Research Article

Victoria N. Kolupaeva, Ann A. Kokoreva, Alexandra A. Belik, Pavel A. Pletenev

Study of the behavior of the new insecticide cyantraniliprole in large lysimeters of the Moscow State University

Abstract: The behaviour of cyantraniliprole was studied in a lysimetric experiment. The experiment was carried out at the lysimeters of the Soil Research Station of Moscow State University from June 2015 to December 2018. The soil of lysimeter is soddy-podzolic silt loam. The insecticide was applied at the recommended and tenfold rates in 2015 and 2016. The maximum depth of migration of cyantraniliprole in the soil profile was 35 cm in October 2015 and 40 cm in October 2016. Cyantraniliprole was found in the leachate of lysimeter water 2 weeks after its first application in 2015 and continued until the end of 2018, that is, 2 years after the last treatment. Cyantraniliprole was found in most of the water samples analyzed. The maximum concentrations of cyantraniliprole in the leachate were 12.5 and 2.6 μg L^{-1} in lysimeters with tenfold and recommended doses, with mean values of - 1.7 and 0.6 μg L^{-1}, respectively.

Keywords: soil; pesticide; leaching; lysimeter; preferential flows

1 Introduction

The use of plant protection products can give an improvement of up to a 25% yield (Ganiev and Nedorezkov 2006).

*Corresponding author: Victoria N. Kolupaeva, Russian Scientific-Research Institute of Phytopathology, Bolshiye Vyazemy, Moscow region, Russia, E-mail: v.kolupaeva@vniif.ru
Ann A. Kokoreva, Alexandra A. Belik, Russian Scientific-Research Institute of Phytopathology, Bolshiye Vyazemy, Moscow region, Russia
Ann A. Kokoreva, Alexandra A. Belik, Lomonosov Moscow State University, Moscow, Russia
Pavel A. Pletenev, Federal Scientific Center of Hygiene named after F.F. Erisman of Rospotrebnadzor, Mytischi, Moscow region, Russia

While during the first half of the 20th century the process of inventing effective and safe molecules went slowly, at the end of the 20th and beginning of the 21st century the number of pesticides used in agriculture increased every year. Refusal to use pesticides is completely impossible due to the catastrophic consequences of the yield decreasing for humanity. Thus, food safety – an element of national security – takes care of sustainability, which means that the national food system of countries develops under the regime of expanded reproduction (Klimin 2014; CFS 2012).

Bob Ferklau (CREON Energy 2016), global market analyst, noted that in the United States and Brazil – the largest pesticide markets – sales of plant protection products amounted to $ 8 billion, followed by China ($ 6 billion), Japan ($ 2.5 billion) and France ($ 2 billion). Russia is not among the top ten countries in terms of pesticides sales: the volume of the Russian market was $ 1.2 billion (at the level of Italy and the United Kingdom, despite the larger area of agricultural lands in Russia). At the same time, according to E. Alekperova (CREON Energy 2016), in 2015, 97% of Russia's grain areas were sown with etched seeds.

Thus, production is on the way to increasing the number of pesticides, mainly generics, and science is trying to reduce their adverse effects on the environment and non-target organisms. Numerous studies have shown the presence of pesticide residues in underground waters around the world (Fava et al. 2010; Akesson et al. 2015; Shaw et al. 2012; Estes et al. 2016; Imran and Jain 1998; Lagana et al. 2002; Haarstad and Ludvigsen 2007; Lapworth and Goody 2006). In south-Swedish public supply wells, pesticides occurred in 18 of the 23 wells, i.e., approx. 80 % of the study sites (Akesson et al. 2015). In Sweden, both the currently used and banned pesticides (such as atrazine – banned since 1989, simazine – since 1994, carbendazim – since 1998, imazapyr – since 2002, terbutilazin – since 2003 and isoproturon – since 2012) were observed. In Italy bentazon, MCPA and 2,4-D were detected in drainage water and groundwater (Lagana et al. 2002). In Norway, a total of 12 compounds were

detected. These included bentazone, dichlorprop, endosulfan, chlopiralid, MCPA, mecoprop, 2,4-D and others. The most frequently detected group of compounds are the phenoxy acids, and they also occurred in the highest concentrations (Haarstad and Ludvigsen 2007). In southeast England between 2003 and 2004 diuron was observed in 90% of groundwater samples analyzed. In 60% of groundwater samples metabolites of diuron were more prevalent than the parent compound. Longer-term (1989-2005) monitoring showed that pollution of the aquifer by atrazine, simazine, and more recently diuron, displayed a positive correlation with periods of high groundwater levels (Lapworth and Goody 2006).

