THE STUDY OF ORGANOPHOSPHORUS PESTICIDE RESIDUES IN SOIL AND VEGETABLE PRODUCTS IN DIFFERENT GROWING SYSTEMS

STUDIUL REZIDUURILOR DE PESTICIDE ORGANOFOSFORICE DIN SOL SI LEGUME, IN DIFERITE SISTEME DE CULTIVARE

HURA Carmen¹, PERJU Cristina¹, MUNTEANU N. ², STOLERU V. ²

e-mail: carmen hura@yahoo.com

Abstract. In this paper are presented the research results obtained in 2010, in SIECOLEG Project, regarding the assessment of some organophosphoric pesticide residues (55 active substances) from 80 samples soils and 25 samples vegetables from different growing systems (ecological, in conversion and conventional). In all samples analysed the organophosphoric pesticide residues were included in admissible limits (Regulation (EC) nr. 396/2005).

Key words: residues, organophosphoric pesticides, soil, vegetables.

Rezumat. În lucrarea de față sunt prezentate rezultatele cercetării obținute în anul 2010, in cadrul proiectului 52141/2008 — SIECOLEG, cu privire la evaluarea unor reziduuri de pesticide organofosforice (55 substante active), din 80 probe sol si 25 probe de legume, în difertite sisteme de cultivare (ecologic, in conversie și convențional). În toate probele analizate reziduurile de pesticide organofosforice s-au incadrat in limitele maxime admise (conform Regulamentului (EC) nr. 396/2005).

Cuvinte cheie: reziduuri, pesticide organofosforice, sol, legume.

INTRODUCTION

Irrational use of pesticides in agriculture causes pollution of large areas of soi land food with nitrate / nitrite, pesticides and heavy metals.

In most cases, pesticides used to protect crops exerts its toxic action not only as to pests and pathogens, but also to animals; there is a risk that people can be affected due to toxic residues ingested with food (Hura, 2005, 2007).

Given the importance of this issue and the fact that in our country amounts were used, it was useful considered to know the content of pollutants in some soils cultivated with vegetables, as well as in fresh vegetable products.

The aim of the research is to assess the extent to which chemical factors are risk factors for plants and humans exceed the limits above which are pollutants. In this way producers and consumers become aware of the importance of organic vegetable production and the negative influence of during the use of pesticides on the ecological balance and the harvest, that human health.

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¹ NIPH/ Regional Center of Public Healthy Iasi, Romania

² University of Agricultural Sciences and Veterinary Medicine Iasi, Romania

MATERIAL AND METHOD

Organophosphorus pesticide residue content was analyzed in 105 samples, of which 85 soil samples and 25 samples of plant products (tomatoes, peppers, eggplants, cabbage, onions), in three cultivation systems (organic, in conversion and conventional), using standard methods. The soil samples were collected during 2010 in two phases, as follows: spring (before the establishment of crops) and summer (at harvest maturity).

Samples of soil (table 1) and plants (table 2) was carried out in certain locations, as follows:

- certified organic land: Bacau Vegetable Research Station SCL and lasi University of Agriculture - USAMV;
 - land in conversion: Andrieseni (Family Association FA Rotariu C.)
- conventional land: Roman (AgroFlamanzi), Tg. Frumos (Family Association FA Maxim I., Family Association FA Vavilov M.), Matca (Family Association FA V. Marin).

Table 1
Number of soil samples analyzed and their codification

| Land status | Location | No. of samples | Samples codification | | | | | | |
|---------------|---------------------|----------------|---|--|--|--|--|--|--|
| | SCL Bacau | 12 | S32, S33,S34, S35,S43 | | | | | | |
| Ecological | USAMV/ spring | 3 | S5, S6, S7 | | | | | | |
| - | USAMV/ autumn | 6 | S26, S31 | | | | | | |
| In conversion | Andrieseni lasi | 11 | S59, S69 | | | | | | |
| | Sere Roman/ spring | 4 | S1, S2, S3, S4 | | | | | | |
| | Sere Roman/ autumn | 4 | S78, S79, S80, S81 | | | | | | |
| Conventional | Tg. Frumos/ spring | 7 | S8, S9, S10, S11, S12, S13, S14 | | | | | | |
| Conventional | Tg. Frumos/ autumn | 14 | S44, S45, S46, S47, S48, S49, S50, S51, | | | | | | |
| | rg. Fruinos/ autumn | 14 | S52, S53, S54, S55, S56, S57, S58 | | | | | | |
| | Matca | 11 | S15, S16, S25 | | | | | | |

In the study were determined organophosphorus pesticide residues (44 active substances) in soil samples and vegetable products.

