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Ecotoxicological view of protection of apple orchards against insect pests in Poland

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Abstract: The paper presents some aspects of relations between modern plant protection of apple orchards and ecotoxicology. Based on significant similarity of the shape and size of apple and tomato fruits the relation between the doses of active ingredients of plant protection products and their residue levels immediately after treatment was derived for the apples and then quality indices and the risks for human health were estimated. It was found that many of the currently in force MRLs need to be revised and the exposure of consumer should not exceed the acceptable daily intakes (ADIs) and acute reference doses (ARfDs) for pesticide residues

Keywords: apples, quality indices, maximum residue limits, risk assessment

INTRODUCTION

For obvious reasons we are becoming more and more sensitive to the conditions and quality of our environment and food. We have the term "healthy food" to describe ecological food. The use of this term is not only misleading but even harmful since it suggests that 95% of Polish food is unhealthy. Is that true? Not really.

Fruit or vegetables not protected from the fungus-related diseases may contain micotoxins, the substances produced by organisms of the fungus kingdom far more dangerous than the fungicides. This is the case of mold on the strawberries,

patulin produced by a variety of molds, particularly *Aspergillus* and *Penicillium* commonly found in rotting apples, or ochratoxin A occurring in commodities like cereals, coffee, and dried fruit [1].

On the other hand, if the chemical treatment is to be effective, plant protection product has to get into contact with the harmful pest or disease, originating and developing on/in the plant or its surroundings. In order to stimulate such contact the agrochemicals are applied directly on the plants, animals, soil or water. As a result of such procedures in the food or elements of environment the residues of pesticides can be found [2]. As far as food of plant origin is concerned, Good Plant Protection Practice (GPP) provide that the initial deposits of fungicides on the plant are the necessary conditions of their effectiveness, while the residues of insecticides have to be considered as redundant but most often unavoidable pollution. Furthermore, desired feature of fungicides, especially those used as a protection agent, is their persistence, while insecticides should undergo detoxication pretty fast, preferably to CO₂, H₂O or a phosphoric acid.

The goal of this paper is to present some relations between modern plant protection programs and the ecology, using the example of controlling of herbivorous insects in apple orchards.

AGRICULTURAL MANAGEMENT SYSTEMS AND ECOLOGY

There are three systems of management: conventional agriculture, integrated agriculture and ecological agriculture. Two of them, integrated agriculture and ecological agriculture, have their own legal status in Poland and other countries of European Union. There are precise regulations specifying the conditions they must meet and the observance of which is monitored by public administration.

Ecological agriculture, also known as biological or organic agriculture, is the system of management of sustainable production of plants and animals in household, based on the substances of biological and mineral origin, not processed technologically, so it does not lead to shift in ecological balance. Ecological agriculture can develop only in the regions free from industrial pollutions. Globally, the demand for ecological products increases, which is proved by, for example BioFach, the World Organic Trade Fair, which traditionally takes place in Nuremberg. Ekogala is the largest Polish organic exhibition for exhibitors and visitors from Poland and other countries like Ukraine, Czech Republic, Slovakia, Germany, France, Russia and offers the perfect setting for presenting organic products to buyers and specialists. Over 100 exhibitors and over 10000 trade visitors met at Ekogala in 2008.

Ecological agriculture in European Union was regulated by the decree of Council Regulation published in Official Journal L 198 on July 22, 1991 [3]. The decree is the legal act superior to the national law and has to be implemented in the national legal system without any modifications (abbreviations, amendments or interpretations) by each member state. In Poland since May 1st, 2004 we have the law on ecological agriculture [4] from April 20, 2004, containing the EU regulations and describing the competencies of Polish bodies working on the issue of ecological agriculture.

The law specifies the products and the condition of their use in the plant protection. These are all the substances of natural origin, such as:

- Azadirachtin (present in the Neem tree seeds), aqueous extract of Nicotiana tabacum, plant oils (mint, pine, caraway seeds), natural pyrethrins extracted from Chrysanthemum cinerariaefolium, extract of Quassia amara containing quassinoids used as insecticides or rotenone,
- microorganisms (bacteria, viruses and fungi) e.g. *Bacillus thuringiensis*, *Granulosis wirus*,
- diamonium phosphate(VI), metaldehyde, pheromone, synthetic pyrethroids (only deltamethrin or cyhalothrin and only in traps!),
- copper in various chemical forms, ethylene, potassium soap, the hydrated aluminum potassium sulphate(VI), paraffin oil, potassium manganate(VII), elemental sulphur.

Observing all these regulations is controlled and when disallowed substances are found it may result in withdrawing certifications for labeling given product as "ecological" [4].

