

# Pesticide monitoring of agricultural soil pollution

*Lyudmila Zhichkina*<sup>1,\*</sup>, *Vladimir Nosov*<sup>2</sup>, *Kirill Zhichkin*<sup>1</sup>, *Vyacheslav Zhenzhebir*<sup>2</sup>, *Yury Abramov*<sup>2</sup>, and *Mira Alborova*<sup>2</sup>

<sup>1</sup>Samara State Agrarian University, 446442 Kinel Uchebnaja str. 2, Samara, Russia

<sup>2</sup>K.G. Razumovsky Moscow State University of technologies and management, 109004 Moscow Zemlyanoy val 73, Russia

**Abstract.** The role of pesticides in modern agriculture is not in doubt; the continuous improvement of drugs and technologies for their use reduces the possibility of environmental pollution and their accumulation in manufactured products. The purpose of the research is to assess the pollution of the soil cover of agricultural land with residual amounts of pesticides in the Samara region conditions. Tasks: - to analyze the content of insectoacaricides and herbicides residual amounts in the soil in the spring and autumn; - establish patterns of residual pesticides migration along the soil profile. As a result of studies conducted in 2016-2018. it was found that the content of total DDT related to the first hazard class in the studied samples decreases, a similar situation is observed for organochlorine insectoacaricides HCH and HCB, their residual amounts were found in the soil in the autumn and spring periods of 2016. Residual quantities of the organophosphorus insect metacosacaricide were detected annually (the exception was the autumn period of 2017). Regarding the content of residual amounts of herbicides in the soil (2,4-D, dalapon, simazine, atrazine, promethrin, trifluralin, THAN), it can be noted that during the years of research their content was mainly reduced. A study of the pesticides vertical migration showed that the content of their residual amounts in the soil increases with depth, reaching a maximum at a depth of 1.0-1.6 m.

## 1 Introduction

The problem of protection and rational use of natural resources has now become one of the most urgent for humanity [1-3]. In Russia, agricultural nature management depends on a number of social and economic factors, representing the interaction of society with the environment. The development of territorial planning and adaptive landscape farming systems design will allow the production of economically and environmentally determined quantity and quality, ensuring the stability of agricultural landscapes and the soil fertility reproduction [4, 5]. The system of measures to combat pests, pathogens and weeds is an integral part of the adaptive landscape farming system and is aimed at creating favorable

---

\* Corresponding author: [zskirill@mail.ru](mailto:zskirill@mail.ru)

conditions for growing cultivated plants and suppressing harmful organisms. The decrease in the pests number when using pesticides should take into account the intrapopulation relations of species within agroecosystems and agrolandscapes. The pesticides use in modern conditions allows not only to reduce crop losses from pests and maintain the resulting products quality [6-9]. The soil-protective and minimal tillage is impossible without the pesticides use; it is possible to reduce the effectiveness of other measures, for example, the application of fertilizers and ameliorants [10-12].

Insecticides and acaricides, nematicides, rodenticides, molluscicides, repellents, pheromones, fungicides, herbicides, desiccants, plant growth regulators - are pesticides [13-18]. In 2018, about 1,500 types of drugs related to pesticides based on chemicals and biological principles were registered in Russia. The agricultural land area treated with pesticides in the Russian Federation in 2018 amounted to 94.731 million hectares (42.7% of the agricultural land total area), which is 7.711 million hectares (3.5%) more than in 2016 and 2.480 million ha (1.1%) less than in 2017. In the Samara region conditions in 2016, pesticides were applied on an area of 1562.4 thousand ha (Table 1), the area of pesticides in 2017 and in 2018 increased by 10.6 and 132.0 thousand ha respectively.

**Table 1.** The dynamics of the crops area treated with pesticides in the Samara region.

Year	The cultivated area, thousand ha				
	insecticides, acaricides	fungicides	herbicides	desiccants	Total
2016	383.1	251.9	880.0	47.4	1562.4
2017	369.1	329.8	851.5	22.6	1573.0
2018	3707	297.1	973.1	53.5	1694.4

According to the pesticides chemical composition, they belong to three groups: organic, inorganic, preparations of biological origin [19-21]. Pesticides may include organochlorine, organophosphorus and inorganic compounds of mercury, lead, arsenic and other elements. All pesticides used in agriculture are more or less toxic to animals and humans [22-25].

