The Sources of Income and the Dynamics of Heavy Metals in the Soil of Different Agro-Ecosystems with Their Long-Term Agricultural Use

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Abstract. In the present work, an attempt was made to determine the dynamics of the content of gross forms of heavy metals in long (50 years) field experiments of various agroecosystems on various fertilizer backgrounds. In the ecosystem of the field five-field grain-crop crop rotation, the dynamics of the content of heavy metals was more clearly expressed due to their higher removal due to a higher yield of crops entering the crop rotation, as well as more significant inflows of heavy metals to the soil with mineral fertilizers and manure at a dose of 20 tons / ha per rotation sowing volume. The main sources of heavy metals in the soil are the mineral and especially organic fertilizers. Introduction of mineral and organic fertilizers, even in moderate doses for 10 rotations has contributed to the content of heavy metals in the ploughed layer typical black earth and resulted in exceeding the concentrations of individual elements (Pb, Cd), having high background values.

1. Introduction

Agrochemical soil survey of the Kursk region indicates the presence of large areas with a high content of heavy metals [1,2]. There is a clear trend of increasing the content of heavy metals in soils, especially suburb zones and industrial enterprises [3,4]. It’s found that the main soils polluters in Kursk region are such heavy metals as Pb, Zn, Cu and Cd. The high content of these elements are both in natural ecosystems and in the agro-ecosystems [5].

Being accumulated in the soil in large quantities, heavy metals have had a negative impact on the biological properties of the soil (microbiological activity, the activity of soil enzymes) humus condition, structure, pH environment, etc. The result is a partial and, in some cases, the total loss of soil fertility [6,7].

The main sources of heavy metals in the soil are: industrial enterprises, which use them in technological processes; thermal station of fossil fuels burning, vehicle emissions, as well as organic and mineral fertilizers [8,9]. The use of mineral fertilizers in agriculture aimed at improving the elements content in the soil for power plants, increasing crop yields. However, apart from the basic components of fertilizers (elements of mineral nutrition) there is a composition of impurities of heavy metals and metalloids [10,11]. The contents of these contaminants is closely dependent on the quality of the source of raw materials and technologies of processing [12,13].
The most enriched one is with chemical elements and impurities with phosphorus fertilizers. So, in fertilizers produced from phosphate, there is high content of Mn up to 0.1%, the VA and Zn up to 0.01-0.05 %, F up to 0.6% [14]. Nitrogen and potash fertilizers can contain up to 100-400 mg/kg Mn, Cr, Ni, Zn, Ti [15]. A long and systematic application of various forms of mineral fertilizers can contribute to the accumulation of heavy metals in soils and agricultural products [16,17].

Therefore, to study the effect of fertilizer on the accumulation of heavy metals in the ploughed layer of the soil in different agro-ecosystems with their long-term agricultural use, it is essential for chemical monitoring of soils of the Central Chernozem region of Russia. Of particular importance there are studies conducted in the long-term fixed field experiments, the experimental data which can become the basis for the practical background of chemical monitoring of soil and agro-ecological monitoring at the reference areas [18].

The most complete monitoring of soil contaminated with heavy metals will be done with the system of indicators to assess the degree of contamination, change the properties of soils under the influence of the toxics and sustainability of soils to be contaminated [19].

In the work there is an attempt to determine the dynamics of the content of the gross forms of heavy metals in the long (50 years) field experiments of different agroecosystems at different levels of fertilized backgrounds.

2. Methods
The studies were conducted on the typical chernozem in the multi-year permanent Petrinsky’s establishment of the Soil Institute named after V.V. Dokuchaev and Kursk federal agricultural research center. Long-term stationary experiments laid in 1968 in crop short rotations on two backgrounds: without fertilizers and with applying N200R250A250 and 20 t/ha of manure per the rotation. The experiments have been deployed in time and space in three times cycle with a total area of 370 and a checking area of 200 m2. In parallel experiments there was carried out the cultivation of agricultural crops in the permanent clean fallow.

