RESEARCH ARTICLE
Indian Journal of Agricultural Research, Volume Issue : ()

Heavy Metal Contamination of Gray Forest Soil in Oilseed Agrocenoses using Mineral Fertilizers

D.V. Vinogradov[1], T.V. Zubkova[2]

10.18805/IJARe.AF-698

ABSTRACT

Background: The purpose of the research is to study the features of contamination of dark gray forest soils with heavy metals and to establish the yield of oil cabbage crops as a result of the use of various levels of mineral nutrition in the conditions of the Non-black earth zone of Russia.

Methods: The experiments were carried out on the dark gray forest soils of Ryazan region in crops of spring rape, white mustard and gray mustard (Sarepta). Soil sampling to determine HMs was carried out before the experiment. Determination of heavy metals was carried out by atomic absorption spectrometry using a semi-quantitative spectral method on a spectrophotometer in the laboratory of the State Station of the Agrochemical Service "Ryazanskaya" and the laboratories of the university.

Result: The studied types and combinations of mineral fertilizers had effect on the growth and development of plants. The effectiveness of the use of mineral nutrition doses proves its high efficiency in studies with oilseed crops in the conditions of the Non-Chernozem zone of Russia. The highest yields, for spring rapeseed (19.3 dt ha^{-1}), for gray mustard (13.7 dt ha^{-1}) and white mustard (12.2 dt ha^{-1}), were observed in the variants with the action of $N_{90-120}P_{60}K_{60}$.

Key words: Fertilizers, Heavy metal, Oilseed, Productivity, Soil.

INTRODUCTION

The production scale for the cultivation of oilseeds has greatly increased recently. These crops are raw materials of renewable energy, which is associated with the creation of new conditions for their use (Ralphe *et al.,* 2006; Günnur and Nilgün, 2013).

The main share in the production of such oilseeds as spring rapeseed and mustard falls on China, India, Canada and the EU (Carre and Pouzet, 2014).

In the structure of oilseed crops in the non-chernozem zone of Russia, such plants as spring rapeseed and sunflower occupy a significant share, at the same time, this oilseed direction of the crop industry as a whole has not yet been rebuilt according to the principle of high adaptability and productivity. In this regard, the introduction, expansion of the range of oilseeds, the selection of new highly productive crops, varieties, hybrids become decisive factors for optimizing production systems. The list of cultivated crops used for cultivation for oilseeds is expanding in the region. In addition to the traditional sunflower and rapeseed, oilseed flax, ginger, white and blue mustard, soy and some essential oils are of interest. In addition, a comprehensive study of oilseeds, the study of their adaptive and productive potential, the development of innovative technologies for the storage and processing of oilseeds is relevant.

Taking into account a number of organizational, technical, agricultural and economic measures to solve the problem of increasing the production of vegetable oil, both for food and for technical purposes, concentrated high-protein feed in the country only at the expense of rapeseed and sunflower, as the main traditional crops, is impossible in the near future. There is a need for widespread introduction of new crops, approved by world and domestic science and practice, into agricultural production, among which white mustard and blue mustard (Sarepta) are promising.

Cultivation of these crops requires constant improvement of technology elements, considering mineral and organic nutrition (Pin Koh and Ghazoul, 2008; Rondanini *et al.,* 2012). The cultivation of these crops is reduced to the use of their seeds in the food industry. At the same time, the main attention is paid to the quantitative ratio of fat and protein in oil seeds (Gunhild *et al.,* 2000; Arif *et al.,* 2012). It is known that, in addition to the cultivation technology, the quality and yield of oil are influenced by the time of harvesting, the period of seed development and local soil and climatic conditions (Nykter *et al.,* 2006). Under conditions

[1]Department of Agronomy and Agricultural Technologies, Faculty of Technology, Ryazan State Agrotechnological University Named after P.A. Kostychev, Ryazan, Russia.
[2]Department of Technology of Storage and Processing of Agricultural Products, Agro-industrial Institute, Bunin Yelets State University, Yelets, Russia.

Corresponding Author: T.V. Zubkova, Department of Technology of Storage and Processing of Agricultural Products, Agro-industrial Institute, Bunin Yelets State University, Yelets, Russia.
Email: ZubkovaTanua@yandex.ru

How to cite this article: Vinogradov, D.V. and Zubkova, T.V. (2024). Heavy Metal Contamination of Gray Forest Soil in Oilseed Agrocenoses using Mineral Fertilizers. Indian Journal of Agricultural Research. doi: 10.18805/IJARe.AF-698.