The term integrated agriculture means the system of management which is the compromise between the consumer's demands for:

- more environment-friendly agriculture, especially reducing the use of chemical plant protection products, and,
- production of food that is safe, affordable for everybody, fresh, free from damages and insects, of perfect shape and size.

Integrated agriculture is therefore challenging idea, which has to be translated into practical guidelines for the food producers.

This short characteristic of management systems shows that the ecological agriculture is by definition environment-friendly but there are many barriers to its wide introduction and its importance is at the moment quite limited. Integrated agriculture, on the other hand, has quite an ambitious goal — sensitivity to the natural environment without resigning of use of modern plant protection products.

PROTECTION OF APPLE ORCHARDS

Herbivorous insects and diseases are the main threats to the crops. Maintaining or increasing the crops requires constant development of plant protection methods, which can be divided into three main categories: plants quarantine, agrotechnical and breeding methods and the direct control methods [5]. The goal of the latter is control already existing agrofags and prevention of their spreading with use of the following methods:

- biological pathogenic viruses, bacteria and fungi and parasitic and predatory animals,
- mechanical and physical factors (temperature, light) and mechanical treatments,
- chemical direct destruction of pathogens and pests, or affecting their development (chitin synthesis inhibitors, juvenile hormones) or behavior (pheromones, insect repellents, antifeedants) using the chemical substances.

Using at least two of the above mentioned methods of control of pests and diseases, the art. 4 of the Law on plant protection calls integrated plant protection (IPP). The second method is usually biological method [4, 6].

Chemical method of pest and disease control

Chemical methods, more and more often used following the discovery of insecticidal features of DDT (dichloro-diphenyl-trichloroethane), is almost from the beginning widely criticized [7] and often treated as a main threat to those working with them, as well as consumer and environment [8, 9]. It is underestimated, however, that there has been great progress in this area resulting in the changes of the choice and technique of application of plant protection substances and in education of food producers.

At the moment, under the regulations of the Directive 91/414 [10], all active substances which since 1993 were used in the chemical preparations, are subject to reevaluation and registration. This process was finished in 2008 and it is clear that there will be further limits of active substances allowed for use in EU. It is worth mentioning that large number of active substances forbidden or withdrawn results not in the risk they bring but rather in the producers' decision not to re-register them.

Even if we take into account the substances allowed after 1993, the overall number of available chemical products has significantly decreased. It affects mostly minor crop production, including many species of vegetables, flowers and berries [9]. The most important effect of the limitation of the number of registered substances is the lack of opportunity of realizing rational method of

plant protection. At the moment there are 750 plant protection products registered, which is about 66% of the number registered at the end of 2003.

Maximum residue limits and the doses of insecticides

Unwanted effects of use of chemical products are the residues of their active ingredients (a.i.), often very toxic both for humans and other organisms. In order to ensure safe use of these products the law regulates the use of it, introducing protection periods for bees and humans, and the waiting times (tolerances, preharvest intervals, PHI) and the Maximum Residue Limits (MRLs).

MRLs are established on the basis of field researches done strictly to the rules of good agriculture practice (GAP) and toxicological examinations, aiming at determining the allowed levels of intake of given substance. As a result of such examinations the limits of legally allowed residues in fruit and vegetables are determined. Therefore, each case of finding the substance's residues not recommended for the protection of given plant or exceeding the allowed MRL is the proof of not meeting the standards of good agricultural practice.

The average residue level of any pesticide in fruit and vegetables depends primarily on the application rate of its active ingredient. Despite of an obvious association between these two factors in the available literature, no papers with attempts at its quantitative determination have been found except by Frank et al. [12]. No wonder, therefore, that no consistent system of pesticide residue evaluation has been created up to now. The initial content of some substances can only be determined on the basis of their degradation studies in a given crop [12-18]. The relation between the doses of active ingredients of plant protection products and their residue levels immediately after treatment was determined for greenhouse tomatoes. It is described by the following formula:

$$R = 0.24 \times D \text{ (mg kg}^{-1}),$$

where D means authorized dose of an active ingredient of plant protection product, necessary for the effective protection from diseases and herbivorous insects and, 0.24 is the coefficient of proportionality describing the residue expected after its application at the dose of 1 kg per ha [19]. This formula may be helpful in establishing consistent MRL system and allows for resignation from time consuming and costly procedures of their determining for each new substance destined to the protection of greenhouse tomato.

