Russian scenarios for exposure assessment of pesticides to soil organisms

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Abstract. Standardized exposure scenarios are important in pesticide authorization procedures. They are used for the estimation the effects of pesticides to soil organisms. Scenarios are needed for evaluation the pesticide concentrations in soil profile. Nine Russian scenarios for exposure assessment were drafted. These scenarios were implemented as input files to the pesticide fate model PEARL. To evaluate the influence of the soil and weather conditions of the scenarios on the level of pesticide in soil, the model PEARL was used to calculate the annual maximum (at the day of application) and 56-day areic content and concentration of test compounds in the soil during long-term pesticide application (for 20 years). It appears the content differences between the nine regulatory zones were no more than a factor of two. These differences were comparatively small in view of the considerable variations in climate and soil characteristics between these zones. Calculations showed the highest pesticide content was observe in Novosibirsk, and the lowest ones were in Krasnodar and Saratov. Keywords: pesticide, exposure scenarios, soil organisms, pesticide fate model PEARL, soil, risk assessment, concentration of pesticides.

1. Introduction

The using of plant protection products can bring immediate benefits to crop production, although their adverse environmental impacts may affect yields in the medium to long term [1-2]. Pesticide risk assessment at the European Union started in 1991 under Directive 91/414/EEC. However, only in 2002 the specific methods to assess potential risks of pesticides to non-target soil fauna were established [3-5]. In the Russian Federation, the procedure for estimation the risk of pesticides is also carried out in accordance with European standards. To this end, as part of the harmonization of Russian and European approaches to pesticide registration, many OECD guidelines for testing chemicals have been translated into Russian and approved as state standards, for example, guidelines for determining toxicity for earthworms [6-7]. The thresholds used in environmental risk assessment are determined by the relationship between pesticide toxicity endpoints (EC or NOEC values) and their predicted environmental concentrations (PEC) - the so-called toxicity exposure ratio (TER). It should be compared with the trigger value, which is currently 5: if the TER is below the trigger value, this indicates a potential risk to the organisms being assessed. Thus, predicting pesticide concentrations in the environment is an important part of such exposure assessment. In EU numerical pesticide fate model such as MACRO [8], PEARL [9], PELMO [10] and PRZM [11] are used in combination with a limited number of standard scenarios to calculate the PECs. The scenario consists of a set of soil, climate and crop parameters to be used in the simulation. Standardized scenarios are necessary because they increase the similarity of the assessment process by minimizing the impact of
methodology and the person fulfillment the PEC estimation. Nine standard scenarios which represented major agricultural regions were designed to assess risk of pesticide to groundwater in Russia in 2005. The scenarios were revised in 2015 and 2020 [12] to increase their vulnerability to groundwater contamination by chemicals and to develop realistic worst-case scenarios.

The aim of this work was to create standard soil and climatic scenarios for assessing the impact of pesticides on soil organisms based on the previously conducted climatic zoning of agricultural areas in Russia; to compare the standard scenarios with each other on the level of pesticide quantities in soils, using the PEARL model to calculate the maximum (for acute toxicity) and 56-day (for chronic toxicity) their concentration in soils for the case of long-term (26 years) application.

2. Materials and methods

Climatic and soil data. The weather data was taken from the NASA site [13] and from the site of the Russian Research Institute of Hydrometeorological Information [14]. Information on the distribution of soils in Russia and a description of soil profiles were obtained from the Unified State Register of Soil Resources [15].

Model PEARL. Calculations of pesticide content in soil were carried out with PEARL model, which is used when registering pesticides in the EU and Russia [16].

Test-substances. For testing the standard scenarios, four theoretically possible test pesticides and one metabolite with certain properties were used: pesticide A (DT50 = 60 days, Koc = 103 dm$^3$ kg$^{-1}$), pesticide B (DT50 = 20 days, Koc = 17 dm$^3$ kg$^{-1}$), pesticide C (DT50 = 20 days, Koc = 172 dm$^3$ kg$^{-1}$), that forms metabolite C (DT50 = 100 days, Koc=52 dm$^3$ kg$^{-1}$), and pesticide D (DT50 = 20 days, Koc = 60 dm3 kg$^{-1}$). These test pesticides and one metabolite were included in the model by the developers for validation.

PECs calculation. Spring pesticide spray applications without crop in the rate of 1 kg ha$^{-1}$ during 26 years were simulated. A maximum annual and 56-day predicted areic (calculating per unit area) content of pesticides in soil profile were determined. A simulation period of 20 years was used to evaluate pesticide content in soil. In order to appropriately set soil moisture and temperature in the soil profile prior to the simulation period and because pesticide residues may increase more than one year to reach plateau values, a six year “warm-up” period was added to the start of the simulation period. Simulation results during the warm-up period were ignored in the assessment. Twenty maximum annual (or 56-day) content values were ranked from lowest to highest. The seventeenth value (fourth highest) was used to represent the 80% percentile value associated with weather for the specific simulation conditions.

