling in laboratory mill,  
17 simulating the industrial processing.  
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24 Milling was carried out in a fractionating laboratory mill Buhler MLU 202. Eight  
25 fractions: bran, semolina, groats (3 fractions), flour (3 fractions) were obtained and  
26 were submitted for analysis as well as whole grain.  
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### 30 *Chemicals*

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32 *Pesticide standards.* Analytical standards of pirimiphos-methyl, purity 99.8% and  
33 chlorpyrifos-methyl, purity 99.9% were obtained from LGC Promochem (Wesel,  
34 Germany). Stock solutions ( $1.0\text{ mg}\cdot\text{ml}^{-1}$ ) of each pesticide were prepared in ethyl  
35 acetate and stored in a freezer at  $-23^{\circ}\text{C}$ . Working standard solutions at concentration  
36 rates of  $10\text{ ng}\cdot\text{ml}^{-1}$  -  $500\text{ ng}\cdot\text{ml}^{-1}$  were prepared by diluting of stock solutions with ethyl  
37 acetate and stored at  $4^{\circ}\text{C}$  in dark.  
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### 43 *Solvents and reagents.*

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45 All organic solvents were of gas chromatography grade and were obtained from  
46 Merck KGaA (Darmstadt, Germany). Double distilled water was used when needed in  
47 experiments. Solid phase extraction (SPE) sorbent: graphitized carbon ENVI-Carb  
48 120/400 mesh, surface area  $100\text{ m}^2/\text{g}$ , was obtained from Supelco (Bellefonte, PA,  
49 USA).  
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### 54 *Instrumentation.*

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57 Hewlett-Packard gas chromatograph Model 5890 Series II equipped with  $^{63}\text{Ni}$   
58 electron capture detector (ECD) and nitrogen-phosphorus detector (NPD) was used.  
59 Split-splitless injector operated in the splitless mode. Capillary column AT<sup>TM</sup>-5ms, (30  
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3 m × 0.25 mm × 0.25 μm) was obtained from Alltech Associates, Inc. (Lokeren,  
4 Belgium). Nitrogen of purity 99.9995 % was used for gas chromatography.  
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7 Vacuum manifold (Varian BV) was used for SPE.  
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### 10 **Analytical method**

11 *Extraction.* The weight of the analytical samples taken of different products varied  
12 depending on the expected levels of residue concentrations. The whole wheat grain  
13 laboratory samples were homogenised by mixing, analytical samples of 10 g were  
14 weight, 50 ml mixed solvent acetone-water (8:2) were added and samples were  
15 extracted by shaking for 30 min on a shaking machine and left over night. Analytical  
16 samples of 10 g were weight of bran and semolina and extracted with 100 ml of the  
17 solvent. 20 g analytical samples of flour and groats were extracted with 100 ml of the  
18 solvent. The row extracts were filtered through filter paper and 25 ml aliquot of each  
19 extract was taken for further SPE cleanup and pre-concentration.  
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### 30 *Sample clean up.*

31 25 ml of the acetone extracts were diluted with 200 ml bidistilled water and the diluted  
32 extracts were submitted to SPE clean-up/preconcentration. SPE was carried out by  
33 using polypropylene cartridges manually packed with 400 mg ENVI-Carb, conditioned  
34 with 10 ml ethyl acetate:methanol (8:2) followed by 5 ml methanol and washed with  
35 10 ml water. The sorbent was never allowed to dry up during the conditioning and  
36 sample loading steps. The samples were forced to pass through the sorbent under  
37 vacuum at rate of 10 ml min<sup>-1</sup>. After the passage of the sample, the cartridge was  
38 washed with 0.5 ml of methanol and dried under vacuum for 30 min. The pesticides  
39 were eluted with 6 ml ethyl acetate:methanol (8:2) at rate of 1 ml.min<sup>-1</sup> and collected  
40 in 10 ml graduated tubes. The final volumes of the samples were adjusted by dilution  
41 or evaporation under gentle nitrogen flow in order to obtain analyte concentrations  
42 appropriate to quantitative determination.  
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### 53 *Gas-Chromatographic determination.*

54 GC-NPD operating conditions: carrier gas nitrogen, at flow rate 2.5 ml min<sup>-1</sup>; make up  
55 nitrogen 30 ml min<sup>-1</sup>; hydrogen – 4 ml min<sup>-1</sup>; air – 100 ml min<sup>-1</sup>; injector temperature  
56 270°C; detector temperature 300°C.  
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GC-ECD operating conditions: carrier gas nitrogen, at flow rate 2.5 ml min<sup>-1</sup>; make up nitrogen 30 ml min<sup>-1</sup>; injector temperature 270°C; detector temperature 300°C.

