CHLORPYRIFOS RESIDUE LEVELS IN LOCAL CROPS FROM THE REPUBLIC OF MOLDOVA AND ROMANIA

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INTRODUCTION

Chlorpyrifos **(ChP)** is a broad-spectrum, chlorinated organophosphorus (OP) insecticide, acaricide and nematicide. Chlorpyrifos is used on agricultural food and feed crops, cattle ear tags, golf course turf, industrial plants and vehicles, non-structural wood treatments including processed wood products, fence posts and utility poles, and to control public health pests such as mosquitoes and fire ants.

Therefore population (adults and children) are widely exposed through occupational use, contact with treated surfaces, breathing air in treated buildings or near treated fields or orchards. It is a widespread contaminant of fruit and vegetables, but is also found in grains, beans, dairy products, meat, fish, tea, and soft drinks. It is even found in processed products such as bread, hamburgers, jam, meat pies, muesli, olive oil, pasta, pizza, sausages, and snack bars.

Chlorpyrifos has at least three main modes of action in mammals:

- ▼inhibits the enzyme acetylcholinesterase (AChE) causing overstimulation of the nervous system;
- ▼causes oxidative stress, a process involved in many human diseases, including cancer, Parkinson's disease, Alzheimer's disease, diabetes, and heart failure;
- ▼causes endocrine disruption.

ChP is pervasive in the environment. Research has shown that runoff after heavy rains can remove up to a third of the amount of chlorpyrifos that was recently applied to plants.

Until recently ChP was one of the most widely used insecticides in the world. In 2018 in the Republic of Moldova 29 products containing chlorpyrifos under different trends have been registered and intensively used (*e.g.* Dursban 480 EC, Fosban 480 EC, Pyrinex 480 EC, Nurelle D505, etc.). However, since 2019, it has been excluded from the list of active substances approved for use in the PPP.

THE AIM OF THE STUDY

Determination of Chlorpyrifos contamination level in local most commonly consumed foods of plant origin

SAMPLE PREPARATION & ANALYSIS

Between May 2017 and August 2018, various fresh plant products were collected in the pilot districts of the Republic of Moldova and Romania, from local producers to determine the residuals of ChP. The values obtained for the content of ChP in foods were compared with the Maximum Residue Levels according to EU legislation (see Table 1).

Sampling of fruits and vegetables was carried out in the following pilot districts:

Moldova:

- ▼districts with intensive use of pesticides (Straseni and Ialoveni),
- ▼areas with low level of pesticide use (Telenesti and Causeni).

Romania:

- ▼ known areas polluted with heavy metals. post-industrial areas (Copsa Mica);
- ▼unpolluted areas (Alba county)

A total of seventy-six samples of local most commonly consumed products of plant origin (apples, grapes, potatoes, onion, carrot, lettuce, tomatoes, cucumbers, beets) were collected from markets, food deposits, farms and homesteads for the analyses.

Analytical method for the determination of residues of ChP in crops: Gas chromatographic method with mass spectrometry. Equipment: gas chromatograph "Agilent Technologies" 6890N, equipped with selective mass detector MSD "Agilent Technologies" 5973 and autosampler "Agilent Technologies" 1530N.

RESULTS AND DISCUSSION

The basic structure of the food ration of a consumer from the Republic of Moldova consists of about 30-40 food products of plant origin. Scientific research has shown that vegetable products such as tomatoes, potatoes, peppers, green salad, strawberries, green beans, celery, grapes, pears, peaches and apples are at major risk of being contaminated with pesticide residues based on the technologies of cultivation.

The analytical results showed that ChP residuals were determined in 24 samples collected in the pilot districts in Moldova and Romania which accounted for 32% of the total number of samples, including: in 26% of the samples in Moldova and in 53% - in Romania. It should be noted that 13% of the total number of analyzed samples contained chlorpyrifos residues above the MRL.

The obtained results indicate that ChP residues were determined in:

Moldova	Romania
- 56% of apples samples;	- 100% of apples samples;
- 56% of carrots samples;	- 66 % of carrots samples;
- 50% of onions samples;	- 60% of onions samples;
- 20% of cabbage samples;	- no cabbage samples;
- 10% of potatoes samples;	- 33% of potatoes samples.

In the pilot areas with intensive use of pesticide, the number of samples contaminated with chlorpyrifos was 2.5 times higher than in the districts with low level of pesticide use.

Table 1. **Levels of the contamination of the vegetable products with the residuals of chlorpyrifos in Moldova and Romania**

Type of the product	MRLs* (mg/kg)	Residuals of chlorpyrifos (mg/kg) in local food (mean measured)	
		Republic of Moldova	Romania
Apples	**0.01**	**0.029**	**0.034**
Quinces	**0.40**	0	**-**
Plums	**0.30**	0	-
Grapes	**0.01**	0	-
Potatoes	**0.01**	**0.0027**	**0.015**
Beetroots	**0.05**	0	**-**
Carrots	**0.10**	**0.021**	**0.046**
Onions	**0.20**	**0.013**	**0.026**
Tomatoes	**0.10**	**0**	**-**
Sweet peppers	**0.01**	0	**-**
Cucumbers	**0.01**	0	-
Pumpkins	**0.01**	0	-
Head cabbages	**0.01**	**0.005**	**-**

**** MRL –maximum residue levels for chlorpyrifos in accordance with Reg (EU) 2020/1085*** .

Moldova ▼the highest detected concentrations of the ChP in crops sampled in the pilot areas were: in apples - 0.132 mg/kg (MRL= 0.01 mg/kg); in carrots - 0.052 mg/kg (MRL=0.1 mg/kg); cabbages - 0.023 mg/kg (MRL= 0.01 mg/kg); onions - 0.029 mg/kg (MRL= 0.2 mg/kg); potatoes – 0.027 mg/kg (MRL= 0.01 mg/kg). ▼samples of the grapes and fruits, other than apples, were free from residuals of ChP.

Romania ▼The highest detected concentrations of the ChP in apples sampled in pilot districts were - 0.032 mg/kg; in carrots - 0.048 mg/kg; in onions - 0.052 mg/kg; potatoes – 0.047 mg/kg.

CONCLUSIONS

Considering that ChP residues have been detected in the most commonly consumed vegetables and fruits in Moldova and Romania, it can be assumed that one of the important sources of penetration of OP pesticides into the human body is products of plant origin, which may present a high risk to human health in acute and long-term perspective.

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