Table 2 Number of plant samples analyzed in different areas

| Land status | Location | No. of samples | Samples codification |
|--------------|-----------------|----------------|----------------------|
| Ecologic | SCL Bacau | 4 | V9, V10, V11, V12 |
| In conversie | Andrieseni lasi | 7 | V19,V25 |
| Conventional | Tg. Frumos | 6 | V13,V18 |
| Conventional | Matca | 8 | V1, V2,V8 |

Determination of pesticide residues was performed according to standards, as follows: SR EN12393-1, 2, 3:2009 – Fat-free foods. Multireziduu methods for determining pesticide residues GC and SR EN 15662 / 2009 - Foods of plant origin. Determination of

pesticide residues by GC-MS and / or LC-MS/MS after extraction / partition with acetonitrile and purified by dispersive method SPE-QuEChERS.

After processing the samples by extraction with organic solvents (acetonitrile, petroleum ether), pesticide residues were analyzed by gas chromatography method using a Shimadzu GC, model 2100, equipped with autosamples and using NPD detector for analysis of organophosphorus pesticides. Were used as standards for determining pesticide residues by gas - chromatography, these mixtures of pesticides: Pesticides Mix 17, Mix 154, Mix 155, Dr. Ehrenstorfer.

Interpretation of results on pesticide residues was carried out in accordance with Regulation (EC) no. 396/2005 on maximum residue limits of pesticides in fruits, vegetables, cereals and other plant products.

RESULTS AND DISCUSSIONS

Results on organophosphorus pesticide residues content (23 active ingredients - Mix 154) in soil samples collected from vegetable farms in 2010, are presented in table 3. Organophosphorus pesticide residues were not detected in any sample analyzed at the farm USAMV (samples S5, S6, S7). The soil samples collected from vegetable farms in Roman (samples S1, S2, S3) and Tg. Frumos (S8, S9, S10, S11, S12, S13, S14) were detected Omethoate residues, Phorate and Phosmet.

Organophosphorus pesticide residues (21 active ingredients - Mix 155) in soil samples collected from farms studied in 2010 were not detected in any sample analyzed. In table 4 the results on the content of organophosphorus pesticide residues (23 active ingredients - Mix 154) in soil samples collected from vegetable farms in the survey taken in August / 2010.

These residues were not detected in any sample analyzed from USAMV farm (samples S26 - S31). In the soil samples collected from conventional vegetable farms Tg. Frumos (sample S15 - S25), residues were detected in low concentrations Omethoate and Phosmet. Omethoate content ranged from 0.005 (S23) and 0.02 mg / kg (S20). Phosmet content ranged from 0003 (S15, S18) and 0.01 mg / kg (S17, S20).

Organophosphorus pesticide residues (21 active ingredients - Mix 155), from soil samples collected from vegetable farms studied in 2010 - were not detected in any sample analyzed.

In table 5 are shown the contents of organophosphorus pesticide residues in vegetable samples collected from areas Targu Frumos and Matca. The pesticide residues were not detected in most samples analyzed. Residues like Omethoate (V3-V8, V14 - V17), Phorate and Metribuzin in tomatoes fruit (V7) and Phosmet (V1 - V4, V7 - V8 and V13-V17) were detected, but within acceptable limits (< 0.01 mg / kg).

In table 6 are shown the contents of organophosphorus pesticide residues in vegetable samples collected from organic farms or in the process of conversion. The content of these pesticide residues have been detected in fresh produce from certified organic farms, in contrast to FA Rotariu have found remains of Omethoate (V20-V24) and Phosmet (V20, V21, V24, V25) but within acceptable limits (< 0.01 mg / kg).

Contents of organochlorine pesticide residues (Mix 154) from soil samples In phase I (mg/kg)

Table 3

| | in phase i (ing/kg) | | | | | | | | | | | | | |
|--------------------------------|---------------------|----------------------|------|-------|----|----|------------|------|-------|-------|-------|-------|-------|-------|
| Pesticides | | Samples codification | | | | | | | | | | | | |
| (active substances) | S1 | S2 | S3 | S4 | S5 | S6 | S 7 | S8 | S9 | S10 | S11 | S12 | S13 | S14 |
| Methamidophos | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Mevinphos | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Molinate | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Heptenophos | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Omethoate | 0.02 | 0.03 | 0.01 | 0.02 | nd | nd | nd | 0.02 | 0.05 | 0.05 | 0.04 | 0.01 | 0.05 | 0.05 |
| Naled | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Monocrotophos | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Phorate | nd | 0.001 | nd | nd | nd | nd | nd | nd | 0.002 | 0.002 | 0.001 | 0.003 | 0.02 | 0.003 |
| Fonofos | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Metribuzin | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Parathion- | | | | | | | | | | | | | | |
| methyl | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Metalaxyl | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Malathion | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Fenthion | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Parathion-ethyl | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Isofenphos | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Mecarbam | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Phenthoate | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Myclobutanil | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Fensulfothion | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Phosmet | 0.004 | 0.006 | 0.01 | 0.006 | nd | nd | nd | 0.01 | 0.006 | 0.007 | 0.006 | 0.008 | 0.006 | 0.007 |
| Phosalone | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Demeton-S- methyl-sulfoxide | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

