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TIMELINE EVOLUTION OF MAXIMUM RESIDUE LEVELS FOR ACTIVE SUBSTANCES IN PLANT PROTECTION PRODUCTS

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Abstract: Setting maximum limits for residues of plant protection products is particularly important in order to avoid negative effects on food security and consequently on human health. Over time the maximum acceptable values of residue levels have been modified according to the legislation. To highlight timeline evolution of these MRL for the active substances in plant protection products, the paper presents the residue limits within tree representative official documentation which in chronological order are as follows: Detailed hygiene rules regarding foods and sanitary protection, standardized in M.S Order. no 611/1995, compared with the order M.A. regarding maximum levels for pesticide residues in plants and plant products no. 95/224/2001 and the legislation at European level, the REGULATION (EC) No 396/2005 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 February 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin and amending Council Directive 91/414/EEC. The results of the analysis show that during the period studied, the maximum acceptable residue levels of plant protection products on harvested vegetables, have decreased significantly, which demonstrates a strong focus on food safety and consumer protection.

Key words: *maximum residue levels, residues, active substance, consumer protection*

INTRODUCTION

Treatments with plant protection products leave marks on or in plant leaves called residues which cannot be removed by simply washing. They decompose in time by sunlight or by metabolism. Plant protection products used have higher or lower toxicity and thus residues have a level of dangerousness directly proportional to it. Therefore, to ensure consumer protection, authorities have the responsibility to take all measures to ensure that such residues will not affect people's health, especially those less resistant such as children and elderly people. (Schorr, 2011)

Measures to be taken when residues pose a health risk consist in setting a maximum limit for residues, as well as a pre harvest interval (PHI), which is the interval between the last treatment applied and the time of harvesting, basically the moment when products treated reach consumers directly or the food industry.

Maximum residue level (MRL) is the highest level of pesticide residues tolerated in or on food or feed, when pesticides treatments are applied according to Good Agricultural Practices. These MRLs are not set for plant protection products but for active substances, expressed in mg s.a. / kg food. (FAO 2012)

Purpose of this paper is to highlight the importance of establishing maximum limits values for residues for active substances in foodstuffs and demonstrating their evolution in order to protect consumers, as is remarked in legislation.

Since 1985, at the 23rd FAO Conference, it was developed and approved the International Code of Conduct on Pesticides Management, which includes methodologies for testing pesticides and reducing health and environmental risks.

The 2001 law regarding maximum residue levels of pesticides in plants and food, by the order of the Agricultural Food and Forestry Minister, was adopted after the European law which was applicable at the time.

MATHERIALS AND METHOD

Before MRL is set or amended EFSA assesses the residue behavior of the pesticide and possible consumer health risks from residues in food. Chronic long-term and acute short-term dietary consumer exposure to pesticide residues are estimated using a calculation model developed by EFSA (PRIMo – Pesticide Residue Intake Model). This model is based on national food consumption data and unit weights which are provided by Member States and implements internationally agreed risk assessment methodologies (FAO &WHO, 2009).

The methodology for calculating the maximum residue levels is based on the chronic toxicity tests, by determining the dose administered daily for 2 years, for which is not observed any negative effect on the experience animal. From this value (NOAL - No Observed Adverse Effect Level), by applying a safety factor of 100, it is obtained the value for ADI (acceptable daily intake), meaning the amount in mg/kg, which may be taken by the consumers without any risk to their own health, for the rest of their life.

Given the eating habits of different countries, is calculated theoretical maximum daily intake (TMDI), assessing the amount of foodstuff consumed in a day, being very important the percentage for these residues consumed in theory of the accepted daily intake (ADI). Residues present no risk when TMDI value is lower than the acceptable daily one (ADI) (WHO, 1997; 2003).

$$TMDI = \frac{\text{intake}\left(\frac{\text{kg}}{\text{day}}\right) * \text{MRL}}{\text{body weight}}$$

For the analysis of the MRLs values, in plants and plant products, we had as legislative base, the following official documents:

- ORDER no. 611/03.04.1995 for approving the rules regarding foods and sanitary protection under the Law no. 98/1994 concerning the establishment and sanctioning infringements of the legal hygiene and public health; (I.P.S.M.P)
- ORDER no. 95/224 2001 Minister for Agriculture, Food and Forestry and the Minister of Health on establishing maximum levels for pesticide residues in plants and plant products - Official Gazette of Romania - Part I Acts, Decrees, Resolutions and other documents No. 339;
- REGULATION (EC) no 396/2005 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 February 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin and amending Council Directive 91/414/EEC.

