Accounting of heavy metals in agricultural land use

Mikhail Mikhailovich Geraskin1*, Zhanna Nikolaevna Bakanova1, Vasily Ivanovich Kargin2, Natalia Nikolaevna Ivanova2, and Nikolay Nikolaevich Neyaskin1

1 State University for Land Administration, 15, Kazakova St., Moscow, 105064, Russian Federation
2 Ogarov Mordovia State University, 430005, 68 Bolshevik St., Saransk, Russian Federation
3 State Center of Agrochemical Service “Mordovskiy”, 430904, 35 Pionerskaya St., Yalga, Russian Federation

Abstract. People use many chemicals in their economic activities, which leads to the fact that they become involved in a cycle of anthropogenic transformations of the environment. It was proved that microelements and heavy metals are the most toxic among pollutants. Microelements in the arable layer of the soil depend on the type of soils, their location and content in soil-forming rocks. The studies revealed that the content of heavy metals in the soil in all cases is lower than the APC (MPC). The products obtained in the test areas are safe in relation to the content of heavy metals. Adaptive landscape farming systems can serve as an additional and significant step in optimizing the environmental situation when the soils are contaminated with heavy metals.

1 Introduction

People use many chemicals in their economic activities, which leads to the fact that they become involved in a cycle of anthropogenic transformations of the environment [1–2]. Often, due to imperfect cleaning systems, these substances enter the soil, water and air, thus contaminating and poisoning them.

It was proved that microelements and heavy metals are the most toxic among pollutants. They are the main indicator of anthropogenic impact on the environment, in particular on the soil [3]. It should be noted that these pollutants rank second in terms of hazard, second only to pesticides. In the future, they can become more dangerous than solid waste and waste from nuclear power plants.

Since metals are mobilized in the soil and various migratory forms are formed, it is in it that the main cycles of migration of heavy metals in the biosphere occur. Besides, the soil can serve as a source of secondary pollution of water and air. From the soil these substances are absorbed by plants, which in the worst way can get into human food.

All heavy metals are combined into a fairly large group of chemical elements, the main criterion is their atomic mass. Of these, three elements can be distinguished as especially toxic – mercury, lead and cadmium. The rest belong to microelements: zinc, cobalt, vanadium, copper, tin, molybdenum and nickel [8].

Most of the agricultural land is polluted by elements such as mercury, tin, bismuth, arsenic, lead, copper, which enter the soil with poisonous chemicals, biocides, plant growth stimulants, and structure-forming agents. The introduction of unconventional fertilizers derived from all kinds of waste, and alternative fertilizers made from various wastes into agricultural production often contain a significant set of pollutants in fairly high concentrations.

The purpose of the study is to monitor the content of microelements and heavy metals in the soils of the Republic of Mordovia and crops growing on them with the subsequent introduction of optimal crop rotations agricultural land planning in enterprises engaged in the production of food crops.

2 Materials and methods

Since 1993, the State Center of the Mordovian Agrochemical Service has been conducting a system of regular observations in 13 reference areas on the territory of the republic. By 2010, the number of reference plots reached 23 in 20 districts in 21 farms of the Republic of Mordovia. They are located in various natural and climatic zones and reflect the climatic and economic features of the main soil types (Table 1).

Conventional methods were used to study the accounting of the content of heavy metals in the soil: determination of the content of mobile and acid-soluble forms of heavy metals was carried out by the atomic absorption method; detection of heavy metals in plant tissues was carried out by atomic absorption method in flame of an air-acetylene burner.

3 Results and discussion

Microelements in the arable layer of the soil depend on the type of soils, their location and their content in soil-forming rocks. The content of boron and molybdenum in all reference areas ranges from medium to high (Table 2). Most
of them are contained in reference plots No. 5, 7, 8. The content of zinc, manganese, cobalt is lower. Conversely, all reference areas contain high amount of copper in the arable layer. This pattern is observed over the entire study period [4].