nd - undetectable

Table 4
Contents of organochlorine pesticide residues (Mix 154) from soil samples in phase II (mg/kg)

| | Samples codification | | | | | | | | | | | | | | | | |
|--------------------------------|----------------------|-------|------|-------|-------|------|-------|------|-------|-------|-------|-----|-----|-----|-----|-----|-----|
| Pesticides (active substances) | S15 | S16 | S17 | S18 | S19 | S20 | S21 | S22 | S23 | S24 | S25 | S26 | S27 | S28 | S29 | S30 | S31 |
| Methamidophos | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Mevinphos | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Molinate | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Heptenophos | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Omethoate | 0.008 | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 | 0.007 | 0.01 | 0.005 | 0.01 | 0.008 | nd | nd | nd | nd | nd | nd |
| Naled | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Monocrotophos | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Phorate | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Fonofos | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Metribuzin | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Parathion-methyl | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Metalaxyl | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Malathion | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Fenthion | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Parathion-ethyl | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Isofenphos | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Mecarbam | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Phenthoate | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Myclobutanil | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Fensulfothion | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Phosmet | 0.003 | 0.004 | 0.01 | 0.003 | 0.004 | 0.01 | 0.004 | nd | 0.007 | 0.005 | 0.006 | nd | nd | nd | nd | nd | nd |
| Phosalone | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Demeton-S-methyl-sulfoxide | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

nd - undetectable

| Species / cultivar | Samples | Pesticides (active substances) | | | | | | | | |
|---------------------|--------------|--------------------------------|---------|------------|---------|--|--|--|--|--|
| opecies / cultival | codification | Omethoate | Phorate | Metribuzin | Phosmet | | | | | |
| Peppers/California | V3 | 0.007 | nd | nd | 0.004 | | | | | |
| Peppers/Fidelio | V4 | 0.01 | nd | nd | 0.002 | | | | | |
| Tomatoes/Magnus | V5 | 0.01 | 0 | nd | nd | | | | | |
| Cucumbers/Merengue | V6 | 0.003 | nd | nd | nd | | | | | |
| Tomatoes/Magnus | V7 | 0.002 | 0.001 | 0.002 | 0.003 | | | | | |
| Cucumbers/Mirabelle | V8 | 0.001 | nd | nd | 0.001 | | | | | |
| Cucumbers/Merengue | V14 | <0.01 | nd | nd | <0.01 | | | | | |
| Peppers/Maradona | V15 | <0.01 | nd | nd | <0.01 | | | | | |
| Tomatoes/Belladona | V16 | <0.01 | nd | nd | <0.01 | | | | | |
| Cucumbers/Merengue | V17 | <0.01 | nd | nd | <0.01 | | | | | |

Table 6
The content of organophosphorus pesticide residues (Mix 154) in plant samples collected in 2010 (mg/kg)

| Species / cultivar | Samples | Pesticides (active substances) | | | | | | | | |
|--------------------|--------------|--------------------------------|---------|------------|---------|--|--|--|--|--|
| Species / cultivar | codification | Omethoate | Phorate | Metribuzin | Phosmet | | | | | |
| Peppers/Belladona | V19 | nd | nd | nd | nd | | | | | |
| Tomatoes/Primadona | V20 | <0.01 | nd | nd | <0.01 | | | | | |
| Eggplant/Aragon | V21 | <0.01 | nd | nd | <0.01 | | | | | |
| Cucumbers/Merengue | V22 | <0.01 | nd | nd | nd | | | | | |
| Onion/Stuttgart | V23 | <0.01 | nd | nd | nd | | | | | |
| Green beans/Saxa | V24 | <0.01 | nd | nd | <0.01 | | | | | |
| Cabbage/Gloria | V25 | nd | nd | nd | <0.01 | | | | | |

CONCLUSIONS

- 1. In most of the analyzed samples of soil and plant products on the soils, the content of the main chemical contaminants have been detected and analyzed were within the maximum allowed under European and national regulation.
- 2. In conventional farms from Roman, Tg. Frumos and Matca a series of organophosphorus pesticide residues (Phorate, Phosmet, Omethoate) were detected, in majority of soil samples analyzed.

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