Submitted: 29-09-2021 **Accepted:** 27-01-2024 **Online:** 23-02-2024

of intensive technogenic load, there is a strong pollution of the soil and air with heavy metals. This occurs in regions where large industrial centers are located and a lot of automotive vehicles are concentrated. In such areas, biogeochemical provinces are formed with a high content of heavy metals in soil, water and plants, which reduces the biological value of plant products and leads to the appearance of heavy metals in the food chain (Butsiak *et al.* 2021; Martyshuk *et al.,* 2016; Gutyj *et al.*, 2017; Rudenko *et al.*, 2019; Boiko *et al.*, 2020). Consequently, it is important in the technology of growing agricultural crops to control the agrochemical parameters of the soil, considering the used mineral fertilizers and pesticides.

Therefore, the aim of the research was to study the effect of different doses of mineral fertilizers on the yield of rapeseed and mustard in conditions of techno-genic pollutants.

MATERIALS AND METHODS

The experiments were carried out on the dark gray forest soils of Ryazan region in crops of spring rape, white mustard and gray mustard (Sarepta).; Coordinates: 54.03556° north latitude and 39.77944° east longitude. The research was conducted during 2018-2020 on the basis of the Ryazan State Technological University Named after P. A. Kostychev. According to agrochemical parameters, the soil was characterized by an increased content of phosphorus - 16.2-18.0 mg/100 grams of soil and potassium 12.9-14.1 mg/ 100 grams of soil. Humus was 2.4-3.8% depending on the depth of sampling. pH_{se} was on average 4.8-5.6 over a layer of 0-40 cm.

The study of the content of various forms of heavy metals (HMs) was carried out at a site located within the reach of man-made pollutants - industrial enterprises of the city of Ryazan, within a radius of 22-25 km.

Soil sampling to determine HMs was carried out before the experiment. Determination of heavy metals was carried out by atomic absorption spectrometry using a semi-quantitative spectral method on a spectrophotometer in the laboratory of the State Station of the Agrochemical Service "Ryazanskaya" and the laboratories of the university.

Crop cultivation technology was generally accepted for this zone (Zubkova *et al.,* 2020; Gulidova *et al.,* 2017; Butov *et al.,* 2019; Zubkova *et al.,* 2021). The variety of spring rape was Ratnik, white mustard was Rhapsody and gray mustard was Rushena. The seeding rate was 2.5 million viable seeds per hectare. Sowing was carried out in the first decade of May. Ammonium nitrate, double superphosphate and potassium salt were used in terms of the active ingredient.

RESULTS AND DISCUSSION

The studies revealed that the average indicators of the content of lead, cadmium, zinc, copper in the soil are higher than Clarke, but did not exceed the MPC. Determination of mobile forms of HMs showed their variability in the upper soil layers. Natural HM levels in soils were subject to fluctuations and depended on their geochemical background, topography, climate and anthropogenic input of industrial emissions to the earth's surface. A number of principles, such as nickel, chromium, arsenic, cadmium, lead, mercury, having no definite functional significance for plants and animals, have a toxic effect on the ecosystem as a whole.

The solution to the problem of obtaining environmentally friendly products in contaminated areas is impossible without considering the migration and accumulation of elements. The soil serves as a natural barrier for HMs, which somewhat hinders their entry into plants and migration to adjacent environments.

It is known that as long as HMs are firmly bound to the constituent parts of the soil, they are difficult for plants to access and their negative effect on the soil and plants will be insignificant (Vinogradov *et al.,* 2019; Lupova *et al.,* 2020; Khabarova *et al.,* 2018; Zubkova *et al.,* 2021). However, if changing soil conditions allow the transfer of HMs into the soil solution, there is a direct danger of their use by plants (Vinogradov and Zubkova, 2021; Mustafayev and Mazhaysky, 2018; Shchur and Valckho, 2016). Plants most actively assimilate actual reserves (extractant NH_4Ac) HMs and potential ones (1-n HCl) are used as they enter the soil solution. Table 1 and 2 show the results of the content of HMs in 1-n HCl and NH_4Ac buffer.

