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Full Length Research Paper

The process of migration of a benzoylurea derivative in the soil-water system

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Abstract

Soil in comparison with other objects in the human habitat, is the place of maximum pesticide accumulation. Soil is a link in the biosphere that is both the start and the end of many migration routes of xenobiotics along the soil-water-air and food chains. Therefore, it is necessary to strictly control the xenobiotic content of soil as an additional criterion for the degree of contamination of adjacent environments at acceptable levels. The purpose of the present experimental study was to investigate the migration-water hazard indicator of a benzoylurea derivative pesticide active ingredient and its formulation and to establish an evidence-supported threshold concentration for the pesticide in soil according to this hazard indicator. The migration-water hazard indicator characterizes the processes of pesticide migration from soil to groundwater.

The study was conducted under the standard and comparable soil and microclimatic conditions using a soil model standard and special laboratory filtration units. The method of laboratory modeling is a mandatory step in the study of the migration of pesticides in soil.

Keywords: Pesticide, Benzoyl urea derivative, Migration-water hazard indicator

INTRODUCTION

Among the global chemical pollutants of the environment that pose a real threat to the human health, including child health, pesticides occupy a special position. This is due to the characteristics of their use: they are deliberately imported into agrophytocenoses to achieve domestic goals; the ability to migrate and circulate in natural biocenoses (soil-water-human, soil-air-human, soil-plant-human, soil-microbiocenosis-human), as well as the possibility of contact between these highly biologically-active ingredients and the general public. In addition, the scale of their use in agriculture is constantly growing since the use of various pesticide preparations (formulations) allows saving at least one-third of the crop production (Popova et al., 2018, Gromova et al., 2011).

According to the ISO 11074-1 international standard, soil is the upper layer of the Earth's crust, consisting of mineral particles, organic matter, including protein components, water, air and living organisms. It is a biological system-a genetic reservoir that provides for the vital activity of plants, animals and humans (Fomin & Fomin, 2001).

About half of the pesticides applied to the arable land reach the soil level. During the pesticide application of agricultural land. This results in soil being the place of maximum pesticide accumulation in comparison with other objects in the habitat. Being a link of the biosphere, where the numerous chains of migration along the soil-water-air and food chains begin and end, the need arises to strictly regulate the content of pesticides in soil (Kryatov et al., 2009).

Pesticides are found in soil in a labile state and, therefore, can move along soil profile in the horizontal and the vertical directions. This process occurs under the action of molecular diffusion with capillary moisture, downward current of gravitational water, the root system of plants and as a result of displacement during tillage. Pesticides move greater distances with a stream of water, occurring after rain or irrigation. The speed and depth of the vertical movement depend on the solubility of the pesticide product, the characteristics of its adsorption and desorption, volatility, as well as the intensity of the evaporation of soil moisture. In the event of prolonged rain or irrigation, poorly adsorbed hydrophilic substances move down the soil profile along with water, which can lead to groundwater pollution.

Conducting experimental studies of the effects of pesticides on the migration-water hazard indicator in the soil-water system is relevant and timely (Goncharuk et al., 1986; Rakitsky et al., 2016).

The migration-water hazard indicator characterizes the ability of a pesticide to migrate from soil to groundwater. The threshold concentration for this hazard indicator is set at the value of the maximum amount of the regulated pesticide (mg/kg of absolutely dry soil), at which no concentration in groundwater is created that exceeds the maximum permissible concentration of the pesticide under study in the water of reservoirs (MPC in water).

Considering that the pesticides based on benzoylurea are highly persistent in soil, and are used as a systemic and contact fungicide in agriculture against late blight disease on potatoes and tomatoes with high rate of application and multiple treatments, the experimental study on the migration of the active ingredient and its formulation was conducted in the soil-water system.

