

Original Article

The effect of difenoconazole-based fungicides on the destruction of insecticides from various chemical classes in apple fruits and leaves

Efeito de fungicidas à base de difenoconazol na degradação de inseticidas de diferentes classes químicas em frutos e folhas de maçã

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Abstract

The work studied the ability of fungicides with the active substance difenoconazole from different manufacturers to change the rate of destruction of such active insecticide substances as dimethoate, imidacloprid and lambda-cyhalothrin. During the summer growing season, apple tree plants were treated with pesticides Score, CE (250 g/l difenoconazole) and Raek, CE (250 g/l difenoconazole), and the single-component insecticide Sirocco, CE (400 g/l dimethoate) and the two-component insecticide Borey, SC (150 g/l imidacloprid+50 g/l of lambda cyhalothrine). The treatment of plants with preparations and the subsequent collection of plant samples were carried out on the territory of the Moscow Timiryazev Agricultural Academy Fruit Station in the city of Moscow during 2023-2024. The experiment consisted of variants using tank mixtures of the preparations in question and the separate use of insecticides, control variants on all apple varieties were treated with water and were not treated with pesticides. At regular intervals, we selected the leaves and fruits of the apple tree from each variant, this happened within 50 days after spraying. The level of pesticide residues was determined in the laboratory "Agroecology of Pesticides and Agrochemicals", Moscow Timiryazev Agricultural Academy, which is GLP accredited. The levels of insecticides and fungicides in the selected plant parts were determined using approved, standard chromatography methods. In the course of experimental studies, it was revealed that a combination of difenoconazole-based fungicides with insecticides of three different groups can affect the rate of decomposition of the active substances of insecticides. The data obtained during the experiments confirmed that the presence of difenoconazole in the tank mixture leads to a change in the rate of decomposition of the active substances in the leaves and fruits of the apple tree. When using a tank mixture consisting of the insecticide Borey, SC and the fungicide Score, SC, there was a slight slowdown in the process of destruction of imidacloprid an increase in the period of complete decay -DT95 by 51.4% in leaves and 38.4% in fruits) and lambda-cyhalothrin (an increase in the period of complete decay -DT95 by 39.4% in leaves and 16.5% in fruits). At the same time, the combination of the insecticide Sirocco, CE with the fungicide Raek, CE contributed to the acceleration of the breakdown of the active substance dimethoate in all the studied apple tree tissues with a reduction in the period of complete insecticide degradation of 26.9% in leaves and 11.6% in fruits.

Keywords: pesticides, apple tree, residual amounts, fungicides, insecticides.

Resumo

O presente trabalho investigou a capacidade de fungicidas contendo difenoconazol como substância ativa, provenientes de diferentes fabricantes, de alterar a taxa de degradação das seguintes substâncias ativas inseticidas: dimetoato, imidacloprido e lambda-cialotrina. Durante o período de crescimento estival, plantas de macieira foram tratadas com os pesticidas Score, CE (250 g/l de difenoconazol) e Raek, CE (250 g/l de difenoconazol), com o inseticida monocomponente Sirocco, CE (400 g/l de dimetoato) e com o inseticida bicomponente Borey, SC (150 g/l de imidacloprido + 50 g/l de lambda-cialotrina). O tratamento das plantas com os produtos e a subsequente coleta de amostras vegetais foram realizados no território da Estação de Fruticultura da Academia Agrícola Timiryazev de Moscou, na cidade de Moscou, durante os anos de 2023 e 2024. O experimento consistiu em variantes com o uso de misturas dos produtos em tanque e o aplicação isolada de inseticidas. As variantes de controle, em todas as variedades de maçã, foram tratadas apenas com água e não receberam pesticidas. Em intervalos regulares, coletaram-se folhas e frutos de macieiras de cada variante, durante um período de 50 dias após a pulverização. O nível de resíduos de pesticidas foi determinado no laboratório "Agroecologia de Pesticidas e Agroquímicos" da Academia Agrícola Timiryazev de Moscou, que possui acreditação pelas Boas Práticas de Laboratório (GLP). Os níveis de inseticidas e fungicidas nas partes selecionadas das plantas foram determinados utilizando métodos cromatográficos padrão e aprovados. No decorrer de estudos experimentais, constatou-se que a combinação de fungicidas à base de difenoconazol com inseticidas de três grupos diferentes pode afetar a taxa de decomposição dos princípios ativos dos inseticidas. Os dados obtidos nos experimentos confirmaram que a presença de difenoconazol na mistura em tanque leva a uma alteração na taxa de decomposição dos princípios ativos nas folhas e frutos da macieira. Ao utilizar uma mistura em tanque composta pelo inseticida Borey, SC e pelo fungicida Score, SC, observou-se uma ligeira desaceleração no processo de destruição do imidacloprido (aumento do período de decomposição completa - DT95 - em 51,4% nas folhas e 38,4% nos frutos) e da lambda-cialotrina (aumento do período de decomposição completa - DT95 - em 39,4% nas folhas e 16,5% nos frutos). Paralelamente, a combinação do inseticida Sirocco, CE com o fungicida Raek, CE contribuiu para a aceleração da degradação da substância ativa dimetoato em todos os tecidos da macieira estudados, com redução do período de degradação completa do inseticida de 26,9% nas folhas e 11,6% nos frutos.

