Ecological and agrochemical assessment of the effect of fertilizers on the behavior of cadmium and lead in soil

T S Morozova, V I Geltukhina, L A Manokhina, E Y Kolesnichenko
Belgorod State Agricultural University named after V Gorin, 1 Vavilova st., p. Mayskiy Belgorodskiy rayon, Belgorodskaya oblast, Russia

E-mail: Manohina_LA@bsaa.edu.ru

Abstract. In the southwestern part of the Central Chernozem Region, mineral fertilizers enhance the mineralization of organic matter. The introduction of manure contributed to an increase in the content of humus in the soil. The maximum humus content in the soil - 5.23% was noted in the variant with aftereffect of 80 t/ha of manure. Between 2013 and 2019, the application of mineral fertilizers led to acidification of the soil solution. The effect of manure at a dose of 40 t/ha and the application of mineral fertilizers at a dose of N90P60K60 against the aftereffect of 80 t/ha of manure has a positive effect on the reaction of the soil environment, the absolute pHKCL increases to 5.88 units and 5.84 units respectively, which corresponds to a neutral soil reaction. Regular application of mineral and organic fertilizers and their joint application change the content of active forms of cadmium in the soil. The systematic application of mineral fertilizers, organic fertilizers and the application of mineral fertilizers against the manure aftereffect leads to an increase in active forms of cadmium in the soil and, therefore, can have a negative impact on the agroecological state of the soil. The use of fertilizers in different doses did not significantly affect the change in the content of gross forms of cadmium, however, its slight increase was observed in all cases, its content in the soil was 0.38-0.14 mg/kg lower than the UEC. The highest content of gross forms of cadmium was noted on variants with the introduction of mineral fertilizers against the aftereffect of manure. The mobility coefficient of cadmium from 2013 to 2019 changed upwards in the variants with the introduction of mineral fertilizers, aftereffect of manure and the introduction of mineral fertilizers against the aftereffect of 40 t/ha of manure. The introduction of mineral fertilizers against a background of 80 t/ha of manure led to a decrease in the cadmium mobility coefficient.

Currently, the pollution of soils with heavy metals is a very urgent problem. Their increased content in the soil leads to a change in the biological properties of the soil, humus state, acidity, etc., which as a result leads to the accumulation of heavy metals in agricultural products. The most dangerous are the metals of the 1st hazard class - Zn, Cd and Pb [1, 2, 3]. Prediction of heavy metal contamination of soil and crop production is possible based on continuous monitoring of the ratio of various forms of heavy metals in the tilth-top soil [4, 5, 6]. Heavy metal pollution can also occur due to the agriculture, the main sources of which are chemicals: organic and mineral fertilizers, pesticides, etc. [7, 8]. Thus, objectively assessing the existing environmental situation and predicting the results of anthropogenic load on the soil as a result of the systematic use of fertilizers allow studies only in long-term stationary experiments.

Studies on the effect of the systematic use of fertilizers on cadmium and lead accumulation in soil were carried out on the basis of many years of stationary field experience in the laboratory for
monitoring and soil fertility of the Federal State Budget Scientific Institution Belgorod FANC RAS, established in 1987 on typical heavy loamy chernozem on loesslike loam with the following characteristics: humus content 5.0%, the amount of absorbed bases 34.2-36.4 mEq / 100 g of soil, hydrolytic acidity 2.5-2.7 mEq / 100 g of soil, pH salt 5.6-5.8; the content of mobile phosphorus and exchange potassium (according to Chirikov) is 55-60 and 105-125 mg / kg of soil, respectively [9, 10].

Determination of agrochemical parameters of the soil was carried out in an accredited testing laboratory of the Federal State Budget Scientific Institution "Belgorod FANC RAS": pHKCI - according to the TsINAO method (GOST 26483-85); humus according to Tyurin - GOST 26213-93; the amount of absorbed bases - according to the Kappen-Gilkovits method (GOST 27821-88); hydrolytic acidity - according to the Kappen method in the modification of TsINAO (GOST 26212-91).

The content of mobile forms of cadmium and lead, gross forms of cadmium were determined in the testing laboratory of the FSBEI HE Belgorod State Agrarian University by atomic absorption method (GOST 30178-96 and MU TsINAO).

