Assessment of Russian regions vulnerability to groundwater pollution with pesticides

Victoria Kolupaeva*, Victor Gorbatov, and Inna Nuhina
Russian Scientific-Research Institute of Phytopathology, Bolshye Vyazemy, Moscow region, Russia

Abstract. The predisposition of the region to groundwater pollution by pesticides depends on climatic and soil factors, characteristics of the aquifer system, the type of the territory management, physicochemical properties of used pesticides and timing of their application. The applying of computer models for vulnerability assessment allows to consider the influence of factors affecting the migration of substances through the soil profile. Agricultural districts of Russia were grouped by basic climatic parameters - average annual temperatures and rainfall. 9 large regions with uniform climatic characteristics were obtained. The combination of climatic and soil parameters of each region made up a standard scenario, which was implemented as input files to the pesticide fate model PEARL. As an indicator of the vulnerability of groundwater to pesticide contamination, we used the predicted weighted average annual pesticide concentrations in leachate at a depth of 1 m. Calculations showed the highest vulnerability was in Nizhny Novgorod, Moscow, Pskov, Vladivostok, intermediate one - in Novosibirsk, and the lowest ones - in Kurgan, Saratov, Kursk and Krasnodar. Key words: pesticide, groundwater, zoning, migration, mathematical model, standard scenario.

1 Introduction

Numerous studies carried out around the world indicate the contamination of groundwater with pesticides. Groundwater is an important source of drinking water. 87% of the total water consumption is water from underground sources in Russian rural settlements. In addition, climatic conditions in most regions of the Russian Federation (low temperatures and large amounts of precipitation) contribute to the migration of pesticides into groundwater. Preventing a penetration of pesticides into groundwater is an important task, since groundwater is a vulnerable natural object that is practically incapable of self-purification. Low temperature, lack of microbiological activity and poor sorption capacity of grounds lead to the fact that pesticides can remain in groundwater for a long time in an unchanged state.

Insufficient data on the rate of decomposition of pesticides are available. A few studies consider aerobic aquifer conditions [1, 2], but most studies are conducted in the top soil. Some authors reported that MCPP half-lives of 0.5 to 1 years were measured for aerobic ground water conditions [3-5]. MCPP degradation in anaerobic conditions is highly uncertain due to lack of data. On the basis of the few existing studies, the anaerobic degradation rates

* Corresponding author: v.kolupaeva@vniif.ru
are expected to be very slow, with a half-life of 5 years or more [6, 7]. Another study showed that no degradation nor sorption was observed for the two pesticides (mecoprop and atrazine) in an anaerobic aquifer [8]. The pesticide monitoring program implemented by the Federal Service for Hydrometeorology and Environmental Monitoring does not include investigation of groundwater. Now there is an urgent need for monitoring pesticides in groundwater. In order for monitoring to be more informative and useful, it is necessary to identify the most vulnerable regions to groundwater pollution.

In its broadest context, groundwater vulnerability means whether or not the underlying aquifer will be contaminated by activities on the surface of the earth. For the purposes of this article, the vulnerability of groundwater to pollution is defined as: “the relative ease with which a contaminant (in this case a pesticide) applied on or near the land surface can migrate to the aquifer of interest under a given set of agronomic management practices, pesticide characteristics and hydrogeological sensitivity conditions” [9].

The environmental and non-environmental vulnerability of groundwater is usually shared [9,10]. Environmental vulnerability depends on climatic and soil conditions as well as hydrogeological situation. Specific vulnerability depends on land use intensity, timing of pesticide applications and properties of pesticides. A large variety of vulnerability assessment approach has been drawn up. Generally, these approaches can be divided into three classes: index-based, process-based, statistical. The advantages of index approaches are their simplicity and relatively low data requirements. Indexes are obtained by aggregating parameters that define an intrinsic or specific vulnerability [11, 12]. The principle underlying statistical approaches is to identify the correlation between the vulnerability of groundwater to migration and the presence of pollutants in groundwater. This could be the observed presence of pesticides in groundwater based on monitoring data, or potential occurrences calculated using models. Statistical methods rely on data for a specific region. The weakness is that they may not be valid in other regions without any configuration [13, 14]. Process-based models can be used to more detailed review of physical and chemical processes. Mainly, these approaches are based on pesticide fate models that are parameterized for a large number of scenarios representing specific locations [15, 16]. The aim of the study was to implement climatic zoning of agricultural districts of Russia, to identify regions vulnerability to groundwater pollution by pesticides with pesticide fate model PEARL, to build a schematic map of pesticide potential to leach to groundwater.

