Heavy metals in the soil and vegetation cover of agricultural landscapes in the steppe southern European Russia (Rostov region as a case study)

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Abstract. Recently, there has been an active development of all industries, transport, agriculture within the steppe zone of southern Russia. The agro-industrial complex is widely developed within the Rostov region, characterized by highly efficient crop production, grain and sunflower production. The article examines the soil cover and agricultural products of the region. A change in the distribution of trace elements in the upper soil layer with the use of various agricultural technologies was revealed. It was revealed that the most favorable conditions for the accumulation of most of the studied microelements are formed in the soils under rice fields and vineyards. In the course of the research, the differentiation of the main crops for a number of heavy metals was studied. An analysis of the data obtained indicates the existence of a tendency for the average content of trace elements to increase from grain crops to forage grasses, which is associated with soil conditions and specific biological characteristics. According to the content of elements in soils, the coefficient of biological absorption and biogeochemical activity of the studied crops were calculated, which made it possible to rank them according to their ability to accumulate heavy metals.

1. Introduction

The steppes of the south of the European part of Russia are a zone of intensive agricultural production, where about 80% of the country's agricultural production is grown. In terms of the cost of agricultural products produced in 2019, the Rostov Region ranks 2nd in Russia, second only to the Krasnodar Territory, a region with much more favorable natural and climatic conditions [1]. The main branch of the region's agriculture is crop production. In 2019, the Don Territory produced 11.7% of the all-Russian harvest of sunflower, 10% of grain, 4.1% of vegetables and 3.4% of fruits and berries. Agricultural lands occupy more than 84% of the total area of the region. Arable land accounts for 59% of its entire territory [2]. The sown area, which sharply declined in the 1990s, has steadily increased since 2001. At the same time, the agro-industrial load on the territory is increasing, which is manifested in the growth of the applied mineral fertilizers. Over the past 3 years, the dose of applied fertilizers has exceeded 80 kg per 1 ha of crops [3]. This is the maximum value in the entire history of agriculture on the Don.

In accordance with the classification of N.S. Kasimov [4] in the Rostov region, the following departments of agricultural landscapes are distinguished: field, garden (vegetable), rice plantations and landscapes with perennial crops (orchards and vineyards). With further division into classes, when the features of water migration are taken into account, rain-fed (rain-fed) and irrigated landscapes are...
distinguished, represented by vegetable and rice plantations. Field rainfed landscapes absolutely dominate the area of the Rostov region. Due to the shortage of water resources, the area of irrigated land has decreased by 2 times compared to the 1980s and now accounts for about 3.6% of the total arable land area. Orchards and vineyards take up even less space - less than 1%.

The soil cover of agricultural landscapes is formed mainly by chernozems and chestnut soils. Chernozems occupy the main part of the Rostov region; chestnut soils are developed in the arid east and southeast. Among the soils of the chernozem series, the following subtypes are distinguished: southern chernozem, ordinary, northern Azov and Ciscaucasian, as well as meadow-chernozem soils. Chestnut soils are represented by dark chestnut, chestnut and light chestnut subtypes. Their distinctive feature is solonetsousness, which grows eastward.

The introduction of large amounts of mineral fertilizers leads to disruption of the biogeochemical migration cycles of elements and the accumulation of heavy metals (HM) in all blocks of agroecosystems. Thus, the study of the distribution of HMs in the soil and vegetation cover of various agricultural landscapes is an important and urgent scientific and practical task.

2. Models and Methods
The work is based on the results of ecological and geochemical survey on the territory of 42 agricultural enterprises of different agricultural specialization, located in various natural and agricultural zones of the Rostov region. Sampling included sampling of the surface (0–20 cm) soil horizon and agricultural crops.

Ecological and geochemical survey was carried out over a network of 0.5 × 0.5 km. The sampling of soil samples was carried out by the envelope method from a test plot measuring 10 × 10 m. During the work carried out, 477 samples were taken.

At each site, a sample of the productive part of the agricultural crop was taken simultaneously with the soil. Testing was carried out when crops reached commercial maturity. As a result, 311 samples of agricultural plants were taken, of which: 187 samples of grain and leguminous crops, 74 - forage grasses, 29 - fruits, 21 - vegetables.