Palavras-chave: agrotóxicos, macieira, quantidades residuais, fungicidas, inseticidas.

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1. Introduction

To reduce costs in the production of agricultural products, such a technique as the preparation of tank mixtures of pesticides from various chemical classes is very often used (Antonenko et al., 2024; Hernández et al., 2017; Popov et al., 2003; Weisner et al., 2021). This technique makes it possible to more effectively organize the control of pests and plant diseases. The use of tank mixtures makes it possible to reduce the cost of chemical treatment and cover a wider range of harmful objects. As in the cultivation of field crops, mixtures of fungicides and insecticides are often used in orchards (Barrón Cuenca et al., 2022; Hernández et al., 2017; Popov et al., 2003; Schabacker et al., 2020; Serrie et al., 2024; Weisner et al., 2021). Also, preparations containing not one but several active substances are considered the most effective, this applies to both fungicides and insecticides (Man et al., 2023; Popov et al., 2003; Silva Pinto et al., 2020). One of the positive aspects of tank mixtures of preparations in pest and disease control is the "potentiation effect" noted by a number of researchers (Ferguson et al., 2022; Popov et al., 2003; Silva Pinto et al., 2020; Zhao et al., 2020), which consists in enhancing the effect of each component on a harmful object. Nevertheless, the use of tank mixtures of pesticides can also have a negative aspect, which is to increase the harmful effects on the human body and animals. A number of modern researchers speak about the increased negative effects on the animal body with simultaneous exposure to several pesticides (Acosta-Dacal et al., 2025; Antonenko et al., 2024; Cabrera et al., 2024; Barrón Cuenca et al., 2022; Hernández et al., 2017; Popov et al., 2003; Schabacker et al., 2020; Yun et al., 2022; Zhao et al., 2020).

Since the period of control of the most common apple tree diseases coincides with the mass reproduction of pests on this crop, a mixture of fungicides with insecticides from various chemical classes is often used. Due to the similar principle of action on organisms of warm-blooded animals and insects, insecticides are the most dangerous for humans (Popov et al., 2003; Barrón Cuenca et al., 2022; Silva Pinto et al., 2020). The study also examined the effects of the use of preparation mixtures on the rate of destruction of the active ingredient of the fungicide - difenoconazole. The study is of scientific and practical importance, since the active ingredients of insecticides such as dimethoate, imidacloprid and lambda cyhalothrin, as well as the fungicide difenoconazole, are widely used in the Russian Federation and in many other countries (Russia, 2023).

