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Original Article

Variation of the rate of pesticides decomposition used together in the process of agricultural production

Variação da taxa de decomposição dos pesticidas utilizados em conjunto no processo de produção agrícola

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Abstract

The use of tank mixtures of pesticides makes it possible to increase the efficiency of chemical treatment. The aim of the study was to establish the relationship between the joint use of pesticides and the rate of decomposition of active substances. The study was carried out on the crops of spring wheat, spring barley, peas, spring rapeseed, seed potato. Chemical treatments were carried out with insecticides and fungicides – the insecticide (imidacloprid and λ-cyhalothrin), suspension concentrate; the fungicide (propiconazole), emulsifiable concentrate; the insecticide (imidacloprid), soluble concentrate; the fungicide (copper sulfate tribasic), suspension concentrate. Determination of residual amounts of active substances of pesticides was carried out using methods of gas-liquid chromatography and high-performance liquid chromatography. The acceleration of decomposition of the active substance - imidacloprid on pea crops and spring rapeseed was caused by the combined use of the insecticide (imidacloprid) and the fungicide (propiconazole). The use of the fungicide (copper sulfate tribasic) in a tank mixture with the insecticide (imidacloprid and λ-cyhalothrin) on potatoes caused a slowdown in the decomposition of the active substances imidacloprid and λ-cyhalothrin. Also, there was a change in the level of intake by plant of active substances in the first three hours after spraying, when using tank mixtures, in comparison with the separate use of compounds. The data obtained on the change in the rate of decomposition of active substances of pesticides, when they are used together in mixtures, indicate the need to continue research in this area. In this regard, it is important to study the dynamics of the decomposition of individual active substances of pesticides in plant tissues when they are used in tank mixtures, it is also necessary to conduct research using compounds most commonly used in agricultural production.

Keywords: decomposition, field crops, pesticides, residues.

Resumo

A utilização de misturas em tanques de pesticidas permite aumentar a eficiência do tratamento químico. O objetivo do estudo foi estabelecer a relação entre a utilização conjunta de pesticidas e a taxa de decomposição das substâncias ativas. O estudo foi realizado nas culturas de trigo de primavera, cevada de primavera, ervilha, colza de primavera e batata-semente. Foram realizados tratamentos químicos com inseticidas e fungicidas − o inseticida (imidaclopride e valuetech-cialotrina), concentrado em suspensão; o fungicida (propiconazol), concentrado emulsionável; o inseticida (imidaclopride), concentrado solúvel; o fungicida (sulfato de cobre tribásico), concentrado em suspensão. A determinação das quantidades residuais de substâncias ativas dos pesticidas foi realizada utilizando métodos de cromatografia gás-líquido e cromatografia líquida de alta eficiência. A aceleração da decomposição da substância ativa – imidaclopride nas culturas de ervilhas e colza de primavera foi causada pela utilização combinada do inseticida (imidaclopride) e do fungicida (propiconazol). A utilização do fungicida (sulfato de cobre tribásico), que contém cobre, numa mistura de tanques com o inseticida (imidaclopride e valuetech-cialotrina) em batatas provocou um abrandamento da decomposição das substâncias ativas imidaclopride e valuetech-cialotrina. Além disso, verificou-se uma alteração no nível de ingestão por planta de substâncias ativas nas primeiras três horas após a pulverização, quando se utilizam misturas em tanques, em comparação com a utilização separada de compostos. Os dados obtidos sobre a alteração da taxa de decomposição das substâncias ativas dos pesticidas, quando utilizadas em conjunto em misturas, indicam a necessidade de prosseguir a investigação neste domínio. Por isto, é importante estudar a dinâmica da decomposição de substâncias ativas individuais de pesticidas nos tecidos vegetais quando são utilizados em misturas em tanques, e realizar pesquisas que empreguem compostos mais comuns na produção agrícola.

Palavras-chave: decomposição, culturas de campo, pesticidas, residuais.