2 Methods and Materials

A necessary condition for establishing the level of pollution of the soil cover is the regulation of the pollutant content in the soil [26]. As an indicator of finding the maximum amount of pollutant that does not cause negative consequences, the MPC (maximum permissible concentration) of a harmful substance in the soil acts [27]. According to state standard (GOST) 17.4.1.03-84 Nature protection. The soil. Terms and definitions of chemical pollution, MPC of soil pollutant is the maximum concentration of a pollutant that does not cause a negative direct or indirect impact on the environment and human health. Approximate permissible concentrations (APC) of pollutants in soils with different physicochemical properties are also used in practice. The values of MPC and APC are given in normative documents Hygienic Standards (GN) 1.1.7.2041-06, GN 2.1.7.2511-09, GN 1.23111-13. According to GOST 17.4.04-85, the category of “contaminated” should include soils in which the amount of pollutants is at or exceeds the MPC (APC).

The purpose of the research is to assess the pollution of the soil cover of agricultural land with residual pesticides in the Samara region conditions.

Tasks: - to analyze the content of insectoacaricides and herbicides residual amounts in the soil in the spring and autumn; - establish patterns of residual pesticides migration along the soil profile.

Observations of soil pollution were carried out in 2016-2018. in accordance with Operating Guidelines (RD) 52.18.697 (Observations of residual pesticides in environmental objects. Organization and procedure) and RD 52.18.156 (Nature protection. Soils. Methods

of taking combined soil samples and assessing agricultural pollution by residual amounts of pesticides). Soil samples were taken in the spring and autumn. The residual amounts of the following pesticides were determined in the soil: 1) organochlorine insecto-acaricides: dichlorophenyl trichloroethane (DDT), its metabolite dichlorodiphenyl dichloroethylene (DDE), alpha, beta, gamma-hexachlorocyclohexane (HCCCH), hexachlorobenzene; organophosphorus: metaphos; 2) herbicides: simazine + atrazine, promethrin, trifluralin, 2,4-dichlorophenoxyacetic acid (2,4-D), dalapone, sodium trichloroacetate (THAN).

In 2016, fields in the Bezenchuksky and Stavropolsky districts, orchards in the Syzransky district, soils of the Samarskaya Luka National Natural Park and the Agroforestry and Land Reclamation Station AGROS were examined. The total survey area was 1818 ha. In 2017, studies were carried out in the fields of the Bezenchuksky and Kinelsky districts, in the gardens of the Syzransky district, soils of the Samarskaya Luka National Nature Park and the Aglos Agroforestry and Reclamation Station. The total survey area left 2270 hectares. In 2018, the survey was conducted in the fields of the Bezenchuksky, Stavropolsky, Pestravsky districts and in the gardens of the Syzransky district, as well as on the soils of the Samarskaya Luka National Natural Park and the Aglos Agroforestry and Reclamation Station with a total survey area of 1705 ha.

On the territory of Sadovod OJSC (Lesnaya Polyana, Syzransky district), a soil section was laid 2 m deep, where 20 samples were taken from various genetic horizons to determine 10 pesticides.

Soil contamination with pesticides can occur with the use of increased consumption rate, violations of the timing and application technology, prolonged use in the same area, in emergency case. Pesticides identified in the soil belong to the first, second and third hazard classes (Table 2).

3 Results and Discussion

Dichlororiphenyl trichloroethane (DDT) is a chemical active substance from the class of organochlorine compounds, contact, intestinal action, is currently not listed in the permitted pesticides list, has previously been used in agricultural production for pest control. Under normal conditions, it can persist in soil for up to 12 years. The rate of its decomposition is influenced by soil temperature, anaerobic conditions. It belongs to the first hazard class; during the years of research, its content in the spring varied from 0.022 to 0.080 mg / kg, in the fall from 0.008 to 0.022 mg / kg of soil.

Table 2. The average content of residual pesticides in the Samara region soils in 2016-2018.

