An investigation upon toxicological reasons of pest control system choice in apple orchards

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ABSTRACT

The present study simulates degradation of pesticides in the soil of the apple orchard based on a half-life of active ingredients. Throughout the paper, pesticide degradation is described by exponential regression equations. The calculation of the content of active substances has been carried out in dynamics during one year for two pest control system models, which involve 11 active ingredients – insecticides and fungicides. Model № 1 differs in one insecticide, flubendiamide, which is replaced by dimethoate in Model №

2. Furthermore, the toxic hazard assessment of those two models is carried out according to non-parametric Argo-Eco-Toxicological Index (AETI). If AETI>0.5 then toxication is estimated to be dangerous for the environment. In designed models duration of dangerous soil intoxication level decreases by 3.2 times due to replacement of flubendiamide by dimethoate. In this respect, the proposed prognostic mathematical method in the present study can be successfully used while choosing the safest pest control system.

Key Words: Pest management in orchards; Toxic hazard; Pesticide degradation in the soil; Active ingredients; Mathematical models

INTRODUCTION

Modern investigations undertaken in various countries of the world present different approaches to estimation of toxic hazards for humans and the environment, caused by pesticides during pest control in orchards. Thus, in South Tyrol (Northern Italy), it was found that pesticide concentrations in human habitats (including playgrounds) were associated with areal proportion of apple orchards in the surroundings. Pesticides are blown out by the wind during soil erosion in orchards. That is why, on wild herbs of playgrounds were found pesticides such as phosmet, imidacloprid, chlorpyrifos-methyl, methoxyfenozide, cypermethrin, fluazinam, penthiopyrad, difenoconazole, dodine, penconazole, tetraconazole and etc. The present study demonstrates that topographical and meteorological conditions such as use of land, rainfall, wind speed, and direction have an impact on pesticide drift Linhart et al. [1].

Experts detected through analytical methods that there were 10 highly frequently used chemicals in the soil of Chinese apple orchards including carbendazim, imidacloprid, acetamiprid, triadimenol, triadimefon, tebuconazole, chlorbenzuron, difenoconazole, chlorpyrifos, buprofezin Rongguang et al. [2]. Meanwhile, the soil pesticide contents were all below MRLs (Maximum Residue Limits) of China (0.5-5.0 mg/kg) and the European Union (0.01-3.00 mg/kg), indicating their low acute toxic risks. From our point of view, such a conclusion looks too optimistic when other studies are taken into account.

The duration of pesticide use in one place is of great significance. This is especially true for gardens where no crop change exists in the process of crop rotation. In particular, the fungicide penconazole (Topaz) in Krasnodar region of South Russia during first use had a very short half-life (i.e. – $T_{05}=7$ days). However, following the use of Topaz for three years, the half-life of penconazole in the soil increased to $T_{05}=14$ days; and residual traces of xenobiotic were present in the surface layer of the soil even during the harvest period six years later Podgornaya et al. [3]

The average use per hectare of the active ingredient of insecticides, fungicides, and acaricides in Turkish orchards were determined to be 13.7 kg, 11.4 kg and 2.2 kg, respectively. It was calculated that economic loss of pesticides was € 549.71 per hectare resulting from overdose use of agricultural chemicals. The percentages of this loss for insecticides, fungicides and acaricides were 86.00, 0.52 and 13.47%, respectively. There are altogether 42 active ingredients, including extremely hazardous parathion-methyl, highly hazardous azinphosmethyl, methidathion, omethoate and moderately hazardous cyhexatin, cypermethrin, deltamethrin, dicofol, difenoconazole, fenpyroximate,

fenthion, fenvalerate, imidacloprid, indoxacarb, phosalone, tebufenpyrad, thiacloprid, triadimenol, and trifloxystrobin. In Turkey, consumers have been experiencing increasing concern about the use of pesticides in food production. Turkey is one of the most important countries in the world when apple production is considered. In this respect, increasing the use of pesticides in apple production has been accompanied by concern over health effects associated with pesticide use and abuse. Nevertheless, the majority of the farmers are suggested to be unaware of the recommended dose, time, and application method of the pesticides Yilmaz et al. [4].