Infiltration through riverbeds and riverbanks and leaching through the soil and unsaturated zones are the main pesticide input routes into groundwater (Reichenberger et al. 2007; Arias-Estévez et al. 2008). Therefore, groundwaters are vulnerable to pollution (Gurdak 2014). The factors (chemical, physical, and biological) influencing the leaching of the pesticides are varied including physical-chemical properties of the pesticide (water solubility, vapor pressure, adsorption coefficient, etc.), permeability of the soil, texture and organic matter content of the soil, site characteristics (hydrogeological conditions), and method/dose of pesticide application. Sorption and degradation processes, both influenced by chemical-physical properties of the soils and compounds, and weather conditions, mainly affect the movement of water and dissolved pesticides through the soil. According to Rodríguez-Cruz (2009), adsorption and desorption are the processes that regulate the magnitude and speed of leaching, and a pesticide should not be affected by other processes while it is adsorbed to the humic-argillic complex. Besides adsorption, the leaching of pesticides in soils also depends on the amount of water moving through the soil (Si et al. 2009). For example, Tiktak et al. (2004) demonstrated that pesticide leaching generally increased with increasing annual rainfall amount. However, areas with a high temporal variability of rainfall were also found to be associated with greater leaching (Larson et al. 1999).

Cyantraniliprole is a new insecticide that is currently being assessed for use in the EU. It was introduced in 2008. Therefore, scientific papers on the behaviour of cyantraniliprole in the environment are not yet available, with the exception of reports from regulatory agencies in different countries.

The dissociation constant (pKa = 8.8 at 20°C) indicates that the behaviour of the substance in the environment may be affected by pH. It is known that degradation of cyantraniliprole in aerobic soil can be classified as readily degradable (DT_{50} < 20 d at 20°C and pF2) to slightly degra-

dable (DT_{50} 60-180 d). DT_{90} values ranged from 66.2-376 d. Dissipation of cyantraniliprole was investigated in soil dissipation studies under field conditions carried out at ten different locations in Europe, Canada, and the United States. The DT_{50} values at the ten field sites ranged from 9.7 to 44 days (geomean = 17.2 d), whereas the DT_{90} values ranged much more widely, from 55.5-333 d (geomean = 157 d). The longest field DT_{90}s (246 to 333 d) were in cold locations in New York, Missouri, Manitoba and Germany, where soil was frozen for some portion of the study durations (APVMA 2013).

Cyantraniliprole is expected to be mobile in most soils based on low adsorption coefficients. The leaching potential also increases with increased persistence. For cyantraniliprole, the persistence is variable depending on soil conditions. For the most conservative persistence and mobility parameters, the groundwater ubiquity score (GUS) of cyantraniliprole indicates that this compound is a probable leacher. Under field conditions, it was generally found in the upper soil layer although small amounts of cyantraniliprole moved to a depth of 15 cm below soil surface (PRD 2013). In Arizona (USA) cyantraniliprole was included in Groundwater Protection List (ADEQ 2015). When a pesticide Minecto Pro containing cyantraniprole is applied in Nassau and Suffolk counties of New York State, the label indicates "one of the active ingredients in this product, cyantraniliprole, has properties and characteristics associated with chemicals detected in groundwater. Cyantraniliprole may leach into groundwater if used in areas where soils are permeable, particularly where the water table is shallow" (MinectoPro 2018). According to the conclusions of the review report (The European Parliament 2009), on both the antranilic insecticide cyantraniliprole and chlorantraniliprole indicated that all Member States shall pay particular attention to the protection of groundwater, when the compounds are applied in regions with vulnerable soil and/or climatic conditions.

The mobility of two relatively new antranilic diamide insecticides, cyantraniliprole and chlorantraniliprole in soil was examined by means of disturbed columns loaded with a typical semiarid Mediterranean soil (Calcaric fluvisol) under laboratory conditions (Vela et al. 2017). Both insecticides appeared in leachates, with 52% cyantraniliprole and 41% cholantraniliprole of the initial mass added present. Based on the recieved DT50 and K_{oc}, the calculated Groundwater Ubiquity Score (GUS) index was higher than 5 for both, indicating they have the potential to leach. In other experiments the columns with undisturbed soil monoliths were used to study cyantraniliprole movement (Shein et al. 2017). There were monoliths with a height of 30 cm and a diameter 10 cm taken from two

soils: medium loamy agrosoddy-podzolic soil (organic carbon content (OC) = 1.1%) and light loamy silty alluvial gray-humus soil (OC = 2.1%). The experimental study of cyantraniliprole migration in the columns has shown that the content of the pesticide in the filtrate from agrosoddy-podzolic soil significantly increases with time, while its content in the filtrate from alluvial grey-humus soil is insignificant, despite the rather high mobility of the substance. Differences in organic matter contents explain the differences in the migration of cyantraniliprole in soils: the organic matter content in the alluvial soil is higher than in the soddy-podzolic soil. The cyantraniliprole content in alluvial grey-humus soil decreases down the column. The pesticide content in the top layers of this soil column is considerably greater when compared to the soddy-podzolic soil, which is directly related to its adsorption.

According to the available data, it can be assumed that under the conditions of the Moscow region, cyantraniliprole may persist in the soil for a long time and migrate to the deep layers (DT_{50} in the sod-podzolic soil for 50 days (Kolupaeva et al. 2016), Koc – 332 ml g^{1} – for upper 20–cm layer, 67 ml g^{1} – for the 20-40 cm layer (Kolupaeva V.N. and Nyukhina I.V., unpuplished data).