MATERIALS AND METHODS

Objects of research: active ingredient $C_{14}H_8Cl_3F_3N_2O$-a derivative of the benzoylureas chemical class (benzamides), molecular weight-383.5g, solid beige substance with a phenolic odor, water solubility at 20°C-2.8 g/L (pH 4-7), solubility in organic solvents in mg/100 mL at 24°C: ethyl acetate-37.7 g/L, n-hexane-0.2 g/L, ethanol-19.2 g/L, toluene-20.5 g/L, acetone-74.7 g/L, dichloromethane-126 g/L, dimethyl sulfoxide-183 g/L. N-octanol/water partition coefficient: K_{ow}logP=2.9 (pH 4, 7.3, 9.1) (The Pesticide Manual. 17th Edition, 2015), highly persistent in soil-DT_{90} >365 days (EU, WHO, SanR&N 1.2.2584-10) (Food and Agriculture Organization of the United Nations, 2000; The University of Hertfordshire Agricultural Substances Database Background and Support Information, 2017; Sanitary rules and regulations, 2010); formulation based on a benzoylurea derivative; model sample filtrates; control water samples-a blank sample filtrate. The obtained water samples were stored in a darkened container in a refrigerator for no more than a week (2-6°C).

Experimental Conditions

The experiments were conducted in standard and, therefore, comparable soil and microclimatic extreme conditions (temperature, humidity, intensity of ultraviolet irradiation), contributing to the maximum migration of pesticide from soil to water. 1 m tall laboratory filtration columns, 10 cm in diameter, with a filtrate collection system, filled with drainage and soil having the maximum filtration and minimum sorption capacity, with a constant granulometric and physical-chemical composition- Model Soil Standard (MSS), were used in the experiments. The MSS was a mixture of medium and fine-grained sand, extracted from an open quarry from the depth of 3 m, with an organic carbon content of 0.5%-1.5%, pH of the aqueous extract was 6.5-7.5; the absorption capacity was <5.0 (mg-eq/100 g of soil), the sum of exchange bases was 3.0 (mg-eq/100 g of soil); mechanical composition -the number of particles with a diameter of more than 0.1 mm-95%, the number of particles with a diameter of less than 0.1 mm-5%, the content of particles with a diameter of 0.1-0.25 mm - ≥ 50%, the maximum particle diameter ≤ 1%, with the content of the normalized substance - <natural background).

Three doses of the active ingredient and the formulation, as calculated according to the active ingredient content in 3 replicates, and control were studied. The first concentration corresponded to the maximum recommended application rate in agriculture (1N) (1.6 l/ha) - 0.04 mg/kg and 0.7 mg/kg, respectively; the second was 10 times lower than the maximum rate (0.1N) - 0.004 mg/kg and 0.07 mg/kg; the third was 10 times higher than the maximum rate (10N) - 0.4 mg/kg and 7.0 mg/kg (the persistence of the substance in soil is more than one vegetative period).

The concentrations were added to the top 20 cm layer of the filtration columns in the form of pre-made aqueous solutions considering the total amount of water for daily watering. The experiments were performed in the dark. Watering of experimental units, sampling, and analysis of sample filtrates were carried out daily. The content of the rationed substance was determined continuously in every 100 mL of filtrate. The study continued until the test substance concentration reached the level of the previously established MPC in water - 0.01 mg/dm³.

Calibration solutions of a mixture of water: acetonitrile with a concentration of 1 µg/cm³ were used for the preparation of model water samples with the addition of the substance. An analytical standard sample of the substance with 99.2% content was used, as presented in Figures 1-3.