Table 1. Topographic survey of reference plots and presence of pollutants.

| Region             | Nearest inhabited locality | RP No. | RP area, ha | Leached chernozem | Podzolized chernozem | Dark-grey forest soil | Grey forest soil | Sod-podzolic soil | Alluvial soil |
|--------------------|---------------------------|--------|-------------|--------------------|----------------------|----------------------|-------------------|-------------------|---------------|
| Oktyabrsky         | Nikolaevka                | 5      | 46          | 54° 10' 45° 15'   | 0.5                  | 10                   | 1                 | 0.5               | 15            |
| Oktavsky           | Saransk                    | 8      | 29          | 54° 10' 45° 15'   | 5                    | 0.2                  | 25                | 5                | 2             |
| Lyamibrsky         | Lyambir                    | 12     | 70          | 54° 15' 45° 07'   | 1.5                  | 15                   | 15                | 20               | 0.01          |
| Chamizinsky        | Sabur-Machkasy             | 21     | 112         | 54° 23' 45° 45'   | 0.3                  | 3                    | –                 | –                | 0.001         |
| Romodanovsky       | Maloe Chufarovo            | 22     | 57          | 54° 03' 45° 25'   | 1.5                  | 20                   | –                 | 22               | 0.2           |
| Ardatovsky         | Ardatov                    | 28     | 27          | 54° 50' 46° 13'   | 1.5                  | –                    | –                 | –                | –             |
| Atyashevsy         | Atyashevo                  | 34     | 45          | 54° 43' 46° 18'   | 1.0                  | –                    | –                 | –                | 0.02          |

Table 2. Characteristics of the arable layer by the content of mobile forms of microelements, sulfur, fluorine and iron.

| Region             | Year | RP No. | B    | Mo   | Cu   | Zn   | Co   | Mn   | Fe   | S   | F   |
|--------------------|------|--------|------|------|------|------|------|------|------|-----|-----|
| Leached and podzolized chernozem |
| Oktavsky           | 2011 | 5      | 2.12 | 0.12 | 5.6  | 0.92 | 1.38 | 54   | 18.9 | 6.4 | 0.99|
| Oktavsky           | 2012 | 5      | 2.36 | 0.22 | 4.9  | 0.93 | 1.86 | 38.8 | 17.1 | 3.4 | 0.83|
| Oktavsky           | 2013 | 7      | 0.84 | 0.11 | 5.4  | 0.91 | 0.91 | 74   | 18.7 | 4.3 | 0.66|
| Oktavsky           | 2014 | 8      | 2.28 | 0.21 | 5.1  | 0.85 | 1.44 | 39.7 | 31.9 | 2.5 | 0.60|
| Oktavsky           | 2015 | 8      | 1.89 | 0.17 | 4.3  | 1.02 | 1.46 | 44   | 18.5 | 5.7 | 1.02|
| Oktavsky           | 2016 | 8      | 2.09 | 0.22 | 4.3  | 0.78 | 1.79 | 41.3 | 10.4 | 1.7 | 0.74|

The iron content in reference plots No. 6, 10, 29 is much higher than in other areas. The sulfur content in the soils of the reference areas is low and ranges from 1.6 to 6.0 mg/kg. Fluorine is the most active and reactive metalloid. Fluorine and its compounds in microdoses are necessary, in high doses – toxic to humans, animals, plants. The sulfur content in reference areas No. 5, 8, 21 is slightly higher compared to other areas – 0.83; 0.74; 0.76 mg/kg of soil, but the results obtained do not exceed the maximum permissible concentrations in soil.

An increased content of mobile forms of heavy metals and arsenic (Table 3) is observed at reference plots No. 7, 8, 10, 32, which are located near hazardous pollution sources. For example, plot No. 7 is located next to the runway of Saransk airport, area No. 8 is located near the rubber factory on one side and the railway bed on the other side.