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1. Introduction

In recent decades the intensification of agricultural production, which has been observed, provides an increase in the level of production with a reduction in labour costs and material resources to obtain it. Agricultural producers tend to use highly effective compounds, often containing two or three active substances in their composition. Besides, pesticide mixtures are widely used to reduce the cost of protective measures (Cloyd, 2012; Galani et al., 2020; Roselló-Márquez et al., 2019). The use of tank mixtures of pesticides makes it possible to increase the efficiency of chemical treatment. It increases the range of controlled harmful objects and reduces the amount of mechanical damage to cultivated plants by equipment (Cloyd, 2012; Whitford et al., 2018; Galon et al., 2021). Companies producing and selling pesticides are developing recommendations for the preparation of tank mixtures (Crépet et al., 2019; Ma et al., 2019; Roselló-Márquez et al., 2019; Yang et al., 2018). One of the most frequent combinations of the compound during protective measures is the use of a mixture of fungicides and insecticides (Almasri et al., 2020; Jansen et al., 2017; Srinivasulu et al., 2012; Tamburini et al., 2021). It is often recommended to use tank mixtures containing herbicides (Shalaby and Abdou, 2010; Whitford et al., 2018; Zubkov et al., 2020). The use of such tank mixtures is widespread on crops of field vegetable and grain crops, as well as in horticulture. However, intensive use of pesticides always poses a risk to human health and the environment, so their use should be strictly regulated (Chaikasem and Na Roi-et, 2020; Galani et al., 2020; Ibrahim et al., 2018; Ma et al., 2019). Procedures regulate the method of treatment with the compound, its consumption rate, they also indicate the waiting period for harvesting, i.e. the period between the treatment with the compound and the time when agricultural products become safe for humans (OECD, 2021; Dolzhenko, 2009b; HPAATRF, 2022). Furthermore, the applicable regulations do not take into account the possible joint use of several pesticides in one mixture, which often occurs in practice. It is known that the use of tank mixtures often causes the effect of potentiation, i.e. mutual enhancement of the properties of active substances of pesticides, when they are used together (Dolzhenko, 2009a; Dolzhenko and Rakitsky, 2018; HPAATRF, 2022). In the works of several scientists, there is an increase in the penetration of pesticides into plant tissues when they are used together, and the possible influence of the active substances of pesticides in solution on each other is noted (Hale et al., 2019; Ma et al., 2019; Roselló-Márquez et al., 2019; Yang et al., 2018). Some researchers obtained data on the intensification of the negative effect of pesticides on the animal body when they are used together (Kalliora et al., 2018; Shalaby and Abdou, 2020; Yang et al., 2018). The aim of the study was to establish the relationship between the joint use of pesticides and the rate of decomposition of active substances.

2. Materials and Methods

2.1. Site characteristics

The field section of the study was conducted during 2020-2021 on the territory of the educational and experimental farm of the Russian State Agrarian University-Moscow Timiryazev Agricultural Academy, the laboratory part was carried out in the Educational and Scientific Consulting Center "Agroecology of pesticides and Agrochemicals" in the northern part of Moscow. The soil in the experimental territory is Albeluvisol (IUSSWGWRB, 2006), sod-podzolic, medium loam on podzolic loam, with a capacity of the arable horizon of 24 - 25 centimetres (cm), potential of hydrogen (pH) = 6.2, humus content - 2.1%.

2.2. Crop varieties

During the experiment, the varieties of crops included in the State Register for the Central Region of the Russian Federation were used: spring barley of the Nur variety, spring wheat of the Ivolga variety (early time maturation), spring rapeseed of the Geros variety (medium time maturation) period, peas of the Pharaoh variety (medium time maturation), potatoes of the Nevsky variety (medium time maturation).

