Ecological and agrochemical features of chemical agents use on soils contaminated with cadmium and copper in the link of vegetable rotation

S D Litsukov¹, E G Kotlyarova, S A Linkov, L N Kuznetsova, T S Morozova and A V Shiryaev

Belgorod State Agricultural University named after V. Gorin (Belgorod SAU), Vavilova Street, 1, 308503 Mayskiy, Belgorod region, Russia

¹E-mail: s.litzuckov@mail.ru

Abstract. The article presents mobility coefficients of cadmium and copper, biological absorption coefficients of toxic metals by the main products of potatoes, beetroot and beans, depending on the chemicalization agents used on black soil with a typical heavy loamy granulometric composition. The introduction of lime, the combined application of lime and manure have a positive effect on reducing the coefficient of cadmium mobility. The high content of cadmium and copper in the soil does not have a negative effect on the synthesis of basic organic substances in vegetable products (starch, sugar, protein). The accumulation of nitrates in vegetable products occurs as a result of the mineral and organic fertilizers application; heavy metals do not have a significant effect on the accumulation of nitrate nitrogen during the cultivation of vegetable crops. The coefficient of biological absorption is influenced not only by lime, manure, mineral fertilizers, but also by the physiological characteristics of the crops themselves, which need toxic elements as micro and ultramicroelements for nutrition and synthesis of organic substances. The results of studies on crops of beetroot show that the application of lime, manure and the combined application of lime and manure reduce the intake of cadmium, copper, lead and zinc in root crops and tops of beetroot. A double dose of mineral fertilizers reduces the intake of copper and lead, but insignificantly, and does not have a positive effect on reducing the accumulation of cadmium and zinc. On soils contaminated with heavy metals (Cd, Cu), according to the value of biological absorption coefficient of the studied crops, heavy metals are distributed as follows: when growing potatoes - Cd > Cu; when cultivating table beet - Cu > Cd; when growing beans - Cu > Cd.

1. Introduction

Vegetables hold a special place in the world among food products. Potatoes have become one of the main food crops, the role of which in solving the nutritional problem is very large. Red beet and beans are of great importance for a balanced diet. Basic amount of vegetable crops is not processed in the food industry, but are delivered to the consumer’s table immediately after harvesting. Soils contaminated with heavy metals can become unsuitable for crop production for many years [1]. One of the main toxic elements is cadmium, since it is the most mobile in the soil and can accumulate in crop products. The mobility of cadmium decreases with an increase in the humus content in the soil [2]. However, fertilizers
increase the supply of cadmium to plants, while the share of the toxicant in the yield of the main product in relation to the by-product increases [3-5].

The main measures that reduce the intake of toxic elements are the introduction of chemical ameliorants, which reduce the intake of heavy metals in crop products [6, 7]. The migration of heavy metals in agroecosystems is determined by a number of factors. Among them, the most important are soil conditions and biological characteristics of the plants themselves. This requires deep research in the soil - fertilizer - plant system. The study of techniques that reduce the intake of heavy metals in plants is one of the main tasks in the production of agricultural products.

Therefore, when growing these crops, especially in areas with a high content of toxic elements in the soil, it is necessary to pay special attention to them, first of all, on the accumulation of heavy metals. In addition, almost all vegetable farms are located around large cities and the likelihood of soil contamination of vegetable products with these elements increases. Therefore, we believe that conducting research on vegetable crops in order to obtain environmentally friendly products is one of the most important tasks of agricultural production. The objects of our research to study the use of chemicals on soils contaminated with heavy metals are potatoes, red beet and beans.

2. Methods

Studies to study the intake of heavy metals in potato tubers, red beet and beans were carried out according to the following scheme:

- Control;
- N180P180K180;
- N180P180K180 + CuSO₄ (176.8 g / m²) + CdSO₄ (10.3 g / m²);
- N180P180K180 + Lime (4 t / ha) + CuSO₄ (176.8 g / m²) + CdSO₄ (10.3 g / m²);
- N180P180K180 + Manure (50 t / ha) + CuSO₄ (176.8 g / m²) + CdSO₄ (10.3 g / m²);
- N180P180K180 + Lime (4 t / ha) + Manure (50 t / ha) + CuSO₄ (176.8 g / m²) + CdSO₄ (10.3 g / m²);
- N360P360K360 + CuSO₄ (176.8 g / m²) + CdSO₄ (10.3 g / m²);
- N360P360K360 + Lime (4 t / ha) + CuSO₄ (176.8 g / m²) + CdSO₄ (10.3 g / m²);
- N360P360K360 + Manure (50 t / ha) + CuSO₄ (176.8 g / m²) + CdSO₄ (10.3 g / m²);
- N360P360K360 + Lime (4 t / ha) + Manure (50 t / ha) + CuSO₄ (176.8 g / m²) + CdSO₄ (10.3 g / m²);
- N360P360K360 + Lime (4 t / ha) + Manure (50 t / ha) + CuSO₄ (176.8 g / m²) + CdSO₄ (10.3 g / m²);
- N360P360K360 + Lime (4 t / ha) + Manure (50 t / ha) + CuSO₄ (176.8 g / m²) + CdSO₄ (10.3 g / m²);
- N360P360K360 + Lime (4 t / ha) + Manure (50 t / ha) + CuSO₄ (176.8 g / m²) + CdSO₄ (10.3 g / m²);
- N360P360K360 + Lime (4 t / ha) + Manure (50 t / ha) + CuSO₄ (176.8 g / m²) + CdSO₄ (10.3 g / m²);
- N360P360K360 + Lime (4 t / ha) + Manure (50 t / ha) + CuSO₄ (176.8 g / m²) + CdSO₄ (10.3 g / m²);

The amount of heavy metals applied to the experimental plots was calculated on the basis of pure metal. The research was carried out on typical heavy loamy chernozem with granulometric composition. The experiment was repeated four times.

