Effects of Long-term Fertilization Systems on Heavy Metals Residues in Sod-podzolic Soil and Oats Yield

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ABSTRACT

Background: The paper presents the results of studies conducted on the basis of the former Smolensk branch of Pryanishnikov Institute of Agrochemistry, in the village of Olscha, Smolensk district, Smolensk region. In a long field experiment, various fertilizer systems were studied, their effect and aftereffect on the qualitative and quantitative crop yield, soil properties.

Methods: A stationary field experiment was established in 1978. The aftereffect of fertilization systems on oats has been studied since 2009. The aftereffect was studied in 2015-2016 and 2017. With one dose of organic fertilizer (compost based on cattle manure - cattle), over 30 years of experience, 17.4 tons of organic matter, 435 kg of total nitrogen, 198 kg of phosphorus (P₂O₅), 621 kg of potassium (K₂O) entered the soil. A single calculated dose of nitrogen, phosphorus and potassium corresponded to 25.5 kg of active ingredient per ha¹.

Result: With prolonged use of fertilizers, the content of heavy metals in the soil did not exceed the calculated permissible concentration. However, at a fivefold norm (N150P150K150 + 15 t ha⁻¹), the cadmium content was overestimated. An ecologically justified dose of aftereffect in the Smolensk region on sod-podzolic soil should be considered a fourfold dose of mineral components and compost (N120P120K120 + 12 t ha⁻¹).

Key words: Accumulation of cadmium, Accumulation of heavy metals, Compost, Grain yield, Heavy metals, Mineral fertilizers, Mobile forms of heavy metals, Oat, Soil.

INTRODUCTION

The main goal of the study is to analyze the long-term aftereffect of organic and mineral fertilizers in different doses and combinations on the agrochemical and environmental indicators of sod-podzolic light loamy soil, yield and quality of oat grain.

In the experiment laid down in 1978, various types of fertilizers were used, since 2009 fertilizers have not been introduced, which allowed the authors to focus on possible changes in the content of heavy metals in the soil of the arable layer and the final product.

Currently, the problem of pollution and degradation of agricultural lands is coming to the fore (Malcev et al., 2002, Fedulova et al., 2018).

The importance of crops for producing environmentally safe and biologically valuable products has been noted by many authors (Ellmer et al., 2002, Kostadinova et al., 2002, Syganov et al., 2008, Stewart et al., 2014).

Foreign scientific sources studying the yield of legumes in Africa report (Islam, M. and Sebetha, E. 2020) that, the interaction of cultivar × location had significant contribution on the yield parameters such as number of pods per drybean plant and hundred seed mass. In future studies, the locations with lower levels of soil phosphorus should be considered for production of drybean under higher P rates.

In research (R. Sharmugasundaram, M. Malarkodi and B. Gokila 2019) утворюючо, the nutrients, that maintenance of available N, built up of P and depletion of available K was observed as compared to initial available status. Non application of micronutrients fertilizer also resulted in depletion of micronutrients in post-harvest soil. This suggests that mineral fertilizer with organic manure shall be adopted for sustaining crop yield and soil fertility in continuous cropping system.

Interesting studies are presented in experiments (Waseem et al., 2019), was found that both organic as well as inorganic fertilizers have substantial residual effect on growth and yield of succeeding fodder oat crop in fodder sorghum-oat cropping sequence, which indicates that a certain proportion of recommended fertilizer dose to oat fodder can be reduced, however results needs to be further investigation for confirmation.
Scientific reviews indicate that each year this problem will become of particular importance in many agricultural areas bordering large industrial zones (Minkina et al., 2013) or in areas with mixed industrial agriculture, including the functioning of Russia’s largest livestock complexes of various specifics (Jakovlev et al., 2016, Jakovlev et al., 2018, Novikov et al., 2018).

In the scientific justification for the use of organic and other fertilizer systems, it is appropriate to present the results of a field experiment in Rotamstead (England), where organic fertilizers were applied for decades and variants using mineral fertilizers were also studied. It is reported that only when using the organic system in the soil of the arable layer did the total nitrogen content increase to 0.2%, the mineral system did not contribute to the increase in the total nitrogen and organic matter in the soil. Currently, against the background of insufficient application of organic and mineral fertilizers, the argument remains undeniable that the main method of increasing crop yields is the use of fertilizers (Kudeyarov, 2019), in particular this applies to the Smolensk region (Gordee et al., 2001, Kozlova et al., 2014, Slusar, et al., 2018).