2.3. Pesticides

The application of pesticides was carried out within the recommended time limits and consumption rates allowed for use. The study examined the use of the following pesticides: Borei, suspension concentrate (SC) (150 g/L imidacloprid+50 g/L lambda-cyhalothrin (λ-cyhalothrin) (Avgust, Russia) at a consumption rate of 0.1 L/ha; Tilt, emulsifiable concentrate (EC) (250 g/L propiconazole) (Syngenta, Switzerland) at a consumption rate of 0.5 L/ha; Imidor, soluble concentrate (SL) (200 g/L imidacloprid) (Schelkovo Agrohim, Russia) at a consumption rate of 0.6 L/ha; Kumir, SC (345 g/L copper sulfate tribasic) (Avgust, Russia) at a rate of 5 kg/ha (Khan et al., 2020). Pesticides: the insecticide (imidacloprid and λ-cyhalothrin) contains substances from the class neonicotinoids and pyrethroids, the fungicide (propiconazole) belongs to the class azoles, the insecticide (imidacloprid) belongs to the class neonicotinoids, the fungicide (copper sulfate tribasic) belongs to the class copper compounds. The treatment with the preparations was carried out in the phases of the development of cultivated plants, which are recommended by the regulations of use, in calm weather to exclude the decomposition of the working solution. Working solutions of the preparations were applied within one hour after their preparation. In each experiment, control variants were present - without treating the culture with pesticides. A sampling of plant products, packaging, transportation and storage were carried out following approved guidelines (Dolzhenko and Rakitsky, 2018; SANTE, 2021; OECD, 2021). In all variants of the experiment, sampling was carried out 3 hours after spraying, followed by sampling at intervals of 5 days, for 40 days, from each variant of the experiment, after treatment with compound and their mixtures. Samples of plant parts were collected according to OECD (2021). Eight samples of each crop in each variant were taken during experiment. The weight of sample of peas and cereals was at least 1 kg, the weight of sample rapeseed and potatoes was at least 2 kg. Each sample was collected from 12 different points of the field. Collected samples of plant parts were frozen and stored at - 18 ºC. Determination of residual amounts of active substances of pesticides was carried out using methods of gas-liquid chromatography and high-performance liquid chromatography. Approved guidelines were used for these purposes: Methodological guidelines 4.1.1430-03; Methodological guidelines 4.1.2380-08; Methodological guidelines 4.1.1390-03; Methodological guidelines 4.1.2923-11; Methodological guidelines 4.1.2784-10; Methodological guidelines 4.1.2784-10.