3. Results

The basis for the development of the exposure standard scenarios was the climatic zoning carried out earlier in the development of the groundwater scenarios. Since the scenarios were supposed to be used in the state procedure for registration of pesticides, then for the convenience of planning monitoring and making decisions on regulation, the district of the Russian Federation was chosen as the minimum unit of consideration. For each district, the average climatic (average annual air temperature and total precipitation) and soil (a set of the most common zonal and intrazonal soils) characteristics were determined. After that, all districts were grouped in such way that they formed regions that were relatively homogeneous in these indicators. Thus, nine climatic zones were identified for the elaboration of nine standard scenarios (table 1).

The next stage of our work was a selection of the soils for each zone. For groundwater realistic worst-case was defined as the 90th percentile of PEC values within the agricultural area, which consists of 80% of the soil percentile and 80% of the weather percentile. For this, from a number of zonal and intrazonal regional soils, soils with properties that facilitate the migration of pesticides were selected. These were soils with a low organic matter content and a light particle size distribution. To assess the effects of pesticides on soil organisms, it was decided that for the scenarios the typical and most used agricultural soils of the region should be selected and the realistic worst-case should be
received temporal 80% percentile over period 20 years. The characteristics of the developed standard scenarios are presented in table 1.

### Table 1. Russian scenarios for exposure assessment of pesticides to soil organisms.

| Zones          | Air temperature range, °C | Precipitation range, mm | Soil texture class | pH   | Organic matter, % |
|----------------|---------------------------|-------------------------|-------------------|------|-------------------|
| Moscow         | 2.5 - 5.6                 | 619 - 650               | Silt loam         | 6.0  | 2.7               |
| Kursk          | 6.2 - 8.0                 | 492 - 568               | Silt loam         | 6.5  | 7.6               |
| Saratov        | 5.3 - 7.3                 | 299 - 468               | Silty clay loam   | 7.0  | 3.4               |
| Krasnodar      | 11.2 - 12.6               | 438 - 646               | Silty clay loam   | 7.1  | 5.7               |
| Novosibirsk    | 0.6 - 1.6                 | 369 - 578               | Silty clay loam   | 6.3  | 9.2               |
| Vladivostok    | 1.0 - 8.4                 | 576 - 744               | Silt loam         | 5.7  | 5.6               |
| Pskov          | 2.5 - 4.8                 | 453 - 653               | Sandy clay loam   | 6.4  | 1.4               |
| Nizhniy Novgorod | 3.6 - 5.0            | 423 - 644               | Silt loam         | 5.9  | 3.9               |
| Kurgan         | 1.2 - 2.8                 | 247 - 390               | Silty clay loam   | 7.3  | 11.2              |

To calculate initial (after application) level of pesticide content in soil, we applied physically based model PEARL. This pesticide fate model is used for risk assessment in Russia and EC. To parametrize this model, the soil (particle size distribution, pH, organic matter content, bulk density, van Genuchten parameters for all soil horizons) and climatic (daily global radiation, average vapor pressure, average wind speed, maximum and minimum air temperature, precipitation for 26-year period) characteristics for all scenarios were compiled and implemented as input files to the model. The results of simulation are presented in tables 2 and 3. Calculations for test-substances revealed that the background content (for example, in 56 day) is generally small compared to the maximum pesticide quantity directly after application. It is worth explaining that the peak content (directly after application) consists of two components: an application rate and the background content that remain in soil just before application. Since all test compounds were applied in the same rates, the differences in peak amounts resulted from the differences in residual amounts in the soil at the time of application, that is, due to the differences in persistence of compounds in the soil. For this reason, the content of medium persistent substance A (DT50 = 60 days) and metabolite C (DT50 = 52 days) was higher than the low persistent substances B, C and D (DT50 = 20 days). But substance properties did not have a significant effect on the content in total soil of short-lived substances (as in European studies [17]). Due to this effect, the range of content in total soil for the individual substances was generally small (approximately a factor of two between the lowest and the highest quantity for peak content and a factor of five for 56-day content).

To estimate differences between scenarios the sum of the amounts of test compounds in the soil for each scenario were calculated. In table 2, the scenarios were ranked in growing order of the sums of the peak amount of pesticides in the soil. The maximum quantities were in Novosibirsk, followed by Nizhniy Novgorod, Moscow. The lowest ones were in Krasnodar and Saratov. A sequence of scenarios for increasing the amount of pesticides was slightly different for 56-day sums. For example, since the summer in Nizhny Novgorod is warmer than in Moscow, the amount of pesticide in 56 days after application was lower.