In soil and plant samples, the content of vanadium, cadmium, manganese, copper, nickel, lead, chromium and zinc was determined by atomic absorption spectrometry. For soil samples, the concentration and dispersion coefficients of heavy metals were calculated in relation to the local geochemical background. The intensity of accumulation of heavy metals in agricultural crops was expressed through the biological absorption coefficient (BAC) obtained by dividing the content of a chemical element in a plant by its content in the soil.

3. Results and Discussion
To assess the level of anthropogenic transformation of agricultural landscapes, it is necessary to know the content of chemical elements in the landscapes of the background territories. Reference background landscapes should be located outside the zone of influence of industrial and agricultural pollution [4]. Intensive agricultural development of the territory led to the disappearance of natural steppes, therefore, many scientists use HM concentrations in the soils of local protected natural areas as background values [5]. In this work, the natural geochemical background is assumed to be the content of HMs in the soils of pastures, the most remote from the main sources of pollution in the regions of the Rostov region [6, 7]. Regional background concentrations of HMs in soils are presented in table 1.

| regional natural background | Cr  | Mn  | Cu  | Zn  | Pb  | Cd  | Ni  | V   |
|-----------------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| 61.5                        | 750.0 | 34.8 | 84.3 | 24.0 | 0.21 | 43.8 | 97.0 |
As already noted, the most common agricultural landscapes within the Rostov region are non-irrigation landscapes characterized by minimal agrogenic transformation of the soil environment. Their example can be used to study the distribution of chemical elements in different types of soils in the region (table 2).

**Table 2.** HM contents in different types of soils of non-irrigated field landscapes of the Rostov region [8–13].

|                | Southern chernozems | Ciscaucasian chernozems | Ordinary chernozems | Azov chernozems | Meadow-chernozem | Chestnut |
|----------------|---------------------|-------------------------|---------------------|-----------------|------------------|----------|
| Cr             | 60                  | 61                      | 65                  | 67              | 68               | 62       |
| Mn             | 742                 | 724                     | 707                 | 695             | 718              | 712      |
| Cu             | 29.5                | 31.0                    | 33.0                | 30.7            | 33.6             | 28.0     |
| Zn             | 72.4                | 82.5                    | 78.7                | 75.0            | 85.0             | 72.4     |
| Cd             | 0.25                | 0.26                    | 0.23                | 0.25            | 0.25             | 0.24     |
| Pb             | 28.3                | 29.0                    | 25.8                | 27.2            | 26.7             | 26.9     |
| Ni             | 41                  | 42                      | 45                  | 42              | 44               | 36       |
| V              | 92                  | 99                      | 96                  | 92              | 97               | 110      |

Analysis of the content of elements in the soils of rainfed landscapes revealed insignificant differences in the concentrations of HMs within different types of soils in rainfed landscapes. This is explained by the general direction of the soil-forming process and the weak lithogeochemical differentiation of the parent rocks. According to the peculiarities of distribution in soils, the following groups of elements are distinguished:

1) Cr, Cu, Zn и Ni, for which a slight increase in concentrations is observed in the following order: chestnut - subtypes of chernozem - meadow-chernozem soils;

2) V, accumulating mainly in chestnut soils;

3) Mn, Cd и Pb, for which weak differentiation of elements in different soil subtypes was established.

In general, the average content of trace elements in the soils of non-irrigated landscapes is close to the background values. The exceptions are cadmium and lead, the content of which exceeds the natural pedogeochemical background by 1.1–1.2 times, as well as copper and zinc, whose concentrations are 1.1–1.25 times lower than the background.

Reclaimed landscapes and perennial plantations experience a more powerful agro-industrial impact due to the intensive application of mineral fertilizers and pesticides, deep plowing, the introduction of chemical elements with irrigation water, etc. irrigation, soil, drainage) - soil, additional input of chemical elements with fertilizers and pesticides, and sometimes changes in the structure of the soil cover. These factors cause a more significant differentiation of the content of elements in the upper soil cover of agricultural landscapes (table 3).

The average contents of Cr, Cu, Cd, and Pb in the soils of reclaimed types of landscapes exceed the natural soil-geochemical background by 1.1–2.6 times; the average contents of Cu in rice paddies, Zn in soils of gardens, and V in soils of landscapes of perennial plantations are comparable with background values. The concentrations of Mn in the soils of irrigated landscapes and Ni in the soils of vegetable plantations and rice paddies are 0.7–0.8 parts of the background.