On the other hand, reducing the use of pesticide is challenging in orchards where pesticides are recurrently applied to control numerous pests and diseases, and thus crucial to improve fruit production sustainability Simon et al. [5]. Authors report the level of pesticide use and agri-environmental performances of three protection systems in apple orchards surveyed in France from 2005 to 2008 which involve conventional, low-input, and organic. Assessment of pesticide use is esteemed through treatment frequency index (TFI). It is classified as a simple indicator based on grower's practices and is used at different scales to assess the intensity of pesticide use. In an orchard where n - compounds are applied across the season, TFI is defined as follows;

$\sum_{i=1}^{n} \left[\left(ADi / RDi \right) \times SAi \right]$

with ADi – presenting the applied dose per hectare, RDi – indicating the lowest registered dose for the crop and target pest, disease or weed, as suggested in official databases and SAi – displaying the treated surface area proportion ($0 \le SAi \le 1$). TFI has an additive construction, which suggests that TFI increases with pesticide applications, but does not consider compound toxicity Simon et al. [5]. This approach towards the problem, from our point of view, is too crude as an environmental assessment of chemical risks, while protecting gardens from pests and diseases.

Although pesticides are developed to function with reasonable certainty and minimal risk for human health and the environment, many studies have raised concerns about health risks. Several indicators have been used to assess the potential risk of pesticides for human health and the environment. However, their use indicates reduced certainty, suggesting a need for development of alternative indicators that could increase the accuracy and reliability of pesticide risk assessment and thus contribute to reduction of possible adverse effects of pesticides on human health and the environment Damalas et al. [6].

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Poltavsky AN, et al.

In this respect, an alternative indicator was developed by Russian scientist; however, it is not widely known in other countries. This indicator is presented in the following section.

MATERIALS AND METHODS

The present study aims to esteem the potential hazard of pest control systems for apple orchard. Wide nomenclature of pesticides to solve this problem includes many active ingredients with different toxic properties. We have modeled the dynamics of pesticide degradation in the soil, based on the halflife of active ingredients (Table 1). This integrated indicator involves all forms of biotic and abiotic transformations of pesticides (i.e. photolysis, hydrolysis and biological degradation). The Agro-Eco-Toxicological Index (AETI) is a nonparametric ecological indicator for assessment of ecological danger of total pesticide amount, which is applied for pest control Zinchenko et al. [7].

In the present study, the AETI has been modified for assessment of the pollution dynamics in the soil with pesticides applied in apple orchards in Krasnodar region of South Russia, as indicated below;

 $AETI=(10 \times V \times (1 + V) 3) / (1 + V) \times 4 + 5000)$

Where «V» - refers to the level of pesticide pressure;

V=D/(Q × I); D=M/S

Where «D» – offers ecotoxicological dose, «M» – the mass of pesticide, «S» – area of application (in our calculations S=one hectare), and «I» – self-cleaning index of the soil. In all our calculations, it is found that I=1,0 – for the heavy black soils, which are characteristics of the south of European Russia.

$$Q = (1/M) \times \sum_{i=1}^{n} COi \times m_i$$

where mi – presents the amount of i-pesticide and COi – shows average degree danger of applied range of pesticides; $CO=(\kappa_a + \kappa_b) - 1$.

Coefficient K_a – depends on toxicity of active ingredient for animals, estimated as DL_{50} for rats. If DL_{50}
+15 mg/kg is, then K_a =1; if DL_{50} =16-150 mg/kg; K_a =2; if DL_{50} =151-5000 mg/kg; K_a =3; if DL_{50} >5000, and K_a =4.

Coefficient K_b – depends on persistence of pesticide in the soil, estimated as T₅₀ – half-decay period in the soil. If T₅₀>20 days, then K_b=1; if T₅₀=20-5 days; K_b=2; if T₅₀=5-3 days; K_b=3; if T₅₀< 3, and K_b=4.