A sample of water with a volume of 10 cm³ was filtered through a membrane filter with a pore size of 0.2 µm, and then 10 mm³ of formic acid were added. The sample was then analyzed using tandem mass spectrometry with high-performance liquid chromatography (reversed-

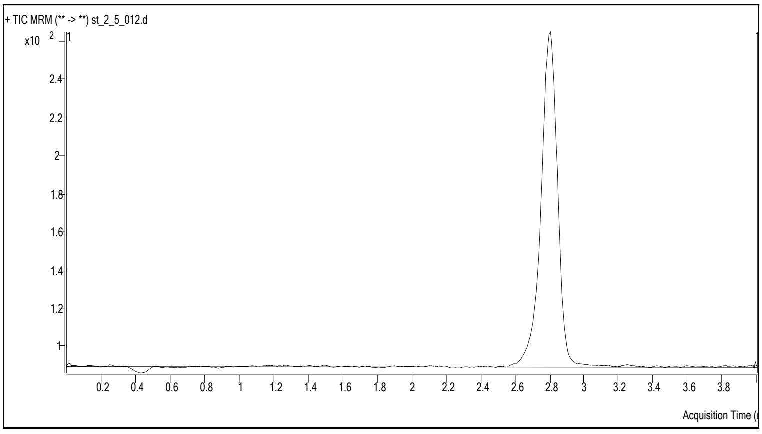

Figure 1. Analytical standard chromatogram, the concentration of the benzoylurea derivative 0.0025 μg/ML.

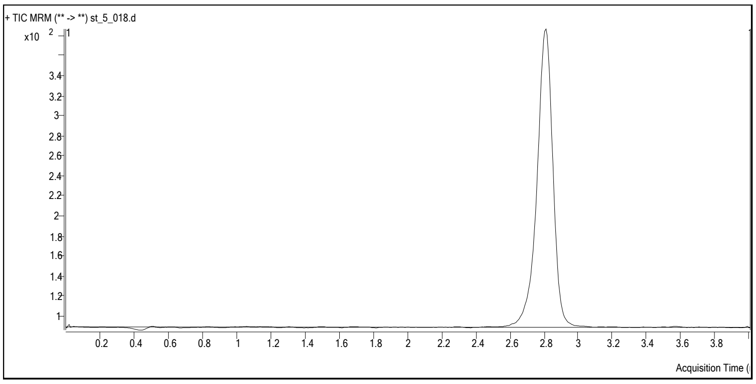

Figure 2. Analytical standard chromatogram, the concentration of the benzoylurea derivative 0.005 μg/mL.

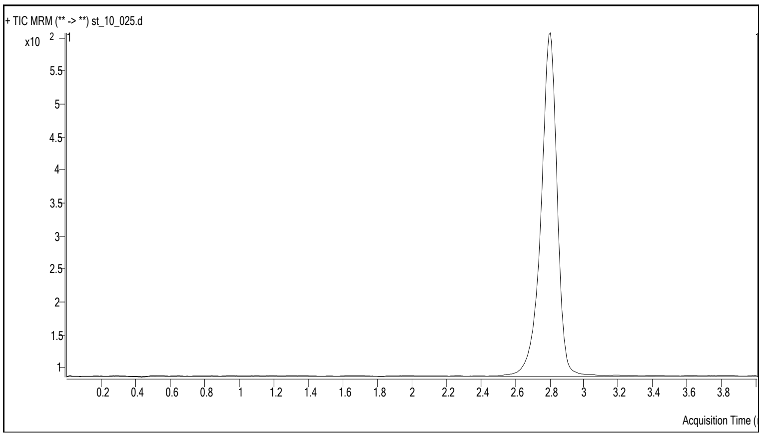

Figure 3. Analytical standard chromatogram, the concentration of the benzoylurea derivative 0.01 μg/mL.

phase) with triple quadrupole detector (HPLC, Study No. 03- 27: Method AR 307-03) - the lower limit of quantitation of 0.0025 mg/dm^3 (LOD) 0.0025 μg/L (Rakitskiy et al., 2015).

Analytical studies were performed on "Agilent 1290 Infinity LC" liquid chromatograph, equipped with a mass selective detector "Agilent Triple Quad 6460", binary pump, column thermostat and auto sampler.

Quantitative determination of the substance was carried out by the method of absolute calibration based on the calibration dependence of the peak area of substances on their concentration in the analyzed solution, as presented in Figure 4.