Most countries have legal regulations governing the use of pesticides. A number of criteria for the level of pesticides in water have been adopted. For example, Directive 98/83 / EC of the Council of the European Union of November 3, 1998 limits the concentration of individual pesticides in drinking water to a level of 0.1 µg L^{1} and for total pesticide content of 0.5 µg L^{1} (Council Directive 1998). In Russia, for assessing the quality of water, a system of maximum permissible concentrations – Russian water toxicological human index for each individual pesticide is used. For cyantraniliprole it is 0.1 mg L^{1} – 1000 times more than drinking water levels in the EU. Moreover, in order to assess the ecological risks of pesticides in Russia, experimental data obtained in the EU are used. This is an incorrect approach, because Russia is north of most of the EU countries, the climate is colder, and the amount of precipitation is much higher than in Europe, which leads to a higher risk of migration of pesticides to groundwater (Steffens et al. 2013; Kolupaeva and Gorbatov 2015). This is also facilitated by the migration of pesticides with preferred water flows through macropores and cracks (Rosenboom et al. 2005; Shein et al. 2018). The assessment of the risk of pesticides leaching into groundwater during their registration is mainly based on the results of laboratory studies of the sorption and migration of pesticides, data from field small-scale experiments, as well as the results of modeling. However, these types of studies do not provide an

objective characterization of pesticide leaching in real ones. Outdoor lysimeters were developed to avoid or at least decrease the differences obtained between laboratory and field conditions (Kordel and Klein 2006). Lysimetric studies allow us to study the behavior of toxicants in the soil under conditions as close to natural as possible and to obtain information about their concentrations in the groundwater flow, which, to a certain extent, makes it possible to fill in the missing monitoring data.

The purpose of the research was to study transport of the insecticide cyantraniliprole in and down the soil profile to assess its leaching potential.

2 Methods

2.1 Cyantraniliprole

Cyantraniliprole is an active substance (AS) with insecticidal activity for a wide range of crops. It is an effective remedy against many pests (whitefly, thrips, aphids and fruit fly). The structural formula of cyantraniliprole is shown in Figure 1. Cyantraniliprole is used as an AS of the following preparations: Cyazypyr, Benevia, Exirel. Cyantraniliprole is moderately persistent (DT_{50} = 34.4 days) medium-mobility (Koc = 241) substance (EFSA 2014). In the laboratory experiment (at a temperature of 20°C and soil moisture content of 60% of ultimate field water capacity) in the sod-podzolic soil of the Moscow Region, the cyantraniliprole DT_{50} period was 49.9 days (Kolupaeva et al. 2016).

Cyantraniliprole is practically a non-toxic substance for mammals and birds, and slightly toxic for earthworms. However, it is a toxic substance for all tested species of hydrobionts: slightly toxic to fish and extremely toxic to daphnia and algae. In addition, cyantraniliprole is extremely toxic to bees (Table 1).

The experiment was carried out on the lysimeters of the Soil Research Station of the MSU from June 2015 to December 2018 (Figure 2).
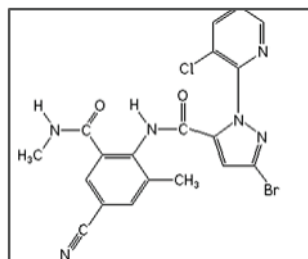

Figure 1: Structure diagram of cyantraniliprole

Table 1: Physical, chemical and ecotoxicological properties of cyantraniliprole (PPDB 2019)

Solubility in water (mg L^{-1})	14.2
Octanol-water partition coefficient, Log P	2.0
pKa	8.8
Vapour pressure (mPa)	5.133x10^{-15}
DT 50, days	34.4
Koc, l/kg	241
Acute oral toxicity (mammals), LD$_{50}$ (mg kg^{-1})	>5000
Acute toxicity (birds), LD$_{50}$ (mg kg^{-1})	>2250
Acute toxicity (fish), LC$_{50}$ (mg kg^{-1})	>12.6
Acute toxicity (aquatic invertebrates), EC$_{50}$ (mg L^{-1})	0.020
Acute toxicity (aquatic plants), EC$_{50}$ (mg L^{-1})	>12.1
Contact acute (honeybees), LD$_{50}$ (µg bee^{-1})	0.0934
Acute toxicity (earthworm), LC$_{50}$ (mg kg^{-1})	>945

The lysimeters of the soil research station of Lomonosov Moscow State University (MSU)

