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RESEARCH ARTICLE

HEALTH RISK RELATED TO THE INTAKE OF PESTICIDES IN THE REPUBLIC OF MOLDOVA

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Abstract

The present research was conducted to assess the health risk associated with consumption of vegetables and fruits contaminated with pesticides by the population of the Republic of Moldova. Pesticide residues were determined in four vegetable crops and three fruit crops, namely: tomato, cucumber, eggplant, head cabbage, apple, plum, and grapes. Obtained results indicate that concentration levels exceeding their Maximum Residue Levels (MRLs) were detected in 6% of apple samples, in 8% of samples of head cabbage and in 5% of samples of plums. The most detectable pesticides were dimethoat, captan, carbendazim, acetamiprid, copper, and cymoxanil. The MRL exceedance for dimethoat, tebufenpyrad, phosalone, carbendazim, indoxacarb was registered (31% of all detected pesticides). The estimated daily intakes (EDIs) have been estimated between 0.000015 and 0.0012 mg/kg of body weight/day. The calculated hazard indices (estimated daily intake/acceptable daily intake [EDI/ADI]) ranged from 0.00041 and 0.42 for the analyzed pesticides. The highest value of hazard index for detected pesticides was calculated for a dimethoate – 0.42. We conclude that the long-term consumption of vegetables and fruits does not pose a health risk for the population of Republic of Moldova.

INTRODUCTION

The Republic of Moldova is an independent country located in the South-East of Central Europe and in the North-East of the Black Sea between Romania and Ukraine. The agricultural and industrial sector occupies a central place in the national economy. According to the 2008 data of the National Profile for Chemical management in the Republic of Moldova, over 32% of the country's working population labours in the agricultural sector.

As of 1 January 2013, the country's agricultural sector has allowed the application of 740 plant protection products (PPPs) that are produced on the basis of 315 active substances from different chemical groups: compounds of copper and sulfur, carbamates and thiocarbamates, organophosphorus, chlorophenoxy, synthetic pyrethroids, neonicotinoid derivatives, sulfonyl-urea, strobilurin, among others (according to Government Decision of the Republic of Moldova no. 567 of 16 July 2014). The widespread applications of PPPs as a result of technical and scientific development causes substantial increases in agricultural production, but often with the risk to produce negative effects on the food safety. Some pesticides used in agriculture are classified as carcinogenic, mutagenic or causing hormonal system disorders. The results of laboratory analysis of multiple samples of the food of plant origin shows that residues of pesticides commonly persists in food commodities, therefore monitoring the pesticide levels is a substantial contemporary public health problem to guarantee food quality and to evaluate the health risk.

The basic structure of the diet of a consumer in the Republic of Moldova consists of about 30-40 foods of plant origin. Studies (Boon et al., 2008; Darko G., Akoto O., 2008; Berrada et al., 2010; Sinha et al., 2012;

Knezevic et al., 2012; Lozowicka B. et al, 2012; Eissa et al., 2013; Mosleh et al., 2014; Chandra et al., 2014; Ali U. et al., 2014; Syed Jabir Hussain et al., 2014; Chowdhury et al., 2015) have shown that tomatoes, peppers, lettuce, broccoli, strawberries, spinach, green beans, celery, grapes, pears, peaches and apples have major risks of being contaminated with pesticide residues. These contaminants pose a risk to public health because they are present in most types of food (Ali U. et al., 2014). In this context, dietary intake of pesticides is one of the main routes of exposure to different pesticides (Egeghy et al., 2011; Ibarluzea et al., 2011; Gasull et al., 2011). This means that population is subjected to the continuous action of pesticides, which may have serious consequences for health, especially on future generations. Pesticide contamination is a priority public health concern in the Republic of Moldova.

The present research was conducted to assess the health risk associated with consumption of vegetables and fruits contaminated with pesticides by the population of the Republic of Moldova.

Material and Methods

Sample collection

170 samples (47 samples of apples, 25 samples of tomatoes, 25 samples of cucumbers, 5 samples of eggplants, 25 samples of head cabbage, 19 samples of plum, 24 samples of table grapes) from the harvest of 2014 were collected from different agricultural fields of the Republic of Moldova. 50 g of homogenized samples of fruits and vegetables were taken for analysis.

Instrumentation

The pesticide residues' analysis was carried out by the multiresidue procedures. Selected samples were analyzed by using of gas chromatography/mass spectrometry (GC/MS).

Quality assurance

Samples were analyzed according to the quality assurance system SM SR EN ISO / IEC 17025: 2006.

Hazard identification and characterization

Results of identification and estimation of pesticide residues in selected samples were compared with maximum residue levels (MRLs). National MRLs were established in Health Regulation (2010), partially transposing Regulation no. 396/2005 of the European Parliament and of the Council of 23 February 2005.

Estimation of human intake

The estimated daily intake (EDI) was calculated using the following equation:

EDI = C x F/ W, where C – is the sum of the concentration of pesticide residues in each commodity (mg/kg), F – is the mean daily intake of food per person, W – is the mean body weight (60 kg).