The main source of heavy metals in the soil is phosphorus fertilizers, followed by nitrogen and then potash fertilizers close to them (Bezuglov et al., 2011). Metals such as: Zn, Pb, Cd, Cr, Cu, Hg, Co have a negative effect: they pollute agricultural products, inhibit soil microbiota and worsen soil properties (Aseeva, 2012).

When assessing the impact of heavy metals on the agricultural system as a whole, it is noted that a slight (relative to background indicators) increase in gross concentrations of heavy metals in technologically contaminated soils can be accompanied by a noticeable increase in the concentrations of mobile and loosely bound forms. In turn, this can contribute to the accumulation of pollutant elements in plant products and their transition into watercourses (Golubev, 1990, Dabahov et al., 2005, Minkina et al., 2017, Chernov et al., 2019).

In conducted by V.B. Trotz (2015) studies revealed that the application of mineral fertilizers increases the gross soil content of metals such as Cd, Pb, Zn, Cu, Co, Mn by 10-36% and increases the mobility of Zn, Cu, Co and 25% on average Mn. The total volume of HM inflow into the phytomass of spring cereals, including oats, on average decreases by 5-30% with an increase in the level of mineral nutrition of crops. However, lead migration is stimulated to spring wheat plants, Cd, Zn and Cu to barley and oat plants and Cd and Mn to pea biomass, it is noted that most metals accumulate in the root system of plants and are transported in relatively large quantities to inflorescences can Zn and Cu.

In connection with the foregoing, it was decided at the final stage of the experiment to analyze the content of heavy metals in soil and plant samples on the experimental options.

**MATERIALS AND METHODS**

The studies were carried out on the basis of the former Smolensk branch of VIUA, in the village of Olisha, Smolensk district, Smolensk region. The region is located in the central part of the East European (Russian) Plain. Most of it lies on the Smolensk-Moscow Upland, the northwestern part of the region is located in the Baltic lowland, in the south - the Dnieper lowland. The region is characterized by undulating relief, with hilly areas and deeply cut river valleys.

The region’s climate is temperate continental, characterized by moderately warm summers (average July temperature + 16-17°C) and moderately cold winters (average January temperature -8°C-10°C). The continentality increases towards the northeast. Average annual temperatures range from + 3.5°C to + 5°C. The annual range of average monthly temperatures is 25-27°C. Differences in temperature in parts of the region are insignificant, however, in the southern regions the temperature is about 1-2°C higher. The first half of winter is warmer than the second. The sum of the active temperatures of the region is close to 2000°C.

A stationary field experiment was established in 1978. In a crop rotation with the following alternation of crops: in the first rotation (1979–1989) - potatoes - barley - winter rye - pea-oat mixture - winter wheat - barley - perennial grasses of the 1st and 2nd years of use - winter rye - oats; in the second (1990–1995) and third (1996-2001) rotations - potato - barley - perennial grasses of the 1st and 2nd years use - winter wheat - oats; in the fourth (2002-2008) and fifth (since 2009, with the aftereffect of fertilizers) rotations - annual grasses (oats for green fodder) - winter rye - barley - perennial grasses of the 1st and 2nd years use - spring wheat - oats. In the first rotation of the crop rotation, organic fertilizers were applied under potatoes and winter wheat; in the second and third rotations - for potatoes; in the fourth rotation - for winter rye. Fertilizers contained 0.46% total nitrogen per raw substance, 0.08% ammonium nitrogen, 0.21% P₂O₅, 0.66% K₂O. Organic matter content on dry matter - 59%, C: N ratio - 19. Gross content of heavy metals in fertilizer: Cd - 0.1, Cr - 1, Ni - 0.6, Cu - 7 mg kg⁻¹ dry mass.