Insecticides used for the protection of apple orchards from herbivorous insects contain active ingredients in the amounts from 25 g in one liter and up to 500 g in 1000 g of plant protection product (except for: Owadox 1000 EC and Sumithion

Super 1000 EC, containing 100% of fenitrothion). These products are applied with different amounts of water (in apple orchards: 500-700 l ha⁻¹ and in greenhouses: 1500-2000 l ha⁻¹) but at the same concentration, giving similar coverage of tomato plants and apple trees. It means that for the effective protection of apple orchards we need almost three times (precisely 2.86 times) smaller amount of active substance per hectare. Given the significant similarity of the shape and size of apple and tomato fruits we can derive the relation between the dose and the level of residues for the apples. It is described by the following formula:

$$R = 2.86 \times 0.24 \times D = 0.69 \times D \text{ (mg kg}^{-1}\text{)}.$$

According to the above formula there were estimated the levels of residues, R, which may be found in apples immediately after the application of the recommended insecticides (Table 1), and then the quality indices for these residues expressed by the ratios R/MRL. The residues should not exceed the allowed MRLs, thus these indices should not exceed 1. The quality indices for many substances now recommended for pest control in apple orchards significantly differ from 1 and are:

- 0.5-1.5: diazinon, chlorpyrifos, thiodicarb, pirymicarb, spirodiclofen, fenazaquin, spinosad and cyhexatin,
- 0.1-0.3: 16 other insecticides,
- below 0.1: 4 substances, among which cypermethrin,
- 31-77: fenitrothion, dimethoate and dichlorvos.

The above proves that MRLs are significantly inconsistent. Only for some insecticides, for which R/MRL is in the range of 0.5-1.5, their values remain within the limits of expected levels. For majority of active substances, for which quality indices are below 0.3, MRLs were established on too high level, e.g. for cypermethrin (MRL = 1 mg kg⁻¹). It may be assumed on the basis of the dose of this synthetic pyrethroid, its residue even after the significant overdose, or several usages, will not reach 1 mg kg⁻¹. The above has been proven by the real residue levels found in apples in 2007 and their indices of quality for cypermethrin (see Table 2).

Finally, for three insecticides the quality indices are between 31-77, which means that for these substances current MRLs were lowered to 0.01-0.02 mg kg⁻¹, but they were not withdrawn from the market and from plant protection programs. To conclude, we should say that the system of Maximum Residue Limits in current regulations in Poland is, to large extend, inconsistent. Exceeding the standards of MRLs in the sample of apples in cases of majority of insecticides is practically impossible but it does not mean the observance by the producer guidelines of Good Agriculture Practice.

Table 1. Insecticides currently used in apple orchards, their application rates (D), expected residues (R), MRLs [20], ADI [21, 22] and, risk indices (R/ADI)

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Active substance	Chemical group	D	R	MRL	ADI	R/ADI
diazinon	Organothiophosphate	0.56	0.38	0.30	0.002	190.0
chlorpyrifos	Organothiophosphate	0.75	0.51	0.50	0.003	170.0
dichlorvos	Organophosphate	0.83	0.57	0.01	0.004	142.5
dimethoate	Organothiophosphate	0.90	0.62	0.02	0.01	62.0
fenitrothion	Organothiophosphate	1.13	0.77	0.01	0.005	154.0
thiodicarb	oxime carbamate	0.38	0.26	0.20	0.01	26.0
pirimicarb	Dimethylcarbamate	0.38	0.26	0.50	0.002	130.0
lambda-cyhalothrin	Pyrethroid 0.01 0.01 0.10				0.02	0.5
deltamethrin	Pyrethroid	0.02 0.01 0.20		0.01	1.0	
beta-cyfluthrin	Pyrethroid	0.02	0.01	0.01 0.20		0.5
esfenvalerate	Pyrethroid	0.02	0.01	0.05	0.02	0.5
alpha-cypermethrin	Pyrethroid	0.04	0.03	1.0	0.05	0.6
cypermethrin	Pyrethroid	0.05	0.03	1.0	0.05	0.6
tau-fluvalinate	Pyrethroid	0.05	0.03	0.2	0.08	0.4
bifenthrin	Pyrethroid	0.06	0.04	0.3	0.01	4.0
novaluron	phenylurea insecticide	0.08	0.05	no data	0.01	5.0
teflubenzuron	phenylurea insecticide	0.11	0.08	0.50	0.01	8.0
diflubenzuron	phenylurea insecticide	0.30	0.21	1.00	0.02	10.5
acetamiprid	Nicotinoid	0.04	0.03	0.10	0.07	0.4
thiamethoxam	Nicotinoid	0.05	0.03	0.10	0.01	3.0
thiacloprid	Nicotinoid	0.10	0.07	0.30	0.01	7.0
pyrethrins	Pyrethrins	0.04	0.03	no data	0.04	0.8
hexythiazox	Thiazolidine	0.05	0.03	0.50	0.01	3.0
indoxacarb	Oxadiazine	0.06	0.04	0.30	0.01	4.0
fenpyroximate	Pyrazole	0.08	0.05	0.50	0.01	5.0
pyriproxyfen	pyridine derivative	0.08	0.05	0.20	0.1	0.5
spirodiclofen	tetronic acid	0.10	0.07	0.10	0.015	4.7
methoxyfenozide	Hydrazide	0.10	0.07	0.30	0.1	0.7
fenazaquin	Quinazoline	0.14	0.10	0.10	0.005	20.0
pyridaben	Pyridazinone	0.15	0.10	0.50	0.03	3.3
clofentezine	Tetrazine	0.18	0.12	0.50	0.03	4.0
spinosad	Lactone	0.20	0.14	0.20	0.02	7.0
cyhexatin	Organotin	0.36	0.25	0.20	0.008	31.3
propargite	sulfite ester	1.14	0.78	3.00	0.01	78.0
paraffin oil	Hydrocarbons	2.25	1.54	no data	no data	_
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Name of the substance	n	R (mg kg ⁻¹)	MRL	R/MRL		
Diazinon	7	0.01-0.06	0.30	0.03-0.20		
Chlorpyrifos	7	0.01-0.24	0.50	0.02-0.48		
Cypermethrin	4	0.02-0.04	1.0	0.02-0.04		
Phosalone	3	0.03-1.03	2.0	0.02-0.52		
Fenitrothion	2	0.01-0.05	0.01	1.00-5.00		
Dimethoate	1	0.17	0.02	8.50		

