EFFECT OF INDUSTRIAL PROCESSING ON THE LEVEL OF ORGANOCHLORINE PESTICIDE RESIDUES IN GREEN PEAS

EFECTUL PRELUCRĂRII INDUSTRIALE ASUPRA NIVELULUI UNOR REZIDUURI DE PESTICIDE ORGANOCLORURATE DIN MAZĂREA VERDE

ANDREI Corina[1], ȚÂRCĂ Felicia[2],
ANGHEL Roxana [1], BARCAN (BĂETU) Alina[1]
e-mail: corinandrei84@yahoo.com

Abstract. *The main objective of this study was to investigate the effect of industrial processing on the level of organochlorine pesticide residues in samples of green peas. Pesticide residues were quantified by gas-chromatographic method (GC-TSD) after each stage technology, including washing, blanching, sorting and sterilization. The results indicated that the reduced amount of waste washing with 12.28 to 50%. Blanching step allowed for a decrease in the concentration of residues between 15.8 to 66.6%. Blanching is an effective step to remove pesticide residues. Heat treatment in combination with large amounts of water improves disposal of the residues. Cumulative loss in concentration varied between 35 and 82.1% for pesticide residues, except β - endosulfan, where content increased from processing green peas bean. Industrial processing tended to reduce or eliminate (aldrin, eldrin) substantially pesticide residues in a synergistic manner.*
Keywords*: organochlorine pesticides, industrial processing, green peas*

Rezumat. *Obiectivul principal al acestui studiu a fost de a investiga efectul prelucrării industriale privind nivelul unor reziduuri de pesticide organoclorurate din probele de mazăre verde. Reziduurile de pesticide au fost cuantificate prin metoda gaz-cromatografică (GC-TSD), după fiecare etapă tehnologică, incluzând spălarea, blanşarea, sortarea şi sterilizarea. Rezultatele au indicat că procesul de spălare a redus cantitatea de reziduuri, cu 12,28 – 50%. Etapa de blanşare a permis o scădere a concentraţiei de reziduuri, între 15,8 – 66,6%. Blanşarea este un pas eficient pentru a elimina reziduurile de pesticide. Tratamentul termic în combinaţie cu o cantitate mare de apă îmbunătăţeşte eliminarea reziduurilor. Pierderea cumulată în concentraţie a variat între 35 şi 82,1% pentru reziduurile de pesticide, cu excepţia β endosulfan, unde conţinutul a crescut în urma prelucrării mazării verzi. Prelucrarea industrială a avut tendinţa de a reduce sau elimina (aldrin, eldrin) în mod substanţial reziduurile de pesticide într-un mod sinergic.*
Cuvinte cheie: *pesticide organoclorurate, prelucrare industrială, mazăre verde*

[1] University of Agricultural Sciences and Veterinary Medicine of Iaşi, Romania
[2] National Sanitar Veterinary and Food Safety, Iaşi-branch, Romania

INTRODUCTION

Persistent organic pollutants (POPs) are characterized by a long half-life in the environment and a potential bioaccumulation in the food. In this category are organochlorine pesticides (POcl), based on DDT and others, based on chlordane, aldrin, dieldrin, endrin, heptachlor and toxaphene. After 1988, these types of pesticides were not allowed, or were restricted, currently the only organochlorine pesticide lindane used as the base (which is not on the list of the Stockholm Convention on **P**ersistent **O**rganic **P**ollutants). After numerous investigations and public concern about the dangers of their use, the Government has imposed restrictions and bans on this class of pesticides (the proper use of pesticides in relation to the authorisation and registration, as well as compliance with Maximum Residue Limits). Despite the limitation on the use of these pesticides (in the 1970s and 1980s), they continue to persist in the environment today.