A number of authors have noted the possibility of the effect of fungicides from the triazole class on plant growth and development through physiological changes, that is, their effect as growth regulators (Jakl et al., 2021; Li et al., 2023; Man et al., 2023; Zheng et al., 2023). It is known that the use of any pesticide in Russia is regulated, waiting periods are defined for each crop (Russia, 2023), when agricultural products become safe for the human body after treatment with the preparation. Nevertheless, it should be noted that when developing regulations for the use of pesticides in Russia and other countries, cases where the use of pesticides occurs in a mixture are not

considered. This question is being asked by a number of modern researchers (Antonenko et al., 2024; Serrie et al., 2024; Zhao et al., 2020).

The listed arguments related to this topic indicate to us that the study of the possibility of changing the rate of destruction of insecticides when used in a mixture with difenoconazole-based fungicides is an urgent topic for study.

2. Materials and Methods

The experiment used preparations approved for use in the Russian Federation: fungicides Score, CE (250 g/l difenoconazole) (Syngenta, Russia) and Raek, CE (250 g/l difenoconazole) (Avgust, Russia) were used at the same consumption rate of 0.2 l/ha; insecticide Sirocco, CE (400 dimethoate) (Avgust, Russia) was used at a consumption rate of 1.5 l/ha; Borey insecticide, SK (150 g/l imidacloprid+50 g/l lambda cyhalothrin) (Avgust, Russia) at a rate of 0.3 l/ha. These products and the consumption rates used are approved for use on apple trees in the Russian Federation (Russia, 2023).

The treatment of apple tree plants with preparations followed by sampling of leaves and fruits was carried out in the Fruit Crops department of the ESPC of Horticulture and Vegetable Growing n.a. V.I. Edelstein of the FSBEI HE RSAU-MAA named after K.A. Timiryazev. According to the soil analysis data on the experimental plots, the soil was sod-podzolic with a pH of 6.3 with a humus content of 2.2%. Apple tree plants of the same age and variety were treated with the preparations. In the variants using the preparations Raek, CE and Sirocco, CE, the Melba apple variety was used; in the variant with the preparations Score, CE and Borey, SC (150 g/l imidacloprid +50 g/l lambda-cyhalothrin)– the Verboye variety. Both varieties are included in the State Register of varieties of the Russian Federation. The Melba variety belongs to the summer varieties, and the Verboye variety belongs to the late varieties. The Melba trees were 8 years old at the time of the treatments, in Verboye - 10 years. For each variant of the experiment, 10 trees were used, from which an average sample of fruits and leaves was collected after processing.

Apple tree plants were treated with preparations in the "fruit growth" phase, with a fruit size of 5 cm. The treatment of plants with these preparations was carried out in compliance with all requirements for chemical treatment and registered standards of use (Russia, 2023).

For two months after the day of spraying, samples of apple fruits and leaves were taken separately with an interval of 3 days in the first 2 weeks and then with an interval of 7 days (Dolzhenko, 2009a, b; Dolzhenko and Rakitsky, 2018). The weight of the fruit sample was 2 kg, and the weight of the leaves was at least 0.5 kg (Dolzhenko, 2009a, b; Dolzhenko and Rakitsky, 2018; European Union, 2021). When collecting plant samples from various experimental variants, all measures were taken to prevent contamination, using disposable rubber gloves and plastic bags with individual labeling for each experimental variant and others necessary for these types of research (European Union, 2021).

The laboratory “Agroecology of pesticides and Agrochemicals” of the Moscow Timiryazev Agricultural Academy analyzed selected plant samples to determine the level of residual amounts of pesticides in them. It should be noted that this laboratory is accredited according to the international GLP (Good Laboratory Practice) standard. Certified equipment was used in the laboratory part of the study. Data were analyzed for validity using univariate analysis of variance performed in the Statistica program.

To determine the residual amounts of the insecticide lambda cyhalothrin, the procedure described in MUK 4.1.2380-08 was used. It is based on the use of capillary gas-liquid chromatography with an electron capture detector after extraction of a substance with an organic solvent. The completeness of recovery of this method was 86.9% for leaves and 97.6% for fruits.

To analyze the content of the insecticide imidacloprid, the method from MUK 4.1.1977-05 was used. It is based on high-performance liquid chromatography using an ultraviolet diode-matrix detector. The completeness of recovery of this method was 84.6% for leaves and 93.9% for fruits.