Agrochemical indicators of the experimental site: humus content - 5.8%, pHkcl - 5.6, mobile phosphorus - 312 mg / kg, exchangeable potassium - 174 mg / kg, easily hydrolyzed nitrogen - 175 mg / kg, cadmium - 0.92 mg / kg, copper - 19.1 mg / kg, lead - 21.5 mg / kg, zinc 44.4 mg / kg. The sown area of the plot is 4.5 m², the accounting area is 3.25 m². Crop accounting was carried out manually. The results were processed by the method of variance analysis. Agrochemical parameters of the soil were determined by the following methods: pHkcl - potentiometric method; humus - according to Tyurin; easily hydrolysable nitrogen - according to Cornfield; phosphorus - according to Chirikov; potassium - according to Chirikov.

Determination of heavy metals was carried out according to the methodological instructions developed by CISAS (1993). For the experiment, a nitrophosphate was used. Mineral, organic and lime fertilizers were applied simultaneously to the soil surface and sealed them while manually digging the site. Heavy metals were introduced each separately, after mixing their salts with soil so that there was no direct contact between them. Then the soil of the plot was dug up.

To study the influence of heavy metals on the quality of agricultural products and their interaction with the soil, it is necessary to conduct research at the level of crop rotation. Therefore, we carried out research on typical black soil when growing potatoes, red beet and beans on a stationary plot in the link of vegetable rotation. The first crop rotation is potatoes, the second is beetroot and the third is beans.
3. Results
The addition of cadmium and copper to the soil increased their content. The presence of total forms of heavy metals on plots did not decrease over three years, but there was a redistribution between the options. The movement of heavy metals in soils can occur with liquid and suspension, with the help of plant roots or soil microorganisms. The adsorption of metals by plant roots leads to the depletion of the lower part of the horizon A of the soil with these elements and the enrichment of its upper part due to the decomposition of plant residues. Spring melt water and rainfall during the growing season of vegetable cultivation have a special influence on the redistribution of heavy metals between the variants. The content of total forms of toxic elements before the experiment was set on average for all options: cadmium - 0.92 mg / kg, copper - 19.1 mg / kg.

The ACL in the soil is: cadmium - 1.0 mg / kg, copper - 66 mg / kg. The introduction of water-soluble salts of cadmium and copper led to an increase in the content of their total forms on average: cadmium in 13-21; copper in 2-2.8 times from the level of ACL and amounted to: 13.57-28.55 mg / kg; 122-168 mg / kg, respectively (table 1). Data on the content of cadmium and copper total forms are presented in table 1.

The artificially created increased content of heavy metals in the soil makes it possible to establish the effect of various chemical agents on the yield, quality and accumulation of toxic elements in the main and by-products of potatoes, red beet and beans.

Table 1. Content of cadmium and copper total forms in soil on average for three years, mg / kg.

| Experiment variants          | Samples       | potatoes | red beet | beans | On average |
|------------------------------|---------------|----------|----------|-------|------------|
| Control                      |               | Cd       | Cu       | Cd    | Cu         | Cd       | Cu       | Cd       | Cu       |
|                             |               | 0.85     | 24.03    | 1.19  | 20.63      | 1.05     | 24.9     | 1.03     | 23.19    |
| N180P180K180                 |               | 0.79     | 22.17    | 1.17  | 20.39      | 1.04     | 22.4     | 1.00     | 21.65    |
| N180P180K180 + Cu, Cd       |               | 17.77    | 148.0    | 25.52 | 168.37     | 21.23    | 150.4    | 21.51    | 155.59   |
| N180P180K180 + Cu, Cd+ lime |               | 15.97    | 122.4    | 23.28 | 168.22     | 19.73    | 148.8    | 19.66    | 146.47   |
| N180P180K180 + Cu, Cd+ manure|               | 15.77    | 140.8    | 22.77 | 144.63     | 20.13    | 155.1    | 19.56    | 146.84   |
| N180P180K180 + Cu, Cd+ manure+ lime | | 15.21    | 156.7    | 24.25 | 154.50     | 20.21    | 159.4    | 19.89    | 156.87   |
| N360P360K360+ Cu, Cd        |               | 13.57    | 143.7    | 28.55 | 161.30     | 21.64    | 154.7    | 21.25    | 153.23   |

Since the most dangerous are the mobile forms of cadmium and copper, when cultivating agricultural crops, it is necessary to know their content in the soil and ways to reduce them. The main physical and chemical factors that control the mobility of heavy metals include the following soil characteristics:
- acid-base conditions;
- redox conditions;
- grading;
- the amount of organic matter.

Mobile forms of cadmium and copper, which are presented in table 2, have the main influence on the intake of toxic elements in crop production.

Table 2. Content of mobile forms of Cd and Cu in soil on average for three years, mg / kg.

| Experiment variants | Samples       | potatoes | red beet | beans | On average |
|---------------------|---------------|----------|----------|-------|------------|
| Control             |               | Cd       | Cu       | Cd    | Cu         | Cd       | Cu       | Cd       | Cu       |
| N180P180K180        |               | 0.85     | 24.03    | 1.19  | 20.63      | 1.05     | 24.9     | 1.03     | 23.19    |
| N180P180K180 + Cu   |               | 17.77    | 148.0    | 25.52 | 168.37     | 21.23    | 150.4    | 21.51    | 155.59   |
| N180P180K180 + Cu+ lime |           | 15.97    | 122.4    | 23.28 | 168.22     | 19.73    | 148.8    | 19.66    | 146.47   |
| N180P180K180 + Cu+ manure |       | 15.77    | 140.8    | 22.77 | 144.63     | 20.13    | 155.1    | 19.56    | 146.84   |
| N180P180K180 + Cu+ manure+ lime | | 15.21    | 156.7    | 24.25 | 154.50     | 20.21    | 159.4    | 19.89    | 156.87   |
| N360P360K360+ Cu    |               | 13.57    | 143.7    | 28.55 | 161.30     | 21.64    | 154.7    | 21.25    | 153.23   |