Name of designated pesticide	Hazard Class	MPC / APC, mg / kg	The average content, mg / kg (spring)			The average content, mg / kg (autumn)		
			2016	2017	2018	2016	2017	2018
Total DDT	1	0.1/	0.080	0.075	0.022	0.011	0.022	0.008
Total HCH	1	0.1/	0.076	0.0	0.000	0.020	0.0	0.000
HCB	1	/0.03	0.009	0.0	0.000	0.006	0.0	0.001
Metaphos	1	0.1/	0.020	0.006	0.001	0.002	0.0	0.004
2,4-D	2	0.1/	0.30	0.027	0.026	0.041	0.019	0.022
Dalapon	2	0.5/	0.029	0.302	0.221	0.019	0.140	0.118
Simazin	2	0.2/	0.001	0.021	0.012	0.002	0.006	0.013
Atrazine	1	0.5/						
Prometrine	3	0.5/	0.001	0.0	0.009	0.000	0.0	0.002
Trifluralin	3	/0.1	0.019	0.049	0.005	0.014	0.015	0.000
THAN	3	/0.2	0.138	0.420	0.080	0.000	0.100	0.137

Hexachlorocyclohexane (HCH), an insecticide of contact, intestinal and some fumigant action, paralyzing the insects nervous system, belongs to the first class of danger, is not currently used. The residual amount of insecticide was found in the soil in the spring and autumn of 2016 and amounted to 0.076 and 0.020 mg / kg respectively.

Hexachlorobenzene (HCB) is an organochlorine compound with an insecticidal and fungicidal effect on harmful organisms, which belongs to the first hazard class. Residual quantities of this drug were discovered only in 2016, the average content in the soil in the spring was 0.009 mg / kg, and by the fall it had dropped to 0.006 mg / kg.

Metaphos belongs to the first class of danger, an organophosphorus contact insect acaricide with a wide spectrum of action. Residual amounts of metaphos were present in the soil annually, the highest content was noted in the spring of 2016 and amounted to 0.020 mg / kg.

2,4-D herbicide, which penetrates plants mainly through leaves, violates the physiological processes - hazard class 2. Residual quantities of herbicide were found in all years of research.

Dalapon is a herbicide that penetrates plants through leaves and roots, hazard class 2. The maximum residual amount of herbicide in the soil was noted in the spring of 2017 and amounted to 0.302 mg / kg.

Simazin is a soil systemic herbicide related to chlortriazines that inhibits photosynthesis - hazard class 2. Atrazine is a soil herbicide effective against most annual weeds, hazard class 1. Residual amounts of simazine and atrazine were detected in the soil annually. So the average content in the soil in the spring ranged from, 0.001 to 0.021 mg / kg, in the fall from 0.002 to 0.013 mg / kg.

Promethrin is a soil herbicide of systemic action, characterized by a short aftereffect, related to triazines. It is well associated with organic and mineral components of the soil, decomposes mainly by microbiological means. When conducting studies, residual amounts of promethrin were detected in the spring of 2016 (0.001 mg / kg) and 2018. (0.009 mg / kg), in the autumn period only in 2018 (0.002 mg / kg).

Trifluralin is a systemic herbicide of soil action related to dinitroanilines. The drug decomposes in the soil throughout the growing season, some of its metabolites can last from one to three years. In 2016-2018 in the spring, the average residual content of trifluralin varied from 0.005 (2018) to 0.049 mg / kg (2017); in the autumn of 2018, no herbicide residues were found in the soil.

Sodium trichloroacetate (THAN) - used to combat monocotyledonous weeds, low toxicity to animals and humans - hazard class 3. During the years of research, the highest content of residual amounts of the herbicide was found in the fall in 2017 and amounted to 0.420 mg / kg.

As a result of the studies, it was found that in the spring of 2016, residual amounts of the following pesticides were found in the selected soil samples: total DDT, total HCH, HCB, metaphos, 2,4-D, dalapon, difluracil and THAN. The maximum level of chloroorganic insectoacaricides residual amounts in the soil varied from 1.7 to 4.3 MPC, organophosphorus was 1.3 MPC, and herbicides from 0.2 to 0.9 MPC, i.e. did not exceed permissible concentrations (table. 3).

In the autumn period of 2016, the content of residual amounts of insectoacaricides in the soil decreased: total DDT (3.1 MPC), metaphos (0.1 MPC), however, the content of total HCH (5.2 MPC), HCB (2.5 APC) increased. In addition, the content of residual amounts of 2,4-D herbicides in the soil increased to 1.1 MPC.

In the spring of 2017, soil plots contaminated with insecto-acaricide, total DDT (3.3 MPC) and herbicides were found: THAN (4.5 APC), dalapon (4 MPC), trifluralin (1.6 APC). Excess residual pesticides in the fall of 2017 were observed only for the herbicide THAN (1.6 APC).