Chromatography Conditions

Liquid chromatograph with a tandem mass spectrometry detector: triple quadrupole with an ionization source equipped with coaxial supply of hot nitrogen for effective ion desolvation.

As a stationary phase, a reverse-phase chromatographic column 50 mm long with an internal diameter of 2.1 mm and containing ZORBAX Eclipse Plus RRHD C18 was used. Column temperature-25 ° C;

As a mobile phase, a mixture of solvents A-solution of 0.1% formic acid (by volume) in water; B-solution of 0.1% formic acid (by volume) in acetonitrile. Isocratic elution mode A:B (50:50). The flow rate of eluent was 0.3 cm^3/min. The volume of sample injected 5 mm^3. Approximate retention time-2.8 min. Linear detection range: 0.0025-0.05 mg/dm^3.

Operating mode of the MS detector: registration of positive daughter ions after the destruction of maternal ions (registration of the “transition” in the multi-reaction monitoring mode: 383.0 → 172.9 (quantitative transition), 383.0 → 74.1 (confirmation transition)) (Meng, 2008).

To confirm the reliability and reproducibility of the results, the method was pre-validated on 5 model water samples with the addition of substance at 2 levels of the lower limit of quantitative determination of 0.005 mg/dm^3 (corresponding to ½ MPC in water) and 20 levels of the lower limit of quantitative determination of 0.05 mg/dm^3 (Demoliner et al., 2010), as presented in Figures 5 and 6. The established range of completeness of extraction for the soil was 75%-118% (average 93%). Standard deviation is 17.6%.

The accumulation, correction, processing, analysis and visualization of the obtained data were performed by mathematical-statistical methods with modern information technologies employing typical licensed and original software (IBM, PC/AT) (Council BCP, 2015).

RESULTS

The conducted experiments demonstrated that the level of migration of a substance in the soil-water system depends on the concentration in soil.

Until the 11th day of the experiment, the residual amounts of the substance were not detected in any of the studied concentrations.

On the 12th day of the experiment, the active ingredient in the filtrate samples of concentrations of 0.1N, 1N, 10N was detected at the level of-0.003 mg/dm^3, 0.006 mg/dm^3, 0.14 mg/dm^3, respectively, and the residual amounts of the substance at a concentration of 10N for the formulation (in terms of the active ingredient content) were at the level of 0.0036 mg/dm^3.

On the 13th day, the residual amounts of the substance (active ingredient and the formulation) were detected, respectively:

- at the concentration of 0.1N-0.002 mg/dm^3 and 0.0004 mg/dm^3;