The stability of POcl and that residues can remain in foodstuffs, processed or unprocessed, increases the danger to human health. Industrial processing could modify or degrade the chemical structure of analytes and matrix may change in food. Typical stages used in the processing of vegetables and fruits, such as washing, peel, blanching and sterilization plays a role in reducing residues (Geetanjali et al., 2009). Effects of industrial processing of foodstuffs on the pesticides was examined in detail by researchers such as Holland P.T. et al. (1994) and Geetanjali K. et al.; (2009). These authors concluded that there was a reduction in the level of pesticide residues, due to techniques for processing, unless the by-products were concentrated to obtain fruit and vegetables and the pressing or extraction of oil from seeds. It has been suggested that the effects of processing on the levels of pesticide residues may be influenced by the physical location of pesticides and physico-chemical properties such as solubility, volatility, water partition coefficient - octanol (log Kow) and thermal degradation.

This paper was designed to quantify the effects of the washing, blanching, sorting and final sterilization of organochlorine pesticide residues in green peas bean being taken on the technological process of obtaining canned green peas bean in brine.

MATERIAL AND METHOD

In general, production procedures canned green peas bean include four steps, washing, blanching, sorting and final sterilization. In the current study, green peas was analyzed in five stages (green peas - unprocessed, washing, blanching, sorting and final sterilization) and taken to determine and investigate the variation in the content of pesticide residues during processing. Each processing step (see below) was considered a point of sampling for residue analysis.

(i) Washing: Green peas was subjected to washing steps (four washes) with sorting has been done in pre-sorted and hydraulic conveyor.

(ii) Blanching: Stage of scalding (blanching) was carried out in continuous scalding machine at a temperature of 98°C for 3 minutes.

(iii) Final sort: After blanching was carried out in a rapid cooling to a temperature of 30°C for 1 minute; at the same time there was a further washing. After cooling was achieved a final sorting conveyor belts.

(iv) Sterilization has been carried out in an autoclave at a temperature of 120°C for 15-35 minutes, followed by cooling of the vessels (jar) on the outside, cooling is provided at 40 minutes, during which time the product is brought to a temperature of 40°C. Immediately after removal of the unit of processing fruit and vegetables, samples were placed in plastic bags and stored at -20°C until analysis, and analyzed as such.

Criteria for selecting pesticides was based on some of the major organochlorine pesticides (α, β and γ HCH, pp '- DDT, op' - DDT, pp '- DDE, α and β endosulfan and endosulfan sulfate, aldrin, dieldrin, endrin and heptachlor) monitored at EU level monitoring program for pesticide residues. In all cases, the selected pesticides are used in general have been used to control a variety of pests and diseases. Current established maximum residue limits for pesticides in the study were given the limits of admissibility the regulated by the EU Reg EC No 396/2005.

Determination of pesticide residues was carried out according to standards: EN 12393-1, 2, 3:2009 - Foods of plant origin. Multireziduu methods for determining pesticide residues GC. For the quantitative determination of residues of POcl performed in this study was used as the gas chromatography apparatus of Varian 450 coupled to the detector TDS, where the samples were injected automatically separated and purified by a pre-processing thereof by solvent extraction organic (acetonitrile, petroleum ether).

To report levels of pesticide residues were using two parameters: mean value and standard deviation (s) from three identical samples for each sampling point, expressed in mg/kg. Data were subjected to analysis of variance (ANOVA).

RESULTS AND DISCUSSION

Results of the study on organochlorine pesticide residues analyzed along four processing steps are shown in Table 1.

Effect of processing steps on residues of HCH and its metabolites is shown in table 1. The fortified the content in α and γ HCH showed the highest values detected in the raw material, while for β HCH and HCH the highest concentrations were obtained after washing steps. Effect of sterilization phase has proven to be most pronounced on green peas. The washing resulted in decreased concentrations of α HCH and γ HCH respectively 16% and 14%. Blanching stage residue level decreased by 60% for β HCH isomer, 55% for HCH, with up to 16% in the case of 6% for α HCH and γ HCH. Effect of sorting phase was found to be more pronounced on β HCH isomer and the least effect was obtained on γ HCH residues. The process of sterilization decreased α and γ HCH residues up to 67%, the lowest effect was found when HCH residues while β isomer HCH concentration has not changed.