The soils of an experienced land are presented by typical powerful thick loamy semi humus chernozem. The distribution of humus in soil profile is typical for ploughed chernozem: even reducing its content down the profile from 6.2% in the layer 0-25 cm to 2.4-3.2% at a depth of 100 cm. The density of the ploughed layer is 1.05-1 to 0.10 g/cm3, the total density is 58-63%, the amount of absorbed grounds is 32.9-33.9 mg per 100 g of soil, the degree of saturation of the soil grounds is 88.9-90.1%.

| Level  | pH | Humus, % | Phosphorus according to Chirikov | Potassium according to Maslova | Lead, Pb | Zink, Zn | Copper, Cu | Cadmium, Cd | Nickel, Ni |
|--------|----|----------|----------------------------------|-------------------------------|----------|---------|-----------|------------|-----------|
| 0-10   | 5.9| 6.2      | 14.5                             | 16.4                          | 48, 66   | 39,61   | 8.2       | 1.44       | 87.3      |
| 10-25  | 6.3| 6.0      | 14.6                             | 16.8                          | 39, 34   | 20,39   | 4.9       | 0.96       | 66.6      |
| 0-25   | 6.1| 6.1      | 14.6                             | 16.6                          | 44, 00   | 30,00   | 6.6       | 1.20       | 77.0      |
| MPC    |    |          |                                  |                               | 30       | 100     | 55        | 1.0        | 85        |

Table 1. The original agrochemical soil indicators of an experienced land.
The contents of the active phosphorus (according to Chirikov) is 10.1-14.5, the exchange of potassium (according to Maslova) - 14.6-16 1.8 mg/100 g of soil. The Gross content of heavy metals was defined in the 6nHcl on atomic-absorption spectrophotometer AAS -30. Assessment of the gross forms of Cd and Zn in soils is made according to the procedure the Ministry of Agriculture of the Russian Federation.

3. Results and discussion

Analyzes and calculations have shown that with the introduction of mineral fertilizers to the permanent fallow and winter wheat, which has been grown incessantly for 50 years in a dose of N45P60K60 in the soil annually: Pb - 35.133; Zn - 29.496; Cu - 29.982; Cd - 11.94; Ni - 55.63 mg/ha (table 2.2.).

In seeming at first glance insignificant quantities of heavy metals, annually from mineral fertilizers into the soil for a multi-year period their number can achieve substantial quantities, especially in soils with high background indicators of these elements.

Table 2. The projected flow of heavy metals in the soil with fertilizers.

| Element | Heavy metal concentration in fertilizer, mg/kg | The quantity of heavy metals flowing with the N45P60K60, mg/ha | Admission of heavy metals with fertilizer, mg/ha |
|----------|-----------------------------------------------|-------------------------------------------------------------|--------------------------------------------------|
| Pb       | 0.25                                          | 33.0                                                       | 5700                                            |
| Zn       | 0.5                                           | 66.0                                                       | 2130                                            |
| Cu       | 1.0                                           | 132,                                                       | 1950                                            |
| Cd       | 0.3                                           | 39,6                                                       | 525,                                            |
| Ni       | 0.9                                           | 19.3                                                       | 2550                                            |

So, at a rather high background values of Pb and Cd in the typical chernozem application of mineral fertilizers in dose of N45P60K60 per hectare crop rotation square now leads to exceeding the maximum permissible concentration (MPC) of these elements in the soil (tab. 3).

Table 3. The dynamics of heavy metals in agro permanent fallow and permanent crops of winter wheat during the period 1968-2017 years.

| Index | Heavy metal concentration in soil, mg/kg |
|-------|-----------------------------------------|
| Pb    | 44.00                                   |
| Zn    | 30.00                                   |
| Cu    | 6.60                                     |
| Cd    | 1.20                                     |
| Ni    | 77.00                                   |

| Index | Heavy metal concentration in soil, mg/kg |
|-------|-----------------------------------------|
| Pb    | 44.08                                   |
| Zn    | 30.06                                   |
| Cu    | 6.66                                     |
| Cd    | 1.20                                     |
| Ni    | 77.00                                   |
In the ecosystem of the permanent fallow the contents of the gross forms of heavy metals in the ploughed soil layer after 50 years in the variant without the application of mineral fertilizers remained essentially at the source level as well as the sources of income in the soil were there are only to atmospheric precipitation (acid rain, etc.).

In the variant with the annual application of N45P60K60 content of the gross forms of heavy metals in the soil layer 0-25 cm has increased: Pb + 0.70; Zn + 0.58; Cu + 0.60; Cd + 0.03; Ni + 0.11 mg/kg.

In the ecosystem with the permanent cultivation of winter wheat the dynamics of the contents of the gross forms of heavy metals depend on the ratio of: "Entry into the soil - taking away with a harvest" of winter wheat. In the variant without the application of mineral fertilizers, there has been a trend of reducing the content of heavy metals in the soil, since the removal of their yields of winter wheat exceeded the entry with atmospheric precipitation.

