Risk assessment of pesticide leaching into groundwater based on the results of a lysimetric experiment

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Abstract. Mobility of cyantraniliprole, paclobutrazol and metribuzin was investigated on large lysimeters of the Experimental Soil Station of Moscow State University. Pesticides were applied in recommended and tenfold rates for cyantraniliprole and paclobuyrazol and recommended and eightfold rates for metribuzin. All three pesticides were detected in leachate. Cyantraniliprole was detected in most water samples analyzed. The maximum concentrations of cyantraniliprole in the leachate were 2.6 and 12.5 µg L⁻¹ in lysimeters with recommended and tenfold rates, respectively. Paclobutrazol was found 3 and 7 times during the year after application in the lysimeter with recommended and increased rates in concentrations up to 26 µg L⁻¹. Used in accordance with the regulation, metribuzin in leachate was detected once, in eightfold rate - 73% of water samples; maximum concentration was 180 µg L⁻¹. The migration risk into groundwater of all three studied pesticides is assessed as high, risk for people as low, risk for aquatic organisms as high. Risk and danger assessment based on simulation with model PEARL and mobility indexes showed high agreement with the assessment according to the experiment.

1. Introduction

The presence of pesticide residues in groundwater is a serious threat to the health of consumers of drinking water. In Russia, this problem mainly concerns rural settlements, where 87% of the total water supply is water from underground sources. There is a growing concern about the contamination of ground and surface water with pesticides all over the world [1-8]. For example, in Denmark, pesticides are found in 5% of surveyed wells (9). Weather conditions in most regions of the Russian Federation (low temperatures, a long frosty period, large amounts of precipitation, leaching or periodically leaching water regime, structured soils) promote the migration of pesticides beyond the soil profile [10, 11]. Pesticide monitoring conducted by Federal Service for Hydrometeorology and environmental monitoring does not include groundwater investigation. Since the monitoring of the pesticide content in groundwater is not conducted in the Russian Federation, there is no information about the most dangerous pesticides and the most vulnerable regions in terms of groundwater pollution in the Russian Federation.

An environmental impact estimation of a pesticide is a part of the registration process and includes an assessment of its hazard and risk. Terms “hazard” and “risk” are frequently used as synonyms. However, the conceptual meaning of these words is very different. A definition of the term “hazard” was given by an expert group of the OECD [12]: the hazard of a chemical is a function of two broad
considerations, the potential of the chemical to harm biological systems (or damage other systems) and its potential for exposure such that harm or damage can occur. On the contrary, the term “risk” is more complex because it also includes the quantitative estimation of the probability of an adverse effect on a biological target (humans/environment) exposed to a chemical substance. Thus, it could be said that risk assessment goes one step beyond hazard evaluation. Ecological risk assessment “evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors” [13]. The term “adverse ecological effects” includes all biological and nonbiological environmental changes that society perceives as undesirable.

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 objective characteristics of pesticide leaching under actual conditions. Laboratory studies do not consider the variability of weather conditions, and the results of a mathematical prediction largely depend on the type of model selected and the amount and quality of experimental support for the model on soil and pesticide properties. In contrast to laboratory and field experiments, lysimetric studies allow, in conditions as close to natural as possible, to study the behavior of toxicants in the soil and to obtain information about their concentrations in percolate, which to some extent allows filling in the missing monitoring data.

The goal of this work was to study the migration of insecticide cyantraniprole, systemic triazole plant growth regulator with the fungicidal properties paclobutrazol and selective, systemic triazinones herbicide metribuzin in soddy-podzolic soil in a lysimetric experiment, to assess the risk of these pesticides, using data from a lysimetric experiment. It was also planned to compare the results obtained with the risk assessment with mobility indices and simulation with model PEARL. For the study, two new pesticides were chosen - cyantraniprole and paclobutrazol, which have potential for use and contaminate groundwater via leaching in the Russian Federation [14-17], and metribuzin, which is widely used in our country and is often found in groundwater in other countries [18-23].