Table 1

Residue levels during processing of green peas, mg/kg (mean ± SD) (n=3)

Pesticide	Unprocessed peas	Whasing	Blanching	Final sorting	Sterilization
α HCH	0,0073±0,001	0,0063±0,002	0,0053±0,001	0,0040±0,001	0,0013±0,001
β HCH	0,0040±0,004	0,0050±0,002	0,0020±0,001	0,0013±0,001	0,0013±0,001
γ HCH	0,0057±0,001	0,0050±0,001	0,0047±0,001	0,004±0,0006	0,0013±0,0003
HCH	0,0023±0,001	0,0067±0,002	0,0030±0,002	0,0020±0,001	0,0013±0,001
pp' - DDT	0,0067±0,002	0,0047±0,002	0,0020±0,001	0,0013±0,001	0,0017±0,001
op' - DDT	0,0013±0,002	0,0010±0,001	0,0013±0,001	0,0010±0,001	0,0013±0,001
pp' - DDE	0,0053±0,001	0,0030±0,002	0,0040±0,001	0,0027±0,002	0,0017±0,001
α endosulfan	0,0040±0,001	0,0020±0,001	0,0013±0,001	0,0013±0,001	0,0013±0,001
β endosulfan	0,0007±0,0003	0,0007±0,001	0,0003±0,001	0,0003±0,001	0,0013±0,0003
Endosulfan sulphate	0,0023±0,001	0,0013±0,001	0,0013±0,001	0,0013±0,001	0,0013±0,001
Aldrin	0,0043±0,001	0,0047±0,001	0,0030±0,002	0,0040±0,001	nd
Dieldrin	0,0033±0,001	0,0033±0,001	0,0010±0,001	0,0003±0,001	0,0007±0,001
Endrin	0,0020±0,001	0,0013±0,001	nd	nd	nd
Heptachlor	0,0047±0,002	0,0033±0,001	0,0023±0,001	0,0013±0,001	0,0013±0,001

Results concerning metabolites DDT's are shown in table 1. Own investigations on the content of pp '- DDT, presented the values that showed a significant decrease it by 57% after blanching stage compared to stage washing of 0.0047 mg/kg to 0.0020 mg/kg and a decrease of 35% after sorting step. The washing step has reduced the content in the pp' - DDT by 29%, from 0.0067 mg/kg (unprocessed green peas) to 0.0047 mg/kg. After the sterilization step has occurred increase in the concentration of pp '- DDT whith up to 31%. The results concerning isomer op '- DDT, is characterized by a different behavior, with small increases and decreases as follows: comparative between stages of blanching vs. washing and sterilizing vs. final sorting noticed an increase of concentration by 30%, from 0.0010 mg/kg at 0.0013 mg/kg. The level concentration of pp '- DDE obtained at samples of unprocessed green peas comparative with samples of green peas taken after the washing, registered a decrease by 43%, a value that after blanching stage increased by 33%, from 0.0030 mg/kg at 0.0040 mg/kg. Process of final sorting has resulted in a decrease in the concentration of 32.5%, from 0.0040 mg/kg at 0.0027 mg/kg. Sterilization phase resulted decrease with 37% in the concentration of pp '- DDE in samples of green peas that have been sorted.

The effect of industrial processing on residues of α and β endosulfan and endosulfan sulphate is shown in table 1. Samples of green peas unprocessed analyzed for content of α endosulfan showed a mean value of 0.0040 mg/kg, a value that subsequently decreased after the washing step by 50% to 0,0020 mg/kg. After the blanching step, the contents decreased by 35%, up to 0.0013 mg/kg. The final sorting step, followed by sterilization did not influence content of α endosulfan, the concentration registered remaining at level of the 0.0013 mg/kg.

