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Migration of herbicides in the soil of agrophytocenoses and the possibility of managing the risk of contamination of environmental components

G.E. Larina[1,*], L.M. Poddymkina[2,*], S.L. Belopukhov[2], R.F. Baibekov[3] and I.I. Seregina[2]

[1]All-Russian Research Institute of Phytopathology, 5 Institute Srt., RU143050 Bolshie Vyazemy, Moscow Region, Russia
[2]Russian State Agrarian University - Moscow Timiryazev Agricultural Academy, 49 Timiryazevskaya Str., RU127550 Moscow, Russia
[3]Agrochemical innovation center for the development of agricultural science and production – 12 Kostyakova Str., RU127422 Moscow, Russia
[*]Correspondence:larina.galina2014@gmail.com, poddimkina@gmail.com

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Abstract. The migration of residual amounts of sulfonylurea and imidazolinone herbicides under conditions of washing water regime (sum of precipitation in forest and forest-steppe natural zone within 400–600 mm) in practice of intensive agricultural production has been studied. Vertical moisture transport in the soil determines the number of large pores, voids and cracks, and herbicide mobility depends on solubility of the active substance in water and adsorption equilibrium between the soil solution and the soil solid phase. The herbicide was applied to the soil surface, as is the case in practice. Then, pure water (without herbicide) was fed into the column from above, and the movement of water along the soil profile, as well as the adsorption of the herbicide by the soil and the desorption of the active substance by water, were simulated. The water supply to the column was stopped when the portions of water collected after filtering the water through the column contained less than the detection limit of herbicide residues chromatographically. The percentage content of sulfonylurea and imidazolinone herbicides residues in the soil solution varied depending on the nature of the active substance (maximum determined for imazapyr and lowest - metsulfuron-methyl) and soil type (more in acidic soil, compared to neutral and slightly alkaline soil). Effective management of pollution risks of the components of the natural environment (soil, surface and groundwater) provides a set of agrotechnological measures to reduce the number of large pores, voids and cracks in the arable layer.

Key words: pesticide, vertical mobility in soil, sulfonylurea, imidazolinone, plant protection product, pollution of groundwater.

INTRODUCTION

Intensive agricultural production is impossible without the use of chemical protection against pests. Weeds make the greatest contribution to crop yield loss, control of which includes not only agrotechnical methods, but also the use of herbicides. At present, the range of active substances and preparative forms based on them is quite wide and includes a choice of herbicides with different mechanisms of action, method of penetration and movement in the plant, spectrum of action (selectivity), etc. (Larina, 2014; Obraztsov et al., 2018; Sinitskaya, et al., 2018). In recent decades, there has been high interest in herbicides of the class of imidazolinone derivatives and sulfonide-urea derivatives, which have a broad spectrum of action, high biological activity and high selectivity, systemic prolonged action and resistance in biological media (Aichele & Penner, 2005; Paporisch, et al., 2020). But there is also an acute question about the distribution in the soil and the size of the real danger of contamination by residual amounts of herbicides of different classes of natural environment components (surface and groundwater, deep soil layers, etc.). The total balance of pesticide residues in agrophytocenoses consists of 20–65% of the applied pesticide, which is stored and destroyed at the application site, up to 10% accumulates in organic soil layers, 30–55% evaporates, 4–20% penetrates and moves through the plant, up to 5% moves into the lower (mineral) soil layers and can migrate into aquifers (Bauer & Calvet, 1999; Visokova et al., 2019; Larina & Spiridonov, 2000).

There is not enough information about the factors (soil, climate, regional features) that directly or indirectly affect the mobility of residual amounts of modern pesticides in the soil profile of different soils. It is necessary to have an idea about the nature of distribution in the soil and the extent of the real danger of soil (ground) water pollution by residual amounts of chemical plant protection products. Herbicides based on imidazolinone and sulfonylmocene derivatives have been vertical mobility in soil. What are the environmental consequences of their use? How can the risk of hazardous contamination be reduced in soil management practices? Model experiments with soil cores are a convenient tool for modeling herbicide migration under controlled conditions under the influence of a limited number of factors, study the patterns and scales of the vertical migration of the active substance in the soil profile. It is believed that if the solubility of a substance in water exceeds 10 ppm, then it is mainly carried out with the aqueous phase of the runoff. The drug with lower solubility is adsorbed on soil particles and is transported mainly with solid runoff.