The lead content has exceeded Clarke (10 mg/kg) in almost all soil samples, that indicated its accumulation. Lead can reduce the mobility of molybdenum, iron, chromium, phosphorus, sulfates, carbonates in the soil. The maximum content of mobile forms of lead has been noted in the 0-20 cm layer of gray forest soils of the experimental site, which is about 40% of the total reserves. At the same time, the pollution with this element is characterized as "moderately hazardous" and "average", respectively.

Significant fluctuations in HMs was observed in the studied soils. The excess of Clarke and MPC was observed in 41% of samples of gray forest soils of the experimental site. Therefore, according to the scale of environmental regulation, on average, gray forest soils can be classified as heavily polluted.

Copper, like mercury, inhibits enzymes, causes rupture in plant cell membranes and an increase of copper in soils causes an increase of fulvic acids in humus. These fluctuations range from 8 to 99 mg/kg in the 40-60 cm layer, which is almost 1.2 times higher than Clarke and MPC. These soils are classified as highly contaminated on the scale. The actual reserves of mobile forms of copper are insignificant, but the mobility of copper is 2 times higher in layers 0-20 and 20-40 cm than in the lower ones.

The content of total chromium in soils is below Clarke. Chromium, soluble in 1-n HCl, is along the profile of gray forest soil in the range from 1.5 to 2.0 mg/kg, that is, according to the scale of TMs ecological standardization "moderately hazardous".

The conducted studies of the samples taken from the experimental site show that there is a relatively unfavourable

Table 1: Content of zinc, lead, cadmium in gray forest soils of the experimental site, mg/kg (average for 2018-2020).

Soil sampling	Zinc			Lead			Cadmium		
depth, cm	Total	1-n HCl	NH_4Ac	Total	1-n HCl	NH_4Ac	Total	1-n HCl	NH_4Ac
0-20	73	10.5	1.91	19.3	7.6	0.3	1.25	0.13	0.03
	57-79	5.5-17.1	0.13-6.88	11-30	5-19		0.3-2.0	0.1-0.2	
20-40	70	9.9	1.79	19.0	4.4	0.3	1.25	0.12	0.03
	62-88	5.3-19.4	0.17-7.26	8-32	2-6		0.3-2.0	0.1-0.2	
40-60	66	9.6	1.50	15.0	4.0	0.3	1.0	0.1	0.03
	57-80	5.3-18.1	0.13-5.81	9-31	1-5.0				
60-80	66	5.8	0.76	13.9	4.0	0.3	1.0	0.1	0.03
	53-79	5.0-12.0	0.20-2.56	5-23	1-6				
80-100	63	5.5	1.13	15.8	3.8	0.3	1.0	0.1	0.03
	56-66	0.9-5.8	0.10-2.79	8-28	2-6				
100-120	-	5.4	0.65	-	4.5	0.3	1.0	0.1	0.03
		2.9-8.8	0.13-3.14		3-5				
Clarke		50			10			0.5	

Table 2: Content of copper, chromium, nickel in gray forest soils of the experimental site, mg/kg (average for 2018-2020).

Soil sampling	Copper			Chromium			Nickel		
depth, cm	Total	1-n HCl	NH_4Ac	Total	1-n HCl	NH_4Ac	Total	1-n HCl	NH_4Ac
0-20	46	6.7	0.13	102	1.9	0.087	58	7.8	0.41
	12-129	3.9-13.4	0.05-0.33	39-185	1.4-3.0	0.08-0.13	33-134	3.3-11.0	0.15-0.74
20-40	39	5.5	0.085	114	2.0	0.084	54	5.1	0.42
	10-116	3.0-12.0	0.05-0.17	74-175	1.0-2.5	0.08-0.10	33-126	1.7-7.8	0.12-0.74
40-60	57	3.6	0.062	120	2.0	0.090	47	4.2	0.33
	10-99	1.2-5.7	0.05-0.09	85-185	0.5-2.5	0.08-0.13	39-89	1.5-6.3	0.11-0.71
60-80	35	2.7	0.1	120	1.6	0.087	50	2.5	0.32
	17-57	0.9-3.8	0.08-0.15	40-176	0.8-2.4	0.08-0.12	36-91	1.3-4.7	0.12-0.49
80-100	31	2.5	0.12	104	1.6	0.090	64	2.5	0.35
	19-38	1.0-3.7	0.08-0.23	43-152	0.6-2.4	0.08-0.12	48-104	1.1-3.5	0.20-0.49
100-120	-	3.2	0.14	-	1.5	0.08	-	2.8	0.38
		2.8-3.6	0.05-0.24		1.2-1.7	0.06-0.11		1.5-4.4	0.17-0.68
Clarke		20			200			40	

The numerator is the average, the denominator is the minimum and maximum content.