The lysimeter station was built in 1960 and modernized in 2015. Each of the lysimeters has an area of 8 m^2 and a depth of 175 cm. Two lysimeters were used for the study. The soil of the lysimeter is soddy-podzolic silt loam with the normal structure of the soil profile. The properties of soil are shown in Table 2 (Karpachevsky and Umarova 2003; Shein et al. 2009).
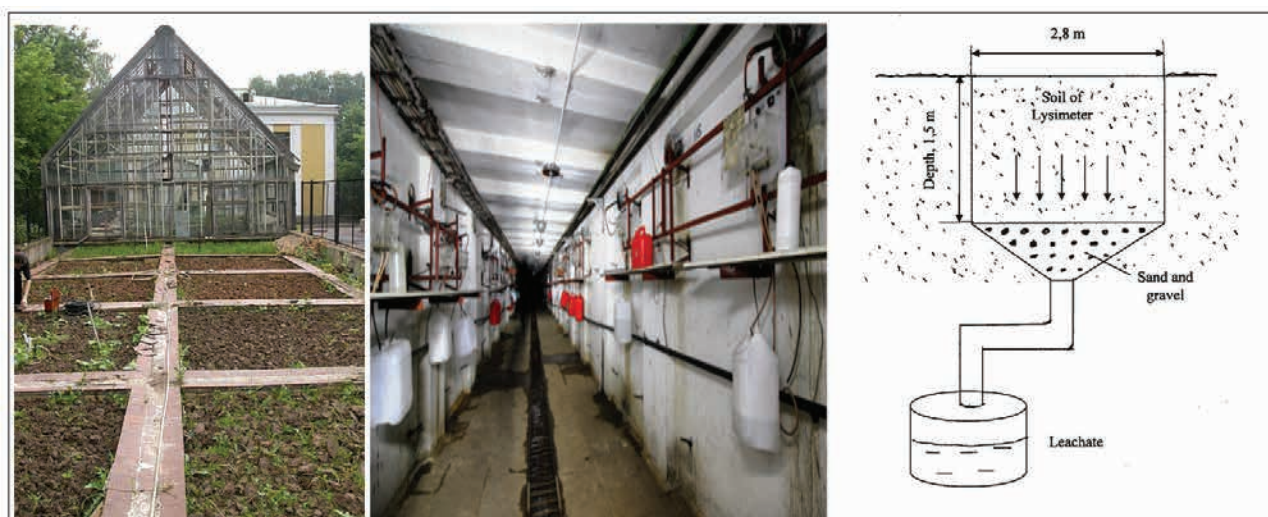
Table 2: Some physical and chemical properties of the soil

Horizon depth, cm	Sand (>50 µm) / Silt (2–50 µm) / Clay (<2 µm), %	ρ, g cm^{-3}	C, %	pH$_{H2O}$	K$_{filtration}$, m day^{-1}
0-20	5.3/89.7/5.0	1.28	2.18	5.81	0.70
20-35	4.1/88.8/7.1	1.45	0.77	5.73	0.54
35-60	5.9/89.8/4.3	1.49	0.65	5.73	0.36
60-120	7.6/86.2/6.2	1.50	0.60	4.50	0.18
120-150	18.4/75.5/6.1	1.56	0.81	4.50	0.08

2.2 Lysimeter experiment

Pesticides were applied into the lysimeters using a knapsack sprayer. Cyantraniliprole was used at the recommended rate (0.4 kg ha^{-1}) in lysimeter 6 and tenfold rate (4.0 kg ha^{-1}) in lysimeter 5 in June 2015 and then in June 2016. For use in the recommended rate, the amount of the pesticide formulation, required for treatment and containing 0.32 g of cyantraniliprole, was dissolved in 2 L of water and applied by spraying. For use at a tenfold rate, the required amount of the formulation, containing 3.2 ml of cyanthraniliprol, was dissolved in 0.2 L of acetone, then 2 L of water was added and sprayed. It should be noted that, despite the fact that the pesticide formulation was dissolved initially in acetone, and only then water was added, a certain amount of undissolved formulation remained in the sprayer.

Water leachate from the lysimeter was collected at least one time per month. Soil samples were collected every 5 cm until a depth of 50 cm in spring and autumn.

Figure 2: Lysimeters of MSU

Samples of soil were taken with a borer (making up a mixed sample of 5 individual ones).

2.3 Cyantraniliprole analysis

The method of cyantraniliprole analysis was based on the extraction of cyanthraniliprole from soil samples with acetonitrile, purification of the extracts with hexane, then on solid-phase extraction (SPE) cartridges C and C_8 with determination of cyanthraniprole by high performance liquid chromatography (HPLC) using a UV detector at 265 nm. The extraction of cyantraniliprole from water samples was carried out with hexane, followed by purification on the cartridge C_8. Detection limits of the analytical method were 0.5 µg L^1 and 2.5 µg kg^1 for water and soil respectively.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and Discussion

The mean annual air temperature in the years of the experiment was close to the mean long-term values (Table 3).

The amount of precipitation in 2016 exceeded the mean annual value by 90 mm, and in the summer – by 121 mm. In 2017, the total annual precipitation was higher than the mean annual value by 223 mm, and during the summer – by 104 mm. In 2015, the mean precipitation values for the year and during the seasons were close to the mean annual rates. It is especially worth noting that despite the fact that the total amount of precipitation coincides with the long-term one, in the summer of 2015 severe showers with a daily rainfall exceeding a quarter of the monthly norm were observed. For 14 days after treatment, 76.3 mm of precipitation fell, for 30 days – 101.6 mm. During the whole experiment (3.5 years) a washing water regime was observed. The volume of monthly water per-

colation ranged from 20 to 120 mm. Differences between lysimeters in the values of water volume were within 10%.

If compared with EU conditions, see Table 4, the conditions of the Russian Federation are much colder and rainy than most of Europe, and the MSU lysimetric station falls into the category of extreme worst, or worst case, according to the classification of the FOCUS group that develops standard scenarios for pesticide migration models.