Single dose of organic fertilizers - 3.2 tons (3 tons with rounding). Together with 1 ton of organic fertilizers, 580 kg of organic matter, 14.5 kg of nitrogen, 6.6 kg of phosphorus, 20.7 kg of potassium per hectare per year were introduced into the soil. With one dose of organic fertilizer added to the soil (cattle manure compost). During the study period (more than 30 years), 17.4 tons of organic matter, 435 kg of total nitrogen, 198 kg of phosphorus (P₂O₅), 621 kg of potassium (K₂O) were added to the soil.

The following mineral fertilizers were applied to the soil: ammonium nitrate, double superphosphate, potassium chloride. A single calculated dose of nitrogen, phosphorus and potassium corresponded to 25.5 kg of active ingredient per ha⁻¹. With mineral fertilizers, 765 kg of nitrogen, phosphorus and potassium were supplied to the soil in 4 rotations per hectare of crop rotation.
The experiment was repeated three times. The total area of the plot is 112 m² (7x16 m), 48 m² (4x12 m) - accounting.

The paper presents the studies carried out in the fifth rotation of the grain-grass crop rotation in two fields where oats of the Skakun variety were grown, with the supporting introduction of ammonium nitrate at a dose of N45 in the background in all field experiments.

The soil of the experimental site is cultivated soddy-podzolic light loamy, characterized by the following agrochemical parameters: pH 6.4, humus content 1.3%, mobile phosphorus (P<sub>2</sub>O<sub>5</sub>) and potassium (K<sub>2</sub>O) (according to Kirsanov) 160 and 130 mg kg<sup>-1</sup>, respectively.

The content of heavy metals in grain was determined: copper, zinc, lead, cadmium (GOST 30178-96); Content of heavy metals in soil: copper, zinc, lead, cadmium, - Procedure for measuring the mass fractions of toxic metals in soil samples by the atomic absorption method Federal Register 1.31.2007.04106; - Arsenic (MU for the determination of arsenic in soils by the photometric method).

RESULTS AND DISCUSSION

The content of heavy metals in the soil is presented in Tables 1-3.

Analysis of the results of determining the total content of heavy metals in the arable soil layer (0-20 cm) according to the variants of the experiment, which was carried out in 2017, made it possible to identify the following patterns.

In all variants of the experiment, the total content of heavy metals in the sod-podzolic light loamy soil did not exceed the approximate permissible concentrations.

The gross content of lead in the soil was higher in the control variant, as well as in the aftereffect of the mineral (N90P90K90) and organomineral fertilizer systems in three-(N90P90K90 + 9 t<sup>-1</sup> ha<sup>-1</sup> of compost) and five-fold doses (N150P150K150 + 15 t<sup>-1</sup> ha<sup>-1</sup> compost) (Table 1).

The content of lead in the soil of the arable layer of the control variant, which amounted to 23.9 mg kg<sup>-1</sup>, exceeds the analogous indicators for the variants where mineral, organic and organomineral fertilization systems were used in the indicated doses.

It is necessary to clarify here that in this case there is a high probability of active removal of lead with the yield when metal ions are absorbed from the soil solution by the root system of experimental plants; we will consider this aspect when analyzing the actual accumulation of lead in oat grain.

The lowest value for the heavy metals under study was achieved in the variant with the use of a threefold dose of nitrogen (variant 2); this is probably due to the fact that ammonium nitrate, acidifying the soil solution, converts acid-soluble forms of metals into mobile salt ions, which is further accompanied by vertical and partly by planar migration in the soil profile.

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An increase in the content in the topsoil was noted for copper when compared with the control (+ 20.8%), which is probably due to the formation of strong bonds of copper with sulfates, carbonates and phosphates and against the background of a weakly acidic reaction of the soil solution, there is no additional factor that can increase mobility copper compounds in the soil absorbing complex. Interesting data were obtained in the variant using the organic system - variant 6. According to the accumulation

Table 1: 2017 Gross content of heavy metals in the soil (0-20cm).