NH_4Ac is ammonium acetate extract, pH is 4.8.

ecological situation in terms of soil contamination with HMs. The soil is highly contaminated with some HMs.

Annual fluctuations in the yield of rapeseed and mustard on differently fertilized backgrounds are strongly associated with changes in weather conditions and soil fertility. An accurate and objective indicator of moisture conditions is the HTI, especially during the period of “rosette of leaves” - “flowering” (Vinogradov *et al.,* 2019; Vinogradov *et al.,* 2020). With insufficient moisture and arid conditions of the marked segment of the growing season of crops, the use of increased doses of fertilizers is ineffective. The increased amount of precipitation throughout the entire period of development of rapeseed and mustard, as well as heat, allowed the maximum use of the applied mineral fertilizers, especially nitrogen fertilizers. While fertilizing for cultivation, signs of nitrogen deficiency were observed in the early stages of development and later disappeared. Nitrogen fertilizers, due to dry conditions, did not move in the soil, so it took a little longer for the roots to gain access to nitrogen.

Regardless of the nutritional background, the dynamics of linear growth of spring rapeseed and mustard plants had the same course: a uniform increase in plant height during the growing season of crops with reaching maximum values before harvesting. The studied types and combinations of mineral fertilizers had an unequal effect on the growth and development of plants.

Thus, the unilateral application of phosphorus-potassium fertilizers did not have a significant effect on the plant height of both rapeseed and mustard and was at the control level: rapeseed - 80 cm, white mustard - 62 cm, gray mustard - 77 cm. Introduction of nitrogen (N_{60}) and full ($N_{60-120}P_{60}K_{60}$) doses of fertilizers significantly increased the considered indicator in the first half of the growing season. In the rosette phase, fertilized plants exceeded the plant height

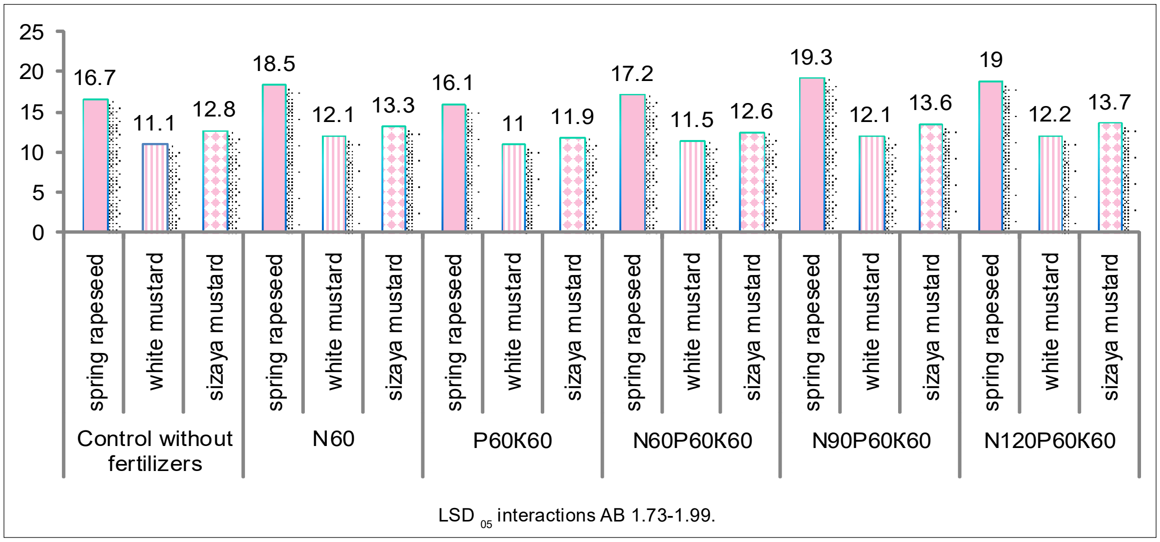

Fig 1: Productivity of oilseeds depending on the level of mineral nutrition (average for 2018-2020).

in the control by 18-36%, which indicated the predominant role of nitrogen in the processes of vegetative growth.