3
Of the two heavy metals studied by us, cadmium is the most mobile on uncontaminated plots. On average, for the rotation of the crop rotation link, the cadmium mobility coefficient in the control was 26.29%, the application of mineral fertilizers reduced the mobility coefficient by 11.80%. In the variant N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} + Cu, Cd, the average mobility coefficient per rotation was 24.71%. In the first year after the introduction of salts of heavy metals, during the cultivation of potatoes, the mobility coefficient of cadmium in the variant N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} + Cu, Cd - 16.43%, in the second year after the introduction of the mobility coefficient of cadmium increased and amounted to 44.5%, and in the third year cultivation decreased to 13.19%.
The maximum mobility of cadmium was in the second year of aftereffect, and then the mobility of cadmium decreased by 31.31%. This is due to the immobilization of this element when interacting with soil colloids, with the formation of insoluble salts with phosphate ions, with carbonates and with the organic part of the soil.

Table 3. Mobility coefficients Cd and Cu on average for three years, %.

| Experiment variants | Samples | Cd   | Cu   | Cd   | Cu   | Cd   | Cu   | Cd   | Cu   |
|---------------------|---------|------|------|------|------|------|------|------|------|
| Control             | potatoes| 21.18| 1.33 | 27.7 | 3.63 | 30.0 | 0.46 | 26.29| 1.81 |
| N_{180}P_{180}K_{180} | red beet| 17.72| 0.86 | 16.2 | 3.73 | 9.56 | 0.32 | 14.49| 1.64 |
| + Cu, Cd            | beans   | 16.43| 2.03 | 44.5 | 3.70 | 13.19| 3.60 | 24.71| 3.11 |
| N_{180}P_{180}K_{180} |         | 12.08| 1.79 | 28.5 | 3.71 | 12.85| 2.93 | 17.81| 2.81 |
| + Cu, Cd + lime     |         | 13.19| 1.92 | 28.2 | 2.62 | 10.3 | 2.46 | 17.23| 2.33 |
| N_{180}P_{180}K_{180} |         | 13.01| 1.79 | 27.3 | 3.31 | 11.38| 2.22 | 17.23| 2.44 |
| + Cu, Cd + manure   |         | 16.06| 1.34 | 29.1 | 4.56 | 10.83| 3.75 | 18.66| 3.22 |

The introduction of lime reduced the cadmium mobility coefficient to 12.08% in the first year of cultivation, in the second year to 28.5% and in the third year to 12.85% compared to the variant $N_{180}P_{180}K_{180} + Cu, Cd$. The introduction of manure also affects the decrease in cadmium mobility coefficient, but its effect is more pronounced in the second and third years of crop cultivation. In the first year of heavy metals introduction, the application of manure reduced the mobility coefficient of cadmium by 3.24%, and lime by 4.35%, in the second year, when cultivating table red beet, the mobility coefficient of cadmium when applying manure was 28.2%, and when applying lime 28.5, i.e. equal influence. During the cultivation of agricultural crops in the third year after the introduction of cadmium, the coefficient of mobility of this toxicant with the introduction of manure was 10.3%, and with the introduction of lime - 12.85%. The combined application of lime and manure also had a positive effect on the decrease in the cadmium mobility coefficient from 13.01% in the first year of cultivation to 11.38% in the third year. The effect of manure on a decrease in the coefficient of mobility of cadmium is manifested in connection with the fact that along with the formation of carbonates and bicarbonates in the soil, the formation of complex compounds with organic matter occurs. A double dose of mineral fertilizers reduced the cadmium mobility coefficient from 16.06% in the first year to 10.83% in the third year of crop cultivation. High doses of complex fertilizers reduce the mobility of this element due to the formation of insoluble compounds with phosphate ions.

The mobility coefficient of copper is significantly lower than the mobility coefficient of cadmium. On the control, the copper mobility coefficient averaged 1.81% per rotation, in the $N_{180}P_{180}K_{180}$ variant - 1.64%. In the variant $N_{180}P_{180}K_{180} + Cu, Cd$, the mobility coefficient in the first year of the introduction of heavy metals was 2.03%, in the cultivation of table red beet, in the second year after the introduction of copper, the mobility coefficient increased and amounted to 3.7% and in the third year after the introduction of heavy metals the copper mobility coefficient decreased by 0.1% and amounted to 3.6%.
The addition of lime reduced the copper mobility on average per rotation to 2.81% or by 0.30% compared to the N_{180}P_{180}K_{180} + Cu, Cd option. The application of organic fertilizers significantly reduced the mobility of copper in the second and third years of aftereffect, and the coefficient of mobility of copper was 2.62% and 2.46%, respectively, which is lower than in the variants with lime application. With the combined application of lime and manure, the copper mobility coefficient was 1.79% in the first year, 3.31% in the second, and 2.22% in the third year. Coefficient of mobility of copper decreases in the third year of cultivation of agricultural crops stronger in variants N_{180}P_{180}K_{180} + Cu, Cd + manure and N_{180}P_{180}K_{180} + Cu, Cd + manure + lime than in variant N_{180}P_{180}K_{180} + Cu, Cd + lime. This is due to the fact that copper is most actively bound by high-molecular fractions of organic matter. A double dose of mineral fertilizers positively affects a decrease in the coefficient of mobility of copper in the first year, and in the second and third years, a decrease in the mobility of copper in comparison with the variant N_{180}P_{180}K_{180} + Cu, Cd was not observed, since when a double dose of mineral fertilizers was applied, the acidity of the soil increased, which contributes to increased mobility of heavy metals (table 4).

According to the value of the mobility coefficient on uncontaminated soils, heavy metals can be distributed as follows: Cd > Cu. On contaminated soils, the distribution of heavy metals by the mobility coefficient can be represented as follows: Cd > Cu. The data in table 4 show that the mobility of cadmium and copper is very significantly determined by the acid-base conditions of the soil. In variants with pH_{ks} less than 5.0, the mobility of heavy metals is higher than in variants with pH_{ks} more than 5.0.