| Experiment variant | Pb   | Zn   | Cd   | Cu  |
|--------------------|------|------|------|-----|
|                    | mg kg<sup>-1</sup> | in%  | mg kg<sup>-1</sup> | in%  |
| Control            | 23.9 | -    | 69.9 | -   |
| N90                | 15.8 | 66.1 | 50.7 | 72.5 |
| P90                | 16.5 | 69.0 | 62.5 | 89.4 |
| K90                | 19.7 | 82.4 | 66.5 | 95.1 |
| 9 t<sup>-1</sup> ha<sup>-1</sup> | 20.2 | 84.5 | 65.8 | 94.1 |
| N90P90K90          | 22.5 | 94.1 | 67.6 | 96.7 |
| N30P30K30 + 3 t<sup>-1</sup> ha<sup>-1</sup> | 16.7 | 69.9 | 63.8 | 91.3 |
| N60P60K60 + 6 t<sup>-1</sup> ha<sup>-1</sup> | 19.1 | 79.9 | 68.2 | 97.6 |
| N90P90K90 + 9 t<sup>-1</sup> ha<sup>-1</sup> | 21.0 | 87.9 | 68.8 | 98.4 |
| N120P120K120 + 12 t<sup>-1</sup> ha<sup>-1</sup> | 19.8 | 82.8 | 55.1 | 78.8 |
| N150P150K150 + 15 t<sup>-1</sup> ha<sup>-1</sup> | 21.1 | 88.3 | 71.8 | 102.7 |
| ADC                | 65   | 110  | 1.0  | 66  |

* compost.
of copper, an increase (+ 2%) in the soil was noted in the aftereffect after prolonged application of organic fertilization. When applying only phosphorus fertilizer (P90), as well as potassium (K90), it should be noted that double superphosphate did not contribute to an increase in the content of analyzed metals, except for cadmium. In variant 4, the increase in comparison with the control was 8.3%, undoubtedly, this is due to the supply of cadmium to the soil with fertilization in previous years.

It should also be explained why, against the background of the use of two-fold doses of mineral fertilizers and manure, the content of heavy metals exceeds the same indicators for the option with three-fold doses. This is primarily due to the removal of heavy metals with the harvest. Table 3 show the results for the yield and the actual content of heavy metals in grain.

A significant accumulation of this metal was also noted in variant 6 (N90P90K90) - with threefold doses of only mineral components and in variant 11 (N150P150K150 + 15 t* ha⁻¹) - with fivefold doses of all mineral fertilizers and manure. Of view of agroecology, the use of five-fold doses on sod-podzolic soil for a long time (30 years or more) can lead to a significant increase in the cadmium content in the root layer. In the future, this can cause contamination of the main products with cadmium. Probably, the application rates presented in option 10 (N120P120K120 + 12 t* ha⁻¹) should be considered the optimal dose of the complex application of mineral components and organic fertilizers. Analysis of the content of metals according to the variants of the experiment in the arable layer of the soil allows us to conclude that the organomineral fertilization system is most expedient from two points of view - an insignificant increase in the content of heavy metals and, at the same time, a guaranteed yield of grain with a given quality, but at lower costs for fertilizers compared option 11.

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The analysis of the accumulation of heavy metals in the grain of oats revealed the following: for all variants of the experiment, the content of permissible levels was not exceeded (Table 3).

**Table 2:** Influence of action and aftereffect of various doses and combinations of organic and mineral fertilizers on the yield of oats c ha⁻¹.

| Experiment variant | Act fertilizers ** | Effect of fertilizers |
|--------------------|-------------------|----------------------|
| Control            | 22.8              | 17.7                 |
| N90                | 30.4              | 19.3                 |
| P90                | 27.9              | 20.2                 |
| K90                | 25.7              | 21.3                 |
| 9 t ha⁻¹           | 26.0              | 21.3                 |
| N90P90K90          | 33.1              | 24.5                 |
| N30P30K30 + 3 t ha⁻¹ | 27.3              | 20.4                 |
| N60P60K60 + 6 t ha⁻¹ | 30.3              | 23.9                 |
| N90P90K90 + 9 t ha⁻¹ | 33.3              | 24.1                 |
| N120P120K120 + 12 t ha⁻¹ | 30.8              | 27.5                 |
| N150P150K150 + 15 t ha⁻¹ | 29.8              | 29.3                 |
| Least significant difference (LSD₀₅) | 3.4 | 3.2 |

*compost.