2. Methods

2.1. Pesticides
Cyantraniliprole is an active substance (a.s.) with insecticidal activity against many pesticides. Cyantraniliprole persistence varies from low to high (DT$_{50}$ = 8.7-91.9 days), mobility is medium ($K_{oc}$ = 157-367 ml g$^{-1}$) [24]. In the laboratory experiment (at a temperature of 20 °C and soil moisture content of 60% of field water capacity) in the soddy-podzolic soil of the Moscow Region, the cyantraniliprole DT$_{50}$ period was 49.9 days [25]. Paclobutrazol persistence varies from moderate to very high (DT$_{50}$ = 27-618 days), mobility – from high to low ($K_{oc}$ 35-665 ml g$^{-1}$). Metribuzin is unstable (DT$_{50}$ 4.7-12.5 days), mobility varies from very high to moderate ($K_{oc}$ = 3.1-81.5 ml g$^{-1}$) [24].

2.2. Lysimeters
The experiment was carried out on large lysimeters of the Experimental Soil Station of Moscow State University (55.71 N, 37.52 E), from June 2015 to December 2018. Experimental Soil Station was built in 1960. Each of the lysimeters has an area of 8 m$^2$ and a depth of 175 cm. The soil of the lysimeter is a model loamy soddy-podzolic soil with the typical structure of the soil profile. The properties of the soil are in table 1 [26]. Soil particle-size distributions (PSD) were analyzed by pipette-method after dispersion with sodium-pyrophosphate. Soil density ($\rho$) was determined by drilling method. Soil organic matter (SOM) was determined by dry combustion an AN-7529M express analyzer [27].

2.3. Lysimeter experiment
Pesticides were applied into the lysimeter using a knapsack sprayer. Cyantraniliprole was used at the recommended (0.4 kg ha$^{-1}$) and tenfold rates twice in June 2015 and then in June 2016; paclobutrazol – at the recommended (0.125 kg ha$^{-1}$) and tenfold rates in June 2015; metribuzin - at recommended
(0.98 kg ha\(^{-1}\)) and eightfold (7.7 kg ha\(^{-1}\)) rates. Water leachate from lysimeter was collected at least one time per month. Soil samples were collected every 5 cm till depth of 50 cm in spring and autumn. Samples of soil were taken with boer (making up a mixed sample of 5 individual ones).

| Horizon depth, cm | Sand (>50 μm) / Silt (2–50 μm) / Clay (<2 μm), % | ρs, kg m\(^{-3}\) | SOM, % | pH\(_{H_2O}\) | Ks, m day\(^{-1}\) |
|-------------------|---------------------------------|-----------------|--------|-------------|----------------|
| P 0-20            | 5.3/89.7/5.0                    | 1280            | 2.18   | 5.18        | 0.70           |
| EL 20-35          | 4.1/88.8/7.1                    | 1450            | 0.77   | 5.73        | 0.54           |
| B1 35-60          | 5.9/89.8/4.3                    | 1490            | 0.65   | 5.73        | 0.36           |
| B2 60-120         | 7.6/86.2/6.2                    | 1500            | 0.60   | 4.50        | 0.18           |
| B3 120-150        | 18.4/75.5/6.1                   | 1560            | 0.81   | 4.50        | 0.08           |

2.4. Pesticide analysis
Analysis of pesticides in water and soil was carried out in accordance with the methodological guidelines approved in the Russian Federation [28-30].

2.5. Migration hazard indexes
An important parameter is the adsorption coefficient which is defined as the ratio between the concentration of the substance in the soil and the concentration of the substance in the aqueous phase at adsorption equilibrium. The adsorption coefficient normalized to the organic carbon content of the soil \(K_{oc}\) is a useful indicator of the binding capacity of a chemical on organic matter of the soil and allows comparisons to be made between different chemicals. Other useful parameter for predicting environmental fate is the Groundwater Ubiquity Score, or GUS, which is derived from the half-life and the sorption coefficient [31]:

\[
GUS = \log(DT_{50}) \cdot (4 - \log(K_{oc}))
\]

2.6. Model PEARL
The PEARL model [32, 33] describes the water flow by the Darcy law and the Richards’ equation and the transport of pesticides in the soil by the convection – dispersion - diffusion equation. Calculations of pesticide concentrations in soils were carried out using the PEARL model, which is used when registering pesticides in the EU and the Russian Federation, and using standard scenarios for Russian regions [10].