**Table 4.** Indicators of exchangeable acidity (pH_{ks}) in the experimental area.

| Experiment variants | 1st year | 2nd year | 3rd year |
|---------------------|----------|----------|----------|
| Control             | 5.4      | 5.2      | 5.3      |
| N_{180}P_{180}      | 5.17     | 5.0      | 5.00     |
| N_{180}P_{180}K_{180} + Cu, Cd | 4.96 | 4.92 | 4.80 |
| N_{180}P_{180}K_{180} + Cu, Cd + lime | 5.30 | 5.32 | 5.10 |
| N_{180}P_{180}K_{180} + Cu, Cd + manure | 5.09 | 5.05 | 5.10 |
| N_{180}P_{180}K_{180} + Cu, Cd + manure + lime | 5.33 | 5.30 | 5.30 |
| N_{360}P_{360}K_{360} + Cu, Cd | 4.89 | 4.77 | 4.70 |

In addition, the application of lime, manure, the combined application of lime and manure, as well as the presence of phosphoric acid salts in the soil also affect the mobility of toxic elements. Consequently, the degree of mobility of heavy metals in the soil is influenced not only by the acid-base, redox conditions of the soil, but also by the presence of carbonates, phosphate ions, and organic matter in the soil.

The main indicators of the quality of vegetable crops are presented in table 5.

The starch content in potato tubers in the control was 68.8% on dry matter, the application of mineral fertilizers increased its content to 69.8%, and on soils contaminated with heavy metals, the starch content was from 71.2 to 71.6%. Consequently, heavy metals did not have a negative effect on reducing the starch content in potato tubers. The sugar content in beet roots in the control was 8.6%, in the variant N_{180}P_{180}K_{180} - 8.8%, which is 0.2% higher than in the control. The addition of cadmium and copper reduced the sugar content in comparison with the variant N_{180}P_{180}K_{180}, but insignificantly, only by 0.2-0.4% in relation to the variant with the introduction of mineral fertilizers. In the variant N_{360}P_{360}K_{360} + Cu, Cd, the sugar content increased to 8.9%. Heavy metals did not have a negative effect on protein content in the cultivation of beans. In the control, the protein content was 17.4%, in the N_{180}P_{180}K_{180} variant - 17.5%, and on the contaminated plots with toxic elements, the protein content was from 17.5 to 17.7%.
Table 5. The main indicators of vegetable crops quality in the link crop rotation on average for three years.

| Experiment variants | Potatoes | Red beet | Beans |
|---------------------|----------|----------|-------|
|                     | Starch content (% on dry matter) | Sugar content, % | Protein content, % |
| Control             | 68.8     | 8.6      | 17.4  |
| N$_{180}$P$_{180}$K$_{180}$ | 69.8 | 8.8 | 17.5 |
| N$_{180}$P$_{180}$K$_{180}$ + Cu, Cd | 71.2 | 8.6 | 17.5 |
| N$_{180}$P$_{180}$K$_{180}$ + Cu, Cd + lime | 71.2 | 8.5 | 17.6 |
| N$_{180}$P$_{180}$K$_{180}$ + Cu, Cd + manure | 71.6 | 8.6 | 17.5 |
| N$_{180}$P$_{180}$K$_{180}$ + Cu, Cd + manure + lime | 71.2 | 8.4 | 17.6 |
| N$_{360}$P$_{360}$K$_{360}$+ Cu, Cd | 71.3 | 8.9 | 17.7 |

Consequently, the high content of heavy metals in the soil (Cd and Cu) does not have a negative effect on the synthesis of basic organic substances in vegetable products (starch, sugar, protein).

One of the indicators of the quality of agricultural products, especially vegetables, is the content of nitrate nitrogen in the main product (table 6).

In the control potato tubers, the content of nitrate nitrogen remained 177 mg / kg, the application of mineral fertilizers increased the content of nitrates by 117 mg / kg, the application of Cu and Cd reduced the content of nitrate nitrogen in relation to the variant N$_{180}$P$_{180}$K$_{180}$ by 7 mg / kg. The application of lime in the contaminated areas reduced the content of nitrate nitrogen in tubers by 16 mg / kg in relation to the variant N$_{180}$P$_{180}$K$_{180}$ + Cu, Cd.

Table 6. The content of nitrate nitrogen in the main product on average for three years, mg / kg.

| Experiment variants | Potatoes | Red beet | Beans |
|---------------------|----------|----------|-------|
|                      |          |          |       |
| Control             | 177      | 780      | 19.5  |
| N$_{180}$P$_{180}$K$_{180}$ | 294 | 874 | 19.3 |
| N$_{180}$P$_{180}$K$_{180}$ + Cu, Cd | 287 | 980 | 22.8 |
| N$_{180}$P$_{180}$K$_{180}$ + Cu, Cd + lime | 271 | 796 | 19.1 |
| N$_{180}$P$_{180}$K$_{180}$ + Cu, Cd + manure | 322 | 1163 | 20.5 |
| N$_{180}$P$_{180}$K$_{180}$ + Cu, Cd + manure + lime | 310 | 857 | 20.5 |
| N$_{360}$P$_{360}$K$_{360}$+ Cu, Cd | 321 | 1151 | 21.5 |
| ACL                 | 250      | 1400     | -     |

On plots with the introduction of manure, joint application of lime and manure and with the introduction of a double dose of mineral fertilizers, the content of nitrate nitrogen in the marketable part of the crop increased and amounted to 322: 310 and 321 mg / kg, respectively. This is primarily due to the introduction of manure and increased doses of mineral fertilizers.