Table 1. Change in the agrochemical parameters of the arable layer of chernozem of typical soil under winter wheat (2013-2019).

| Variant | Humus, % | pHKCI | Ng, mEq / 100 g of soil | S, mEq / 100 g of soil |
|---------|----------|--------|-------------------------|------------------------|
| Control | 4.95     | 5.85   | 2.48                    | 38.2                   |
| N90P60K60 | 4.87     | 5.50   | 2.75                    | 37.9                   |
| N150P120K120 | 4.66   | 5.50   | 2.75                    | 37.8                   |
| Manure 40' | 5.01     | 5.88   | 2.34                    | 37.6                   |
| N90P60K60+ Manure 40' | 4.83     | 5.65   | 2.61                    | 36.5                   |
| N150P120K120+ Manure 40' | 5.03     | 5.53   | 2.68                    | 38.9                   |
| Manure 80'** | 5.23     | 5.69   | 2.48                    | 36.8                   |
| N90P60K60+ Manure 80'** | 5.19     | 5.84   | 2.44                    | 36.5                   |
| N150P120K120+ Manure 80'** | 5.19     | 5.68   | 2.49                    | 37.1                   |

Note: * aftereffect of 40 t/ha of manure: ** aftereffect of 80 t/ha of manure.

The research results show that the humus content in the soil changes under the influence of fertilizers. The use of mineral fertilizers enhances the mineralization of organic matter relative to control. So, with the introduction of N90P60K60, the humus content decreased by 0.08% in relation to the control variant. A double dose of mineral fertilizers saves the process of reducing the content of humus.

The aftereffect of organic fertilizers somewhat reduced the mineralization processes.

An increase in the content of humus in the soil is observed due to the introduction of a double dose of manure and in combination of a double dose of manure with one and two doses of mineral fertilizers. For N90P60K60+ manure 80 t / ha and N150P120K120 + manure 80 t / ha, the humus content in the soil layer is 0-30 cm higher by 0.24%, and in the variant with aftereffect 80 t / ha of manure - 0.28% in relation to control.

Considering the effect of fertilizers on soil acidity, it should be noted that high saturation with mineral fertilizers contributes to acidification of the soil solution reaction. In the variants with the introduction of single and double doses of mineral fertilizers, the pH in the arable layer of typical chernozem decreased from 5.85 to 5.50. A positive effect on the change in the reaction of the soil solution was made by the aftereffect of organic fertilizers and the introduction of mineral fertilizers against aftereffect of manure. Consequently, mineral fertilizers contribute to the acidification of the soil reaction, and organic fertilizers stabilize this indicator.

Long-term application of mineral fertilizers leads to an increase in hydrolytic acidity, compared with the option without the use of fertilizers, its value increased by 0.27 mEq/100 g of soil. The effect of manure and the application of mineral fertilizers against the aftereffect of a double dose of manure has a positive effect, and the value of hydrolytic acidity decreases to the level of the control variant.
The amount of absorbed base is high and, according to the experimental options, varies from 36.5 to 38.9 mEq/100 g of soil, therefore fertilizers did not significantly affect the change in the amount of absorbed bases.

**Table 2.** Dynamics of the content of active forms of cadmium and lead in the arable layer of typical black soil (2013-2019, culture - winter wheat), mg/kg.

| Variant | Cd | Pb |
|---------|----|----|
| Control | 0.14 | 2.10 | 4.40 |
| N<sub>90</sub>P<sub>60</sub>K<sub>60</sub> | 0.12 | 2.13 | 4.56 |
| N<sub>18</sub>0P<sub>20</sub>K<sub>120</sub> | 0.11 | 2.19 | 4.70 |
| Manure 40<sup>+</sup> | 0.08 | 1.95 | 4.70 |
| N<sub>90</sub>P<sub>60</sub>K<sub>60</sub>+ Manure 40<sup>+</sup> | 0.17 | 2.15 | 4.65 |
| N<sub>18</sub>0P<sub>20</sub>K<sub>120</sub>+ Manure 40<sup>+</sup> | 0.08 | 2.19 | 4.77 |
| Manure 80<sup>**</sup> | 0.07 | 1.87 | 4.50 |
| N<sub>90</sub>P<sub>60</sub>K<sub>60</sub>+ Manure 80<sup>**</sup> | 0.07 | 2.18 | 4.10 |
| N<sub>18</sub>0P<sub>20</sub>K<sub>120</sub>+ Manure 80<sup>**</sup> | 0.14 | 2.22 | 4.00 |

Note: * aftereffect of 40 t / ha of manure: ** aftereffect of 80 t / ha of manure.