2.7. Risk assessment for aquatic organism
For risk assessment, acute toxicity indicators of pesticides - LC\(_{50}\) and EC\(_{50}\) (96-hour tests for fish and 48-hour tests for daphnia, respectively) are used, for chronic toxicity - NOEC (14-21 daily tests) for the same aquatic organisms, which are usually given in PPDB [24]. An indicator of the negative impact of a pesticide on aquatic organisms is the relationship between toxicity and concentration in water, which characterizes the risk of a pesticide for aquatic organisms - the lower this ratio, the higher the risk: for acute toxicity LC\(_{50}\) (EC\(_{50}\)) / C\(_{gw}\) > 100 - low risk, 10 < LC\(_{50}\) (EC\(_{50}\)) / C\(_{gw}\) ≤ 100 – medium risk, LC\(_{50}\) (EC\(_{50}\)) / C\(_{gw}\) ≤ 10 – high risk; for chronic toxicity NOEC (EC\(_{50}\)) / C\(_{gw}\) > 10 – low risk, 5 < NOEC (EC\(_{50}\)) / C\(_{gw}\) ≤ 10 - medium risk, NOEC (EC\(_{50}\)) / C\(_{gw}\) ≤ 5 - high risk [34].
3. Results and Discussion

The average annual air temperature in the years of the experiment was close to the average long-term values. The amount of precipitation in 2016 exceeded the average annual value by 90 mm (average for the period from 1997 to 2014 is 732 mm), and in the summer by 121 mm (average – 228 mm). In 2017, the total annual precipitation was more than mean annual value on 223 mm, for the summer - on 104 mm. In 2015, the average precipitation values for the year and during the seasons were close to the average annual rates. It is especially worth noting that although 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 water percolation was observed. The volume of monthly water percolation ranged from 20 to 120 mm. Differences between lysimeters in the volume of water percolate were within 10%.

Cyantraniliprole was found in the lysimetric leachate two weeks after first application in both lysimeters (with the recommended and tenfold doses), the pesticide concentrations were 0.8 and 1.5 μg L⁻¹ respectively. This was facilitated by the precipitation of several showers. This indicates a high mobility of the pesticide in this soil climate conditions and a large influence of rainfall on the rapid arrival of the pesticide beyond the soil profile. Cyantraniliprole was detected in most 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, respectively (table 2).

Paclobutrazol in the lysimeter with the recommended application rate in 2015-2016 was found in lysimetric leachate twice – 2 weeks and 2 months after treatment at concentrations 3.0 and 2.1 μg L⁻¹, respectively, in the lysimeter with a tenfold application rate it was detected 7 times for summer, autumn and spring snowmelt in concentrations up to 26 μg L⁻¹. Used in accordance with the regulation, metribuzin in leachate was detected once 1 month after the first application in 2016 at concentration of 14 μg L⁻¹; (detection limit was 1 μg L⁻¹). Applied in eightfold rate, metribuzin was found in 73% of water samples, the maximum concentration was 180 μg L⁻¹, the average – 25 μg L⁻¹.

It can be assumed that higher detection frequency of pesticides in lysimeter with fold rates explained by the detection limits of the analytical methods not always allows determining the pesticide in leachate in the variant with the recommended rates. The higher frequency of cyantraniliprole detection compared to other pesticides, perhaps, apart from the mobility, is also due to the higher capabilities of the method of analysis — for cyantraniliprole the detection limit was 0.5 μg L⁻¹; for paclobutrazol – 2 μg L⁻¹, for metribuzin – 1 μg L⁻¹.

Table 2. Hazard and risk assessment of pesticide migration to groundwater (worst case scenario).

| Pesticide        | Concentration in leachate, μg L⁻¹ | Koc, ml g⁻¹ | GUS (max.) |
|------------------|----------------------------------|-------------|------------|
|                  | lysimeter, (maximum) lysimeter, (average) lysimeter, (80% percentile) Simulation |            |            |
| Cyantraniliprole | 2.6 0.6 1.2                      | 1.9         | 155 2.8    |
| Paclobutrazol    | 2.5 0.4 1.2                      | 16.9(2.6)*  | 35(210) 5.1(3.5) |
| Metribuzin       | 14.0 0.6 0.0                      | 1.1         | 3 3.0      |

- risk / hazard level high; risk / hazard level moderate; risk / hazard level low