The purpose of the study was to evaluate the vertical migration of herbicides in agricultural soils of various compositions under the conditions of a leaching water regime.

MATERIALS AND METHODS

Multi-year experiments in the period 2016–2020 were carried out on the variants of intensive agricultural production - ploughing and fallow land (without plowing for more than 3 years). Mobility of herbicide residues in soil (imazapyr - Imz, imazamox - Imx, imazetapyr - Imr, metsulfuron-methyl - Sfn) in forest and forest-steppe natural zone of the Central region of Russia was estimated. During the year on this territory falls the sum of precipitation equal to 400–600 mm, so there is a risk of deep penetration of herbicide residues down the profile and getting into natural waters. Grain legumes (peas, soybeans, fodder beans) were sown in the fields where imidazolinone preparations were used, while sulfonylurea preparations were used for grain crops (wheat, barley).

During the vegetation season, soil cores were taken from different depths at the experimental plots of ploughing and follow, in which residual amounts of herbicides were identified (Variant_A, field conditions). The plot size is 20 m^2. The repetition is 4 times.

The vertical migration of herbicides was studied using soil columns in laboratory conditions. Two types of columns were used in the laboratory experiment: stuffed (or several sections, disturbed structure) and monoliths (or non-separable, soil of natural structure). Monoliths (height 40 cm and diameter 10 cm) simulate the processes in the topsoil. Column under pressure was hammered into the field and then dug out without breaking the integrity of the soil core (Variant_B, laboratory conditions, undisturbed structure). In the laboratory, the soil column was dried at room temperature. Stuffed column consists of four sections (pipe 10 cm high and 10 cm in diameter) connected in series (Variant_C, laboratory conditions, disturbed structure). The soil was prepared by the thermal method to an air-dry state and passed through a sieve with a hole diameter of less than 10 mm. Each section of stuffed column was lubricated from the inside with silicone grease and stuffed with air-dry soil. The soil was added in small portions and evenly compacted in the column by light tapping on the side surface. In columns with impaired addition, soddy-podzolic soil was used - Variant_C1 or DP (humus 2.5%; pH_{sol} 4.0; mechanical composition – medium loam), leached chernozem - Variant_C2 or ChV (humus 5.1%; pH_{sol} 6.6; mechanical composition - heavy loam). Then outside, at the bottom of the column, a metal mesh, filter paper and cloth (gauze) were sequentially fixed so as not to lose soil. Then the columns were placed in a container with water and saturated with water without pressure to the level of 80% of the field moisture capacity. The following properties of soil cores were also determined: density increased from top to bottom from 1.17 to 1.68 g cm^{-3}, porosity decreased from top to bottom from 49 to 44%, organic matter content decreased from top to bottom from 3.4 to 0.8%. Then the maximum recommended rate of herbicide was applied to the soil surface. A paper filter was placed on its surface to avoid erosion of the upper soil layer and was automatically supplied by a pump distilled water to the upper edge of the column (maintaining the height of the water layer above the soil surface at least 0.5 cm). Total volume of water was equal to the amount of precipitation in the soil-climatic zone (volume of eluate 500 mm). The solubility of herbicides based on sulfonylurea and imidazolinones depends on the properties of water (pH, impurities), therefore, rainwater was not use in the experiments, due to changes (not stability) of its properties depending on the season and other reasons. Filtrate was collected in portions (volume 50 mL day^{-1}) coming from the column from below and the concentration of tested active substance (a.s.) was determined instrumentally. After the concentration of a.s. in the filtrate reached zero, the columns were dismantled. It was established experimentally that the pore water flow rate in Variant_B was lower and was equal to 3.10 ± 0.44 m day^{-1} (0.47 mm min^{-1}), compared to Variant_C - 8.42 ± 1.19 m day^{-1} (1.21 mm min^{-1}).