The analysis of the results of the study shows that the content of active forms of cadmium in the soil layer of 0-30 cm according to the experimental options ranges from 0.08 to 0.17 mg/kg in 2013 and from 0.09 to 0.77 mg/kg in 2019. The content of active forms of cadmium in the variant without fertilizing increased by 0.08 mg/kg over 6 years, and in the variant with aftereffect of 80 t/ha of manure, the maximum increase in the element content was noted - by 0.2 mg/kg. The application of mineral fertilizers at a dose of N<sub>90</sub>P<sub>60</sub>K<sub>60</sub> and N<sub>18</sub>0P<sub>20</sub>K<sub>120</sub>, against the aftereffect of 80 t/ha led to a decrease in the content of active cadmium to 0.19 mg/kg, which, in our opinion, is associated with the formation of organo-mineral compounds with cadmium.

The content of active lead compounds in the period from 2013 to 2019 increased on average by 2 times for all the studied variants of the experiment. It should be noted that fertilizers do not significantly affect the change in lead content. So, by 2019, the application of mineral fertilizers in a dose of N<sub>90</sub>P<sub>60</sub>K<sub>60</sub> and the aftereffect of 80 t/ha of manure increased the content of mobile forms of lead by 0.3 mg/kg or 6.4%, and the combined action of mineral and organic fertilizers reduced its content by 0.4 mg/kg or 9.1 %

Such an increase in the content of the active form of lead in the soil can be associated, in our opinion, with the powerful technogenic impact and the supply of this element in a form readily soluble in soil waters, for example, in the form of oxides with aerosols released as a result of the combustion of gases, gasoline, etc., since the distance of the experimental section from the M2 Federal Highway is about 700 meters. Fertilizer, in which the element is present in the form of readily soluble salts (carbonates, hydrophosphates), can also be a source of lead in the soil.

Studies have shown that fertilizers have a greater impact on the change in the content of mobile cadmium compounds in the arable soil layer. We determined the content of gross forms of cadmium (Table 3) and calculated the mobility coefficient of cadmium in the soil (Table 4). The mobility coefficient allows you to evaluate the effect of chemicalization on the conversion of cadmium in the soil.
organic fertilizers are applied to the soil, as well as their combinations, a certain pattern is observed. In 2015, the cadmium content in the experimental variants varied from 0.62 mg/kg in the variant with the aftereffect of 40 t/ha of manure to 0.86 mg/kg in the variants with the introduction of mineral fertilizers in one and two doses against the background of the aftereffect of 80 t/ha of manure, in 2019 - 0.64 mg/kg in the variant with aftereffect of 40 t/ha of manure up to 0.91 mg/kg in the variant of applying N150P120K120 against the background of the aftereffect of manure at a dose of 80 t/ha.

In 2013, relative to the control in the variants N90P60K60 + 80 t/ha of manure and N150P120K120 + 80 t/ha of manure, the cadmium content increases by 0.14 mg/kg, and in 2019 its content increased by 0.05 mg/2013 compared to 2013 kg in the variant saturated with fertilizers. Thus, the systematic use of fertilizers did not lead to a substantial accumulation of gross forms of cadmium in the soil.

| Variant | 2013 | Years of study | 2019 |
|---------|------|----------------|------|
| Control | 13.8 | 29.7           |      |
| N90P60K60 | 16.7 | 33.3           |      |
| N150P120K120 | 15.6 | 32.1           |      |
| HaNo3 40’ | 11.1 | 29.7           |      |
| N90P60K60+ manure 40’ | 19.2 | 28.2           |      |
| N150P120K120+ manure 40’ | 17.9 | 31.3           |      |
| HaNo3 80’’ | 13.3 | 28.2           |      |
| N90P60K60+ manure 80’’ | 16.1 | 22.1           |      |
| N150P120K120+ manure 80’’ | 19.4 | 22.1           |      |

Note: * - aftereffect of 40 t/ha of manure; ** - aftereffect of 80 t/ha of manure

The use of fertilizers contributes to an increase in the coefficient of mobility, and in 2019 the coefficient of mobility increased 2.1 times and amounted to 29.7%. From 2013 to 2019, the use of mineral fertilizers increased the mobility coefficient of the metal 2 times.