During the cultivation of table red beet under control, the content of nitrate nitrogen in root crops was 780 mg / kg, in the variant N$_{180}$P$_{180}$K$_{180}$ - 874 mg / kg, and on contaminated soils, the content of nitrates increased and in the variant N$_{180}$P$_{180}$K$_{180}$ + Cu, Cd was 980 mg / kg. The application of lime and the combined application of lime and manure on contaminated soils with heavy metals reduced the content of nitrates to 796 and 857 mg / kg, respectively.
The introduction of manure and a double dose of mineral fertilizers on plots with the introduction of heavy metals increased the content of nitrates to 1163 mg / kg and 1151 mg / kg, respectively, but this is lower than the ACL. The same trend is observed in the cultivation of beans. In the control variant, the nitrate content was 19.5 mg / kg, in the N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} variant - 19.3 mg / kg, and in the N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} + Cu, Cd variant - 22.8 mg / kg or 3.5 mg / kg higher than with background. The application of lime, manure and the combined application of lime and manure reduced the accumulation of nitrates to 19.1 - 20.5 mg / kg. Consequently, the accumulation of nitrates in vegetable products occurs as a result of the introduction of mineral and organic fertilizers; heavy metals do not have a significant effect on the accumulation of nitrate nitrogen during the cultivation of agricultural crops.

The main indicator of agricultural products quality, especially when cultivating them on contaminated soils, is the accumulation of heavy metals in the harvest of the main product.

The content of cadmium and copper in the main products is presented in table 7. On average, over three years, the content of cadmium in potato tubers in the control and in the variant N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} was 0.037 mg / kg.

In the variant N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} + Cu, Cd, the cadmium content in tubers was 0.073 mg / kg, which is 0.036 mg / kg higher than in the control. The application of lime reduced the intake of cadmium to 0.057 mg / kg, the application of manure to 0.067 mg / kg and the combined application of lime and manure to 0.060 mg / kg.

The introduction of a double dose of mineral fertilizers did not have a positive effect on reducing the accumulation of cadmium, and its content in tubers was 0.083 mg / kg, which is 0.01 mg / kg higher than the N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} + Cu, Cd option and 0.053 mg / kg higher than the ACL. Even in the control variant, the cadmium content in tubers is higher than the ACL by 0.07 mg / kg.

The copper content in potato tubers in the control was 0.423 mg / kg, in the N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} variant - 0.373, in the N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} + Cu, Cd variant, the copper content was 0.537 mg / kg. In variants with the introduction of lime, manure, combined application of lime and manure and with the introduction of a double dose of mineral fertilizers, the copper content was 0.597 mg / kg; 0.580; 0.523 and 0.643 mg / kg, respectively, which is 7.7-9.6 times lower than the ACL.

Table 7. Cadmium and copper content of in main products (mg / kg).

| Experiment variants                        | Samples   |          |          |          |          |          |
|-------------------------------------------|-----------|----------|----------|----------|----------|----------|
|                                           | Potatoes  | Red beet | Beans    |          |          |          |
|                                           | Cd        | Cu       | Cd       | Cu       | Cd       | Cu       |
| Control                                   | 0.037     | 0.423    | 0.015    | 0.221    | 0.069    | 0.94     |
| N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} | 0.037     | 0.373    | 0.024    | 0.262    | 0.075    | 0.91     |
| N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} + Cu, Cd | 0.073     | 0.537    | 0.036    | 0.358    | 0.123    | 2.91     |
| N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} + Cu, Cd + lime | 0.057     | 0.597    | 0.025    | 0.258    | 0.063    | 1.08     |
| N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} + Cu, Cd + manure | 0.067     | 0.580    | 0.033    | 0.304    | 0.076    | 1.07     |
| N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} + Cu, Cd + manure + lime | 0.060     | 0.523    | 0.031    | 0.336    | 0.069    | 1.04     |
| N\textsubscript{360}P\textsubscript{360}K\textsubscript{360} + Cu, Cd | 0.083     | 0.643    | 0.036    | 0.339    | 0.103    | 2.86     |
Consequently, when growing potatoes on contaminated soils, the accumulation of copper above the maximum permissible concentration does not occur regardless of the applied chemicals. Copper is the most inactive element of the two studied by us, and the cultivated agricultural crop itself regulates the intake of this element in the required amount.

Red beet cultivated in the crop rotation after potatoes accumulated less cadmium and copper than potatoes, even on contaminated soils. On the control, the content of cadmium in the root crops of table beet was 0.015 mg / kg, in the variant \( N_{180}P_{180}K_{180} - 0.024 \text{ mg / kg} \). On soils contaminated with heavy metals, in the variant \( N_{180}P_{180}K_{180} + Cu, Cd \), the cadmium content was 0.036 mg / kg, which is 0.006 mg / kg higher than the ACL. The application of lime reduced the cadmium content to 0.025 mg / kg, which is lower than the ACL by 0.005 mg / kg, the application of manure also reduced the intake of cadmium in root crops, but insignificantly, its content was 0.033 mg / kg. In the variant with the introduction of lime and manure, the cadmium content was 0.031 mg / kg, and the introduction of a double dose of mineral fertilizers did not reduce the intake of cadmium in the main product.

The content of copper in beet root crops is 0.221 mg / kg in control, which is lower than in potato tubers by 0.202 mg / kg. In the variant \( N_{180}P_{180}K_{180} - 0.262 \text{ mg / kg} \), in the variant \( N_{180}P_{180}K_{180} + Cu, Cd \) - 0.358 mg / kg or 4.642 mg / kg below the ACL level. The application of lime, manure and the combined application of lime and manure in the second year of cultivation reduced the copper input to 0.258; 0.304 and 0.336 mg / kg, respectively. A double dose of mineral fertilizers also reduced the intake of copper in beet root crops by 0.019 mg / kg compared to the \( N_{180}P_{180}K_{180} + Cu, Cd \) option.