The reference plot No. 10 is located in the flood meadows of the Alatyry River, toxic elements settle during the spring flood. Other reasons for the overestimated content of heavy metals are the location of reference plots near motorways (highways).

The mercury content is small in the arable horizon of all reference plots, i.e. compatible with the normal limits, but this element is more contained in RP No. 34 – 0.036 mg/kg of soil. In reference plot No. 32 the content of zinc, lead, nickel, arsenic is the highest – 1.81; 1.35; 1.25; 5.2 mg/kg soil. At the same time, the excess of the MPC in all areas is not observed.

Table 3. Characteristics of the arable layer by the content of mobile forms of microelements, sulfur, fluorine and iron.
Table 3. Characteristics of the arable horizon of reference plots by the content of mobile forms of heavy metals and arsenic.

| Region                  | RP No. | Observation (month) | Mobile forms (acetate-ammoniacal nuffer with pH 4.8), mg/kg |
|-------------------------|--------|---------------------|-------------------------------------------------------------|
|                         |        |                     | Cu   | Zn   | Cd  | Pb  | Ni  | Cr  | As  | Hg  |
| Leached and podzolized chernozem |        |                     |      |      |     |     |     |     |     |     |
| Oktyabrsky              | 5      | 22.04               | 0.20 | 0.93 | 0.060| 0.77| 0.45| --  | 3.8 | 0.020|
| Oktyabrsky              | 7      | 03.05               | 0.22 | 0.85 | 0.080| 0.83| 0.73| --  | 4.0 | 0.027|
| Oktyabrsky              | 8      | 26.04               | 0.26 | 0.78 | 0.050| 1.12| 0.58| --  | 5.4 | 0.019|
| Lambirsy                | 12     | 30.04               | 0.17 | 0.68 | 0.050| 0.87| 0.48| --  | 4.3 | 0.024|
| Ruzaevsky               | 13     | 04.05               | 0.20 | 0.73 | 0.080| 0.62| 1.03| --  | 4.6 | 0.025|
| Chamzinsky              | 21     | 29.04               | 0.38 | 1.01 | 0.060| 0.96| 0.68| --  | 3.8 | 0.020|
| Average                 |        |                     |      |      |     |     |     |     |     |     |

The collection of information on crops and ground adjustment of borders was carried out in those farms where RPs are laid. The measurements were made by height, density, weight from 1 m, fresh productivity in various phases of development, and crop accounting (Table 4). Weed types, their height, productivity, etc. were determined for seeding.
Table 4. Crop chemical composition.