The content of residual amounts of the insecticide dimethoate was carried out by gas chromatography with a nitrogen-phosphorus detector MU No. 3222-85. To determine the main metabolite of dimethoate (o-methoate), gas chromatography-mass-spectrometry was used using a tandem three-quadrupole detector.

The difenoconazole content was produced using the standard guidelines of MUK 4.1.1961-05 – by high-performance liquid chromatography. The recovery completeness of this method was 90.6% for leaves and 89.4% for fruits.

Based on the obtained data on the content of pesticide residues, the decomposition rate constant was calculated for each experimental variant using the following formula: $K = \ln C_1 / C_2 / t$. Where C_1 is the concentration of the pesticide on the first day of sampling, C_2 is the concentration of the pesticide at the time, and t is the time (days). The value of the half-life (DT50) of the pesticide was determined according to the formula: $DT50 = 0.693 / K$, where K is the rate constants of the pesticide decomposition. The value of the decay period of 95% of the substance from its initial level was calculated using the formula: $DT95 = 4.3 \cdot DT50$ (Thomas, 1987).

3. Results

After analyzing plant samples from Sirocco, CE treated plants, it was found that the amount of the active ingredient insecticide dimethoate in the leaves and fruits of the apple tree was almost the same in different experimental variants. For the first day, where the insecticide was applied separately, the dimethoate content in the leaves was 14.98 mg/kg, and in the fruits – 1.49 mg/kg. At the same time, similar samples from a mixture with Raek, CE, contained 14.73 mg/kg and 1.51 mg/kg of dimethoate, respectively (Table 1).

The difference in dimethoate concentrations according to the experimental variants was significantly more noticeable on day 5: 0.752 mg/kg (the non-mixing variant) and 0.296 mg/kg (the mixed version of the experiment), which in percentage terms amounted to 60.6%. Further chromatography showed that mixing of the preparations led to a decrease in the dimethoate concentration in the

Table 1. The dimethoate content in the leaves and fruits of apple trees, during the treatment of plantings with the insecticide Sirocco, CE separately and together with the fungicide Raek, CE, by sampling day mg/kg.

Day of sampling	leaves			fruits		
	Sirocco, CE	Sirocco, CE +Raek, CE	Deviation- “+”/→ «-»	Sirocco, CE	Sirocco, CE +Raek, CE	Deviation- “+”/→ «-»
0 (treatment day)	14.98	14.73	-	1.49	1.51	-
3	1.33	0.742	+	0.262	0.271	+
5	0.752	0.296	+	0.249	0.224	+
7	0.212	0.153	+	0.243	0.200	+
10	0.115	0.111	+	0.219	0.159	+
14	0.094	0.070	+	0.210	0.102	+
21	0.083	0.058	+	0.182	0.125	+
30	0.0768	0.0325	+	0.177	0.062	+
40	0.0661	0.00	+	0.11	0.02	+
50	0.0258	0.00	+	0.06	0.00	+
60	0	0.00	+	0	0.00	+
	K=0.6 DT50= 1.2; DT95= 5.2	K=0.78 DT50= 0.89; DT95= 3.8		K=0.36 DT50= 1.94; DT95= 8.9	K=0.38 DT50= 1.83; DT95= 7.87	

Indicators K, DT50 and DT90 for different experiment options.

leaves. It is important that the complete disintegration of the dimethoate insecticide in the mixed version occurred on the 40th day, when in the version where the insecticide was used separately, its content on the 40th and 50th days was at the level of 0.0661 and 0.0258 mg/kg, respectively (Table 1). The K index for dimethoate is 0.6 (without mixing pesticides), and 0.78 for it in the tank mixture version. The indicators of DT50 and DT90 were, respectively: 0.89 and 3.8 days in the mixed version and 1.2 and 5.2 days in the version with separate application of the insecticide. Obviously, in our experiment, the use of a tank mixture of pesticides has had an effect on accelerating the destruction of the insecticide.