Dietary intake of fruits and vegetables per person was estimated according to minimum norms of the food included in a living-wage food basket (Government Decision of the Republic of Moldova No. 285 of 30.04.2013).

Risk estimation

Calculated estimated daily intake was compared with acceptable daily intake (ADI). This toxicological information is available at http://www.ec.europa.eu/sanco_pesticides. Hazard indices were calculated dividing EDI value by ADI value.

Results and Discussion

Monitoring of priority pesticides in fruits and vegetables

This study was carried out in 2014 in the chemical laboratory of the National Centre of Public Health. We obtained information on the extent of pesticide contamination for different types of vegetables and fruits. The selection of apples, tomatoes, cucumbers, eggplants, head cabbage, plums and table grapes' crops was based on their popularity and high consumption rates by the population of the Republic of Moldova. The obtained data showed that the majority (67%) of the residues monitored were in concentrations below the level of detection (LOD).

The levels and identity of pesticide residues found in the analyzed samples are presented in Table 1. In the analyzed samples, residues of pesticides with different object of application (7 insecticides, 9 fungicides and 1 acaricide) were detected. Sixteen pesticides (dimethoate, mancozeb, tebufenpyrad, phosalone, captan, imidacloprid, cymoxanil, cyprodinil, carbendazim, acetamiprid, indoxacarb, dithianon, copper, pyrimethanil, thiophanate-methyl, chlorothalonil) were found at levels between 0.03 mg/kg and 0.205 mg/kg. Similar levels of carbendazim, acetamiprid and imidacloprid were registered by Sana Sungur and Cetin Tunur (2012).

Analysis of pesticide residue in apple samples shows that two fungicides (dithiocarbamates [mancozeb] and phthalate [captan]) and four insecticides (two organopfosphates [dimethoate and phosalone], triazol [tebufenpyrad] and a imidacloprid from neonicotinoids) were found. Similarly, in samples of plums, captan and dimethoate were present. Besides, fungicide dithianon and copper insecticide were found. In samples of table grapes, both residues of fungicides (thiophanate-methyl, chlorothalonil) and insecticides (cymoxanil, copper) were detected. The MRL value of dimethoate (0.02 mg/kg) was exceeded in sample of apple and plum (0.2 mg/kg and 0.03± 0.007 mg/kg

respectively, table 1). In apples, MRLs exceedance of tebufenpyrad and phosalone were also established (0.28 ± 0.01mg/kg and 0.03 mg/kg respectively, table 1).

Residues of dimethoate 10 times exceeding the MRL, were found in one sample of the analyzed apples. In this case, the following measures have been applied: withdrawal of contaminated products from the market; confiscation and destruction of contaminated products (law, 2004); enforcement sampling of the next coming lot; all MRL exceedances are published at the National Food Safety Agency's website.

Analysis of pesticide residue in samples of vegetables indicates that 5 residues of pesticides: three insecticides (cymoxanil, indoxacarb, acetamiprid) and two fungicides (cyprodinil and carbendazim) were found. The MRLs exceedance of carbendazim and indoxacarb were found in samples of head cabbage (0.12±0.06 mg/kg and 0.25±0.02 mg/kg respectively, table 1).

According to the results, pesticide residues were detected in four vegetable crops and three fruit crops, namely: tomato, cucumber, eggplant, head cabbage, apples, plums, and grapes. Obtained results indicate that concentration levels exceeding their MRLs were detected in 6% of apple samples, in 8% of the samples of head cabbage and in 5% of the samples of plums. The most detectable pesticides were dimethoat, captan, carbendazim, acetamiprid, copper, cymoxanil. The MRL exceedance for dimethoat, tebufenpyrad, phosalone, carbendazim, indoxacarb was registered (31% of all detected pesticides).

Exposure and health risk assessment of pesticides residues in fruits and vegetables.

The results concerning residue levels were used to calculate the estimated daily intake (EDI) expressed as milligram pesticides per kilogram of body weight per day (mg/kg bw/day).

EDI for pesticide residues found in the analyzed vegetables and fruits is a realistic estimate of pesticide exposure calculated according to the international guidelines (FAO, EFSA, WHO). Estimation of exposure levels and risk assessment is recommended by the World Health Organization as an important activity, as it provides reliable estimates of dietary intakes of contaminants.

The EDIs have been estimated between 0.000015 and 0.0012 mg/kg of body weight/day (Table 2). Calculated values of EDIs are lower than the levels of ADI. The study of Claeys W.L., S. De Voghel J.F. (2008) reported that for most pesticide residues the exposure was 100 times lower than ADI. Scientists from Egypt (Mohamed Tawfic Ahmed et al., 2014) also established that EDIs of pesticides ranged from 0.03% to 40% of the ADIs, depending on pesticide concentration and food consumption.