| Region                  | RP No. | Crop          | Product     | Yield, t/ha | Total chemical elements, mg/kg of natural moisture products | Radiological indicators, Bq/kg |
|-------------------------|--------|---------------|-------------|-------------|-------------------------------------------------------------|--------------------------------|
|                         |        |               | Cu          | Zn          | Pb            | Hg            | Cd            | As            | Sr-90 | Cs-137 |
|                         | Leached and podzolized chernozem |       |             |             |                |                |                |                |        |        |
|                         |        |               |             |             |                |                |                |                |        |        |
|                         |        | winter wheat  | grain       | 20.1        | 2.29          | 24.49         | 0.30          | 0.002         | 0.024 | 0.018  | 2.0   | 3.8   |
|                         |        |               | straw       | 26.3        | 2.89          | 15.94         | 1.32          | 0.004         | 0.064 | 0.019  | 3.1   | 7.6   |
|                         |        | oat           | grain       | 18.1        | 1.52          | 20.18         | 0.42          | 0.002         | 0.014 | 0.019  | 1.9   | 4.0   |
|                         |        |               | straw       | 22.3        | 1.63          | 9.71          | 1.71          | 0.004         | 0.039 | 0.019  | 3.3   | 4.2   |
|                         |        | spring wheat  | grain       | 20.4        | 3.06          | 21.38         | 0.27          | 0.002         | 0.015 | 0.018  | 1.9   | 4.9   |
|                         |        |               | straw       | 26.1        | 0.97          | 15.08         | 0.51          | 0.003         | 0.064 | 0.020  | 3.9   | 5.9   |
|                         |        | barley        | grain       | 23.8        | 2.37          | 17.44         | 0.16          | 0.002         | 0.012 | 0.018  | 3.0   | 4.8   |
|                         |        |               | straw       | 20.6        | 0.49          | 4.50          | 0.40          | 0.004         | 0.027 | 0.019  | 3.2   | 6.0   |
|                         |        | winter wheat  | grain       | 27.4        | 1.89          | 17.3          | 0.38          | 0.004         | 0.038 | 0.02   | 3    | 5.9   |
|                         |        | corn          | straw       | 35.2        | 0.54          | 5.06          | 1.31          | 0.006         | 0.034 | 0.021  | 3.8   | 6.5   |
|                         |        |               | herbage     | 16.9        | 0.53          | 4.80          | 0.71          | 0.002         | 0.015 | 0.015  | 1.6   | 5.2   |
|                         |        | perennial     | herbage     | 3.97        | 2.54          | 11.47         | 1.06          | 0.004         | 0.073 | 0.019  | 1.8   | 4.9   |
|                         |        | barley        | grain       | 2.68        | 2.91          | 25.20         | 0.35          | 0.002         | 0.029 | 0.021  | 1.9   | 5.1   |
|                         |        |               | straw       | 2.32        | 1.35          | 7.08          | 1.68          | 0.005         | 0.053 | 0.023  | 2.9   | 6.5   |
|                         |        | winter wheat  | grain       | 21.34       | 30.53         | 0.33          | 0.002         | 0.047         | 0.016 | 1.5    | 3.6   | 42    |
|                         |        | wheat         | straw       | 1.31        | 7.50          | 1.17          | 0.004         | 0.042         | 0.017 | 3.0    | 5.4   | 30    |
|                         |        |               | grain       | 1.82        | 26.87         | 0.31          | 0.002         | 0.023         | 0.016 | 1.8    | 3.8   | 29    |
|                         |        | wheat         | straw       | 2.09        | 10.14         | 1.59          | 0.005         | 0.07          | 0.017 | 2.2    | 4.5   | 172   |
|                         | Dark-grey forest soil |       |             |             |                |                |                |                |        |        |      |      |
|                         |        | perennial     | herbage     | 3.32        | 3.77          | 12.89         | 1.00          | 0.003         | 0.044 | 0.018  | 2.2   | 4.8   |
|                         |        | barley        | grain       | 11.51       | 17.90         | 0.67          | 0.002         | 0.010         | 0.019 | 2.4    | 4.3   | 37    |
|                         |        |               | straw       | 21.67       | 7.35          | 1.09          | 0.006         | 0.031         | 0.023 | 3.2    | 5.6   | 40    |
|                         |        | perennial     | herbage     | 3.84        | 5.15          | 14.34         | 2.56          | 0.005         | 0.144 | 0.022  | 4.8   | 1.9   |
|                         |        | annual        | herbage     | 12.3        | 3.01          | 17.11         | 0.84          | 0.006         | 0.059 | 0.024  | 4.8   | 2.3   |

Chemicals are introduced mainly in those reference plots where grain crops are grown (winter and spring crops). They are used in most cases when sowing in rows (winter and other grains) and in the form of feeding in spring on winter crops. Organic fertilizers were not introduced at any reference plot during the entire observation period, and no chemical soil reclamation was carried out.
As mentioned above toxic elements emitted with spent products of motor engines, railway trains, flooding areas as a result of flood waters, pollution due to fuel ingress at gas stations, etc. settle in the soil and, as a rule, in crop products growing on them.

So at RP 7 there is a high content of lead, zinc in the by-products of oats, at RP 10 and 17 (perennial grass) – cadmium. Some elements are contained in greater quantities at RP 5, 8 than in other areas. These plots are located within the city, near the Rubber Products Plant, during the production of which the atmosphere, soil, and ultimately the agricultural culture growing on it, get polluted.