* - the values in brackets are for the average Koc

In the risk assessment procedure, concentrations of pesticide in groundwater are compared with criteria for acceptable risk. In the EU, a single pesticide concentration above 0.1 μg L⁻¹ and a mixture of pesticides above 0.5 μg L⁻¹ are considered to be threshold [35]. In the Russian Federation, when registering pesticides, concentrations are compared with hygienic standards in drinking water – human indexes (table 3). Preventing pesticide entering the groundwater is an important task, since groundwater is a vulnerable natural object that is almost incapable of self-purification. Temperature conditions, the
lack of microbiological activity and the weak sorption capacity of grounds leads to the fact that pesticides can be very persistent in the groundwater. The value of hygienic indexes significantly exceeds the threshold value adopted in the EU (for example, for cyantraniliprole and metribuzin it is 1000 times higher). Thus, a risk assessment based only on accounting for human harm cannot protect the groundwater itself as a natural object and aquatic organisms from the adverse effects. Therefore, we proposed to take in the Russian Federation as a threshold concentration of pesticide in groundwater – 1 µg L\(^{-1}\)[36]. This concentration is due to the capabilities of most analytical methods for the determination of pesticides using GC and HPLC, approved in RF. In addition, it is proposed for groundwater to estimate risk for aquatic organisms in accordance with the documents adopted in the EU [34], assuming that groundwater and surface water are closely related natural objects. To assess pesticide risk for groundwater, it is suggested to use a two-step procedure, during which the first stage is to assess the risk of migration by comparing predicted and/or experimentally determined concentrations with a threshold value (1 µg L\(^{-1}\)), and at the second stage to conduct a risk assessment for human and aquatic organisms.

Risk assessment was performed only for the variant with the recommended application rate. Thus, using the proposed threshold concentration – 1 µg L\(^{-1}\) and the maximum concentrations in the leachate, the risk of migration to groundwater for all pesticides we studied was assessed as high, for 80% percentile of concentration – risk to groundwater high for cyantraniliprole and paclobutrazol and low for metribuzin.

Table 3. Concentration in leachate, hygienic and toxicological indexes of pesticides (µg L\(^{-1}\)) and risk assessment for mammals and aquatic organisms (dimensionless quantities) (highlighted in color).

| Pesticide   | Lysimeter, (maximum) | Human indexes | Fish | Aquatic invertebrates | Macrophytes |
|-------------|----------------------|---------------|------|-----------------------|-------------|
|             |                      |               | LC\(_{50}\) | NOEC | EC\(_{50}\) | NOEC | EC\(_{50}\) |
| Cyantraniliprole | 2.6            | 100           | 12600 | -   | 20   | -   | 12100   |
| Paclobutrazol    | 2.5             | -*            | 23600 | 3300 | 3200 | 320 | 8       |
| Metribuzin        | 14.0            | 100           | 4000  | 5600 | 49000| 320 | 8       |

[ ] - risk level high, [ ] - risk level moderate; [ ] - risk level low

In the calculations with PEARL model, the average value of DT\(_{50}\) and the minimum value of K\(_{oc}\) from [24] were used as input parameters, thereby simulating the worst case scenario. The calculated and experimental concentrations (maximum values) were close for cyantraniliprole and metribuzin. For paclobutrazol, predicted concentrations were significantly higher. When calculating with average K\(_{oc}\) (shown in brackets, table 2), the value of the predicted paclobutrazol concentration – 2.6 µg L\(^{-1}\) approached the experimental value.

When assessing the environmental impact of pesticide use, the hazard is initially determined. Classes of various kinds of classifications, for example, the mobility indexes of the active ingredients of the pesticides K\(_{oc}\) and GUS, serve as a measure of the environmental hazard of pesticides. The assessment of these indicators almost coincided with the assessment of the results of the experiment (table 2).

For people, the risk of all three studied pesticides is low (table 3). For the maximum experimental concentrations risk for fish is low; the risk of cyantraniliprole for daphnia is high; risk of paclobutrazol and metribuzin for macrophytes – high (table 3).

4. Conclusions

Lysimetric experiments are an informative tool for assessing the migration risk of pesticides. In the experiment, all studied pesticides migrated beyond the soil profile. The risk of migration of cyantraniliprole, paclobutrazol and metribuzin in the conditions of the Moscow region was assessed as high. For people, the risk of pesticides is low, risk for daphnia and macrophytes is high. However, the procedure for assessing the risk of pesticides for groundwater in the Russian Federation, which relies only on hygienic standards, needs to be revised. In addition, when assessing the risk to people, variability
and uncertainty should be considered using safety factors (“fixed safety factors”), which expand the range of possible risks.

**Acknowledgment**

This study was supported by State Project of Russian Scientific-Research Institute of Phytopathology, by the Russian Scientific Foundation, project no. 16-16-04014 and by RFBR according to the research projects no. 18-34-00801.

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