The calculation of the pesticide concentration in soil at time t from the predicted values of the pesticide content was carried out using the following formula (1) (OECD 2002a):

\[
C_t = \frac{(M \cdot 10^6 \cdot d)}{(l \cdot 10^4)}
\]

Where \(C_t\) – concentration in soil (mg kg\(^{-1}\) soil), \(M\) – areic mass (kg ha\(^{-1}\)); \(l\) – thickness of soil layer (m); \(d\) – bulk density of soil (kg m\(^{-3}\)). According to the formula (1), the predicted concentration of
pesticides depends on the soil bulk density, and the higher the density, the higher the concentration. Therefore, the highest peak and 56-day concentrations were derived for the scenarios of Pskov, Nizhny Novgorod, and Moscow, and the lowest ones for Vladivostok. The distinction of the predicted concentrations between the scenarios were small: no more than two times.

Table 2. Peak pesticide content (kg/ha) and concentration (mg/kg) in soils predicted by model PEARL.

| Scenario / substance | A   | B   | C   | D   | Metabolite C | Sum  |
|----------------------|-----|-----|-----|-----|--------------|------|
| Krasnodar            | 1.16| 0.68| 1.04| 0.62| 1.00         | 1.35 |
| Saratov              | 1.21| 0.73| 1.01| 0.60| 1.00         | 1.41 |
| Vladivostok          | 1.36| 0.69| 1.03| 0.52| 1.04         | 1.29 |
| Kursk                | 1.29| 0.71| 1.01| 0.56| 1.01         | 1.55 |
| Pskov                | 1.42| 0.92| 1.04| 0.68| 1.03         | 1.45 |
| Kurgan               | 1.42| 0.78| 1.03| 0.57| 1.03         | 1.61 |
| Moscow               | 1.55| 0.93| 1.06| 0.64| 1.06         | 1.51 |
| Nizhniy Novgorod     | 1.50| 0.94| 1.05| 0.66| 1.03         | 1.68 |
| Novosibirsk          | 1.58| 0.79| 1.06| 0.53| 1.04         | 2.08 |

Table 3. 56-day pesticide content (kg/ha) and concentration (mg/kg) in soils predicted by model PEARL.

| Scenario/substance   | A   | B   | C   | D   | Metabolite C | Sum  |
|----------------------|-----|-----|-----|-----|--------------|------|
| Krasnodar            | 0.67| 0.39| 0.35| 0.21| 0.19         | 0.59 |
| Saratov              | 0.69| 0.42| 0.21| 0.12| 0.19         | 0.66 |
| Vladivostok          | 1.01| 0.59| 0.41| 0.21| 0.35         | 0.59 |
| Kursk                | 0.81| 0.48| 0.23| 0.13| 0.21         | 0.83 |
| Pskov                | 1.00| 0.65| 0.36| 0.23| 0.32         | 0.68 |
| Kurgan               | 0.89| 0.49| 0.27| 0.15| 0.27         | 0.80 |
| Moscow               | 1.09| 0.65| 0.40| 0.24| 0.35         | 0.74 |
| Nizhniy Novgorod     | 1.01| 0.64| 0.30| 0.19| 0.25         | 0.92 |
| Novosibirsk          | 1.05| 0.53| 0.30| 0.15| 0.27         | 1.28 |

The differences in pesticide concentrations within the one scenario by years for the whole simulation period of application were due to the variability of weather conditions. For 56-day concentrations, the coefficient of variation was 11-23%, for peak values less than 8%. Therefore, selection the 80% percentile of all values allowed for a realistic worst-case scenario with high vulnerability.

4. Discussion
Since the differences in pesticide concentrations between the scenarios were observed to be small, it was proposed to reduce the number of scenarios to four: the north of the European part of the Russia with a temperate continental climate (Moscow or Nizhniy Novgorod), the south of the European part of the RF with a warm temperate continental climate (Krasnodar), the Asian part of the RF with a dry continental climate (Novosibirsk) and the Asian part of the RF with a temperate climate (Vladivostok). These scenarios are supposed to be used together in assessment the effects of pesticides on soil...
organisms as major scenarios. The rest of the scenarios can be applied as auxiliary if the crops protected by the pesticide are grown only in this area.

5. Conclusion
The results of simulation indicated that background concentrations were generally small in contrast to the maximum concentration immediately after application. The content in total soil for individual substances varied in the range of approximately a factor of two between the lowest and the highest values for peak quantities and a factor of five for 56-day ones depending on the properties of the pesticides. Differences in the pesticide content between scenarios depended on the climatic conditions; variations in pesticide concentration also was subject to the soil bulk density. Novosibirsk, Nizhniy Novgorod and Moscow were most vulnerable scenarios with maximum pesticide concentration, Krasnodar, Kursk and Saratov were the safest. The variations of the predicted concentrations between the scenarios were within two times. The year-to-year variations of concentrations (for 20-year period) within one scenario and for one pesticide due to weather conditions was within 23% for the 56-day and 8% for the peak values. Considering the differences in concentration between the scenarios were found to be small, four scenarios would be sufficient to assess the effects of pesticides on soil organisms.

Acknowledgments
The work was carried out with the support of the State Project No. 0598-2019-0005 of Russian Scientific-Research Institute of Phytopathology.

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