2.4. Laboratory part

Validation tests were performed to confirm the suitability of the guidelines 4.1.1430-03, 4.1.1390-03 and 4.1.2923-11 for determination of residual amounts in plant material samples. The validation characteristics (parameters) are selected in accordance with SANTE (2021). The following validation characteristics (parameters) were investigated: linearity (acceptance criteria: correlation coefficient not less than 0.995; regression residues showing the degree of deviation of the calculated values of Y from the obtained in the experiment ≤ ± 20%); specificity/selectivity of the method (acceptance criteria: response of the detector signal to the sample of the reagent blank and control samples ≤ 30% limit of quantitation (LOQ)); completeness of recovery/determination (acceptance criteria: mean value of completeness of recovery at two levels of addition of a known amount of substance to the control sample should be in the range of 70-120.0%); precision under repeatability conditions (acceptance criteria: relative standard deviation for each injection level ≤ 20%); accuracy is defined as the total error of the procedure in accordance with Recommendations on Interstate Standardization 61-2010. "Indicators of accuracy, accuracy, precision of quantitative chemical analysis methods. Evaluation Methods"; measurement uncertainty (defined as a non-negative parameter characterizing the scattering of value values attributed to the measured value based on the information used). During the validation studies of the analytical methods used, it has been experimentally proved that with all the changes made, the validation characteristics meet the criteria established by SANTE (2021) and the analytical procedure is suitable for the study of residual amounts of imidacloprid and lambda-cyhalothrin in plant material. The collected samples of plant material were delivered to the laboratory and stored in a freezer at -18 ° C until the day of analysis. The samples of plant material were thawed and crushed using a laboratory mill before carrying out the analysis for the content of residual amounts of active substances. Analysis of the residual amounts of imidacloprid was carried out on an Agilent 1260 Infinity liquid chromatograph with a diode-matrix detector under the following chromatographic conditions: Zorbax Eclipse XDB-C18 column (4,6 millimetres (mm) × 150 mm), 5 micrometre (μm) grain, Zorbax Eclipse XDB-C8 precolumn (2,1 mm × 12,5 mm), 5 μm grain, column temperature: 30 °C, flow rate 0.6 mL/min, wavelength: 268 nanometres (nm), acetonitrile-water mobile phase 25:75 volume per volume (v/v), injection volume 10.0 mm^3. The method is based on the determination of imidacloprid after its extraction from samples by 150 mililiters acetonitrile HPLC gradient grade "Chem-Lab", Belgium, purification of extracts by redistribution in a system of immiscible solvents and purification on concentrating cartridges with grafted amino groups ("Phenomenex Strata NH2" Solid Phase Extraction (SPE), USA). Imidacloprid was identified by retention time and quantification by absolute calibration. Analysis of the residual amounts of lambda-cyhalothrin was carried out on an Agilent 7890B gas chromatograph with an electron capture detector under the following chromatographic conditions: capillary quartz column NR-5, length 30 m, internal diameter 0.32 mm, film thickness 0.25 μm, detector temperature - 300 °C, blowing gas flow (nitrogen) - 30.0 milliliter per minute (ml/min), evaporator temperature - 260 °C, helium gas type, Split mode, pressure 19.9 pounds per square inch (psi), flow division 20:1, total flow 57.6 ml/min, septum blowing flow 3.0 ml/min. The validated method is based on the determination of lambda-cyhalothrin after its extraction by 150 mililiters acetonitrile HPLC gradient grade "Chem-Lab", Belgium samples, purification of the extract by redistribution between the organic and aqueous phases (from 100 mililiters HPLC gradient grade water ("Biosolve BV", Netherlands) to 90 mililiters Hexane-(n) a.r., ASC ("Chem-Lab", Belgium)) and clean-up on florisil columns (5 grams of magnesia silica 0.15 – 0.25 mm "MACHEREY-NAGEL", Germany). Programmed heating of the column from 220 °C (hold 1 min) at 2 degrees per minute (deg/min) to 236 °C (hold 1 min) at 20 deg/min to 300 °C (hold 1 min), constant flow mode, column flow 2.6 ml/min, average speed 50.5 centimeters per second (cm/s), injection volume - 1 mm^3. Lambda-cyhalothrin was identified by retention time and assay by absolute calibration. The results of the studies were subjected to statistical processing by single-factor analysis of variance using the Fisher test in the Excel program.

3. Results

According to the research results, the combined use of the insecticide (imidacloprid and λ-cyhalothrin) in a tank mixture with the fungicide (copper sulfate tribasic) on potato plantings increased the period of complete decomposition of pesticides in the studied culture of active substances - imidacloprid for 10 days and λ-cyhalothrin for 5 days. Thus, in the variant using a mixture of preparations in samples with potato tubers taken 20 days after treatment, the content of λ-cyhalothrin was 0.0394 milligram per kilogram (mg/kg), while in the variant with a separate application of insecticide, complete decomposition of this substance occurred (Figure 1). The content of imidacloprid in the mixed version in the tuber samples after 5 and 10 days after treatment was 0.01 and 0.008 mg/kg, respectively, whereas in the variant with separate use of Boreas, SC after 5 days, imidacloprid was not detected in potato tuber samples (Figure 2).

The application of the fungicide (copper sulfate tribasic) together with the insecticide (imidacloprid and λ-cyhalothrin) on potatoes caused a slowdown in the decomposition of residual amounts of active substances lambda-cyhalothrin and imidacloprid. Furthermore, when using this mixture on potatoes, on the day of processing, there was an increase in the intake of imidacloprid into plant leaves, on average, by 5.3 times (Figure 2), while the intake of lambda-cyhalothrin did not differ from the variant with a separate application of insecticide (Figure 1). The combined application of the insecticide (imidacloprid) on peas together with the fungicide (propiconazole) accelerated the decomposition of the active substance imidacloprid for 10 days. Thus, in the variant with a separate application of the insecticide (imidacloprid), the content of imidacloprid in pea pods 25 and 30 days after treatment was, respectively, 0.021 and 0.02 mg /kg, whereas in the variant using a mixture 25 days after treatment, imidacloprid was not detected (Figure 3).