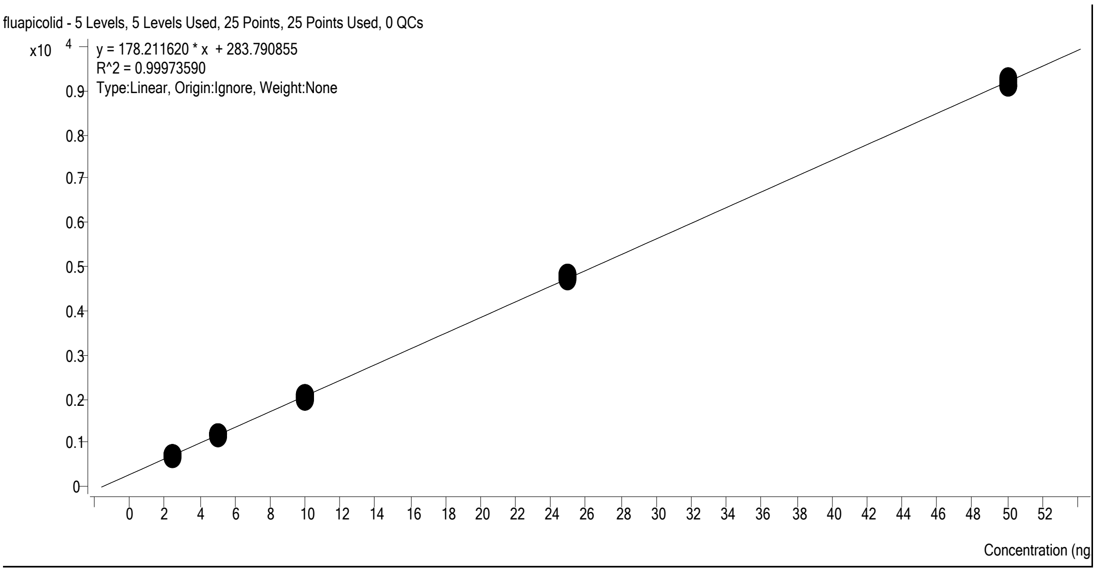

Figure 4. Calibration curve: A plot of the dependency of the chromatographic peak area of the benzoylurea derivative and the concentration in solution. S=178.211620*C 283.790855 (correlation coeficient 0.99973590), where S-the chromatographic peak area, mV·sec; C: concentration of benzoylurea derivative in solution, ng/cm^3.

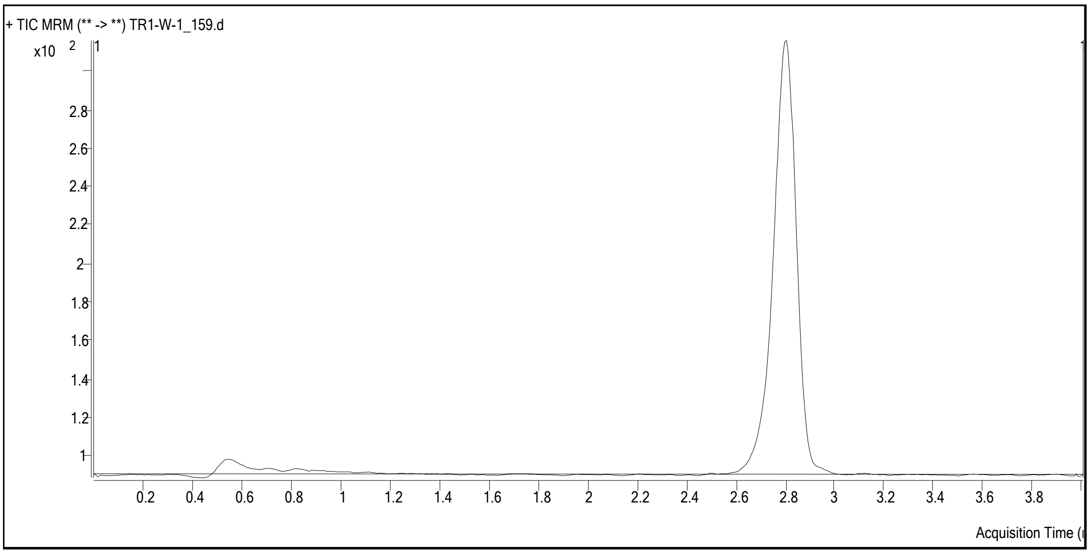

Figure 5. Chromatogram of a sample of water with the addition of 0.005 µg of the benzoylurea derivative, corresponding to 0.0025 mg/dm^3.