**Table 3:** Content of heavy metals and arsenic in oat grain, mg kg⁻¹ dry mass.

| Experiment variant | Cu       | Zn       | Pb   | Cd    | As   |
|--------------------|---------|---------|------|-------|------|
| Control            | 3.46    | 17.6    | 0.06 | <0.01 | <0.01|
| N90                | 2.61    | 22.7    | 0.11 | 0.028 | <0.01|
| P90                | 2.03    | 17.7    | 0.04 | <0.01 | <0.01|
| K90                | 2.62    | 16.6    | 0.06 | <0.01 | <0.01|
| 9 t ha⁻¹           | 2.25    | 12.6    | 0.06 | <0.01 | <0.01|
| N90P90K90          | 2.24    | 24.1    | 0.17 | 0.032 | 0.052|
| N30P30K30 + 3 t ha⁻¹ | 2.33    | 17.1    | 0.05 | <0.01 | <0.01|
| N60P60K60 + 6 t ha⁻¹ | 2.20    | 20.1    | 0.08 | <0.01 | <0.01|
| N90P90K90 + 9 t ha⁻¹ | 2.09    | 18.3    | 0.11 | 0.033 | <0.01|
| N120P120K120 + 12 t ha⁻¹ | 2.12    | 17.1    | 0.07 | 0.012 | <0.01|
| N150P150K150 + 15 t ha⁻¹ | 2.12    | 26.2    | 0.12 | 0.020 | 0.02 |
| Permissible levels, mg kg⁻¹ | 0.5 | 0.1 | 0.2 |       |      |

*compost.
increase in acidity increases the mobility of all salt ions and, consequently, their entry into the plant and their accumulation in the final product.

In the variants with the use of mineral components and compost, the most significant differences are seen in the content of zinc, lead and cadmium and arsenic. So, at a fivefold dose (option 11), the zinc value is maximum and is 26.2 mg kg⁻¹ dry mass, which is probably determined by the acidity of the soil solution, which in this option is 4.6. The organic component and double superphosphate in this variant is no longer a regulating factor for stabilizing the pH in the soil against the background of high doses of nitrogen and potassium, which undoubtedly contribute to acidification.

It is also worth highlighting the ecological function of phosphorus fertilizer against the background of its use, which, in the aftereffect, the acidity of the soil solution is already 5.2, which positively affects the stabilization of the mobility of various cations, including heavy metals. That is why the lowest content of copper and lead was noted here, which was - 2.03; and 0.042, respectively.

The most interesting results were obtained in the variant using a fourfold dose of the organomineral system (N120P120K120 + 12 t ha⁻¹). With a high probability, it can be argued that such a ratio is most suitable for long-term use of the organomineral system in the conditions of the western part of the Smolensk region of the Non-Chernozem zone on sod-podzolic soil.

**CONCLUSION**

In the western part of the Non-Chernozem Zone of Russia, the long-term use of organic and mineral fertilizers in optimal doses and combinations is an effective technique for the cultivation of oats in grain-grass crop rotation on sod-podzolic light loamy soil, which in the aftereffect provides a reliable increase in the yield of biologically valuable and ecologically safe grain products. According to research data in a field stationary experiment, the maximum yield of oats of the Skakan variety was achieved when the organomineral-fertilizer system N120P120K120 + 12 t ha⁻¹ was used in the aftereffect, the grain yield of oats was 27.5 centners ha⁻¹ of grain, which was 55.3% higher than the control without fertilizers.

With long-term use of fertilizers, the content of heavy metals in the soil did not exceed the approximate permissible concentrations, but in the variant with the aftereffect of the organomineral system at the maximum, fivefold dose (N150P150K150 + 15 t ha⁻¹), the cadmium content was higher than in other fertilizers and amounted to 0.44 mg kg⁻¹ with an ODK of 1.0 mg kg⁻¹.

Long-term use of organic and mineral fertilizers in the aftereffect did not affect the accumulation of heavy metals and arsenic in oat grain production. In terms of the content of Cd, Pb, Hg, Ni, Zn, Cu and As, oat grain in the control and in all variants of the aftereffect of organic and mineral fertilizers corresponded to the hygienic levels established by SanRar 2.3.2.1078-01.

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