2 Methods

2.1 Scale

First of all, we should have specified a scale of zoning. Vulnerability assessments are performed over areas ranging from the national level to the level of a small field. We fulfilled assessment at national scale. The minimum unit of zoning we choose was the territorial division of Russia – a district of Russian Federation. The choice of the national scale is due to the fact that the planning and implementation of monitoring activities and the adoption of regulatory decisions based on the monitoring results are best carried out within administrative units.

2.2 Climatic and soil data

The weather data was taken from the NASA site [19] and from the site of the Russian Research Institute of Hydrometeorological Information [20]. Information on the distribution of soils in
Russia and a description of soil profiles were obtained from the Unified State Register of Soil Resources [21].

2.3 Model PEARL

Calculations of pesticide concentrations in leachate were carried out using the PEARL model, which is used when registering pesticides in the EU and Russia [22-24].

2.4 Mapping

For creation a schematic of groundwater vulnerability for regions of Russia program Excel was used to visualize sets of numeric values on a map.

3 Results and discussion

Before zoning, it was identified a territory of interest – the subdivision of Russia with more than 1% of arable land. Then agricultural districts were grouped by basic climatic parameters - average annual temperatures and annual precipitation. In order to regionalize and select the averaged characteristics of each region, more than 50 files of climatic data over a period of 26 years (1988-2013) were considered. 9 large regions with uniform climatic characteristics were obtained. In the Table 1 the climatic characteristics of these zones and the names of the districts included in the zones. In the future, for shortness, we will call the regions by the name of the one of the regional centres.

Table 1. Climatic zoning of Russia.

| Zones       | Districts of Russia (by the name of district center) | Air temperature range, °C | Precipitation range, mm | Soil texture class | Organic matter, % |
|-------------|-----------------------------------------------------|---------------------------|-------------------------|-------------------|-------------------|
| Moscow      | Moscow, Vladimir, Kaluga, Smolensk, Bryansk          | 2.5 - 5.6                 | 619 - 650               | Silt loam         | 3.8               |
| Kursk       | Kursk, Belgorod, Voronezh, Lipetsk, Oryol, Tambov   | 6.2 - 8.0                 | 492 - 568               | Silt loam         | 7.6               |
| Saratov     | Saratov, Volgograd, Orenburg, Samara                | 5.3 - 7.3                 | 299 - 468               | Loam              | 3.5               |
| Krasnodar   | Krasnodar, Rostov-on-Don, Stavropol, Crimea         | 11.2 - 12.6               | 438 - 646               | Silty clay        | 4.3               |
| Novosibirsk | Novosibirsk, Gorno-Altaysk, Kemerovo, Perm, Sverdlovsk, Tomsk, Tyumen | 0.6 - 1.6                 | 369 - 578               | Loam              | 5.2               |
| Vladivostok | Vladivostok, Birobidzhan, Kaliningrad, Sakhalin, Khabarovsk | 1.0 - 8.4                 | 576 - 744               | Silt loam         | 4.2               |
| Pskov       | Pskov, Vologda, Ivanovo, Izhevsk, Yoshkar-Ola, Kirov, Kostrma, Leningrad, Novgorod, Tver, Yaroslavl | 2.5 - 4.8                 | 453 - 653               | Sandy loam        | 3.9               |
| Nizhny Novgorod | Nizhny Novgorod, Kazan, Penza, Ryazan, Saransk, Tula, Cheboksary, Ulyanovsk, Ufa | 3.6 - 5.0                 | 423 - 644               | Silt loam         | 3.9               |
| Kurgan      | Kurgan, Abakan, Barnaul, Omsk, Chelyabinsk          | 1.2 - 2.8                 | 247 - 390               | Loam              | 4.3               |
The next stage of our work was a selection of the soil, which would be worst case scenario for each region. For this, we selected soil types, which represent 80% percentile of vulnerability. Soil selection was carried out using mathematical modelling. For the calculations, we used the PEARL model. For this, the characteristics of more than 100 soil profiles were studied. From a number of zonal regional soils, soils with properties that promote the migration of pesticides were selected. These were the soil with a low content of organic matter and a light particle size distribution. The main characteristics of the selected soils and regions are presented in the Table 1.

To estimate groundwater vulnerability, we applied physically based model PEARL. This pesticide fate model is used for risk assessment in Russia and EC. To parametrize this model, standard scenarios of soil and climatic conditions for the selected 9 zones were developed and implemented as input files to the model.