The combined application of the insecticide (imidacloprid) on spring rape together with the fungicide (propiconazole) also accelerated the decomposition of the active substance imidacloprid. Thus, in the mixed version, the complete disintegration of imidacloprid was recorded 20 days after treatment, while in the variant with a separate application of the insecticide (imidacloprid) on days 20 and 25, the concentration of imidacloprid in rapeseed pods was fixed at 0.051 mg/kg and 0.017 mg/kg, respectively (Figure 4). Also in this experiment, there were differences in the level of intake of the active substance imidacloprid 3 hours after treatment: in the variant with a separate application of the insecticide, its concentration was 0.268 mg/kg, in the mixed version - 0.092 mg/kg (Figure 4).

The combined use of the insecticide (imidacloprid) together with the fungicide (propiconazole) did not affect the rate of decomposition of imidacloprid on spring wheat and spring barley. For example, after 20 days in the green mass of spring barley, the concentration of imidacloprid in the variant with separate use of insecticide was 0.06 mg/kg, and in the mixed version 0.061 mg/kg (Figure 5). Complete disintegration of imidacloprid on these

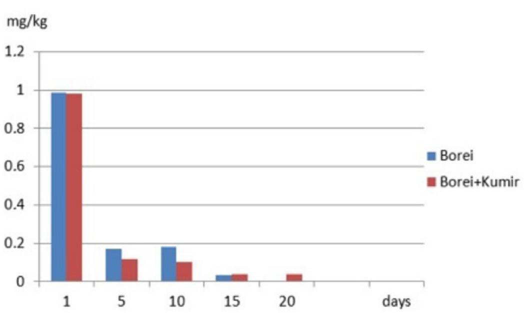

Figure 1. Decomposition of λ-cyhalothrin (mg/kg) on potatoes when using the insecticide (imidacloprid and λ-cyhalothrin) separately and mixed with the fungicide (copper sulfate tribasic).

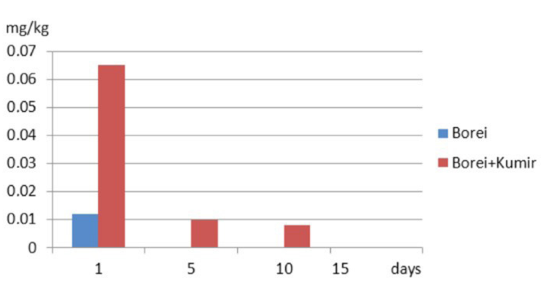

Figure 2. Decomposition of imidacloprid (mg/kg) on potatoes when using the insecticide (imidacloprid and λ-cyhalothrin) separately and mixed with the fungicide (copper sulfate tribasic).

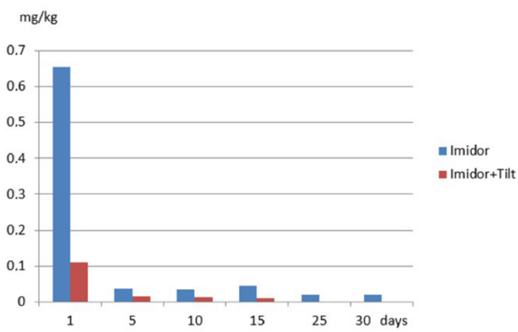

Figure 3. Decomposition of imidacloprid (mg/kg) on peas when using the insecticide (imidacloprid) separately and mixed with the fungicide (propiconazole).

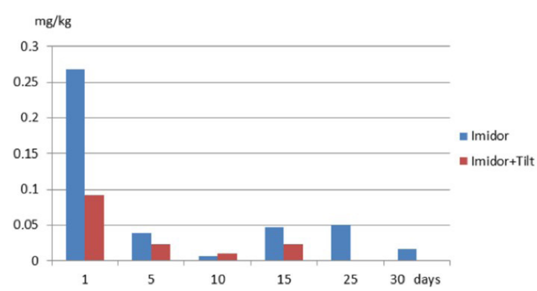

Figure 4. Decomposition of imidacloprid (mg/kg) on spring rapeseed when using the insecticide (imidacloprid) separately and mixed with the fungicide (propiconazole).