Oven temperature programme for both systems was: 100°C, hold 1 min; rate 20°Cmin<sup>-1</sup> to 260°C final temperature, hold 3 min.

Injection volume was 1 µl for all samples. Quantification was performed by using external standards. Matrix-matched calibration standards were used for all quantifications.

The recovery studies were performed by using blank samples of untreated wheat grain. The weights of blanks were the same as the weights of the analytical samples of treated grains. The fortification was done by addition of calculated volumes of working standard solutions in order to obtain 3 concentration levels of the insecticides studied: at MRL (0.01 mg.kg<sup>-1</sup>), below MRL (0.005 mg.kg<sup>-1</sup>) and higher than MRL (0.02 mg.kg<sup>-1</sup>). Five parallel samples were prepared for each fortification level. After waiting time of 1 h for evaporation of the ethyl acetate from standard solutions the fortified samples were analysed according to the method described above.

## Results and discussion

### *Single laboratory method validation:*

The method was validated for the matrices studied.

The ECD response for chlorpyrifos-methyl was linear in the range of 0.005 ng – 0.05 ng and the correlation coefficient  $r^2$  was higher than 0.98 (five-point calibration curve).

The NPD response for pirimiphos-methyl was linear in the studied range of 0.01 ng – 1.0 ng. The correlation coefficient  $r^2$  for the five-point calibration curve was > 0.99.

Concentrations of the analytes in the samples were calculated by using single-level calibration method. This approach is recommended in case the detector response is variable with time (Document No SANCO/10476/2003). In our studies it was confirmed that single-level calibration gave more accurate results than multi-level calibration when the analytes concentrations in samples were adjusted in an interval  $\pm 10\%$  of the calibration level used.

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3 The mean recoveries and the repeatability expressed as standard deviation (SD),  
4 determined at three fortification levels (number of samples n=5) are presented in  
5 table 1.  
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10 The limits of quantification (LOQ) were adopted at 0.005 mg.kg<sup>-1</sup> for both analytes.  
11 The LOQ of the analytical method is strongly dependent not only on the response of  
12 the detector to the analyte but also on the matrix co-extractives in the final extract. It  
13 is possible to obtain higher sensitivity of the method for analytes of lower detector  
14 response if the sample extract does not contain interfering co-extractives. In case of  
15 pirimiphos-methyl the lowest calibrated level (LCL) was 0.01 microgram.ml<sup>-1</sup>. The  
16 clean extracts free of co-extractives made it possible to adjust the matrix  
17 concentration in the sample final solution to 2g.ml<sup>-1</sup> so the LOQ was 0.005 mg.kg<sup>-1</sup>. In  
18 case of chlorpyrifos-methyl the LCL was 0.005 microgram.ml<sup>-1</sup> but the matrix  
19 concentration in the sample final solution was only 1g.ml<sup>-1</sup> because some co-  
20 extractives caused higher chromatographic noise. For that reason the LOQ for  
21 chlorpyrifos-methyl was also 0.005 mg.kg<sup>-1</sup>, despite its higher absolute sensitivity  
22 compared to pirimiphos-methyl. The LOQ was specified for both pesticides at this  
23 concentration level because it ensured compliance with European Commission  
24 criteria for quantitative residue methods (Document No SANCO/10476/2003).  
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### 38 *Processing.*