The soil temperature in the upper layers changed sinusoidally after the air temperature and rarely rose above 20°C even in the summer months, on average remaining at 17°C from June to August (Figure 3).
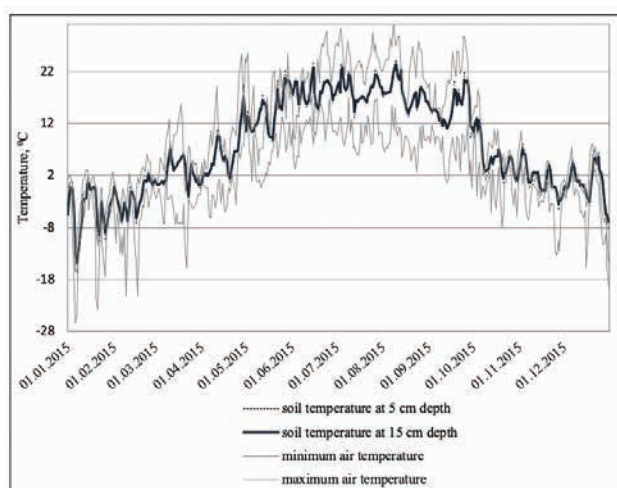
Figure 3: Air and soil temperature in 2015

Table 4: Climatic temperature and rainfall classes for differentiating agricultural scenarios (FOCUS 2015)

Mean autumn & spring temperature, °C	Mean annual rainfall, mm	Assessment of scenarios
<6.6	>1000	Extreme worst case
6.6 – 10	800 – 1000	Worst case
10 – 12.5	600 – 800	Intermediate case
>12.5	< 600	Best case

Table 3: Mean annual and seasonal air temperature and precipitation (meteostation of Moscow State University)

Period	Mean air temperature , °C				Mean precipitation , mm			
	1997-2014	2015	2016	2017	1997-2014	2015	2016	2017
Whole year	5.8	7.1	6.5	6.5	732	761	822	955
Spring	6.0	7.4	7.8	6.7	136	177	146	220
Summer	18.3	17.9	19.5	17.6	228	228	349	335
Autumn	5.6	6.3	4.4	6.2	197	150	200	179
Winter	-6.9	-3.5	-5.7	-4.3	170	204	125	219

Thus, the decomposition of cyantraniliprole in the lysimeter's soil of MSU was slower even in the warm period compared to the mean values from European studies. Despite the fact that cyantraniliprole is medium-persistent a year after the second treatment (in May 2017) a significant amount of pesticide (about 35% of that applied) remained in the soil. The pesticide was distributed to a depth of 30 cm, with a maximum concentration in the upper 5 cm layer. The maximum depth of migration of cyantraniliprole in the soil profile was 35 cm in October 2015 (the year with close to the mean for annual precipitation) and 40 cm in October 2016 (rainy year) (Figure 4). It is known that the degradation rate of cyantraniliprole depends on soil pH [APWMA 2013; EFSA 2014]. The soil of the lysimeter has a pH of 5.8, this can explain the long-term persistence of cyantraniliprole in the soil under conditions of the Moscow region.