In the 5-day samples, the concentration of dimethoate in the two experimental variants (mixed and non-mixed) was close, and the difference in the concentrations of the insecticide became more noticeable after 7 days. In the 7-day fruit sampling in the variant using a tank mixture of preparations, the dimethoate content was recorded at a level 17.7% lower than in the variant where a separate insecticide was used. The difference in the content of residual amounts of the insecticide dimethoate in the 30-day sampling was 65%, in favor of the option with a separate application of the insecticide. Complete destruction of the insecticide was recorded in a 50-day sampling, nevertheless, in the tank mixture variant, it was still fixed at 0.06 mg/kg after 50 days. The K index was 0.36 (the variant without mixing) and 0.38 –the variant with a tank mixture (Table 1). The values of DT50 between the experimental variants in this case differed by only 6%, whereas the values of DT95 in the experimental variants in this case differed by about 1 day (8.9 days in the variant with separate insecticide use and 7.87 days in the variant using a mixture of preparations) (Table 1). It should be noted that the MRL (maximum remains level) for dimethoate in apple fruits is 0.02 mg/kg (Russia, 2021) the set waiting period for apple fruits is 40. and the transition through this value in the variant using a mixture of preparations in

40 daily samples of apple tree leaves, no residual amounts of dimethoate were recorded, while in the variant with separate use of insecticide, the dimethoate content was recorded in the leaves on the 50th day (Table 1).

No dimethoate was detected in the 50-day samples in the co-administered variants. With separate use of the insecticide, complete destruction of dimethoate in apple fruits was observed only on the 60th day.

The composition of the Borey, SC insecticide includes two active ingredients imidacloprid and lambda-cyhalothrin. The active substance imidacloprid belongs to neonicotinoids, has a systemic effect and is able to move well enough in various parts of plants, has a long preservation period in various plant organs (Popov et al., 2003), according to literature data up to 40-60 days (Russia, 2023).

The results of imidacloprid chromatograms showed how the fungicide Quickly affects the flow of insecticide into the leaves on the first day of apple tree treatment. The content of imidacloprid in the leaf samples was 1.94 mg/kg (the first day after the application of Borey, SC) and 1.31 mg/kg (the variant of spraying with a tank mixture) (Table 2).

In the 5-day selection, the leaves contained 0.339 mg/kg of imidacloprid in the mixed version and 0.257 mg/kg in the non-mixed version (Table 2).

10 days after spraying, there was a significant decrease in the imidacloprid content in the leaves. In both studied variants, the indicators turned out to be almost identical: 0.0693 mg/kg in the case of using a tank mixture and 0.078 mg/kg in the case without mixing (Table 2).

The preservation of imidacloprid in apple leaves occurred much longer with the use of a mixed composition of preparations. On the 21st day of treatment, there were no residual amounts of imidacloprid in the non-mixing version, nevertheless, when combining this insecticide with the fungicide Score, the content of the active substance remained at 0.01 mg/kg (Table 2).

Table 2. The content of imidacloprid in the leaves and fruits of apple trees, during the treatment of plantings with the insecticide Borey, SC separately and together with the fungicide Score, CE, according to the selection days, mg/kg.

Day of sampling	leaves			fruits		
	Borey, SC	Borey, SC +Score, CE	Deviation- "+" / → «-»	Borey, SC	Borey, SC +Score, CE	Deviation- "+" / → «-»
0 (treatment day)	1.94	1.31	+	0.257	0.336	+
5	0.257	0.339	+	0.055	0.122	+
10	0.0693	0.078	+	0.0046	0.0099	+
14	0.055	0.011	+	0.0020	0.0108	+
21	0	0.010	+	0	0.0091	+
30	0	0	+	0	0	+
35	0	0	+	0	0	+
	K=0.40	K=0.27		K=0.35	K=0.25	
	DT50=1.72;	DT50= 2.6;		DT50= 2;	DT50= 2.7;	
	DT95=7.4	DT95= 11.2		DT95= 8,6	DT95= 11.9	

Indicators K, DT50 and DT90 for different experiment options.