Maximum limits for pesticide residues in food products, are calculated for a range of active substances for different crops of major interest (VELDE-KOERTS et.al 2003; EPP et al., 2010).

In order to be an objective analysis, it was chose randomly, active substances with insecticidal effect (azinphos- methyl, carbaryl, chlorpyrifos, dimethoate, lindane, malathion, ethion, mevinphos, permethrin), fungicides (captan, folpet, imazalil, dodine, thiabendazole) and herbicides (diquat, glyphosate), for which it was compared the first MRL with the latest,

found in the previously mentioned documents, for crops such as tomatoes, cucumbers, peas, carrots, apples, peaches, apricots (Table 1).

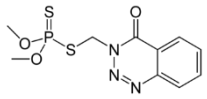
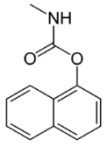
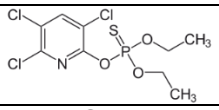
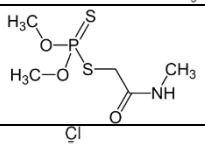
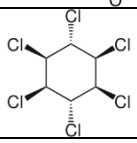
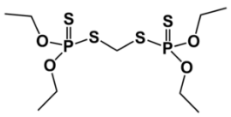
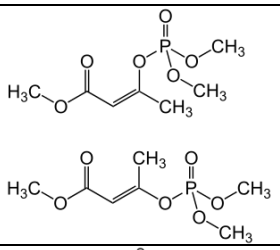
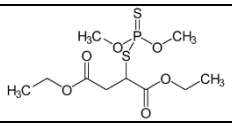
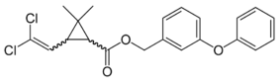
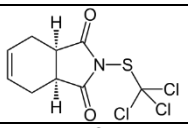
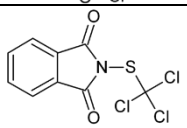
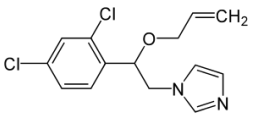
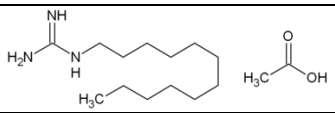
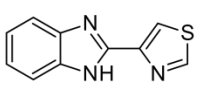
Table 1. Maximum residue levels for a series of pesticides, from different chronological years

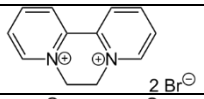
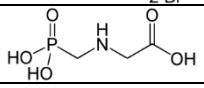
Nr. Crt.	Active substance	Crop	Ord.611/1995 MRLs mg/kg	Ord 95/ 2001 MRLs mg/kg	Reg.EU 396/2005 MRLs mg/kg
Insecticides					
1	**Azinphos-methyl**	Apricot	2,00	0,05	0,05
		Peaches	4,00	0,05	0,05
2	**Carbaryl**	Cucumbers	3,00	1,00	Not approved
		Peaches	10,00	3,00	Not approved
		Tomatoes	5,00	1,00	Not approved
3	**Chlorpyrifos**	Mere	1,00	0,5	0,5
		Carrots	0,5	0,1	0,1
4	**Dimethoate**	Cherry	2,00	1,00	0,2
		Carrots	1,00	1,00	0,02
5	**Lindane**	Tomatoes	2,00	0,5	Not approved
		Carrots	0,2	0,1	Not approved
6	**Malathion**	Cherry/ Peaches	6,00	0,5	0,02
		Tomatoes	3,00	3,00	0,02
7	**Ethion**	Tomatoes	2,00	0,1	Not approved
		Cucumbers	0,5	0,1	Not approved
8	**Mevinphos**	Tomatoes	0,2	0,1	Not approved
		Cucumbers	0,2	0,1	Not approved
9	**Permethrin**	Cucumbers	0,5	0,1	Not approved
		Tomatoes	1,00	0,5	Not approved
Fungicides					
1	**Captan**	Apples	25,00	3,00	3,00
		Cucumbers	10,00	0,1	0,02
2	**Folpet**	Tomatoes	5,00	3,00	3,00
		Cucumbers	2,00	0,1	0,02
3	**Imazalil**	Cucumbers	0,5	0,2	0,2
4	**Dodine**	Peaches	5,00	1,00	0,09
5	**Thiabendazole**	Apples	10,00	5,00	5,00
		Tomatoes	2,00	0,05	0,05
Herbicides					
1	**Diquat**	Potatoes	0,2	0,1	0,05
		Peas	0,5	0,1	0,05
2	**Glyphosate**	Peas	5,00	0,1	0,1

Pesticides are briefly defined as any substance or mixture of substances intended for preventing, destroying, or controlling any pest, unwanted species of plants or animals, causing harm during or otherwise interfering with the production (Table 2).