The addition of lime reduced the cadmium content to 0.063 mg / kg, which is lower than the ACL by 0.037 mg / kg and in comparison, with the variant \( N_{180}P_{180}K_{180} + Cu, Cd \) by 0.06 mg / kg. Manure application also reduced the cadmium content to 0.76 ACL or 0.076 mg / kg. In the variant \( N_{180}P_{180}K_{180} + Cu, Cd + lime + manure \), the cadmium content was 0.069 mg / kg, which is lower than the ACL by 0.031 mg / kg. The introduction of a double dose of mineral fertilizers reduced the content of cadmium in beans, but this is higher than the ACL by 0.003 mg / kg. The copper content in the control was 0.94 mg / kg, 0.91 in the \( N_{180}P_{180}K_{180} \) variant, and 2.91 mg / kg in the \( N_{180}P_{180}K_{180} + Cu, Cd \) variant. The addition of lime reduced the intake of copper by 1.83 mg / kg, and its content was 1.08 mg / kg. The application of manure and the combined application of lime and manure reduced the copper content in the beans to 1.07 mg / kg and 1.04 mg / kg, respectively. A double dose of mineral fertilizers slightly reduced the accumulation of copper, and its content was 2.86 mg / kg.

As a result of our research, it was found that in the third year of cultivation of agricultural crops, the ability of lime and manure to reduce the toxic effects of cadmium and copper is more actively manifested. According to the accumulation of cadmium and copper, vegetable crops can be distributed as follows: beans> potatoes> red beet.

| ACL | 0.03 | 5.0 | 0.03 | 5.0 | 0.1 | 10.0 |
|-----|------|-----|------|-----|-----|------|

To calculate the balance of heavy metals, it is necessary to know their content in by-products. The content of cadmium and copper in by-products is presented in table 8.

Cadmium accumulates in the tops of potatoes more intensively than in tubers. In the control, the cadmium content in the tops of potatoes averaged 0.087 mg / kg over three years. The introduction of mineral fertilizers increased the supply of cadmium to the tops, and its content was 0.097 mg / kg.

On plots contaminated with heavy metals, the cadmium content in the tops was 0.20 mg / kg. The application of lime, manure and the combined application of lime and manure reduced the supply of cadmium to the tops by 0.05; 0.04 and 0.03 mg / kg, respectively. A double dose of mineral fertilizers did not have a positive effect on reducing the intake of this element in the tops of potatoes, and its content was 0.21 mg / kg.
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Table 8. Cadmium and copper content in by-products mg / kg.

| Experiment variant | Samples    |      |      |      |      |      |
|--------------------|------------|------|------|------|------|------|
|                    | Potatoes   | Red beet | Beans |      |      |      |
| Cd                 | Cu         | Cd    | Cu   | Cd   | Cu   |
| Control            | 0.087      | 0.85  | 0.024 | 0.136 | 0.404 | 2.02 |
| N$_{180}$P$_{180}$K$_{180}$ | 0.097      | 1.05  | 0.025 | 0.135 | 0.415 | 2.02 |
| N$_{180}$P$_{180}$K$_{180}$ + Cu, Cd | 0.20      | 2.10  | 0.064 | 0.174 | 1.105 | 8.17 |
| N$_{180}$P$_{180}$K$_{180}$ + Cu, Cd + lime | 0.15      | 1.68  | 0.052 | 0.162 | 0.605 | 3.24 |
| N$_{180}$P$_{180}$K$_{180}$ + Cu, Cd + manure | 0.16      | 1.59  | 0.060 | 0.166 | 0.651 | 3.77 |
| N$_{180}$P$_{180}$K$_{180}$ + Cu, Cd + manure + lime | 0.17      | 1.61  | 0.056 | 0.155 | 0.704 | 3.69 |
| N$_{360}$P$_{360}$K$_{360}$ + Cu, Cd | 0.21      | 2.08  | 0.065 | 0.157 | 1.096 | 8.37 |

The content of copper in the tops of potatoes in the control was 0.85 mg / kg, in the variant N$_{180}$P$_{180}$K$_{180}$ - 1.05 mg / kg. On plots contaminated with heavy metals, the copper content in potato tops was 2.10 mg / kg. The application of lime, manure and the combined application of lime and manure reduced the flow of copper to the tops to 1.68; 1.59 and 1.61 mg / kg, respectively. In the variant N$_{360}$P$_{360}$K$_{360}$ + Cu, Cd, the copper content in the tops was 2.08 mg / kg.

Beetroot cultivated in a crop rotation after potatoes accumulated less cadmium and copper than potatoes. In the control, the content of cadmium in the tops of table beet was 0.024 mg / kg, in the variant N$_{180}$P$_{180}$K$_{180}$ - 0.025 mg / kg. On plots contaminated with heavy metals, the cadmium content was 0.064 mg / kg, which is 0.028 mg / kg higher than in root crops. The introduction of lime reduced the content of this element in the tops by 0.012 mg / kg, the introduction of manure by 0.004 mg / kg, and the combined application of lime and manure by 0.008 mg / kg, and its content was 0.052; 0.060 and 0.056 mg / kg, respectively. The introduction of a double dose of mineral fertilizers did not reduce the intake of cadmium into the beet tops, and its content was 0.065 mg / kg.

The concentration of copper in beet tops is lower than in root crops. In the control, the content of copper in the tops was 0.136 mg / kg, which is lower than in root crops by 0.085 mg / kg. In variant N$_{180}$P$_{180}$K$_{180}$, the copper content was 0.135 mg / kg. In the variant N$_{180}$P$_{180}$K$_{180}$ + Cu, Cd, the copper content in the tops was 0.174 mg / kg, which is 0.184 mg / kg lower than in root crops. The application of lime, manure and the combined application of lime and manure reduced the supply of copper to the tops by 0.012; 0.008 and 0.019 mg / kg, respectively. A double dose of mineral fertilizers reduced the copper content to 0.157 mg / kg.