Obtained data of the sum of EDI were used to calculate the hazard index for the tested compounds. The calculated hazard indices (EDI/ADI) ranged from 0.00041 and 0.42 for the analyzed pesticides (Table 2). The highest value of hazard index for detected pesticides was calculated for the dimethoate – 0.42. In this analyzed sample of apples, the pesticide residues exceeded MRL 10 times. Despite this excess, EDI for dimethoate is less than ADI. This fact can be explained as follows. Dietary intake per person of fruits and vegetables was estimated according to minimum norms of the food included in a living-wage food basket (Government Decision of the Republic of Moldova N 285). According to these norms, consumption of apples is equal to 0.11 kg/day. EDI in this case is equal to 0.0004 mg/kg bw per day. In Moldova, the actual consumption of apples by the population is much higher. Although the consumption data used in this study is the most updated, there is a need for data which reflects real food consumption patterns in Moldova. Here, it should be noted the study of Polly E. Boon et al. (2014) regarding the actual intake levels of pesticide residues, dietary habits and exposure to pesticides in Dutch infants.

Thus, our results of the hazard indices show that the long-term consumption of tested vegetables and fruits could not pose a health risk for the population of Moldova as the hazard indices for all the detected residues were less than one. Knezevic Z., Serdar M., Ahel M. (2012) reported that long term exposure of Croation consumers did not raise health concerns. Authors from Egypt (Mohamed Tawfic Ahmed et al., 2014) also concluded that the EDIs of the different pesticides from vegetable consumption are not considered a public health problem. However, Mahabali S., Spanoghe P. (2015) informed that the highest observed international estimated short-term intake (IESTI) for imidacloprid and chlorothalonil was 74.5 % of the EU acute reference dose, giving rise to concern about pesticide usage.

Thus, we consider that exceedances of MRLs could pose threat to the population health by higher consumption rates of fruits and vegetables polluted by pesticides.

Table 1. Concentration of pesticide residues detected in tested vegetable and fruit samples and maximum residue levels (MRL), mg/kg.

Samples	Detected pesticide	Mean	MRL (national)
Apples	Dimethoate	**0.2** (n=1)	0.02

	Mancozeb	0.13 ± 0.07	5.0
	Tebufenpyrad	**0.28 ± 0.01**	0.2
	Phosalone	**0.03** (n=1)	0.01
	Captan	0.205±0.09	3.0
	Imidacloprid	0.02 (n=1)	0.5
Tomatoes	Cymoxanil	0.15 (n=1)	0.2
	Cyprodinil	0.1 (n=1)	1.0
Cucumbers	Cymoxanil	0.12 (n=1)	0.5
	Carbendazim	0.07± 0.01	0.1
	Acetamiprid	0.15±0.02	0.3
Eggplants	Acetamiprid	0.1 ± 0.01	0.2
Head cabbage	Carbendazim	**0.12±0.06**	0.1
	Indoxacarb	**0.25±0.02**	0.2
Plums	Dithianon	0.26 (n=1)	0.5
	Copper sulphate	0.73±0.09	5.0
	Pyrimethanil	0.11± 0.01	2.0
	Captan	0.03± 0.004	7.0
	Dimethoate	**0.03± 0.007**	0.02
Table grapes	Cymoxanil	0.12± 0.01	0.2
	Copper	1.43± 0.59	5,0
	Thiophanate-methyl	**0.12± 0.01**	0.1
	Chlorothalonil	0.03± 0.005	3.0

Table 2. Acceptable daily intake, estimated daily intake and hazard index for pesticide residues detected in the vegetables and fruits.

Detected Pesticide	∑ EDI, mg/kg bw per day	ADI, mg/kg bw per day	Hazard index (EDI/ADI)
Dimethoate	0.00042	0.001	**0.42**
Mancozeb	0.0002	0.05	0.004
Tebufenpyrad	0.0005	0.01	0.05
Phosalone	0.00006	0.01	0.006
Captan	0.00042	0.1	0.0042
Imidacloprid	0.00004	0.06	0.0007
Cymoxanil	0.00023	0.013	0.017
Cyprodinil	0.00008	0.03	0.0027
Carbendazim	0.00017	0.02	0.0085
Acetamiprid	0.00007	0.07	0.001
Indoxacarb	0.0003	0.006	0.05
Dithianon	0.0002	0.01	0.02
Copper sulphate	0.0012	0.15	0.008
Pyrimethanil	0.00007	0.17	0.00041
Thiophanate-methyl	0.00006	0.08	0.00075
Chlorothalonil	0.000015	0.015	0.001

Conclusions

The monitoring of pesticide residues in fruits and vegetables has an important role in providing data on the pesticide residues of the fresh produce. According to our results, pesticide residues were determined in vegetable and fruit crops, namely: tomato, cucumber, eggplant, head cabbage, apples, plums, and grapes. The MRL exceedance for dimethoat, tebufenpyrad, phosalone, carbendazim, and indoxacarb was registered in 31% of all detected pesticides in analyzed commodities.

Results of our investigations show that the long-term consumption of vegetables and fruits should not pose a health risk for the population of the Republic of Moldova as the hazard indices for all the detected residues were less than one. Nevertheless, exceedances of MRLs could pose threat to population health by higher volume of

consumption of fruits and vegetables polluted by pesticides. We consider that there is need for data which reflects real food consumption pattern in the Republic of Moldova.

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