Table 1. Metrology of the analytical method (HPLC) for the determination of herbicides (*t-test*, $n = 16$, $P > 0.05$)

Active substance (a.s.)	Code	Matrix	Detection limit, ppm	Separation efficiency, *Ci ± ST*, %
Imazapyr	Imz	soil	0.02	86.4 ± 5.0
		water	0.005	88.2 ± 6.3
imazamox	Imx	soil	0.001	89.7 ± 4.4
		water	0.0002	94.6 ± 3.7
imazetapyr	Imr	soil	0.002	85.0 ± 13.4
		water	0.0004	95.5 ± 3.5
metsulfuron-methyl	Sfn	soil	0.004	75.9 ±1.5
		water	0.005	95.7 ± 1.8

Concentration of the tested a.s in the analyzed substrate (soil, water) was determined by chromatographic methods (Table 1). Based on the results of field studies, profile distribution curves of residual amounts of herbicides by soil layers at 10 cm increments to a depth of 50 cm; based on the laboratory experiments, we plotted (or washout curve) the herbicide residual amounts in successive portions of filtrate (water) from the soil core. The experimental data obtained were systematized and analysed using MS Excel 2013, StatSoft Statistica 2010.

RESULTS AND DISCUSSION

Experimental data on the distribution of residual amounts of herbicides in the soil profile of soddy-podzolic soil in dynamics are shown in Fig. 1 (Variant_A). During the growing season, the average depth with the maximum content of herbicides was 16.2 ± 14.5 cm for imazamox, 18.1 ± 14.3 cm for imazetapyr, and 10.1 ± 7.0 cm for metsulfuron-methyl. In different years of observations at the end of the season the content of residual amounts of herbicides in the arable layer was determined (in the range): for imazamox 17–25% of the applied amount, for imazetapyr 12–31% of the applied amount, for metsulfuron-methyl 10–22% of the applied amount.

Under laboratory conditions the curves of herbicide leaching from soil cores were obtained, which are characterized by a high concentration of a.s. in the first portions of the filtrate (Fig. 2). Further the curves have a decaying wave-like character, which, based on the concepts of classical chromatography, can be explained by the presence of voids in the core and heterogeneity of the material, for example due to natural processes occurring in the soil (podzolization, loessivage, etc.). Experimentally established differences in the distribution of residual amounts of herbicides in portions of filtrate obtained by washing soil cores in Variant_B and Variant_C (as an example, the curves for a.s. from the class of imidazolinone derivatives - imazapyr). The general shape of the curve for the arable layer of soddy-podzolic soil (DP) and leached chernozem (ChV) has a fuzzy and indistinct distribution, with a gradual decrease of herbicide concentration in subsequent portions of the filtrate. The shape of the imazapyr washout curve from the core (fallow) was characterized by a narrow peak in the initial section and a long gentle tail. In the first portions of the filtrate, a high concentration of active substances was determined on average 79 ± 6.2% of the applied herbicide rate, compared to soil (ploughing) - 35 ± 2.7% of the applied herbicide rate. This dependence was established for all studied a.s. from the class of imidazolinone derivatives and sulfonylmochetvina derivatives. It was determined that the concentration of herbicides in the filtrate of acidic and less humusy soils (Variant_C1) grew faster, which is important to consider in agricultural practice when imidazolinone and sulfonylurea preparations are applied to the soil surface in the conditions of washing water regime. As a result, residues of imidazolinone and sulfonylurea herbicides in the collected portions of the filtrate were recorded almost after the full application of more than 400 mL of precipitation. With the exception of imazapyr for which the risk of movement of its residues into deep soil horizons (subsoil layer) during the growing season was determined.