Each active ingredient's level for persistence and toxicity required for calculations is available in reference books and websites (i.e. hygienic standards of pesticides content in objects of environment, 2013; the list of pesticides and agrochemicals resolved in the territory of Russian Federation, 2016; Pesticides, 2018) [8-10].

Assessment of AETI levels in the soil is suggested to be as 0-1.0 – harmless, 1.1-5.0 – low danger, 5.1-8.0 – medium danger, 8.0 – high danger.

Calculating active ingredients degradation in the soil with an interval of 10 days, we have got the dynamics of toxic pressure on ecosystem of apple orchard. Mathematical calculations were carried out via Excel processor. The reference sources often report about various T_{05} ranges, which depend on soil type, temperature, and humidity. In such cases, we accept two T_{05} ranges for each active ingredient, that is, T_{05} minimum and T_{05} maximum (Table 1). That is why; some active ingredients have two degradation formulas.

Degradation was calculated separately for cold and warm seasons between transition periods. Such control periods are special for the Krasnodar region's climate (i.e. date and month) as clarified below;

a) T_{05} (max) is used during 21 II – 10 IV and 11 X – 10 XII;

b) T_{05} (min) is used during 11 IV – 10 X;

c) Degradation is not calculated during transition period: 11 XII - 20 II;

d) Calculations are stopped after decreasing active ingredient amount – 1, 0 gr per hectare.

The proportion of pesticides reaching at the soil of the apple orchard depends on spraying equipment, age of trees, and size of apple tree (i.e. dwarf, semi-dwarf, standard). Some experiments report about wide diversity of soil deposit percentages which is 26-92% Allagui et al. [11]. In our models, it was assumed that 50% came to the soil.

RESULTS AND DISCUSSION

The conditions for accumulation of pesticides in soil under apple orchards has specific characteristic, as chemical pressure performs in one place for

TABLE 1

Half-life (T ₀₅ =days)	of active ingredients	in the soil and	I their toxicity for
rats (DL ₅₀ =mg/kg)			

NՉ	Active ingredients	T _{os} min	T _{os} max	DL ₅₀ for rats
1	Abamectin	20	47	14
2	Deltamethrin	12	50	128
3	Dimethoate	2	5	230
4	Dithianon	18	18	600
5	Flubendiamide	210	770	400
6	Fluopyram	6	7	2000
7	Imidacloprid	20	20	450
8	Pyrimethanil	7	54	188
9	Spiromesifen	13	22	229
10	Thiacloprid	6	10	440
11	Trifloxystrobin	3	3	500

many years and the number of annual pesticide treatments is usually quite numerous (i.e. at least 10). Therefore, there is a great risk of undesirable xenobiotic accumulation in the soil, which can worsen the ecological condition of landscape. Our mathematical model represents a pest control system based mainly upon pesticides of «Bayer Crop Science AG» Inc. (Germany).

Apple orchard pest control technology includes the following pesticide applications:

- Green cone spraying on 1.IV against Anthonomus pomorum Linnaeus, 1758 (Curculionidae) with CALYPSO insecticide.
- Spraying when the buds are extended on 15.IV against mildew fungal disease with ZATO fungicide and against Rhynchitinae species with MOVETON insecticide.
- Spraying before blossoming on 1.V against fruit mites with OBERON acaricide.
- Spraying during flowering on 7.V against mildew fungal disease with LUNA TRANQUILITY fungicide.
- Spraying after flowering (i.e. during the fall of 75% petals) on 15.V against mildew and apples scab fungal diseases with LUNA TRANQUILITY fungicide.
- Spraying after flowering on 30.V against a complex of pests with BELT insecticide.
- Spraying during growth of fruits on 15.VI against caterpillars of the 1st generation of *Cydia pomonella* (Linnaeus, 1758) (Tortricidae) with DECIS EXPERT insecticide.
- Spraying during growth of fruits on 30.VI against *Quadraspidiotus* perniciosus Comstock, 1881 (Diaspididae) with BI-58 TOP insecticide.
- Spraying during growth of fruits on 15.VII against caterpillars of the 2nd generation of *Cydia pomonella* with BELT insecticide and mildew fungal disease with DELAN fungicide.
- Spraying during growth of fruits on 30.VII against *Quadraspidiotus* perniciosus with BL58 TOP insecticide and against mildew fungal disease with LUNA TRANQUILITY fungicide.
- Spraying during growth of fruits on 15.VIII against Quadraspidiotus pemiciosus, fruit mites and Cydia pomonella caterpillars with BI-58 TOP insecticide.
- Spraying during the growth of fruits on 30.VIII against the 3rd generation of Cydia pomonella caterpillars with BELT insecticide.
- Spraying during the growth of fruits on 15.IX against caterpillars of the *Cydia pomonella* caterpillars with DECIS EXPERT insecticide.

The Model \mathbb{N} 1 includes 11 active ingredients into 7 pesticides from "Bayer" one from "Keminova" and one from "BASF". For each application of pesticides, the amounts of active ingredients reaching at the soil are calculated (Table 2). Pesticide degradation is described through exponential regression equations (Table 3).

On the other hand, degradation dynamics is presented more clearly in the

TABLE 2

Calculations of the amount of active ingredients reaching at the soil of the apple orchard for Model № 1.

Pesticides, active ingredients and dates of application	gm/litre	gr per hectare	Loss share to soil	Producer
CALYPSO, 1 IV		200		Bayer
Thiacloprid	480	96	0,5	Bayer
ZATO, 15 IV		140		Bayer
Trifloxystrobin	500	35	0,5	Bayer
MOVETON, 15 IV		120		Bayer
Imidacloprid	500	30	0,5	Bayer
OBERON, 1 V		700		Bayer
Abamectin	11,4	4,0	0,5	Bayer
Spiromesifen	228,6	80	0,5	Bayer
LUNA TRANQUILITY, 7 V		1000		Bayer
Fluopyram	125	62,5	0,5	Bayer
Pyrimethanil	375	187,5	0,5	Bayer
LUNA TRANQUILITY, 15 V		1000		Bayer
Fluopyram	125	62,5	0,5	Bayer
Pyrimethanil	375	187,5	0,5	Bayer
BELT, 30 V		400		Bayer
Flubendiamide	480	96	0,5	Bayer
DECIS EXPERT, 15 VI		100		Bayer
Deltamethrin	100	5,0	0,5	Bayer
BI-58 TOP, 30 VI		1500		Keminova
Dimethoate	400	300	0,5	Keminova
BELT, 15 VII		400		Bayer
Flubendiamide	480	96	0,5	Bayer
DELAN, 15 VII		600		BASF
Dithianon	700	210	0,5	BASF
BI-58 TOP, 30 VII		1500		Keminova
Dimethoate	400	300	0,5	Keminova
LUNA TRANQUILITY, 30 VII		1000		Bayer
Fluopyram	125	62,5	0,5	Bayer
Pyrimethanil	375	187,5	0,5	Bayer
BI-58 TOP, 15 VIII		1500		Keminova
Dimethoate	400	300	0,5	Keminova
BELT, 30VIII		400		Bayer
Flubendiamide	480	96	0,5	Bayer
DECIS EXPERT, 15 IX		100		Bayer
Deltamethrin	100	5,0	0,5	Bayer

TABLE 3

Active ingredients degradation equations in the soil of the apple orchard for Model $\ensuremath{\mathbb{N}}\xspace$ 1.