Table 2. Occurrence of the insecticide residues in apples in 2007 and their indices of quality, N=125

N, n – number of samples examined and containing the residues of given substance

Assortment of insecticides and ecology

Despite already mentioned review of the active substances the producer still can choose from wide range of insecticides belonging to different chemical groups. Majority of substances belong to a group of phosphoric(V) acid esters, nerve agents acting on the enzyme acetylcholinesterase. However, their importance in the protection of apple orchards becomes lower and lower, soon the following substances will also disappear from the market: fenitrothion, diazinon and dichlorvos. The first substance was specially popular in Poland for its wide range of use. These substances, similar to *N*-methylcarbamates, are used at the highest doses and belong to the most toxic to other organisms.

Other neurotoxins, synthetic pyrethroids, belonging to the insecticides of total activity, almost all can be found in the programs of orchards protection. For their extremely low doses, their residues, even immediately after the treatment on the fruits already mature, should not exceed 0.05 mg kg⁻¹, and are practically not detected by the currently used methods in some laboratories. Single cases of the appearance of their residues on higher level may indicate violation by the producer the rules of good agricultural practice concerning the dosage or/and frequency of treatment. Therefore negative evaluation of the synthetic pyrethroids is being compensated by the lack of threat to the health of the consumer.

There is also a group of inhibitors of the chitin synthesis showing selective activity, recently present on the market, and in programs of plant protection appeared the products containing active substances belonging to neonicotinoids acting on the central nervous system effective at doses many times lower from the doses of organophosphorus compounds. The possibility of occurrence of their significant residues is scarce. There is also quite interesting wide range of products containing synthetic active substances belonging to different chemical groups, natural pyrethrins or macrocyclic laktones. The assortment of insecticides

is completed by paraffin oil. Persistent organochlorine pesticides have already disappeared from the programs of plant protection.

Interesting and proecological product seems to be Appeal 04 PA (a.i.: 4% of cyfluthrin – substance from the group of synthetic pyrethroids, and 0.1% of codlemone, the codling moth female sex pheromone blend). The recommended dose of the product used against codling moth (*Cydia pomonella*) is 2-3 drops per tree, but not less than 4000 drops per ha. The product is used when regular flights of *C. pomonella* butterflies start. In order to protect the crop from the damages throughout the whole period of flight of first and second generation of the pest the treatment has to be repeated after 6 weeks. It shows the features of perfect proecological product and does not leave the residues.

THREATS TO THE CONSUMER'S HEALTH

The health hazard resulting from the occurrence of residues in fruit and vegetables are precisely defined and the risk to the consumer's health remains closely related to the level of residues of given substance and its toxicity. At the moment there are routine tests performed to assess the risk to consumer's health resulting from short term or regular intake of such pollutions by toddlers and adults [23].