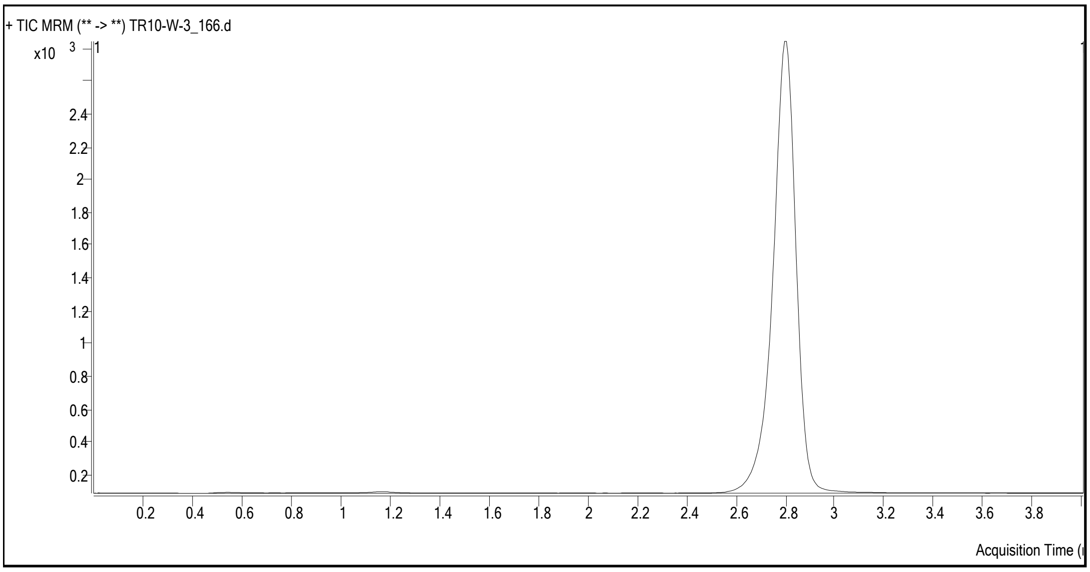

Figure 6. Chromatogram of a sample of water with the addition of 0.05 µg of the benzoylurea derivative, corresponding to 0.025 mg/dm^3.

- at the concentration of 1N-0.026 mg/dm^3 and 0.0003 mg/dm^3;
- at the concentration of 10N-0.8 mg/dm^3 and 0.03 mg/dm^3.

The content of the residual amounts of the substance in the filtrates at all concentrations tested during the experiment gradually increased and reached the maximum values to the 15th day of the experiment:

- at the concentration of 0.1N for the active ingredient-0.006 mg/dm^3;
- at the concentration of 1N for the active ingredient-0.06 mg/dm^3;
- at the concentration of 10N for the active ingredient–3.6 mg/dm^3;
- at the concentration of 0.1N for the formulation (in terms of the active ingredient content)-0.004 mg/dm^3;
- at the concentration of 1N for the formulation (in terms of the active ingredient content)-0.02 mg/dm^3;