Table 2. Chemical properties for the active substances within the study

ACTIVE SUBSTANCE	CHEMICAL STRUCTURE	CHEMICAL FORMULA
Insecticides		

Azinphos- methyl		$C_{10}H_{12}N_3O_3PS_2$
Carbaryl		$C_{12}H_{11}NO_2$
Chlorpyrifos		$C_9H_{11}Cl_3NO_3PS$
Dimethoate		$C_5H_{12}NO_3PS_2$
Lindane		$C_6H_6Cl_6$
Ethion		$C_9H_{22}O_4P_2S_4$
Mevinphos		$C_7H_{13}O_6P$
Malathion		$C_{10}H_{19}O_6PS_2$
Permethrin		$C_{21}H_{20}Cl_2O_3$
Fungicides		
Captan		$C_9H_8Cl_3NO_2S$
Folpet		$C_9H_4Cl_3NO_2S$
Imazalil		$C_{14}H_{14}Cl_2N_2O$
Dodine		$C_{15}H_{33}N_3O_2$
Thiabendazole		$C_{10}H_7N_3S$

Herbicides		
Diquat		$C_{12}H_{12}N_2$
Glyphosate		$C_3H_8NO_5P$

RESULTS AND DISCUTIONS

Data analyzed in this study show a negative trend, starting from the year 1994 with higher values, to a middle period when MRLs were get in line with the European legislation, up to the present, when there are fewer active substances then there used to be, and with decreased values for maximum residue levels.

As for the active substances with insecticidal effect, there shall be noticed carbaryl, for which in 1994, MRL was 3.00 mg/kg for cucumbers, 5.00 mg/kg for tomatoes and 10.00 mg/kg for peaches and after 7 years, in 2001, the values are tree time smaller. By the latest regulation, the active ingredient carbaryl is not approved anymore.

A similar evolution had another series of active substances with insecticidal effect, such as lindane, going from a maximum residue level of 2 mg/kg for tomatoes in 1994 up to not being approved in 2005, as well as ethion, mevinphos and permethrin, for which MRLs were at least halved when Romanian legislation adapted by the European one in 2001, and after four years they were prohibited by the EU Regulation.

Besides these active substances, there is chlorpyrifos which is still approved by the EU Reg 396/2005, but in the late 1994, the value for maximum residue level in apples was two times higher than it is now. At the same time, a.s. azinphos-methyl decreased from 4 mg/kg as MRLs for peach, to 0.05 mg/kg according to the current Regulation. Alongside this, there are a lot more insecticidal active substances whose values decreased since 1994, such as dimethoate, malathion and others.

As regarding active substances with fungicidal effect, it can be noticed a considerable difference between maximum residue levels in apples of 25 mg/kg for captan by the1994 legislation and 3 mg/kg by the 2001 legislation and latest EU regulation. For the same active substance, MRLs in cucumbers decreased from 10 mg/kg accepted in 1994, to 0.1 mg/kg in 2001 and again to 0.02 mg/kg by the EU regulation, meaning it decreased 500 time which is a significant change being safer for consumers health and the environment. A similar situation, for the same product to which MRL apply, but for another active substance, is folpet whose maximum residue level decreased 100 time since 1994, from 2 mg/kg , to 0.1 mg/kg in 2001, up to 0.02 mg/kg by current Regulation.

The same negative trend is followed by another fungicidal active substances, such is thiabendazole with a decreased to half value from 1994 to current regulation, basically from 10 mg/kg to 5 mg/kg, imazalil with an initially MRLs of 0.5 mg/kg for cucumber which decreased to 0.2 mg/kg, and also dodine whose maximum residue level is five times lower now than it was in 1994 for peaches.

The MRLs for the pair of active substances with herbicidal effect for peas , diquat and glyphosate, decreased significantly both since 1994, by 10 times for diquat and 50 times for glyphosate by the current EU regulation 396 /2005.

CONCLUSIONS

The analysis let to the conclusion that throughout the period studied, the maximum levels for residues of plant protection products in harvested vegetable products, decreased significantly which demonstrates a special attention given to food safety and consumer protection.

Currently the number of active substances in plant protection products is lower than it used to be in 1994, for toxicological and ecotoxicological reasons, mostly in the benefit of the consumers' health and the environment but at the same time, to the detriment of agricultural practice.

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