Beans were cultivated for the third year after potatoes and red beet. Among the three vegetable crops studied by us, beans accumulated the most intensively cadmium and copper. In the control, the cadmium content in the bean straw was 0.404 mg / kg, in the variant N$_{180}$P$_{180}$K$_{180}$ - 0.415 mg / kg. On contaminated soils, the cadmium content was 1.105 mg / kg. The application of lime, manure and the combined application of lime and manure reduced the cadmium content in the straw to 0.605; 0.651; 0.704 mg / kg, respectively. In the variant N$_{360}$P$_{360}$K$_{360}$ + Cu, Cd, the cadmium content was 1.096 mg / kg, which is 0.009 mg / kg lower than in the variant N$_{180}$P$_{180}$K$_{180}$ + Cu, Cd, that is, it practically did not decrease.
copper content in straw on the control in variant $N_{180}P_{180}K_{180}$ was 2.02 mg / kg, which is 1.08 mg / kg higher than in beans. On plots contaminated with heavy metals, the copper content in the straw was 8.17 mg / kg. The introduction of lime reduced the input of copper into the straw by 2.52 times, the introduction of manure - by 2.17 times, the combined application of lime and manure - by 2.21 times. A double dose of mineral fertilizers did not have a positive effect on the reduction of copper in the straw, and its content was 8.37 mg / kg.

As a result of our research, it was found that in the link of vegetable crop rotation, a crop that absorbs large quantities of cadmium and copper as the main and by-product is beans.

Adding lime reduces the intake of cadmium in the main and by-products of vegetable crops. In the first year of cultivation after the introduction of heavy metals, the application of lime reduced the cadmium content in potato tubers by 21.9%. In the root crops of table red beet, the accumulation of cadmium during the introduction of lime decreased by 30.5%, and in the third year, during the cultivation of beans, the cadmium content in the beans decreased by 48.8%.

The introduction of organic fertilizers had a positive effect on reducing the intake of cadmium in the main production of vegetable crops. The intake of cadmium in potato tubers decreased by 8.2%, in beet roots by 8.3% and in beans by 38.2%.

The combined application of lime and manure reduced the supply of cadmium to potato tubers by 17.8%, to beet roots by 13.9% and to beans by 43.9%. The introduction of a double dose did not have a positive effect on the intake of cadmium in potato tubers and beet roots, and in beans the cadmium content decreased by 16.3%. The copper content in potato tubers is 7.8-9.3 times lower than the ACL even on soils contaminated with this element. In beet root crops, the intake of copper is insignificant and ranges from 0.358 mg / kg in the variant $N_{180}P_{180}K_{180} + Cu$, Cd to 0.258 mg / kg in the variant $N_{180}P_{180}K_{180} + Cu, Cd + lime$, which is 14-19.4 times lower than the ACL. If in the first year of potato cultivation after the introduction of heavy metals, the introduction of lime, manure and a double dose of mineral fertilizers did not affect the decrease of this element in the tubers, then during the cultivation of table red beet, the intake of copper in root crops decreased in the variants with the introduction of lime, manure, joint application of lime and manure and when applying a double dose of mineral fertilizers by 27.9; 15.1; 6.1 and 5.3%, respectively. The content of copper in beans on plots contaminated with heavy metals ranged from 2.91 mg / kg to 1.04 mg / kg, which is 3.4-9.6 times lower than the ACL. The application of lime reduced the copper content by 62.9%, the application of manure by 63.2%, and the combined application of lime and manure by 64.3%. A double dose of mineral fertilizers slightly reduced the copper content in the beans. The intensity of the accumulation of heavy metals in the by-products of the studied crops is higher than in the main one. The application of lime, manure and the combined application of lime and manure reduce the intake of these toxicants in the tops of potatoes, beetroot and bean straw. Moreover, the introduction of lime reduces the supply of cadmium to the tops of potatoes by 25%, to the tops of beetroot by 18.8% and to the bean straw by 45.2%. The application of manure reduces the supply of cadmium to the tops of potatoes by 20%, to the tops of beet by 6.3% and to the straw of beans by 41.1%. The combined application of lime and manure also has a positive effect on reducing the intake of cadmium, and its content decreases by 15% in potato tops, by 12.5% in beet tops and by 36.3% in bean straw. A double dose of mineral fertilizers had no effect on reducing the intake of toxicants in by-products. The intake of copper in the by-products of the studied crops decreased with the introduction of lime by 20% in the tops of potatoes, by 6.9% in the tops of beetroot and by 60.3% in the straw of beans; the introduction of manure reduced the intake of this element by 24.3%; 4.6% and 53.8%, respectively, the combined application of lime and manure reduced the accumulation of copper in potato tops by 23.3%, in beet tops by 10.9% and in bean straw by 53.4%. The introduction of a double dose of mineral fertilizers slightly reduced the supply of copper to the tops of beetroot.

We calculated the coefficients of biological absorption of Cu and Cd by vegetable crops, which are presented in table 9.

The biological absorption coefficient is the ratio of the content of an element in a plant to the total content in the soil. In the control variant, the most active heavy metals accumulated in beans, and the biological absorption coefficient of cadmium was 6.57% and copper - 3.78%.
The application of mineral fertilizers increased the coefficient of biological absorption of cadmium in uncontaminated plots by 0.45% in potatoes, by 1.55% in beetroot and by 0.64% in beans, and the coefficient of biological absorption of copper increased only with the cultivation of red beet and beans on 0.21 and 0.28%, respectively.

In the cultivation of table red beet and beans, the application of mineral fertilizers contributed to an increase in the biological absorption coefficient of zinc by 0.48 and 0.24%, respectively. Consequently, according to the value of the coefficient of biological absorption of potatoes, red beet and beans on uncontaminated soils, heavy metals are distributed as follows: Cd > Cu.

On soils contaminated with heavy metals, the coefficient of biological absorption of cadmium was from 0.14% in red beet to 0.58% in beans, copper - from 0.21% in red beet to 1.93% in beans. On soils contaminated with heavy metals, the coefficient of biological absorption of cadmium and copper decreased.