The results for the concentration of β endosulfan at raw material and after washing, presented an average content of 0.0007 mg/kg. Blanching stage has

reduced, by 57% to 0.0003 mg/kg. An increase in concentration of β endosulfan was registered by a sterilization step, from 0.0013 mg/kg at 0.0003 mg/kg. The analyzes performed for the average content of endosulfan sulphate indicated a reduction after washing steps, reducing with 43.5% level recorded for this pesticide in unprocessed green peas. Average concentration of 0.00013 mg/kg was recorded in all samples of peas on the technological flow.

Data obtained from analysis for the concentration of aldrin, dieldrin, endrin and heptachlor, statistically processed, are shown in table 1. The values obtained after the washing step had a concentration of 0.0047 mg/kg, content that has been reduced after the step of blanching with 36% to 0.0030 mg/kg. Stage of sterilization to canned green peas completely eliminated aldrin residues in the product.

Throughout the stages of processing green peas investigated for dieldrin content was obtained a decrease in the organochlorine after blanching step, sorting and sterilization (washing steps not reduced dieldrin content). A reduction of 70% of the average content of dieldrin was recorded after the blanching step, from 0.0033 mg/kg (this value was recorded for samples washed peas) from 0.0010 mg/kg. The sterilization step has resulted a decrease with 70% in the concentration of dieldrin, from 0.0010 mg/kg to 0.0003 mg/kg. For the identification residual endrin, only samples of green peas unprocessed, had a concentration of 0.0020 mg/kg, this value was reduced by the washing steps with 35% to a content of 0.0013 mg/kg. Influence stages of blanching, sorting and sterilization that have been evaluated for endrin content of green peas led at getting undetectable values.

Influence of technological process has reduced the average concentration of heptachlor to green peas. There were decreases in the following order: the washing, reduced concentration of heptachlor, by 29.8%, from 0.0047 mg/kg at 0.0033 mg/kg; after blanching step, decreased by 30%, from 0.0033 mg/kg at 0.0023 mg/kg; sorting step for removing remnants vegetable results after blanching products at 98°C, reduced significantly the content with 43%, from 0.0023 mg/kg at 0.0013 mg/kg.

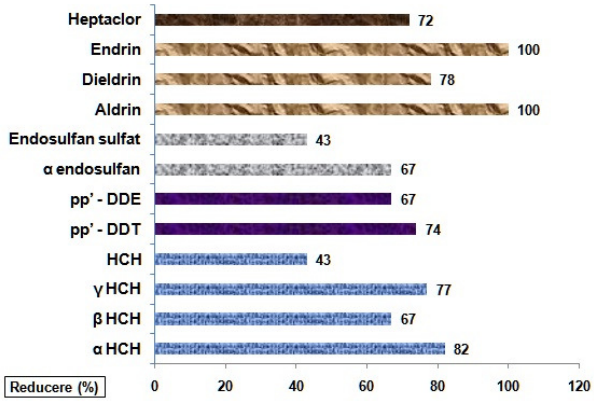

Fig. 1 - Decreased percentage (%) of pesticide residues organochlorine of canned green peas beans in brine

The total amount of pesticides removed by the processing steps combined for each organochlorine (except isomer op '- DDT for which processing effects not changed content in green peas) is shown in figure 1.

In generally removal of residues was more effective (<70%) where α and γ HCH pesticides, pp' - DDT, dieldrin and heptachlor. Following processing green peas, metabolites β HCH, pp' - DDE and α endosulfan were reduced by 67%, while HCH and endosulfan sulphate have shown a reduction of 43% through processing. Residues of aldrin and endrin were completely reduced after subsequent sterilization of canned green peas beans in brine.

CONCLUSIONS

1. Green peas samples taken from the canned green peas beans in brine and analyzed for content in organochlorine pesticide, have resulted in values that significantly decreased after processing raw materials (isomer op' - DDT has not changed concentration after processing).

2. Pesticides aldrin and endrin were recorded as values under detection limit in canned green peas beans in brine;

3. The research results confirms the presence of pesticides in green peas, quantity these being well below maximum limits admissible (MRL's) (EC, 2005).

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