The analysis of the DT50 and DT95 indicators, as well as the K coefficient for imidacloprid, showed the following results: with a separate application of the insecticide, the DT50 and DT95 values were 1.72 and 7.4 days, respectively, while the K coefficient was 0.4; when using a tank mixture, these indicators increased to 2.6 and 11.2 days, and the K coefficient decreased to 0.27.

On the day of treatment, the fruits of trees treated with the tank mixture contained 0.656 mg/kg of imidacloprid, similar samples obtained from the mixed version contained 2.4 times more insecticide (Table 2).

In later samples, a higher concentration of imidacloprid was also found in samples collected in mixed versions, for example, after 5 days, the concentration in fruits in the mixed version of imidacloprid was 55.3% higher (Table 2).

The higher content of imidacloprid in the variants with the combined use of Borey, SC and Score, CE remained until the period of complete disintegration of the active substance imidacloprid. It should be noted that the complete destruction of the preparation in the fruits of the apple tree occurred faster and was recorded 21 days after spraying with the preparation without a mixture. When using a tank mixture of Borey, SC and Score, CE, the presence of imidacloprid was recorded in apple fruits and in samples after 21 days, although at a low concentration of 0.006 mg/kg. The calculated values of K, DT50 and DT95 for imidacloprid in apple fruits were: 2 and 8.6 days, with a value of K = 0.35 – for the variant with separate use of Borey, SC and 2.7 and 11.9 days, with a value of K = 0.25 – for the variant where the use of insecticide and fungicide was combined.

Chromatography of leaf samples showed that the use of a tank mixture with a fungicide delayed the destruction of lambda cyhalothrin.

The concentration of lambda cyhalothrin was 1.21 mg/kg (1 day 1 after spraying with Borey, SC), in the variant using a tank mixture of preparations it was 1.63 mg/kg (Table 3) and differed by 34.7%.

On the 5th day, the leaves contained: 0.94 mg/kg (the variant without a mixture) and 1.31 mg/kg (the variant with a mixture of pesticides). On the 10th and 14th days, the content of lambda cyhalothrin in the variant using a mixture of preparations exceeded that in the variant with separate use of the preparation by 47.9% and 47.6%. Complete destruction of the insecticide in the leaves without the use of a mixture occurred after 21 days, and at the same time, in the mixed version, its concentration was still fixed at 0.01 mg/kg (Table 3). The values of K, DT50 and DT95 for lambda cyhalothrin in apple leaf tissues were 3.3 and 14.2 days and a value of K=0.21 (separate spraying), respectively, in the variant with a tank mixture - 4.6 and 19.8 days with a value of K= 0.15 (Table 3).

The results of chromatography of apple fruit tissues showed that the intake of lambda-cyhalothrin into them on the first day was 1.61 mg/kg (option with tank mixture) and 0.656 mg/kg (option without mixing pesticides). Analysis of apple fruit samples obtained later showed that the preservation of lambda cyhalothrin was high when using a mixture of pesticides. In the apple tree samples obtained on the 5th day after treatment, the content of lambda cyhalothrin in the mixed version was 0.34 mg/kg, whereas in the variant with separate use of the insecticide, its content was lower and amounted to 0.219 mg/kg. On days 10 and 14, the content of lambda cyhalothrin in the variant with separate use of the insecticide was 0.045 and 0.012 mg/kg, while the similar values in the mixed versions were higher: 0.066 and 0.052 mg/kg, respectively, on the days of accounting. Complete destruction of the insecticide in the leaves without the use of a mixture occurred after 21 days, and at the same time, in the mixed version, its concentration was still fixed at 0.006 mg/kg, which is a very low content, but still not a complete destruction of the substance. The values of K, DT50, and DT95 for lambda cyhalothrine were 2.4 and 10.3 days and a value of K=0.29 (using one preparation), similar values when using a tank mixture were 2.8 and 12 days with a value of K=0.25 (Table 3).