Variant_A

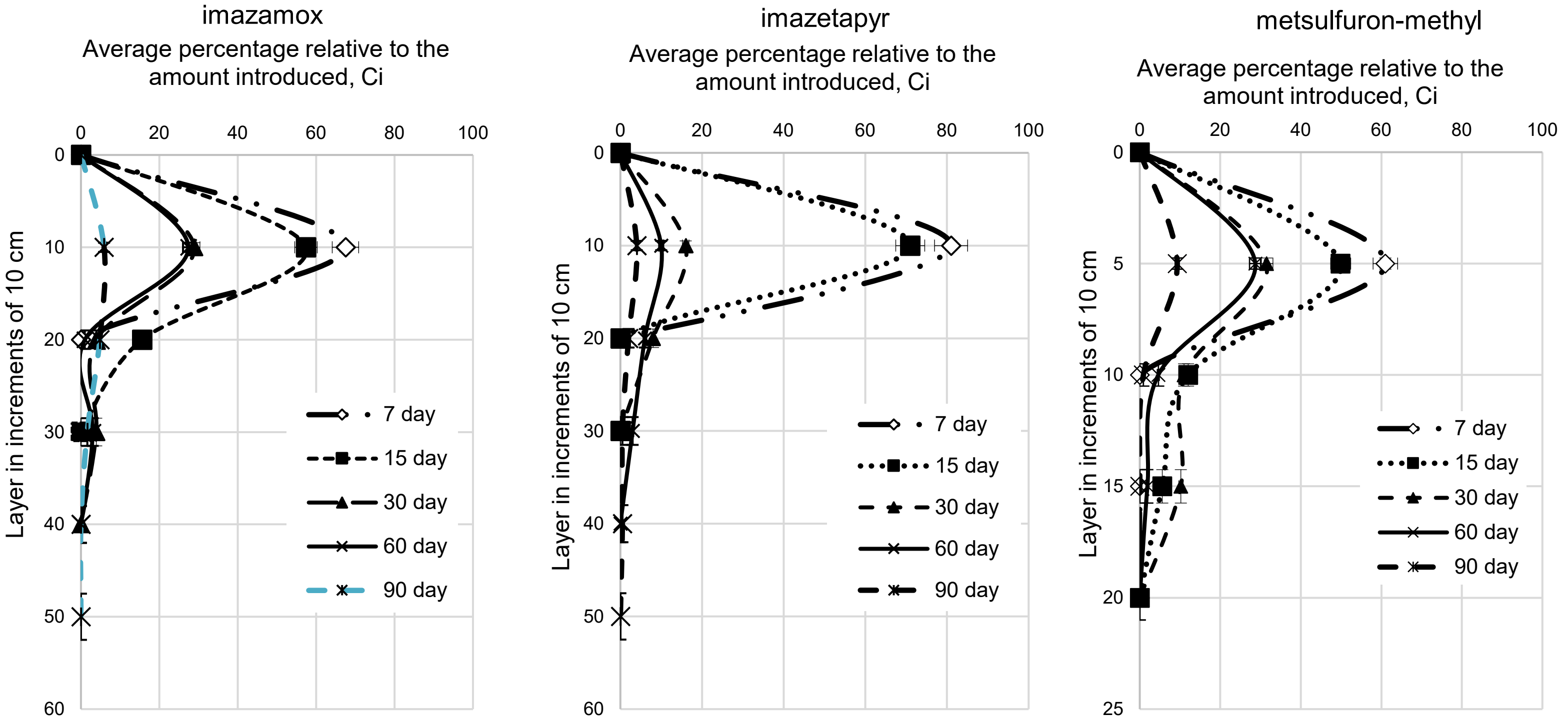

Figure 1. Plots of residual amounts of herbicides at different depths of the soil profile.

The values of adsorption coefficients (L kg^{-1}) for the studied active substances were calculated according to column experiments for different types of soils: *soddy-podzolic soil* - imazapyr (0.200) < imazamox (0.291) < imazethapyr (0.364) < metsulfuron-methyl (2.15); *leached chernozem* - imazapyr (0.023) < imazapyr (0.026) < imazamox (0.029) < metsulfuron-methyl (2.20). The low values of sorption interaction of imazapyr with the soil solid phase confirm the mobility of a.s., as well as the correctness of the assumption about the risks of contamination of natural environment components by residual amounts of this herbicide. In contrast to methsulfuron-methyl, whose residues are highly likely to remain in the place of herbicide application.