Periodically flooded landscapes are distinguished by the most intensive application of fertilizers and pesticides and a long stay of the soil cover under water, which determined the specifics of geochemical processes. In the soils of rice paddies, alkaline-acid and redox conditions of the environment are changeable, and the hydrodynamic regime is unstable [14, 15]. Due to the instability of the soil-geochemical environment, both positive and negative HM anomalies are formed, and rice grown on these soils is often depleted in microelements.
Different agricultural landscapes reveals a clear tendency for the average concentrations of Mn, Cu, Zn, Cd, Pb, and V to increase in the sequence: landraces of perennial plantations, which is associated with the widespread use of copper-containing fungicides - Bordeaux liquid and copper oxychloride [16]. Vineyards, in comparison with orchards, are more often treated with copper-containing preparations, therefore the concentration of the element in the soils of vineyards is much higher.

Comparison of HM contents in soils of different agricultural landscapes reveals a clear tendency for the removal of manganese and the accumulation of chromium, copper, cadmium, lead, and vanadium in the soils of irrigated landscapes and perennial plantations.

Different supply of soils with microelements leads to their different accumulation in agricultural crops. The influence on the chemical composition of plants is exerted not only by the soil-geochemical characteristics of soils, but also by the species belonging of plants, biomorphs, phases of vegetation, natural conditions and other factors.

The content of heavy metals in agricultural vegetation in the Rostov region varies within wide limits (table 4). Manganese exhibits the greatest variability. Its content ranges from 7–11 mg / kg in fruit crops (cherries, apples) to 220 mg / kg in beets. Large variability of contents in different cultures is typical for zinc, cadmium, lead and nickel. At the same time, the concentrations of chromium and copper are in a narrow range. The lowest Cr content is observed in corn (0.14 mg / kg), the highest in sainfoin and cabbage (0.28 mg / kg). The distribution of copper in agricultural crops is very even, with grapes having the highest concentrations (9.6 mg / kg).

Against the background of a wide range of HM contents in the vegetation samples, the following tendency for the average concentrations of Mn, Cu, Zn, Cd, Pb, and V to increase in the sequence: cereals and legumes - vegetables and fruits - forage grasses was revealed. The increase in the average nickel content occurs in a slightly different order: vegetables and fruits - forage grasses - cereals and legumes. This order is formed due to the natural ability of peas to actively accumulate the element, noted by many authors [20–22].

The resulting pattern in the accumulation of trace elements by vegetation can also be explained by which part of the plant is eaten: root crops containing the maximum amount of elements (beets), leaves occupying an intermediate position in the concentration of heavy metals due to additional accumulation of elements with dust and atmospheric precipitation (cabbage ) or fruits (cherries, grapes, tomatoes, apples, cereals). Nevertheless, the distribution of Cr, Mn, Zn, Ni and V in vegetables

| Field arable | Landscapes of perennial plantations | Reclaimed | | | |
|--------------|-----------------------------------|-----------|---|---|
|              | non-irrigated   | gardens   | vineyards | irrigated | periodically flooded |
| Cr           | 64               | 77.1 (1.3)| 86.0 (1.4)| 84.1 (1.4)| 94.2 (1.5)|
| Mn           | 716              | 592 (0.8)| 508 (0.7)| 583 (0.8)| 411 (0.5)|
| Cu           | 31 (0.9)*        | 55.6 (1.6)| 90.2 (2.6)| 38.9 (1.1)| 34.8| |
| Zn           | 78 (0.9)         | 83.2     | 78.3 (0.9)| 77.9 (0.9)| 78.4 (0.9)|
| Cd           | 0.25 (1.2)**     | 0.29 (1.4)| 0.28 (1.3)| 0.26 (1.2)| 0.27 (1.3)|
| Pb           | 27.3 (1.1)       | 30.3 (1.3)| 29.9 (1.2)| 29.4 (1.2)| 29.8 (1.2)|
| Ni           | 42               | 47 (1.1) | 49 (1.1) | 34 (0.8) | 37 (0.8)|
| V            | 98               | 95      | 92        | 105 (1.1)| 124 (1.3)|

* – deconcentration coefficient
** concentration coefficient
and fruits confirms the fact that plants accumulate chemical elements in the following order: roots > leaves > fruits.