Active ingredients degradation equations
Thiacloprid: Y=96e ^{-0,116x}
Trifloxystrobin: Y=35e ^{-0,231x}
Imidacloprid: Y=30e ^{-0,0347x}
Abamectin: Y=4e ^{-0,0385x}
Spiromesifen: Y=80e ^{-0,053x}
Fluopyram: Y=62,5e ^{-0,116x}
Pyrimethanil: Y=187,5e ^{-0,099x}
Fluopyram: Y=62,5e ^{-0,116x}
Pyrimethanil: Y=187,5e ^{-0,099x}
Flubendiamide: Y=96e ^{-0,0033x} , Y=62,511e ^{-0,0009x}
Deltamethrin: Y=5e ^{-0,0578x}
Dimethoate: Y=300e ^{-0,347x}
Flubendiamide: Y=96e ^{-0,0033x} Y=71,332e ^{-0,0009x}
Dithianon: Y=210e ^{-0,039x}
Dimethoate: Y=300e ^{-0,347x}

Pyrimethanil: Y=187,5e^{-0,099x} Fluopyram: Y=62,5e^{-0,116x} Dimethoate: Y=300e^{-0,347x} Flubendiamide: Y=96e^{-0,0033x}, Y=81,3978e^{-0,0009x} Deltamethrin:Y=5e^{-0,0578x}

format of changes in toxic load in soil from each active ingredient (V%). The graphs of V% and AETI are displayed on the same scale "Y" with maximum rate of 100%. The non-parametric AETI index is increased tenfold. The graphs display how the share of each active ingredient in formation of high or low level of AETI indicator changes (Figure 1).

In Model \mathbb{N}_{2} 1, AETI indicator reaches maximum level in mid-May and remains until the end of year (i.e. 85% of the time). Several active ingredients take part in the formation of a dangerous level of toxic load, but the main role is played by the flubendiamide insecticide (BELT). Due to its long half-life in the soil (i.e. T_{05} =210-700 days), flubendiamide tends to accumulate if it is used in pest control in following years. Other active ingredients are degraded in soil during the current season (Figure 1).

The flubendiamide insecticide has negative effects upon the environment. For instance, it produces some toxic metabolites in the soil, and also leads to



Figure 1) The AETI dynamics and levels of toxic load from pesticides (%V) to soil in Model № 1 during the first year of applications.



Figure 2) The AETI dynamics and levels of toxic load from pesticides (%V) to soil in the Model № 2 during the first year of applications.

groundwater pollution if the soil is porous and sandy Shaon et al. [12]. The negative impacts of flubendiamide on many non-target objects (i.e. insects, fishes, and amphibians) have been found out, which therefore makes flubendiamide a serious potential environmental toxicant Shrinivas et al. [13].

In this respect, for environmental reasons, the BELT insecticide containing flubendiamide should not be used in the apple orchard during another two years following the first use. It is better to replace it with more traditional organophosphate insecticide. In our model, calculation was made for BI-58 TOP (dimethoate) by replacing the BELT. In this way, we formed Model \mathbb{N}_2 of the pest control in the apple orchard.

Following that, AETI dynamics chart changed completely. Fungicide pyrimethanyl, as well as insecticides imidacloprid and dimethoate, took the first place in formation of the current toxic load to the soil. Periods with hazardous AETI levels (5>) were short: half a month in April, about a month in May-June and one and a half month in July-August – 26% of the time during the year altogether (Figure 2).

CONCLUSION

Our mathematical models show that the assessment of potential toxic hazards from chemical plant control system using non-parametric AETI

index presents practical consequences. The real process of pesticides accumulation in the soil of apple orchards will depend on many factors such as type of the soil, actual dynamics of temperature and humidity, and activity of microbiota. Nonetheless, theoretical calculation of the toxic hazard of various pesticide complexes applied is carried out for the same degradation conditions. Therefore, Models \mathbb{N}_2 1 and \mathbb{N}_2 2 can be objectively compared. It can be suggested that replacement of only one of the most dangerous toxicant flubendiamide in Model \mathbb{N}_2 1 significantly reduces toxic hazard of Model \mathbb{N}_2 2. Time period with hazardous AETI level in Model \mathbb{N}_2 2 is calculated to be shorter (i.e. 3.2 times) than in Model \mathbb{N}_2 1.

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