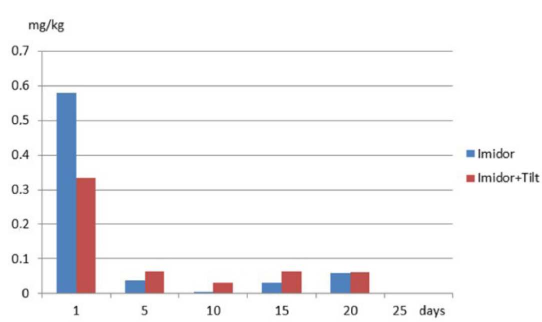

Figure 5. Decomposition of imidacloprid (mg/kg) on spring barley when using the insecticide (imidacloprid) separately and mixed with the fungicide (propiconazole).

crops after treatment with the compound was recorded in the samples collected after 20 days - on spring wheat and after 25 days - on spring barley, in all variants of the experiment. Also, there were differences in the level of intake of the active substance on barley and spring wheat. The concentration of imidacloprid 3 hours after treatment in the variant with a separate insecticide application was 79.3% higher (on wheat) and 73.4% higher (on barley) than in the mixed version.

4. Discussion

In all variants using tank mixtures, variation in the rate of compound of individual active substances was recorded in comparison with their separate use. According to some studies, the combined use of copper-containing preparations with other chemical preparations to varying degrees affects the decomposition of active pesticides in the green mass of plants (Yuliar et al., 2019; Zakharychev, 2020). It is also known that copper-based preparations can also affect the permeability of plant cell walls (Yurkevich et al., 2011; Zakharychev, 2020). Thus, the use of the fungicide (propiconazole) in the tank mixture affected the intake of imidacloprid into the green mass of cultivated plants and, in some variants, affected the decomposition of the insecticide. According to the literature data, fungicides of the azole subgroup, to which the studied fungicide (propiconazole) belongs, EC-propiconazole is a systemic fungicide and, in addition to the fungicidal effect on phytopathogenic fungi, has a growth-regulating effect on plants, affecting it through a change in the synthesis of gibberellins (Zakharychev, 2020). Known effects of azoles are inhibition of internode elongation in cereals, reduction of plant transpiration, and enhancement of photosynthesis (Popov et al., 2003; Zakharychev, 2020). The variation in the amounts of active substances of pesticides entering the plant during treatment with tank mixtures of preparations is most likely due to a change in the physicochemical properties of the resulting working solution when preparing a mixture of several pesticides. A change in the rate or quantities of receipt of active substances of pesticides when they are used together may affect not only the change in the period of decomposition of their residual amounts in culture to a safe level for humans and animals but also affect the biological effectiveness of the solution and affect the occurrence of phytotoxic effects on protected plants. According to other researchers, such problems can arise (Crivellente et al., 2019; Roselló-Márquez et al., 2019; Yang et al., 2018).

5. Conclusion

The data obtained on the change in the rate of decomposition of active substances of pesticides, when they are used together in mixtures, indicate the need to continue research in this area. In this regard, it is important to study the dynamics of the decomposition of individual active substances of pesticides in plant tissues when they are used in tank mixtures, it is also necessary to conduct research using compounds most commonly used in agricultural production. The article was limited to only two types of insecticides: insecticide (imidacloprid and λ-cyhalothrin) and insecticide (imidacloprid), as well as two types of fungicides: fungicide (propiconazole) and fungicide (copper sulfate tribasic). Further study of the decomposition rate of active substances of various pesticides used in a mixture with fungicides from the azole subgroup is of scientific and practical interest. It should be borne in mind that a change in the rate or quantities of receipt of active substances of pesticides when they are used together may affect the biological effectiveness of the solution and affect the occurrence of phytotoxic effects on protected plants.

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