Cyantraniliprole was found in the lysimetric leachate two weeks after its first application in both lysimeters (with the recommended – 0.4 kg ha^{-1} and tenfold – 4 kg ha^{-1} rate), the pesticide concentrations were 0.8 and 1.5 µg L^{-1} respectively (Figure 5). This was facilitated by the precipitation from several showers. This indicates a high mobility of the pesticide in this soil and climate conditions and a large influence of rainfall on the rapid movement of the pesticide beyond the soil profile. It must be said that the period when precipitation falls after the treatment is the most dangerous from the point of view of the migration of pesticides. This is because a large amount of applied pesticide is still in the soil, it is still poorly sorbed within soil particles, and at this time it is rapidly leached in the deep layers of the soil. The data obtained are in good agreement with the results of other authors. Fine-textured soils containing clay minerals and organic matter may act as sorption filters against pesticide leaching. However, this filter is often perforated by soil structural elements such as biopores (earthworm burrows, root channels) or mechanical shrinkage patterns (cracks or fractures). Through these
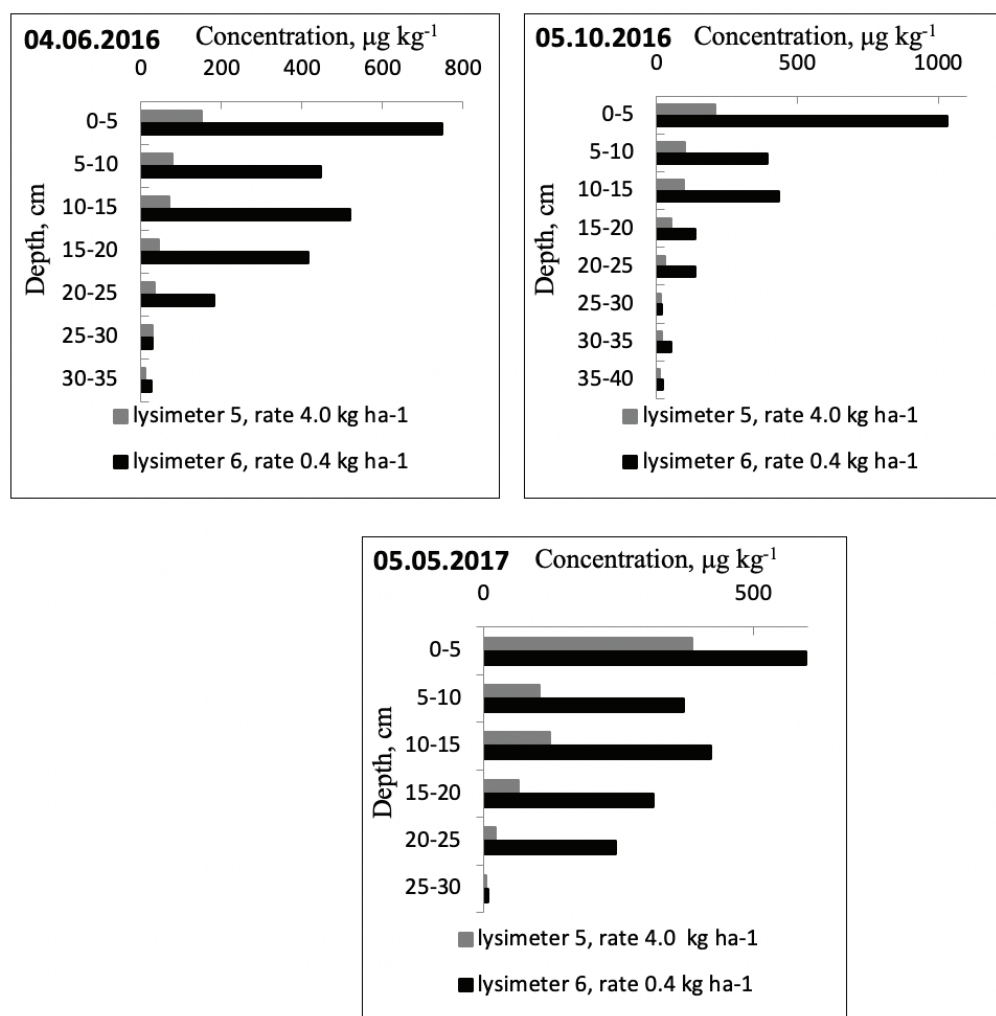

Figure 4: Migration of cyantraniliprole in the soil profile

preferential paths, up to a few percent of the surface-applied pesticide may be channeled below the root zone, particularly during rainstorm events soon after pesticide application (Flury 1996; Kladivko et al. 2001).

Cyantraniliprole was detected in most of the water samples analyzed (Table 5). The highest percentage of detection in the lysimeter with the recommended dose was in 2016 and 2017 – 90 and 82%, respectively, and in the lysimeter with a tenfold dose in 2016-2018 – 82, 91 and 100%, respectively. Thus, we assume that in 2015 the pesticide moved with preferential flows, while in 2016 the border of its movement reached the bottom of the lysimeter, therefore it occurred in all samples. It was also noted that peak concentrations were observed a few days after heavy rain, whereas during heavy rain sometimes a pesticide was not detected in the leachate, as the soil solution was diluted.

The maximum concentrations of cyantraniliprole in the leachate were 12.5 and 2.6 µg L^{-1} in lysimeters with tenfold and recommended dose respectively (Table 6). Concentrations close to the maximum were observed in the lysimeter with a tenfold dose in 2015, 2016 and 2017, in the lysimeter with the recommended dose in 2016 and 2017. In 2017 and 2018, one year and two years after the last treatment, cyantraniprole was detected in water samples in both lysimeters. The 80% percentile of all concentrations was 2.4 µg L^{-1} for a lysimeter with a tenfold dose and 0.9 µg L^{-1} in the lysimeter with the recommended
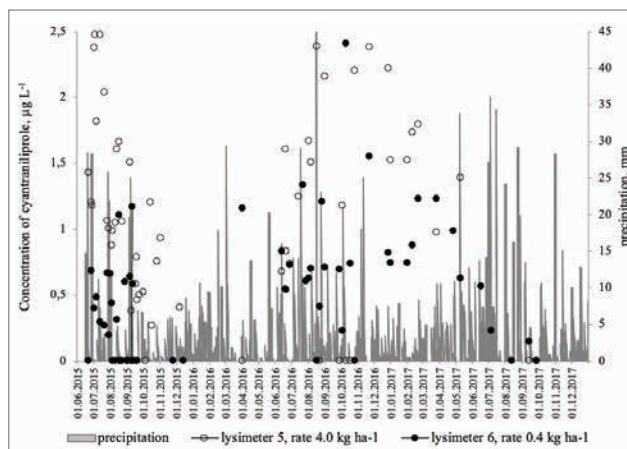

Figure 5: Precipitation and cyantraniliprole concentration in leachate

dose, mean values – 1.7 and 0.6 µg L^{-1}, respectively. The results of the study showed high mobility of cyantraniprole and its ability to migrate beyond the soil profile in the conditions of Moscow region. The reason for this can also be considered due to high persistence of the pesticide in the soil. This is also consistent with the results of the assessment by EFSA (EFSA 2014) and Health Canada Pest Management Regulatory Agency (PRD 2013) that a risk of groundwater contamination with cyantraniliprole cannot be excluded for applications on soils with pH < 6. The detected concentrations in leachate exceeded the permissible limit for drinking water, adopted in the EU, but were significantly lower than the human index used in the