Further an annual water percolation was simulated. Water percolation is an integral indicator of the soil water regime and is a difference between the water that entered the soil with precipitation and its losses from the surface of the soil (evaporation). The amount of water percolation depends on the sum of climatic and soil factors.

The data in figure 1 shown, that maximum percolation was observed in Vladivostok and Krasnodar. Also, high percolation was in Pskov, Moscow, Nizhniy Novgorod and Kursk. In these regions a critically high values of percolation were observed. But, in Krasnodar there was a high annual temperature, that’s why we suppose, that leaching of pesticides in this region is unlikely. In addition, the soils of Kursk and Krasnodar are characterized a high content of organic matter, which also prevents the migration of pesticides. Thus, a preliminary review showed that the groundwater of the four regions is supposedly the most vulnerable to pollution. They are in circles in the Fig. 1.

![Fig. 1. Groundwater vulnerability in Russian regions.](image)

A follow step of the work was a simulation of pesticide transport of pesticides. The migration of four hypothetical substances, which is built into the model, was estimated. These substances have a wide variety of persistence and mobility combination. Pesticide A (DT50 = 60 days, Koc = 103 dm$^3$ kg$^{-1}$) is medium persistent, medium mobile, non-volatile. Pesticide B (DT50 = 20 days, Koc = 17 dm$^3$ kg$^{-1}$) is low persistent, mobile, non-volatile. Pesticide C (DT50 = 20 days, Koc = 172 dm3 dm$^{-3}$ kg$^{-1}$) is low persistent, medium mobile, non-volatile, and forms: metabolite C (Koc=52 dm$^3$ kg$^{-1}$, DT50 = 100 days), which is persistent, mobile.
Pesticide D (DT50 = 20 days, Koc = 60 dm3 kg-1) is low persistent, mobile. These four substances with one metabolite represent most combinations of pesticide properties. Spring pesticide applications without crop in the rate of 1 kg ha-1 were simulated. An average, annual predicted concentrations of pesticides in leachate from soil at the depth of 1 m are shown in the Table 2.

### Table 2. Pesticide concentration (μg L-1) in groundwater leachate at a depth of 1 m.

| Substance     | Moscow | Kursk | Saratov | Krasnodar | Novosibirsk | Vladivostok | Pskov | Nizhniy Novgorod | Kurgan |
|---------------|--------|-------|---------|-----------|-------------|-------------|-------|------------------|--------|
| Substance A   | 11.9   | 0.0   | 0.7     | 0.1       | 2.5         | 18.5        | 33.5  | 17.5             | 0.0    |
| Substance B   | 8.3    | 0.5   | 0.8     | 0.4       | 6.0         | 24.0        | 14.7  | 9.7              | 0.1    |
| Substance C   | 0.0    | 0.0   | 0.0     | 0.0       | 0.0         | 0.0         | 0.2   | 0.0              | 0.0    |
| Substance D   | 1.0    | 0.0   | 0.0     | 0.0       | 0.0         | 3.0         | 1.3   | 0.0              | 0.0    |
| Metabolite    | 35.2   | 5.2   | 2.1     | 7.8       | 35.4        | 48.1        | 46.1  | 46.1             | 0.4    |
| Sum           | 56.3   | 5.7   | 3.6     | 8.3       | 43.9        | 93.5        | 107.4 | 74.58            | 0.56   |

As indicated in Table 2, four regions demonstrated maximum sensitivity to groundwater pollution with sum concentration more than 50 μg L-1. These are Pskov, Moscow, Nizhniy Novgorod and Vladivostok. One region – Novosibirsk – has medium vulnerability. A remaining 4 regions has low vulnerability to groundwater pollution by pesticides. The schematic map of groundwater vulnerability was shown in Fig. 2. Thus, as the study showed, significant territories of Russia are prone to groundwater pollution by pesticides, in particular, in areas in the north of the European part, in the middle Volga region, in the Far East, in the Kaliningrad region (in black on the map). So, our investigation must be continued. We planned to assess regions vulnerability after autumn pesticide application and estimate vulnerability of groundwater in a larger scale for one of highly vulnerable regions (for example, Nizhniy Novgorod).

![Fig. 2. Groundwater vulnerability in Russian regions.](image-url)
4 Conclusion

This study allowed us to divide the regions of Russia into 3 categories: highly vulnerable to groundwater pollution, moderately vulnerable and regions where the migration of pesticides is unlikely. The data obtained on vulnerability of groundwater could help to identify priority areas for pesticide monitoring in groundwater and propose measures to prevent water pollution. This information must also be considered during pesticide registration.

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