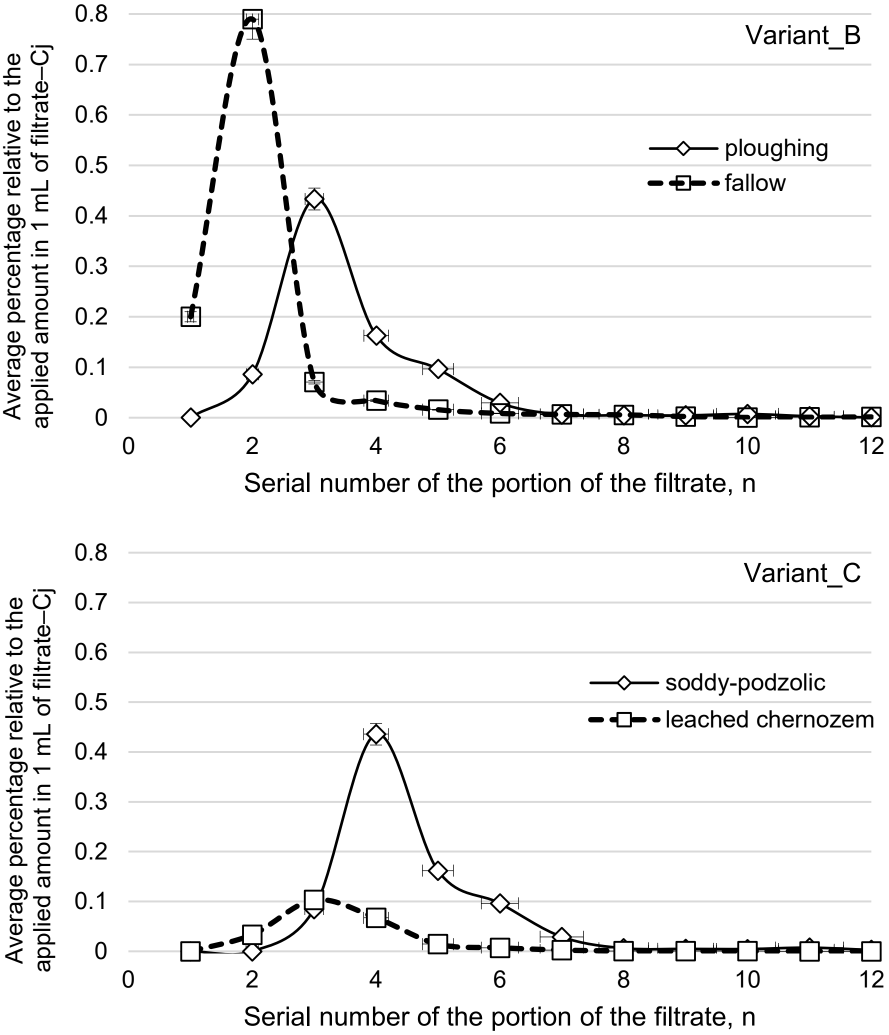

Figure 2. Elution curves of imazapyr from soil cores.

A comparative analysis of the range diagrams showed significant outliers (based on the idea of a normal distribution) for the remains of imazapyr and imazamox in the undisturbed deposit, as well as imazapyr and imazamox in the soddy-podzolic soil and imazapyr in the disturbed chernozem (Fig. 3, a–b). As was revealed in our previous studies, this is due to the heterogeneous composition of the pore space and the presence of cracks and large soil capillaries in the soil from fallow. In the arable layer (Variant_B), the soil has a homogeneous structure after the annual agrotechnical measures (Larina & Spiridonov, 2000; Larina, 2002, 2003). There are practically no cracks and voids in the topsoil, which limits the rapid movement of moisture in the vertical direction along with the herbicide dissolved in it.