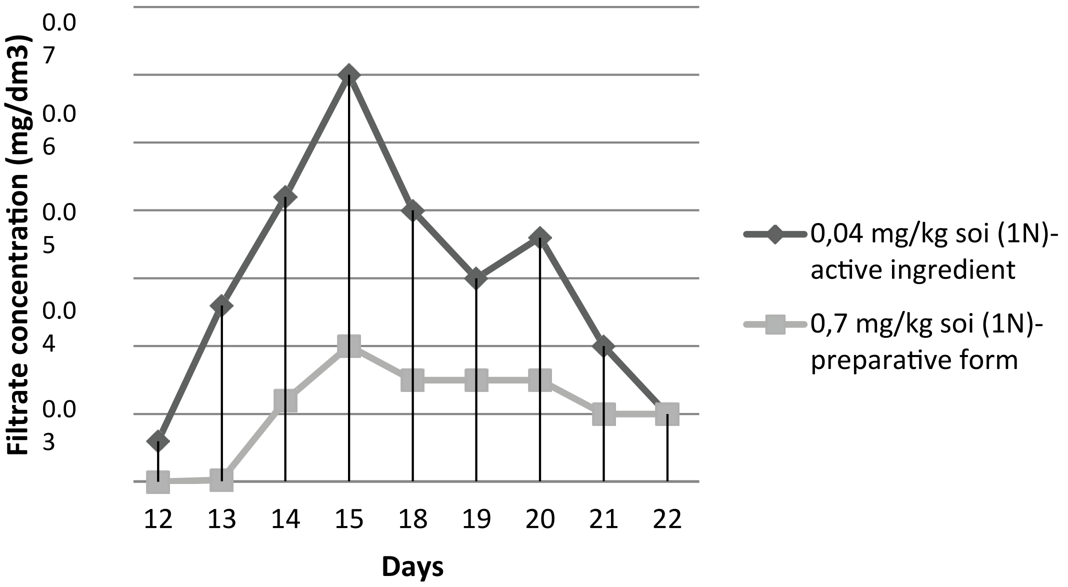

Figure 7: Dynamics of change of the benzoylurea derivative concentration in samples of lysimetric waters (concentration 1N active ingredient, the formulation).

- at the concentration of 10N for the formulation (in terms of the active ingredient content)-0.1 mg/dm^3.

From the 18th day to the 21st day of the experiment, the amount of the substance in the samples of the filtrates gradually decreased in all tested concentrations:

- at the concentration of 0.1N for the active ingredient - 0.004-0.001 mg/dm^3;
- at the concentration of 1N for the active ingredient - 0.04-0.02 mg/dm^3;
- at the concentration of 10N for the active ingredient - 0.2-0.1 mg/dm^3;
- at the concentration of 0.1N for the formulation (in terms of the active ingredient content)- 0.002-0.001 mg/dm^3;
- at the concentration of 1N for the formulation (in terms of the active ingredient content)- 0.015-0.01 mg/dm^3;
- at the concentration of 10N for the formulation (in terms of the active ingredient content)- 0.1-0.04 mg/dm^3.

On the 22nd day of the experiment, the residual amounts in the filtrate samples (1N for the active ingredient and 1N for the formulation) was at the level of MPC in water (0.01 mg/dm^3) and was 0.01 mg/dm^3, as presented in Figure 7.

Starting from the 1st day and until the completion of the study, the substance, tested at a concentration of 0.1N for the active ingredient and for the formulation (in terms of the active ingredient), was either not detected or detected in amounts below the MPC level in water (0.01 mg/dm^3). On the 22nd day of the experiment, the amount of the detected substance in samples at a concentration of 10N for the active ingredient and the formulation (in terms of the active ingredient) was 0.1 and 0.03 mg/dm^3, respectively.

By the 23rd day of the experiment, the substance was detected in samples of the filtrates only in the concentrations of 1N and 10N for the formulation (in terms of the active ingredient content)- 0.004 and 0.03 mg/dm^3, respectively. From the 24th to 27th day of the experiment, the substance was not detected in any of the filtrate samples at all of the tested concentrations.

DISCUSSION

Research on the effects of the benzoylurea derivative pesticide active ingredient and its formulation on the migration-water hazard indicator in the soil-water system, using the Model Soil Standard (MSS) according to our methodology, were conducted for the first time.

The data obtained in the present study of the migration-water hazard indicator for the benzoylurea derivative allowed to establish the threshold concentration for the substance at the level of 0.04 mg/kg (on active ingredient): this concentration was reached on the 22nd day of the experiment when the residual quantity of the substance in the filtrates was at the level of its MPC in water.

A moderate ability for leaching of the benzoylurea derivative and its formulation in the soil-water system was observed in the present study, which allows to consider the compound to be moderately movable and unlikely to penetrate to groundwater when used in agriculture in accordance with the recommended regulations.

The experiments, carried out under extreme conditions, allowed to obtain more stable and comparable results. In this regard, the method of laboratory modeling is a mandatory step for the regulation of pesticides in soil.

CONCLUSION

The obtained value guarantees that the migration of the benzoylurea derivative from soil to groundwater is in the safe amount for human health (≤ 0.01 mg/L MPC in water for the benzoylurea derivative). Therefore, when using formulations based on benzoylurea derivatives with maximum application rates and multiplicity of treatments in agriculture, penetration of an active ingredient to groundwater is unlikely.

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