Table 5: Detection of cyantraniliprole in lysimetric leachate

Lysimeter	Year	Total number of samples	Number of samples with pesticide detected	Detection frequency, %
Tenfold rate	2015	33	29	88
Recommended rate		32	13	39
Tenfold rate	2016	22	18	82
Recommended rate		20	18	90
Tenfold rate	2017	11	10	91
Recommended rate		11	9	82
Tenfold rate	2018	5	5	100
Recommended rate		5	1	20

Table 6: Cyantraniliprole concentration in leachate

Lysimeter	Maximum, µg L^{-1}	Mean, µg L^{-1}	Median, µg L^{-1}	80% percentile, µg L^{-1}	Human toxic index, µg L^{-1}
Tenfold rate	12.5	1.7	1.5	2.4	100
Recommended rate	2.6	0.6	0.6	0.9	100

Russian Federation. This indicates the imperfection of the Russian national method of risk assessment for groundwater, based only on human indices.

4 Conclusions

In conditions of low temperatures, high amounts of precipitation and leaching water regime in soil inherent in Moscow Region, cyantraniliprole migrated beyond the soil profile throughout the entire experiment (3.5 years). In the initial period after application, the movement of the pesticide occurred by means of the mechanism of rapid movement through the macropores, which is observed in fractured structured soils. The pesticide leaching continued for 1.5 years after the last application. The maximum concentrations of cyantraniliprole in water samples were 12.5 and 2.6 µg L^1 in lysimeters with tenfold and recommended dose, respectively. Thus, the results of the experiment indicate that in the conditions of the Moscow Region there is a danger of groundwater pollution with cyantraniliprole.

Acknowledgments

Conflict of interest: Authors declare no conflict of interest.

References

[1]   ADEQ Pesticide Annual report, 2015, 78

[2]   Akesson M., Sparrenbom C.J., Dahlqvist P., Fraser S.J., On the scope and management of pesticide pollution of Swedish groundwater resources: The Scanian example, Ambio, 2015, 44(3), 226–238

[3]   Arias-Estévez M., López-Periago E., Martínez-Carballo E., Simal-Gándara J., Mejuto J.C., García-Río L., The mobility and degradation of pesticides in soils and the pollution of groundwater resources, Agriculture, Ecosystems & Environment, 2008, 123, 247-260

[4]   Coming to terms with terminology. Committee on World Food Security (CFS) Thirty-ninth Session. Rome, Italy, 15-20 October 2012, http://www.fao.org/docrep/meeting/026/md776e.pdf

[5]   Conclusion on the peer review of the pesticide risk assessment of the active substance cyantraniliprole, EFSA J., 2014, 12, 9

[6]   Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. Official Journal of the European Communities, *330, 05/12/1998, 0032 – 0054*

[7]   Estes T.L., Pai N., Winchell M.F., Comparison of predicted pesticide concentrations in groundwater from SCI-GROW and PRZM-GW models with historical monitoring data, Pest Manag Sci., 2016, 72, 1187–1201

[8]   Fava L., Orrù M.A., Scardala S., Alonzo E., Fardella M., Strumia C. et al., Pesticides and their metabolites in selected Italian groundwater and surface water used for drinking, Ann Ist super Sanità, 2010, 46(3), 309-316

[9]   Flury M., Experimental Evidence of Transport of Pesticides through Field Soils-A Review, Journal of Environmental Quality, 1996, 25, 25-45

[10] Ganiev M. M., Nedorezkov V. D., Himicheskie sredstva zashity rastenij, Moskva, Kolos, 2006, 248 (in Russian)

[11] Generic guidance for FOCUS surface water Scenarios, version 1.4, 2015, 105

[12] Gurdak J.J., Groundwater vulnerability. In: Slamian S, ed. Handbook of Engineering Hydrology, Environmental Hydrology and Water Management. Boca Raton, FL: CRC-Press, 2014, 145-162

[13] Haarstad K., Ludvigsen G.H., Ten Years of Pesticide Monitoring in Norwegian Ground Water , Ground Water Monitoring & Remediation, 2007, 27(3), 75–89

[14] Imran A. and Jain S.K., Groundwater contamination and health hazards by some of the most commonly used pesticides, Current Science, 1998, 25(10), 1011-1014

[15] Karpachevsky L.O., Umarova A. B., Bol'shie lizimetry Moskovskogo Gosudarstvennogo Universiteta, Agrokhim Vestn, 2003, 2, 5–6 (in Russian)

[16] Kladivko E.J., Brown, L.C., Baker, J.L., Pesticide transport to subsurface tile drains in humid regions of North America, Crit. Rev. Environ. Sci. Technol., 2001, 31(1), 1 – 62

[17] Klimin I. I. O prodovol'stvennoj bezopasnosti Rossii (1991–2012), SPb, Izd-vo Politekhn. un-ta, 2014, 272 (in Russian)