It should be noted that to determine the degree and completeness of dissolution of the studied heavy metals in soil, such indicators as the effective solubility product of sediments of these heavy metals, effective constants of instability of complexes existing in soil horizons and ion exchange constants in the soil-solution system are used [5].

As a result of the studies it can be stated that the content of heavy metals in the soil in all cases is lower than the APC (MPC). The products obtained in the tested areas are safe in relation to the content of heavy metals. If metals contaminated the soil and vegetation, then the current situation can be corrected using a number of methods. First of all, it is necessary to promptly limit the flow of these substances to agricultural land. In the future, various methods should be applied that help to remove them from the root layer or bind them in the soil into low-dissociating compounds. The selection of crops and varieties that are less susceptible to them helps to reduce the accumulation of heavy metals in plants. Timely assessment of the soil for the presence of free forms of these elements and the compilation of crop rotations with the selection of different degrees of soil pollution for the cultivation of certain crops play an important role here.

In our case, we propose to consider the fifth more efficient method to develop environmental measures with the introduction of optimal crop rotations taking into account the established agrochemical indicators of soils and vegetation in agricultural enterprises of the Republic of Moldova.

It has to be said that the first condition to restrict the entry of heavy metals into the soil must be observed as fundamental. Therefore, the restriction of doses for pollution of agricultural land due to environmental requirements is a prerequisite for the greening of agriculture.

Adaptive landscape systems of agriculture can serve as an additional and significant step in optimizing the environmental situation in case of soil pollution with heavy metals, where it is necessary to introduce optimal crop rotations developed in projects of internal land management on an agrarian landscape basis on these land arrays [6].

In these studies a reference plot means an entire field or a separately processed part of it, which are typical for a given region. The plot is not excluded from crop rotation and is in normal agricultural production conditions.

I. Leached chernozem

RP 5 – Nikolaevka village, Oktyabrsky region, 46 hectares (1994). Main pollutants (railway – 1 km, motorway – 0.5 km, airfield – 3 km). The studied areas were used in agricultural production at different times: grain crops were grown for 10 years, tilled crops – 4 years, perennial grass – 4 years, clean fallow – 1 year.

RP 8 – Greenhouse State Unitary Enterprise, Oktyabrsky region, 29 hectares (1994). Main pollutants (foundry – 3-3.5 km). Use of the plot: grain crops – 16 years, tilled crops – 1 year, vico-oat mixture – 2 years.

RP 12 – Cheremishevskoye LLC, Lambirsky region, 70 hectares (1994). Main pollutants (TPP-2 – 20 km, motorway – 10 m). Use of the plot: grain crops – 15 years, annual grass – 2 years, clean fallow – 2 years.

RP 21 – Saburmakhkasskoye LLC, Chamasinsky region, 112 hectares (1994). Main pollutants (railway – 2 km, cement plant – 3 km, motorway – 2 km). Use of the plot: grain crops – 12 years, tilled crops – 3 years, vico-oat mixture – 1 year, perennial grass – 2 years, clean fallow – 1 year.

RP 22 – KZS and K, Romodanovsky region, 57 hectares (1994). Main pollutants (railway – 2 km, motorway – 0.2 km, industrial zone – 20 km, TPP-2 – 22 km). Use of the plot: grain crops – 12 years, tilled crops – 1 year, perennial grass – 3 years, clean fallow – 3 years.

II. Podzolized chernozem

RP 7 – Lukhovskoye State Unitary Enterprise of the Republic of Moldova, Oktyabrsky region, 26 hectares (1998). Main pollutants (railway – 5 km, motorway – 15 km, airport – 500 m). Use of the plot: grain crops – 4 years, perennial grass – 10 years, clean fallow – 1 year.