The annual introduction of mineral fertilizers in the dose of N45P60K60 under winter wheat growing incessantly resulted in the increase of the gross forms: Pb + 0.68; Zn + 0.56; Cu + 0.31; Cd + 0.02; Ni + 0.10 mg/kg, as in this case, “the ratio of flow into the soil with mineral fertilizers - taking away with a harvest of winter wheat” was in favor of their income.

In the ecosystem of the five-field crop-rotation the dynamics of heavy metal content expressed more clearly as a result of the higher instances at the expense of higher yield of crops in the crop rotation, as well as more substantial revenue of heavy metals in the soil with fertilizers and manure at a dose of 20 tones/ha for the rotation.

In the agroecosystem of five-field cropping without application of organic and mineral fertilizers the contents of the gross forms of heavy metals in the soil layer 0-25 cm at the end of the rotation of 10 (50 years old) decreased in comparison with the original their content: Pb +0.06; Zn +1.25; Cu + 0.28; Cd + 0.02; Ni + 0.03 mg/kg.

Analyzes and calculations show that with the introduction of mineral fertilizers in the dose of N200P250K250 and 20 t/ha of manure of the five-field crop-rotation projected flow of heavy metals in the soil is: Pb - 313122; Zn - 1738306; Cu - 585875; Cd - 4988; Ni - 743216 mg/ha (table 4.).
Table 4. The projected flow of heavy metals (HM) in the soil with organic and mineral fertilizers in the ecosystem of the five-field crop rotation.

| Name | HM contents in fertilizers, mg/kg | The number of HM, flowing with the N200P250K250, for the crop rotation, mg/ha | HM flow with the fertilizers during 5 years, mg/ha |
|------|----------------------------------|------------------------------------------------------------------------------------------------|--------------------------------------------------|
| Pb   | 14.4 147 23750 1225 28800 0 313122 |                                                                                                 |                                                  |
| Zn   | 0.5 14.2 182 86.4 294 8875 1137 17280 0 173806 |                                                                                                 |                                                  |
| Cu   | 1.0 13.0 186 28.8 588 8125 1162 57600 0 585875 |                                                                                                 |                                                  |
| Cd   | 0.3 3.5 4.2 - 176 2187 2625 - 4988 |                                                                                                 |                                                  |
| Ni   | 0.9 17.0 19.3 36.0 529 10625 1206 72000 0 743216 |                                                                                                 |                                                  |

In the agroecosystems of five-field crop rotation with the introduction of organic and mineral fertilizers the contents of the gross forms of heavy metals in the ploughed soil layer at the end of the 10-th rotation improved in comparison with the original their content: Pb +1.22; Zn - 6.92; Cu + 2.04; Cd + 0.06; Ni + 2.86 mg/kg.

Table 5. Dynamics of the contents of the gross forms of heavy metals in the 5-field crop rotation for 10 rotations, 1968-2017 years.

| Index | HM contents in the soil, mg/kg |
|-------|---------------------------------|
|       | Pb    | Zn    | Cu    | Cd    | Ni    |
| Initial HM contents (1968 r), mg/kg | 42.80 29.15 5.80 1.20 76.53 |
| Crop rotation: Pure fallow-winter wheat and sugar beet - corn- barley + clover (without fertilizers) | 42.74 27.90 5.52 1.18 76.50 |
| HM contents in 50 years (2017), mg/kg | -0.06 -1.25 -0.28 -0.02 -0.03 |
| Crop rotation: Pure fallow-winter wheat and sugar beet - corn- barley + clover (N200P250K250 + manure 20 t/ha) | 44.02 36.08 7.84 1.26 79.39 |
| AAC | +1.22 | +6.92 | +2.04 | +0.06 | +2.86 |
| MPC | 130   | 220   | 132   | 2.0   | 80   |
| AAC | 30    | 100   | 55    | 1.0   | 85   |

4. Conclusions

Thus, a comparative analysis of the content of the gross forms of heavy metals in the ploughed soil ecosystems are not fertilized and fertilized permanent fallow has shown that the main source of heavy metals in the soil are the mineral fertilizers, even in small doses of N45P60K60. Heavy metals flow of technogenic nature (with atmospheric precipitation) for the 50-year period was negligible.
In agro-ecosystems with permanent cultivation of winter wheat and crop rotation without the application of fertilizer over the 50-year period there has been a trend of reduction of the gross forms of heavy metals, due to their offset from the main crops and non-timber products. The same mineral and organic fertilizers, even in moderate doses (N200P250K250+manure 20 t/ha for the rotation of the 5-field crop rotation) for 10 rotations has contributed to the content of heavy metals in the ploughed layer of typical black earth and resulted in exceeding the MPC of individual elements (Pb, Cd ), having high background values.

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