**Table 4. HM content in the productive part of agricultural crops grown on the territory of the Rostov region, mg / kg dry matter [8–10, 17–19].**

| Agricultural crops     | Chemical element | Cereals and legumes |          |          |          |          |          |          |
|------------------------|------------------|---------------------|----------|----------|----------|----------|----------|----------|
|                        | Cr               | Mn                  | Cu       | Zn       | Cd       | Pb       | Ni       | V        |
| Wheat                  | 0.16             | 44.3                | 4.3      | 20.7     | 0.065    | 0.63     | 0.35     | 0.046    |
| Barley                 | 0.17             | 42.7                | 4.6      | 22.7     | 0.068    | 0.64     | 0.34     | 0.039    |
| Rye                    | 0.16             | 37.7                | 3.2      | 19.2     | 0.063    | 0.41     | 0.43     | 0.014    |
| Corn                   | 0.14             | 29.1                | -        | -        | 0.080    | 0.77     | 0.30     | 0.039    |
| Sunflower              | 0.15             | 30.2                | -        | -        | 0.080    | 0.77     | 0.24     | 0.052    |
| Peas                   | -                | -                   | 6.8      | 30.7     | -        | 0.10     | 2.09     | 0.020    |
| **Fodder crops**       |                  |                     |          |          |          |          |          |          |
| Alfalfa                | 0.25             | 92.0                | 8.9      | 24.7     | 0.130    | 1.60     | 0.59     | 0.341    |
| Sudanese grass         | 0.21             | 85.2                | 9.4      | 26.0     | 0.130    | 1.64     | 0.46     | 0.248    |
| Sainfoin               | 0.28             | 102.3               | 5.9      | 20.9     | 0.120    | 1.70     | 0.66     | 0.365    |
| **Vegetables and fruits** |                |                     |          |          |          |          |          |          |
| Tomatoes               | 0.23             | 12                  | 7.8      | 13.9     | -        | 0.41     | 0.68     | 0.270    |
| Cabbage                | 0.28             | 48                  | 3.5      | 11.9     | -        | 2.6      | 0.77     | 0.243    |
| Beet                   | 0.40             | 220                 | 6.8      | 18.3     | -        | 0.09     | 1.36     | 0.585    |
| Grapes                 | 0.19             | 12                  | 9.6      | 3.6      | -        | 0.16     | 0.16     | 0.158    |
| Cherry                 | 0.26             | 7                   | 7.9      | 12       | -        | 0.27     | 0.15     | 0.175    |
| Apples                 | 0.24             | 11                  | 3.7      | 7.8      | -        | 0.39     | 0.11     | 0.067    |

To assess the levels of accumulation of heavy metals in plants, biological absorption coefficients were calculated. As the results of the study have shown, agricultural crops, regardless of the place of growth, tend to accumulate lead (BAC 3.2–27.9), which occurs due to a high technogenic load. Plants also actively accumulate copper (BAC 1.14–7.53) and zinc (BAC 1.09–12.43), which is explained by their important biochemical function (table 5).

It is known that zinc belongs to the elements of strong biological accumulation (CBP exceeds one); manganese, nickel, copper and lead are elements of the average biological uptake (BAC = 0.1–1); vanadium, chromium, and cadmium belong to the elements of weak and very weak capture, the BAC of which does not exceed 0.1 [23]. In agricultural crops of the Rostov region, an increase in the values of the BAC of cadmium, lead and copper and moving these elements to a higher level. The transition of chromium to the group of medium biological uptake is noted in wheat (BCI = 0.115), and the transition of vanadium in the Sudanese grass (BCI = 0.233). An increase in the intensity of manganese accumulation is noted in wheat, corn, Sudanese grass, sainfoin and beets, zinc - in peas and wheat (table 5).

Using the indicator of the biogeochemical activity of the species (BAS), obtained by summing the coefficients of biological absorption of individual elements, it is possible to assess the overall ability of the studied culture to the concentration of various microelements. The most intensive involvement of heavy metals in biogenic migration is characteristic of Sudanese grass, wheat and alfalfa, the BAS values of which are 38.05, 37.25, and 36.71, respectively, the least intense - in grapes (BAS = 7.45).