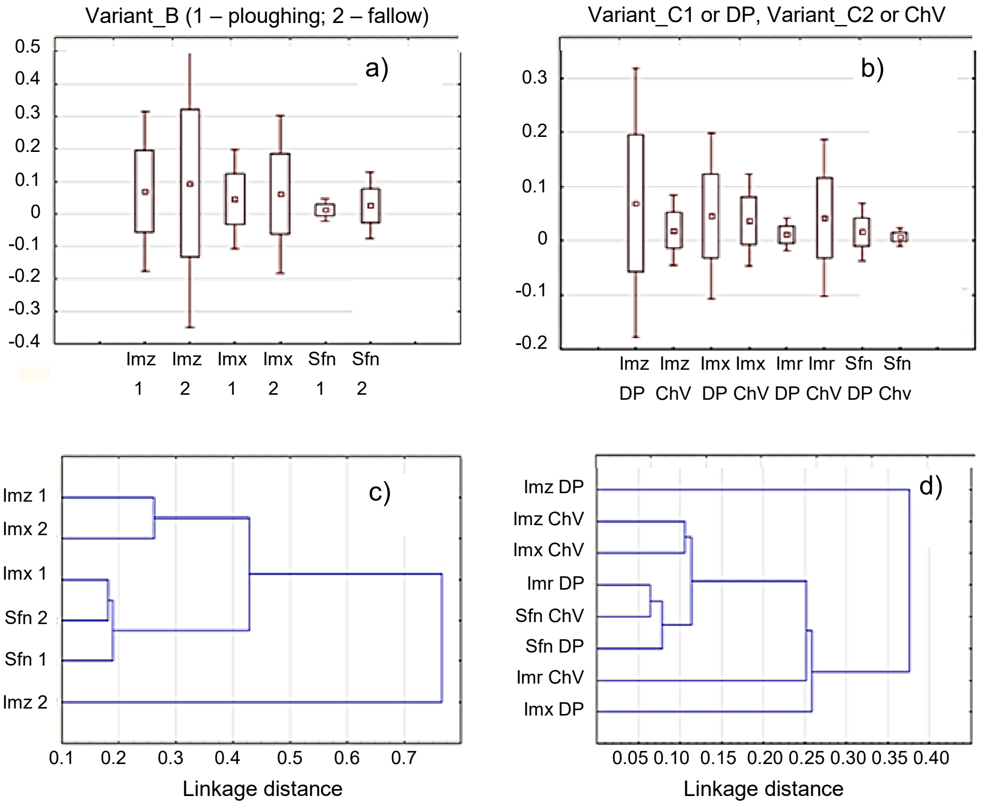

Figure 3. Boxplot (distribution of average values) for the tested herbicides (a–b) and tree diagram for variables (c–d): DP – soddy-podzolic soil, ChV - leached chernozem (*t-test*, $n = 193$, $P > 0.05$).

We carried out a hierarchical classification of the behavior of herbicides in different soils of disturbed and undisturbed addition by the method of a single connection, using the squared Euclidean (Fig. 3, c–d). It is generally accepted that the higher the level of aggregation, the less similarity between members in the corresponding class. It has been established that the behavior of imazapyr in the fallow (Variant_B) and in soddy-podzolic soil (Variant_C1) differs from other options. This fact is explained by the low values of the sorption interaction of imazapyr with the solid phase of the soil and confirms the high risks of pollution of the components of the natural environment with residual amounts over long distances from the place of application.

CONCLUSIONS

The maximum percentage of residual amounts from the applied norm of the herbicide, found in the soil solution, corresponds to imazapyr, the minimum - to metsulfuron-methyl. An intermediate position is occupied by imazamox and imazethapyr. The vertical movement down the profile of water and herbicides dissolved in it depends on the uniformity of the arable layer and the amount of precipitation. In the acidic soddy-podzolic soil, herbicides migrated deeper, in contrast to the weakly alkaline soil (chernozem). The vertical migration of imidazolinone and sulfonylurea preparations was directly dependent on the solubility of the active substance in water and the sorption balance in the soil solution and soil solid phase system. Under the conditions of the leaching water regime (or seasonal showers), the maximum movement of imazapyr residues into the subsoil layer (depth of more than 0.5 m) was observed during the growing season. High environmental risks of pollution of natural (ground) waters by residual amounts of herbicides from the class of imidazolinone derivatives are noted.

Therefore, to manage the environmental risks of the soil, it is necessary to carry out high-quality agrotechnical measures (plowing, harrowing). This will eliminate excessive soil porosity (cracks) and the heterogeneity of the structure of the arable layer and improve the ecological situation of the soil profile.

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