The effect of manure reduces the mobility of cadmium. In the case of manure of 40 t/ha in 2013, its content relative to control decreased by 2.7%. In 2015, the application of mineral fertilizers against the background of the aftereffect of a double dose of manure has the maximum positive effect on reducing the mobility of cadmium in the soil - by 7.6% relative to the control. In the period from 2013 to 2015, the cadmium mobility coefficient in option N150 P120 K120 + manure 80 t/ha (aftereffect) increased by only 2.7%.

The positive effect of manure and mineral fertilizers against the aftereffect of manure on a decrease in the cadmium mobility coefficient is explained by the fact that, along with the formation of carbonates and bicarbonates in the soil, complex compounds of cadmium with organic matter of the soil and phosphate ions are also formed.

Thus, the use of fertilizers in different doses did not significantly affect the change in the content of gross forms of cadmium, however, its slight increase was observed in all cases. The highest content of gross forms of cadmium was observed on variants with mineral fertilizers against the aftereffect of 80
t/ha of manure. In variants with the use of mineral fertilizers, the rate of accumulation of the element is negligible. The application of mineral and organic fertilizers and their joint application from 2013 to 2019 change the content of active forms of cadmium upward. A slight increase in the content of active forms of cadmium in variants with the introduction of mineral fertilizers is, in our opinion, associated with an increase in the acidity of the soil solution, which promotes the transition of cadmium from the gross form to the mobile one. The cadmium activity coefficient varies depending on the dose of fertilizer applied. The greatest mobility of the element can be traced when making mineral fertilizers. The introduction of manure and the application of mineral fertilizers against the background of manure has a positive effect on reducing the coefficient of mobility.

The accumulation and transformation of mobile forms of cadmium and lead in chernozem of typical soils is associated with the reaction of the medium, organic matter content, particle size distribution, vegetation, and metal migration processes in the soil cover [9, 10].

Analysis of the data showed differences in the quantitative distribution of cadmium and lead and nutrients in the soil of the experimental field. As a result of the studies, it was found: in variants with a high humus content, the cadmium and lead content is lower, which is associated with the fixation of mobile forms of heavy metals with organic matter of the soil and the formation of complex insoluble compounds; acidification of the soil solution, especially on variants with the introduction of mineral fertilizers, contributes to the accumulation of active forms of cadmium and lead.

Ecological and agrochemical assessment of the soil indicates the need to control the cadmium and lead content, since there is a tendency to accumulate them in the soil.

Reference
[1] Xu Y G, Yu W T, Ma Q and Zhou H 2015 Potential risk of cadmium in a soil-plant system as a result of long-term (10 years) pig manure application Czech Academy of Agricultural Sciences. Plant, Soil and Environment 61 (8) 352-7
[2] Panin S I, Kolesnichenko E Yu, Morozova T S and Solovyova V I 2014 Assessment of the accumulation of heavy metals by woody plants of the shelterbelts and field crops Vestnik MGOU. Series “Natural Sciences” 1 75-80
[3] Litsukov S D and Akinchin A V 2007 Heavy metal translocation in the soil-plant system (Moscow)
[4] Morozova T S, Litsukov S D and Putyatin L A 2016 The content of mobile cadmium in the soil with prolonged use of fertilizer Sugar beet: scientific and practical journal 1 33-5
[5] Akinchin A V and Linkov S A 2015 Change in the nutrient regime of typical black soil depending on the technology of cultivation of crops Bulletin of the Kursk State Agricultural Academy 8 136-40
[6] Linkov S A, Kuznetsova L N, Akinchin A V and Shiryaev A V 2016 Change in soil fertility depending on factors of intensification of agriculture (Moscow)
[7] Lukin S V 2008 The content of lead, cadmium, mercury and arsenic in the agroecosystems of the Belgorod region Achievements of science and technology of the agro-industrial complex 7 39-41
[8] Sheujen A Kh, Neshchadim N N, Gaidukova N G and Shabanova I V 2019 The influence of natural and anthropogenic factors on the physicochemical properties of leached chernozem and its pollution by heavy metals Agrochemistry 1 19-28
[9] Morozova T S and Kolesnichenko E Yu 2019 Agroecological assessment of the systematic use of fertilizers for the accumulation of cadmium and lead in typical black soil Innovations in the agricultural sector: problems and prospects 4 (24) 226-34
[10] Morozova T S, Linkov S A, Litsukov S D and Kolesnichenko E Yu 2019 Assessment of the agroecological state of chernozem typical in the southwestern part of the Central Chernozem Region Bulletin of agrarian science 6 (81) 123-8