Based on the analysis of the data obtained, it can be argued that forage grasses are characterized by intense accumulation of all the elements under consideration. Also, beets are characterized by intense accumulation of 6 out of 8 considered chemical elements (Cr, Mn, Cu, Zn, Ni and V). This circumstance is due to the fact that we analyzed beet root crops, which store nutrients and are associated with the root system.
The study of the distribution of HMs in different genetic types of soils in rainfed agricultural landscapes revealed lower concentrations of Zn and Cu, as well as increased concentrations of Pb and Cd in comparison with the natural soil-geochemical background. At the same time, the differences in the contents of elements between different types of soil in rainfed landscapes are insignificant, which is explained by the general direction of the soil-forming process and weak geochemical differentiation of parent rocks.

In the soils of reclaimed landscapes, in comparison with non-irrigated ones, there is a clear tendency towards the removal of Mn from soils and the accumulation of Cr, Cu, Zn, Pb, and V. This pattern is due to the level of agrotechnogenic impact, which increases from rainfed agricultural landscapes to rice paddies and vineyards.

When studying agricultural products, the following tendency for an increase in the content of heavy metals was revealed: grain and leguminous crops - vegetables and fruits - fodder grasses. Among vegetables, beets deserve special attention, for which an increased accumulation of most elements (Cr, Mn, Cu, Zn, Ni, V) was noted relative to the other crops under consideration.

4. Conclusion

Table 5. Biological absorption coefficients of HM by agricultural crops of the Rostov region.

| Agricultural crops | Chemical element | БХА |
|--------------------|------------------|-----|
| Wheat              | Cr 0.115 Mn 2.75 Cu 7.53 Zn 12.43 Cd 0.81 Pb 13.2 Ni 0.39 V 0.025 | 37.25 |
| Barley             | Cr 0.066 Mn 0.85 Cu 3.83 Zn 7.53 Cd 0.75 Pb 10.1 Ni 0.18 V 0.016 | 23.32 |
| Rye                | Cr 0.052 Mn 0.91 Cu 3.54 Zn 8.53 Cd 0.77 Pb 8.3 Ni 0.27 V 0.010 | 22.38 |
| Corn               | Cr 0.092 Mn 1.84 Cu - Zn - Cd 0.98 Pb 11.2 Ni - V - | 14.11 |
| Sunflower          | Cr 0.074 Mn 0.87 Cu - Zn - Cd 2.1 Pb 21.3 Ni - V - | 24.34 |
| Peas               | Cr - Mn - Cu - Zn 6.87 Cd 12.4 Pb - Ni 3.03 V 1.22 | 23.53 |

| Fodder crops       | Cr 0.025 Mn 0.79 Cu 3.16 Zn 3.53 Cd 2.3 Pb 26.6 Ni 0.24 V 0.066 | 36.71 |
| Alfalfa            | Cr 0.045 Mn 1.12 Cu 3.33 Zn 3.70 Cd 1.46 Pb 27.9 Ni 0.26 V 0.233 | 38.05 |
| Sudanese grass     | Cr 0.067 Mn 1.39 Cu 2.96 Zn 4.20 Cd 1.08 Pb 12.0 Ni 0.19 V 0.030 | 21.92 |

| Vegetables and fruits | Cr 0.025 Mn 0.43 Cu 2.95 Zn 2.63 Cd - Pb 7.0 Ni 0.29 V 0.038 | 13.36 |
| Tomatoes            | Cr 0.041 Mn 0.72 Cu 1.14 Zn 1.94 Cd - Pb 10.1 Ni 0.24 V 0.032 | 14.21 |
| Cabbage             | Cr 0.065 Mn 2.19 Cu 2.71 Zn 3.65 Cd - Pb 5.1 Ni 0.37 V 0.069 | 14.15 |
| Beet                | Cr 0.020 Mn 0.33 Cu 2.52 Zn 1.09 Cd - Pb 3.2 Ni 0.08 V 0.034 | 7.45 |
| Grapes              | Cr 0.021 Mn 0.23 Cu 3.03 Zn 3.07 Cd - Pb 7.6 Ni 0.08 V 0.035 | 14.07 |
| Cherry              | Cr 0.031 Mn 1.43 Cu 3.40 Zn 4.78 Cd - Pb 14.2 Ni 0.11 V 0.036 | 23.99 |

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