Table 3. The content of lambda-cyhalothrin in the leaves and fruits of apple trees, during the treatment of plantings with Borey, SC separately and together with the fungicide Score, CE, by sampling day, mg/kg.

Day of sampling	leaves			fruits		
	Borey, SC	Borey, SC +Score, CE	Deviation- "+" /→ «-»	Borey, SC	Borey, SC +Score, CE	Deviation- "+" /→ «-»
0 (treatment day)	1.21	1.63	+	0.656	1.61	+
5	0.94	1.31	+	0.219	0.340	+
10	0.23	0.36	+	0.045	0.066	+
14	0.065	0.096	+	0.012	0.052	+
21	0	0.010	+	0	0.006	+
30	0	0	+	0	0	+
35	0	0	+	0	0	+
	K=0.21 DT50= 3.3; DT95= 14.2	K=0.15 DT50= 4.6; DT95= 19.8		K=0.29 DT50= 2.4; DT95= 10.3	K=0.25 DT50= 2.8; DT95= 12.0	

Indicators K, DT50 and DT90 for different experiment options.

4. Discussion

Sirocco, CE insecticide is an insecticide of contact-systemic action, the active substance dimethoate belongs to the class of organophosphoric compounds (a derivative of dithiophosphoric acid) (Popov et al., 2003). This insecticide is able to move well through the plant and enter all tissues and organs.

The preparation Raek, CE and Score, CE are fungicides of systemic action, their active ingredient– difenoconazole belongs to the class of triazoles, it is characterized by rapid penetration into all plant tissues, is able to exert protective effects on the leaves and fruits of apple trees from pathogens of major fungal diseases. It has an immunizing, healing, and protective effect on the plant (Popov et al., 2003). It is known that difenoconazole, in addition to its therapeutic effect, has a positive effect on the plant (increases the area of the leaf blade, the length of the shoot and its foliage by 1.2–1.6 times), ensures the laying of the next year's crop (Jakl et al., 2021; Li et al., 2023; Man et al., 2023; Pan et al., 2023; Zheng et al., 2023).

The data show that mixing of the Sirocco, CE insecticide and the Raek, CE fungicide led to a faster destruction of the insecticide in the apple tree leaves. These differences began to be recorded after three days, when the acceleration of destruction of the insecticide was already 79.2% for the mixing variant.

The minimum allowable level (MAL) of dimethoate content in apple fruits is 0.02 mg/kg (Russia, 2021). The changes in the dimethoate content in the tissues of the apple fruit recorded in the experimental results can be called significant, since the transition through the MAL value in the case of a mixture of preparations occurred earlier (on day 40) than in the variant with separate use of the insecticide (on day 60). The data obtained suggest that over time, the use of the tank mixture accelerated the destruction of the active substance dimethoate in apple leaves, with approximately the same level of insecticide intake in the two experimental variants. This fact can most likely be attributed to the presence of difenoconazole, a number of properties that have a physiological effect on apple plants (Jakl et al., 2021; Li et al., 2023; Man et al., 2023; Pan et al., 2023; Zheng et al., 2023). First of all, a faster decrease in the content of dimethoate in apple leaves, when using a mixture of preparations, may be due to a change in the plant's metabolism caused by the fungicide. Also, due to the ability of difenoconazole to affect the increased growth of apple leaves and its shoots, a possible decrease in the content of the insecticide can be associated with a faster increase in leaf surface mass in the variant where the fungicide was used. The study of the fruit tissue demonstrated that mixing the insecticide with the fungicide led to a faster decrease in the dimethoate concentration. It is known that the movement of dimethoate through the plant occurs mainly along the xylem to all plant parts (Popov et al., 2003). A more rapid decrease in the content of insecticide in apple fruits, in the case of using a tank mixture, we also tend to associate with the physiological effects of the applied fungicide – difenoconazole, which were listed above.

Borey, DC insecticide a two-component product: it contains imidacloprid and lambda-cyhalothrin. Imidacloprid is an insecticide from the group of nitroso-containing neonicotinoids and has a systemic effect. It moves well over all parts of plants. Lambda-cyhalothrin is an insecticide from the group of synthetic pyrethroids, characterized by contact-intestinal and insect repellent effects. It is characterized by good resistance to destruction from ultraviolet radiation, persists on the surface of plants for a long time, and moves poorly around the plant (Popov et al., 2003).