39 The laboratory mill used for processing of the grain was a conventional device used  
40 for simulated fractionation that corresponds closely to the fractionation under the real  
41 industrial process. The results of residue analysis obtained from processing  
42 experiments carried out on stored wheat grain, treated post harvest with chlorpyrifos-  
43 methyl and pirimiphos-methyl are presented in tables 2 and 3.  
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51 Both insecticides were persistent under the conditions studied. After storage period of  
52 270 days the average level of pirimiphos-methyl residues in the whole grain was 5.2  
53 mg.kg<sup>-1</sup> which was 53.6% of the concentration determined in the day of treatment.  
54 Under similar conditions chlorpyrifos-methyl was less persistent. The average residue  
55 level in grain after storage period of 270 days was 3.3 mg.kg<sup>-1</sup> – 42.3% of the initial  
56 concentration determined in the day of treatment. These results show that the  
57 residues on grain following post-harvest treatments with insecticides decline rather  
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3 slowly. This corresponds with the results of long residual effectiveness of post-  
4 harvest applied insecticides on storage pests (Snelson 1987; Holland et al. 1994).  
5 Pirimiphos-methyl was reported as very stable in stored wheat with half-life at 30°C  
6 storage temperature 70 weeks. Chlorpyrifos-methyl under similar conditions was  
7 found to be less stable with half-life 19 weeks (Holland et al. 1994).  
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13 The distribution of chlorpyrifos-methyl and pirimiphos-methyl residues in fractions  
14 from processed wheat is presented in tables 2, 3. The bulk of the insecticides  
15 deposited on the grain remain in the bran. The concentrations of chlorpyrifos-methyl  
16 in the bran are from 3.6 to 4.5 times as high as those present on the whole wheat  
17 grain. The residue levels of pirimiphos-methyl in the bran show a concentrating effect  
18 from 1.6 to 4.7 in comparison with the whole grain. Considerable part of the  
19 insecticides is distributed in the semolina fractions. The residues of chlorpyrifos-  
20 methyl and pirimiphos-methyl determined in semolina are only slightly lower the  
21 residues in bran and are respectively 2.0 -3.6 and 1.3 -3.2 times as high as those on  
22 the whole grain. Generally the residue levels of chlorpyrifos-methyl in flour are 1.6 –  
23 5.6 times lower of the concentration on the whole grain. The concentration interval of  
24 pirimiphos-methyl residues in flour is 2.1 – 3.4 times lower than the residues on the  
25 whole grain. The reduction of residues in flour and groats is mostly due to the  
26 removal of the insecticides with bran and partly with semolina fractions.  
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41 In order to determine the percentage loss of residues during processing the residual  
42 amounts in the separate fractions were calculated on basis of the weight of each  
43 fraction and the corresponding residue concentration. The balance of residues in all  
44 fractions compared to the amount on whole grain before milling, determined in  
45 samples taken after 270 days storage (Table 4), shows that the loss of chlorpyrifos-  
46 methyl during processing is less than 2% of the total amount on whole grain.  
47 Pirimiphos-methyl undergoes comparatively more substantial loss during milling - the  
48 loss of residues is determined to be about 10% (Table 4). Taking into consideration  
49 that volatilisation is one of the basic processes acting on pesticide residues this could  
50 be explained by the higher vapour pressure of pirimiphos-methyl– V.p.(40  
51 °C)=22mPa (Tomlin 2000) and the processes favourable to volatilisation – grinding,  
52 screening etc.  
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## Conclusions

The analytical method used was sensitive enough for reliable determination of chlorpyrifos-methyl and pirimiphos-methyl in wheat at concentration  $0.01 \text{ mg.kg}^{-1}$ .

The storage time and milling of wheat grain, treated post-harvest against stored-product pests with chlorpyrifos-methyl and pirimiphos-methyl at recommended application rates, are not effective enough to reduce the residues in grain and in milled products to levels at/below the general MRL of  $0.01 \text{ mg.kg}^{-1}$  established by EC for any individual pesticide in processed cereal-based baby foods. The bulk of the insecticides deposited on the grain is removed with the bran and partly with the semolina fractions during milling but yet the reduction of residue concentrations in the flour and groats fractions is not sufficient for compliance with the baby foods safety requirements. All EC Directives concerning baby food safety stipulate that the exposure of infants and children to food contaminants is of particular concern because of their possible increased susceptibility for adverse effects. Growing and developing organisms have particular sensitivity to toxic compounds (Dencker and Ericsson 1998). The EC Directives on infant formulas and baby foods state that these products shall not contain any substance in such quantity as to endanger the health of infants and young children. The results of the work presented here indicate that the processed foods based on post-harvest treated wheat grain are not eligible for nutrition of infants and little children.

Taking into consideration the MRLs for foodstuffs of general consumption, the results of this study indicate that processed products (flour, groats) of wheat, treated post-harvest with the insecticides studied, are in compliance with the safety requirements for general population.

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