RP 13 – Demkin farm, Ruzaevsky region, 71 hectares (1994). Main pollutants (railway – 800 m, motorway – 50 m, industrial facilities – 1 km). Use of the plot: grain crops – 16 years, clean fallow – 3 years.

III. Dark-gray forest soil

RP 17 – Vector and K LLC, Zubovo-Polyansky region, 27 hectares (1999). Main pollutants (motorway – 30 m). Use of the plot: grain crops – 3 years, perennial grass – 11 years.

RP 27 – Samaevskoe LLC, Kovykinsky region, 27 hectares (1994). Main pollutants (motorway – 100 m). Use of the plot: grain crops – 8 years, tilled crops – 6 years, annual grass – 1 year, clean fallow – 4 years.

IV. Sod-podzolic soil

RP 14 – Tarkhanovskoye LLC, Rodina branch, Temnikovsky region, 70 hectares (1996-2012). Main pollutants (motorway – 10 m). Use of the plot: grain crops – 3 years, tilled crops – 1 year, clean fallow – 1 year, perennial grass – 12 years.

V. Alluvial granular soil

RP 3 – Kirovskoye LLC, Bolshebereznikovsky region, 22 hectares (1996-2012). Main pollutants (motorway – 10 m, railway – 10 m, airfield – 2 km). Use of the plot: clean fallow – 3 years, perennial grass – 14 years.

RP 6 – Nikolaevka village, Oktyabrsky region, 18 hectares (1994-2012). Main pollutants (motorway – 150 m, railway – 10 m, airfield – 2 km). Use of the plot: vegetable and tilled crops – 11 years, grain crops – 3 years, clean fallow – 3 years, perennial grass – 2 years.

RP 10 – Culture CJSC, Ichalkovsky region, 10 hectares (1994). Main pollutants (railway – 100 m – 2 km). Use of the plot: perennial grass (permanent).

4 Conclusion

In modern agriculture as a result of the increased man-made load the areas of soils contaminated with heavy metals increase, which makes it difficult to obtain high-quality agricultural products. They enter the agroecosystem in
various ways: from gas and dust emissions, with atmospheric precipitation, irrigation waters, etc. It should also be noted that it is during dispersion in ecosystem components that heavy metals enter the environment from technogenic sources, and the most important is the dispersion of aerotechnogenic emissions through the atmosphere. Currently, agrarian landscapes around large cities are subject to anthropogenic impact.

The environmental assessment should distinguish between pollution factors, and the content of heavy metals in suburban agricultural land represents the sum of the components of natural and man-made origin. Thus, it is possible to observe the expansion of the soil range with a reduced environmental value.

It should be noted that the decrease in the accumulation of humus, the decrease in the complexing and structure-forming ability, the biological activity of the soil solution is influenced by the accumulation of heavy metals and accordingly decreases the biological productivity of lands, and enzymatic and microbiological activity is inhibited. All listed processes lead to a decrease in soil resistance to pollution, and, accordingly, to a decrease in soil resistance to overcompaction and the development of gleyization. In fact, the accumulation of heavy metals in the soil leads to an increase in their mobility, to penetration into the deep layers of the soil profile, to pollution of vegetation, to an increase in the content of heavy metals in groundwater. It is also possible to note the unequal nature of transformation in various soils of heavy metals and, accordingly, characteristic buffering.

References

1. Ovchinnikova M. F., Agrochemical Bulletin 1, 2–5 (2013)
2. Tolkach G. V., Bulletin of the Belarusian State Agricultural Academy 4, 118–123 (2017)
3. Sokolov M. S., Agrochemistry 3, 3–18 (2013)
4. Geraskin M. M., IOP Conference Series: Earth and Environmental Science 867, 012060 (2021)
5. Vytnov A. I., Scientific notes of the Russian State Social University 4, 222–227 (2011)
6. Geraskin M.M, Moscow Economic Journal 6, doi: 10.24411/2413-046X-2020-10375