**Table 3.** Pesticide residues in soil samples.

Name of designated pesticide	Maximum level in MPC or APC (spring)			The maximum level in MPC or APC (autumn)		
	2016	2017	2018	2016	2017	2018
Total DDT	4,3	3,3	1,76	3,1	1,0	0,87
Total HCH	2,2	0,1	0,04	5,2	0,0	0,05
HCB	1,7	0,0	0,07	2,5	0,1	0,77
Metaphos	1,3	0,5	0,02	0,1	0,0	0,35
2,4-D	0,5	0,5	0,33	1,1	0,2	0,54
Dalapon	0,2	4,0	0,89	0,2	1,0	0,48
Simazine + atrazine	0,0	0,2	0,51	0,1	0,1	0,32
Prometrine	0,0	0,0	0,13	0,0	0,0	0,01
Trifluralin	0,8	1,6	0,12	0,8	0,6	0,00
THAN	0,9	4,5	0,62	0,0	1,6	1,20

In 2018, in the spring, the maximum level of 1.76 MPC was observed only for the total DDT, in the autumn, only for the preparation of THAN (1.2 APC). In general, from 2016 to 2018. a decrease in the content of residual amounts of the studied pesticides in the soil can be noted.

The movement of pesticides along the soil profile is determined by the properties of the preparation and soil, and by the moisture conditions. If the drug has good solubility, then it is less adsorbed by the soil and moves faster along the profile. In soil samples in 2016, residual amounts of metaphos, 2,4-D, trifluralin and THAN were found; their amount exceeded the MPC and APC. In all analyzed samples in 2017, the residual amount of pesticides did not exceed the values allowed by hygienic standards. In 2018, residual amounts of all pesticides, except for HCB, were found in soil profile samples. Excessive APC was noted only for the preparation of THAN. During the years of research, the content of residual pesticides in the soil increased with depth, reaching a maximum in the water-resistant clay horizon (1.0-1.6 m).

In the soils of the Samarskaya Luka National Natural Park in 2016, the content of HCB residuals exceeded the APC. The content of the remaining determined pesticides was within the normal range. In 2017, observations of the soils of the Samarskaya Luka National Nature Park showed that the residual amounts of DDT, simazine and atrazine exceeded the MPC and APC. The content of other pesticides did not exceed standard values. An analysis of the samples taken in 2018 showed that no excess pesticide residues in the soils of Samarskaya Luka National Natural Park were detected. On the site of the Agroforestry AGROS station, soil samples turned out to be contaminated with residual DDT above the MPC throughout the study period.

4 Conclusion

The problem of protecting soils from pollution is extremely complex, diverse and, of course, relevant in modern agricultural production. The practical implementation of measures to protect the soil cover, its reasonable use is associated not only with the territories natural features, but also with the socio-economic conditions and economic activity. Pursuant to Russia's international obligations, the residual amounts of DDT in the soil are regularly monitored in the framework of the Stockholm Convention on Persistent Organic Pollutants in the Samara Region. As a result of soil pollution studies by residual pesticides carried out in 2016-2018. in the Samara region. It was found that the content of total DDT, belonging to the first hazard class, in the samples studied is reduced. A similar situation is observed for organochlorine insectoacaricides HCH and HCB. Their residual amounts were found in the soil in the autumn and spring of 2016. Residual quantities

metaphos was detected annually (the exception was the autumn period of 2017). Regarding the content of residual amounts of herbicides in the soil (2,4-D, dalapon, simazine, atrazine, promethrin, trifluralin, THAN), it can be noted that in the years of research their content was mainly reduced. A study of the pesticides vertical migration showed that the content of their residual amounts in the soil increased with depth, reaching a maximum at a depth of 1.0-1.6 m.