In the case of the use of Borey, SC insecticide and the fungicide Score, CE, it was recorded that when used in a mixture with a fungicide, there was a change in the rate of destruction of the two active substances of the insecticide – imidacloprid and lambda cyhalothrin, toward slowing destruction. It should be noted that the decomposition rate of DT50 in apple fruits for imidacloprid and lambda-cyhalothrin in the experimental variants differed by less than a day in all experimental variants. A more significant difference was recorded when comparing the indicators of DT95 in different versions of the experiment.

The value of DT95 for imidacloprid when using the mixture was higher by 3.8 days for leaves and 3.3 days for fruits, compared with the option without using the pesticide mixture.

The DT95 index of lambda cyhalothrin in the experimental variant, where the combined use of insecticide and fungicide occurred, exceeded the variant with separate use of insecticide by 5.6 days for leaves and by 1.7 days for fruits.

It should be noted that the MAL value for apple fruits is 0.5 mg/kg (Russia, 2021). Thus, the recorded changes in insecticide degradation recorded in the experiment are not significant in terms of human safety.

The MAL value for the insecticide lambda-cyhalothrin in apple fruits is 0.2 mg/kg (Russia, 2021). The transition through this value was recorded in all variants of the experiment in the same time interval – 10 days, it can be said that the combined use of the insecticide and fungicide in question did not critically affect the product safety period (apple fruits) for the active substance lambda-cyhalothrin.

Thus, analyzing the data obtained, it can be argued that the recorded changes in the timing of the destruction of the active substances of insecticides vary depending on which class the substance belongs to. Obviously, when using the same fungicide, which has the ability to have a physiological effect on the plant, the rate of destruction of the active substances of insecticides varied in different ways and depended on the class of substance.

5. Conclusion

The so-called “green trend” is currently being observed all over the world, aimed at reducing the amount of pesticides in the production of agricultural products. It is necessary to understand that at the moment humanity is unable to completely abandon the use of pesticides, but it is able to significantly reduce their use, pay attention to less toxic preparations, and use resistant varieties. It is also necessary to study the properties of pesticides. The question of possible interactions of pesticides when using tank mixtures remains poorly studied.

Many scientists in various countries are engaged in the search for ways to reduce the risk of crop contamination of field and horticultural products. The results obtained indicate possible causes that may affect the level of the apple crop contamination, which are possible in real conditions of agricultural production. Since the techniques used with the use of tank mixtures are common when spraying apple trees, this study indicates possible cases of changes in the expected destruction time of the active substances of insecticides. The work carried out allows us to form the following conclusions:

1. The addition of the fungicide Raek, CE and the insecticide Sirocco, CE to the tank mixture in the fruits and leaves of the apple tree reduced the decay rates of the insecticide DT50 and DT90;
2. The use of a tank mixture of the fungicide Score, CE and the insecticide Borey, SC led to an increase in the decomposition rates of imidacloprid and lambda-cyhalothrin – DT50 and DT90 in the fruits and leaves of the apple tree;
3. The use of difenoconazole-based fungicides had different effects on the rate of destruction of insecticides from different classes.

The results of the work tell us that in some cases, the change in the rate of destruction of pesticides in agricultural products is significantly influenced by factors that are not considered during registration tests. It is also known that when calculating the hazard of a pesticide, standard information about the preparation and the active ingredients in its composition is usually used. In our study, we point out the need to consider possible changes in the rate of destruction of pesticides when using them in the tank mixture and draw attention to the need to continue such studies. The authors understand that it is often impossible to consider all the factors that can affect the breakdown of active substances in real environmental conditions, but note that it is possible to understand the level of changes that can be achieved using standard plant protection schemes, using the most common active substances of pesticides.

Data Availability Statement

The entire data set that supports the results of this study was published in the article itself.

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