The long-term threat (chronic exposure) may be assessed through comparison of intake of pesticide residue with Acceptable Daily Intake (ADI; mg kg⁻¹ b.w. day⁻¹). Assuming after the EU that the body weight (b.w.) of adult consumer is 60 kg, the average consumption of given fruit or vegetables (C; in kg) and 90 percentile of residues (R; in mg kg⁻¹), intake of the substance in comparison to ADI may be described with the following formula:

Intake =
$$\frac{R}{ADI} \times \frac{C}{b.w.} \times 100\%$$
.

Short-term (within one meal) intake of a given substance (acute exposure) in EU is determined for assumed body weight (b.w.) of adult consumer 70.1 kg, 97.5 percentile of consumption of fruit or vegetables (C), the highest found residues (R_{max}), variability coefficient (v = 2-10) and is compared to the acute reference dose (ARfD; it is determined for only few substances and is on average on the level of 5 times higher then ADI) according to the following formula:

Intake =
$$\frac{R_{\text{max}}}{ARfD} \times \frac{C}{b.w.} \times v \times 100\%$$
.

The exposure of consumer did not exceed the acceptable daily intakes (ADI and ARfD).

In both cases the assessment of health hazard is done on the basis of variable values R/ADI and $R_{max}/ARfD$, which can be named as index of the risk. The highest risk index, resulting from the relatively high dose and significant toxicity expressed by high ADI level, is found to be for diazinon (Table 1). Intake, calculated for the consumer of 60 kg weight with daily consumption (0.3 kg) of apples containing the highest expected residues (Table 1), is:

Intake =
$$0.38 / 0.002 \times 0.3 / 60 \times 100\% = 95\%$$
 ADI.

This assessment does not show the possibility of occurrence of disallowed intake. The risk indices for other organophosphorous insecticides and methylcarbamates inhibitors of acetylcholinesterase are on slightly lower level.

Synthetic pyrethroids, mostly due to their low doses, bring for the consumer the risk about two orders of magnitude lower that the organophosphorous insecticides do. Among the large group of other insecticides currently used in programs of the protection of orchards, the highest risk can be expected after application of acaricides fenazaquin and propargit. Generally, insecticides, if applied in apple orchards in accordance with rules of Good Agriculture Practice, seem to be quite safe for humans.

THREATS TO BENEFICIAL ORGANISMS

In orchards there are plenty of predatory and parasitic organisms that may reduce the population of herbivorous insects. As stated in the Program of Protection of Orchard Plants for 2008 [21] we have the complete knowledge only of *Typhlodromus pyri* (*Phytoseiidae*), a key factor in the biological control of European red mite (*Panonychus ulmi*).

From among 37 insecticides and acaricides currently used in apple orchards 16 were qualified as non-selective compounds. In the group of non-selective substances there are all recommended organophosphorous insecticides and synthetic pyrethroids. Already mentioned fenitrothion (Owadofos 540 EC) has shown toxic action on predatory *Hemiptera*, *Coccinellidae*, *Syrphidae Neuroptera* and parasitic *Hymenoptera*. Knowledge on the action of other insecticides on beneficial animals is however fragmentary and uncertain [20].

Pirimicarb (Pirimor 500 WG) is a carbamate compound used to control

aphids on vegetable, cereal and orchard crops by inhibiting acetylcholinesterase activity. It acts by contact, vapor, and systemic action, and is useful against organophosphorous-resistant strains. Pirimicarb is relatively nontoxic to beneficial predators, parasites, and bees. Due to its selective action, this substance is useful in integrated programs of plant protection.

Selective action is also shown by plant protection product, trade mark Appeal 04 PA, containing cyfluthrin, insecticide from the group of synthetic pyrethroids. But the selective action of this chemical is not the result of the features of its active substances but the methods of its application. It is worth noticing also, that almost all fungicides show selective action.

CONCLUSION

The analysis of some elements of modern protection of apple orchards prove that in the last years there has been significant qualitative changes in this matter. As a result of the review of the active substances of plant protection products significant reduction of assortment of active substances of such agrochemicals available on the market will take place and it will affect mostly protection of minor crops. It should be emphasized, however, that these changes go in the right direction since they gradually lead to the elimination of the most toxic substances, replacing them with substances far less toxic.

Another factor worth appreciating is the increasing awareness of orchard owners of the practical knowledge of biology of herbivorous insects, including the thresholds of their harmfulness. The system of state control of pesticide residues in food functions better and better. Rare cases of exceeding the allowed limit of residues mostly result from not-coordinated changes of Maximum Residue Levels and the assortment of substances available on the market. But many of the currently in force MRLs need to be revised. Finally, the knowledge of the beneficial organisms and the features of insecticides is still insufficient.

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