## References

1. H. Tan, Q. Li, H. Zhang, C. Wu, (...), Y. Li, *Sci. Tot. Environ.* **722**, 137856 (2020)
2. L. Zhichkina, V. Nosov, K. Zhichkin, P. Starikov, A. Vasyukova, Z. Smirnova *IOP Conf. Ser.: Mater. Sci. Eng.* **862** 062061 (2020)
3. E. Carazo-Rojas, G. Pérez-Rojas, M. Pérez-Villanueva, C. Chinchilla-Soto, J.S. Chinchilla-Pampillo, P. Aguilar-Mora, (...), Z. Vryzas, *Environ Pollut* **241**, 800-809 (2018)
4. V. Nosov, M. Tindova, K. Zhichkin, M. Mirgorodskaya, *IOP Conf. Ser.: Earth Environ. Sci.* **337**, 012014 (2019)
5. A.C. Chiaia-Hernandez, A. Keller, D. Wächter, C. Steinlin, L. Camenzuli, J. Hollender, M. Krauss, *Environ Sci Technol* **51** (18), 10642-10651 (2017)
6. M.A. Daam, S. Chelinho, J.C. Niemeyer, O.J. Owojori, P.M.C.S. De Silva, J.P. Sousa, C.A.M. van Gestel, (...), J. Römbke, *Ecotoxicol. Environ. Saf.* **181**, 534-547 (2019)
7. J. Gao, H. Zhou, G. Pan, J. Wang, B. Chen, *Sci. Tot. Environ.* **443**, 7-13 (2013)
8. M. Hvězdová, P. Kosubová, M. Košíková, K.E. Scherr, Z. Šimek, L. Brodský, M. Šudoma, (...), J. Hofman, *Sci. Tot. Environ.* **613-614**, 361-370 (2018)
9. E.M. John, J.M. Shaike, *Environ Chem Lett* **13** (3), 269-291 (2015)
10. R. Kodešová, M. Kočárek, V. Kodeš, O. Drábek, (...), K. Hejtmánková, *J Hazard Mater* **186** (1), 540-550 (2011)
11. L. Zhichkina, V. Nosov, K. Zhichkin, M. Mirgorodskaya, V. Avdotin, *IOP Conf. Ser.: Earth Environ. Sci.* **421**, 062021 (2020)
12. S.-K. Lammoglia, F. Brun, T. Quemar, J. Moeys, E. Barriuso, B. Gabrielle, L. Mamy, *Environ. Model. Softw* **109**, 342-352 (2018)
13. Q. Li, Y. Lu, P. Wang, T. Wang, Y. Zhang, S. Suriyanarayanan, R. Liang, (...), K. Khan, *Environ. Pollut* **239**, 233-241 (2018)
14. A. Mudhoo, V.K. Garg, *Pedosphere* **21** (1), 11-25 (2011)
15. E. Pose-Juan, M.J. Sánchez-Martín, M.S. Andrades, M.S. Rodríguez-Cruz, E. Herrero-Hernández, *Sci. Tot. Environ.* **514**, 351-358 (2015)
16. C. Qu, S. Qi, D. Yang, H. Huang, J. Zhang, W. Chena, H.K. Yohannes, (...), X. Xing, *J Geochem. Explor* **149**, 43-51 (2015)
17. N. Rafique, S.R. Tariq, D. Ahmed, *Environ. Monit. Assess.* **188** (12), 695 (2016)
18. V. Silva, H.G.J. Mol, P. Zomer, M. Tienstra, C.J. Ritsema, V. Geissen, *Sci. Tot. Environ.* **653**, 1532-1545 (2019) doi: 10.1016/j.scitotenv.2018.10.441
19. L. Wang, C. Xue, Y. Zhang, Z. Li, (...), Y. Liu, *Environ. Pollut.* **243**, 734-742 (2018)
20. F. Maggi, D. la Cecilia, A. McBratney, *Sci. Tot. Environ.* **717**, 137167 (2020)
21. W.A. Battaglin, M.T. Meyer, K.M. Kuivila, J.E. Dietze, *J Am Water Res Assoc* **50** (2), 275-290 (2014)
22. C.M. Benbrook, *Environ. Sci. Eur* **28** (1), art. no. 3, 1-15 (2016)
23. M. Danne, O. Musshoff, M. Schulte, *Land Use Policy* **86**, 189-207 (2019)
24. D. la Cecilia, F. Maggi, *Environ. Pollut* **233**, 201-207 (2018)
25. D. la Cecilia, F.H.M. Tang, N.V. Coleman, C. Conoley, R.W. Vervoort, F. Maggi, *Water Res* **146**, 37-54 (2018) doi: 10.1016/j.watres.2018.09.008
26. E. Wołejko, A. Jabłońska-Trypuć, U. Wydro, (...), B. Łozowicka, *Appl. Soil Ecol.* **147**, 103356 (2020)

- 
27. K. Zhichkin, V. Nosov, L. Zhichkina, V. Zhenzebir, O. Sagina, IOP Conf. Ser.: Earth Environ. Sci. **421**, 022066 (2020)