The interphase period - rosette-budding - was characterized by intensive growth of aboveground plant organs. The advantage of the options with the action of fertilizers remained, but the difference between fertilized plants and control was leveled in linear growth. Nevertheless, the introduction of various nitrogen-containing backgrounds increased the height of plants in comparison with the natural agrochemical background in the budding phase by 10-18%, in the flowering phase by 5-15% and in the full ripeness phase by 3-17%.

The use of higher doses of nitrogen fertilizers N_{90-120} under spring rape did not have any significant effect on the onset and duration of the development phases and the growing season. However, they increased the amount of dry matter accumulation and consumption of nutrients in rapeseed. The processes of dry matter biosynthesis by rapeseed and mustard proceeded most intensively during the interfacial period “rosette of leaves - flowering”, when more than half of the final harvest was formed and more than 70% of nitrogen and potassium, as well as about 60% of phosphorus were consumed. Studies of spring rapeseed, white mustard and gray mustard plants on a higher background of mineral nutrition showed the increase of yield structure elements and, as a consequence, the yield (Fig 1).

Against the background of $N_{120}P_{60}K_{60}$, the number of rapeseed siliquae per plant was 9.6 higher than in the control. The indicator of the mass of 1,000 seeds during the study period in rape plants was within 2.7-3.5 g, it was 2.1-2.6 g in gray mustard and 3.4-3.9 g in white mustard, which corresponded to the average values for these crops. A higher level of mineral nutrition contributed to an increase in the mass of 1,000 seeds for rapeseed and gray mustard and had practically no effect on an increase in the mass of seeds for white mustard. The number of seeds in the pod of white mustard practically did not depend on the level of mineral nutrition, possibly due to the short growing season of the crop.

The highest yields, both for spring rapeseed (19.3 dt ha^{-1}) and for gray mustard (13.7 dt ha^{-1}) and white mustard (12.2 dt ha^{-1}), were observed in the variants with the action of $N_{90-120}P_{60}K_{60}$. The oil content in spring rape was 42-45 % and 36.5 % in gray mustard. Low oil content was observed in white mustard (about 30%). The yield of rapeseed and mustard seeds per hectare under the action of increased norms of mineral fertilizers increased, in comparison with the control, by 15-33.5 %, which clearly proved the high responsiveness of these crops to additional nutrition.

Nitrogen had a significant effect on rapeseed and mustard, where it became stronger as the application rate increased. At the same time, cabbage crops showed that they were crops for which the early damage of lack of fertilization was overcome by compensating growth. End-season harvest has not dropped as much as might have been expected given the damage at the start of the season.

Accumulating in stems and roots of plants, heavy metals practically do not get into the seeds, therefore, rapeseed, mustard and other cabbage crops from the contaminated zone can be used for oil production and further processing.

CONCLUSION

Thus, nitrogen had a significant effect on rapeseed and mustard, where it became stronger as the application rate increased. The highest yields of rapeseed and mustard were shown by variants $N_{90-120}P_{60}K_{60}$. Spring rape was more responsive to nitrogen fertilization than mustard. Increasing plant nutrition increased the quality of rapeseed. The highest yields, both for spring rapeseed (19.3 dt ha^{-1}) and for gray mustard (13.7 dt ha^{-1}) and white mustard (12.2 dt ha^{-1}), were observed in the variants with the action of $N_{90-120}P_{60}K_{60}$. The oil content in spring rape was 42-45% and 36.5% in gray mustard. Low oil content was observed in white mustard (about 30%). The yield of rapeseed and mustard seeds per hectare under the action of increased norms of mineral fertilizers increased, in comparison with the control, by 15-33.5%, which clearly proved the high responsiveness of these crops to additional nutrition. The effectiveness of the use of mineral nutrition doses proves its high efficiency in studies with oilseed crops in the conditions of the Non-Chernozem zone of Russia. According to the scale of environmental regulation, on average, gray forest soils can be classified as heavily polluted. The conducted studies of the samples taken from the experimental site show that there is a relatively unfavorable ecological situation in terms of soil contamination with heavy metals.

Conflict of interest

All authors declared that there is no conflict of interest.

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