[18] Kolupaeva V., Gorbatov V. Developing groundwater scenarios for Russia and comparison of their vulnerability with European groundwater scenarios, Proceeding of XV Symposium in Pesticide Chemistry, 2015, 133

[19] Kolupaeva V.N., Gorbatov V.S., Nyukhina I.V., Opredelenie parametrov razlozheniya ciantraniliprola v dernovo-podzolistoj pochve v laboratornyh, Vestn. NGAU, 2016, 2(39), 82-91 (in Russian)

[20] Kolupaeva V.N., Nyukhina I.V., The study of cyantraniliprole sorption in the soils of the Russian Federation (Unpuplished data)

[21] Kordel W., Klein M., Prediction of leaching and groundwater contamination by pesticides, Pure and Applied Chemistry, 2006, 78, 1081-1090

[22] Laganà A., Bacaloni A., De Leva I., Faberi A., Fago G., Marino A., Occurrence and determination of herbicides and theirmajor transformation products in environmental waters, Anal Chim Acta, 2002, 462, 187–198

[23] Lapworth D. J., Gooddy D. C., Source and persistence of pesticides in a semi-confined chalk aquifer of southeast England, Environ Pollut, 2006, 144, 1031–1044

[24] Larson S., Gilliom R., Capel P., Pesticides in streams of the United States: initial results from the national water-quality assessment program, Tech. rep., United States Geological Survey, Water Resources Investigations Report, 1999, 98–4222

[25] MinectoPro https://assets.greenbook.net/13-03-24-10-08-2018-100-1592_MinectoPro_L1B_0718_Label.pdf

[26] Post-release of the conference "Pesticides 2016", CREON Energy. http://www.creonenergy.ru/consulting/detailConf.php?ID=123760 (in Russian)

[27] Proposed Registration Decision for cyantraniliprole – PRD2013-09, Pest Management Regulatory Agency Health Canada, 2013, 215, healthcanada.gc.ca/pmra

[28] Public Release Summary on the Evaluation of the New Active Constituent cyantraniliprole in the Product DuPont Exirel Insecticide, APVMA Product Number 64103, 2013, 56, www.apvma.gov.au

[29] Rodríguez-Cruz M.S., Sánchez-Martín M.J., Andrades M.S., Sánchez-Camazano M., Modification of clay barriers with a cationic surfactant to improve the retention of pesticides in soils, Journal of Hazardous Materials, 2009, 139, 363-372

[30] Reichenberger S., Bach M., Skitschak A., Frede H.G., Mitigation strategies to reduce pesticide inputs into the groundand surface water and their effectiveness, A review, Science of the Total Environment, 2007, 384, 1-35

[31] Rosenbom A., Ernstsen V., Jensen K.H., Refsgaard J.C., Sonnenborg T.O., Larsen F., Preferential flow and transport in variably saturated fractured media, Kgs. Lyngby: DTU Environment, 2005, 21

[32] Shaw M.S., Silburn D.S., Lenahan M., Harris M., Pesticides in groundwater in the Lower Burdekin floodplain, Department of Environment and Resource Management, Brisbane, Queensland Government, The State of Queensland (Department of Environment and Resource Management), 2012, 25

[33] Shein E. V., Kokoreva A.A., Gorbatov V.S., Umarova A.B., Kolupaeva V.N., Perevertin K.A., Sensitivity Assessment, Adjustment, and Comparison of Mathematical Models Describing the Migration of Pesticides in Soil Using Lysimetric, Eurasian Soil Science, 2009, 42, 7, 769-777

[34] Shein E. V., Belik A.A., Kokoreva A.A., Kolupaeva V.N., Pletenev P.A., Prediction of Pesticide Migration in Soils: the Role of Experimental Soil Control, Moscow University Soil Science Bulletin, 2017, 72(4), 185-190

[35] Shein E.V., Belik A.A., Kokoreva A.A., Kolupaeva V.N., Quantitative estimate of the heterogeneity of solute fluxes using the dispersivity length for mathematical models of pesticide migration in soils, Eurasian Soil Science, 2018, 51(7), 797-802

[36] Si Y., Wang M., Tian C.,, Zhou J., Zhou D., Effect of charcoal amendment on adsorption, leaching and degradation of isoproturon in soils, Journal of Contaminant Hydrology, 2011, 123, 75–81

[37] The European Parliament and the Council of the European Union (2009) Regulation (EC) No 1107/2009 of The European Parliament and the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC The Official Journal of the European Union, L 309/1–50

[38] Tiktak A., de Nie D.S., Piñeros Garcet J., Jones A.,Vanclooster M., Assessment of the pesticide leaching risk at the pan-European level: the EuroPEARL approach, J. Hydrol., 2004, 289, 222–238

[39] Steffens K., Larsbo M., Moeys J., Kjellström E., Jarvis N., Lewan E, Predicting pesticide leaching under climate change: Importance of model structure and parameter uncertainty, Agr. Ecosyst. Environ, 2013, 172, 24–34

[40] Vela N., Pérez-Lucas G., Navarro M. J., Garrido I., Fenoll J., Navarro S., Evaluation of the Leaching Potential of Anthranilamide Insecticides Through the Soil, Bull. Environ. Contam. Toxicol., 2017, 99(4), 465-469