**Table 9. Coefficients of biological absorption of cadmium and copper by the main products of vegetable crops, %**

| Experiment variants | Samples |
|---------------------|---------|
|                     | Potatoes | Red beet | Beans |
|                     | Cd       | Cu       | Cd    | Cu       | Cd    | Cu    |
| Control             | 4.33     | 1.84     | 1.26  | 1.07     | 6.57  | 3.78  |
| N180P180K180        | 4.78     | 1.81     | 2.81  | 1.28     | 7.21  | 4.06  |
| + Cu, Cd            | 0.45     | 0.38     | 0.14  | 0.21     | 0.58  | 1.93  |
| N180P180K180        | 0.40     | 0.51     | 0.11  | 0.15     | 0.34  | 0.73  |
| + Cu, Cd + lime     | 0.63     | 0.50     | 0.14  | 0.21     | 0.38  | 0.69  |
| N180P180K180        | 0.50     | 0.37     | 0.13  | 0.21     | 0.34  | 0.65  |
| + Cu, Cd + manure   | 0.60     | 0.46     | 0.13  | 0.21     | 0.48  | 1.85  |
| + Cu, Cd + lime     |         |          |       |          |       |       |

Consequently, when cultivating crops on contaminated soils, the accumulation of Cu and Cd by plants is determined to a greater extent by the physiological characteristics of the plants themselves than by their content in the soil.

The introduction of lime reduced the coefficient of biological absorption of cadmium by 0.05% in the cultivation of potatoes, by 0.03% in beetroot and by 0.24% in beans. The application of organic fertilizers in the year of application and the first year of aftereffect did not affect the decrease in the coefficient of biological absorption of cadmium, and in the second year of the aftereffect in the cultivation of beans, the coefficient of biological absorption of cadmium decreased by 0.20%. In the variant N180P180K180 + Cu, Cd + manure + lime, the coefficient of biological absorption of cadmium during potato cultivation was 0.50%, which is higher than in the variant N180P180K180 + Cu, Cd by 0.05%, in the first year of the aftereffect of manure and lime during cultivation For table red beet, the coefficient of biological absorption of cadmium decreased by 0.01%, and in the second year of the aftereffect of manure and lime - during the cultivation of beans - by 0.24%. A double dose of mineral fertilizers
contributed to an increase in the biological absorption coefficient of cadmium in potato cultivation by 0.15% compared to the N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} + Cu, Cd option, while in the cultivation of table red beet and beans - a decrease of 0.01% and 0.10%, respectively.

The biological absorption coefficient of copper during the cultivation of potatoes in the variants with the introduction of lime, manure and with the introduction of a double dose of mineral fertilizers did not decrease and ranged from 0.51% in the variant N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} + Cu, Cd + lime to 0.46% in the variant N\textsubscript{360}P\textsubscript{360}K\textsubscript{360} + Cu, Cd, which is 0.13% - 0.08% higher as compared to the variant N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} + Cu, Cd. The combined application of lime and manure reduced the coefficient of biological absorption of copper, but insignificantly - by 0.01%. In the cultivation of table red beet in the second year after the introduction of lime and manure, the coefficient of biological absorption of copper decreased in the variant with the introduction of lime by 0.06%. In the variants with the introduction of manure, the combined application of lime and manure and with the introduction of a double dose of mineral fertilizers, the coefficient of biological absorption of copper was 0.21%, i.e. at the level of variant N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} + TM. In the cultivation of beans, the application of lime, manure and the combined application of lime and manure, in the second year of aftereffect, reduced biological absorption coefficient of copper by 1.2%; 1.24% and 1.28%, respectively, and a double dose of mineral fertilizers reduced biological absorption coefficient of copper by only 0.08%.

As a result of our research, it was found that the biological absorption coefficient is influenced not only by lime, manure, mineral fertilizers, but also by the physiological characteristics of the crops themselves, which need toxic elements as micro and ultramicroelements for nutrition and synthesis of organic substances.

According to the intensity of accumulation of heavy metals (Cd, Cu), the studied plants can be distributed as follows: beans> potatoes> red beet. On soils contaminated with heavy metals (Cd, Cu), according to the value of biological absorption coefficient of the studied crops, heavy metals are distributed as follows:

- when growing potatoes - Cd> Cu;
- when cultivating red beet - Cu> Cd;
- when growing beans - Cu> Cd.

According to the value of biological absorption coefficient of potatoes, red beet and beans in the control variant and on plots with fertilization on uncontaminated soils, heavy metals can be distributed as follows: Cd> Cu.

On contaminated soils, the accumulation of heavy metals by plants is determined not only by the introduction of lime, manure and the joint application of lime and manure, but also by the physiological characteristics of the plants themselves. According to the intensity of accumulation of cadmium and copper, the studied plants can be distributed as follows: beans> potatoes> red beet.

4. Conclusion

On average, cadmium is the most mobile of the two heavy metals studied by us during the rotation of the crop rotation link. The maximum mobility of cadmium was in the second year after the introduction of this element into the soil and amounted to 44.5%, and in the third year the mobility of cadmium decreased to 24.71%. Adding lime reduces the mobility coefficient of cadmium. The application of manure also affects the decrease in the mobility of cadmium, but its effect is manifested in the second and third years after application. The combined application of lime and manure also has a positive effect on reducing the mobility of cadmium. Lime also had a positive effect on reducing copper mobility, however, in the second and third years, the introduction of manure and the joint application of manure and lime have a more significant effect on reducing the mobility of this toxicant than lime alone.

Heavy metals do not have a significant effect on the quality of vegetable crops. The addition of lime and the combined application of lime and manure reduce the supply of copper and cadmium to the main products of the studied crops. Manure application reduces cadmium input in potato, red beet and beans cultivation. The supply of copper to potato tubers in the first year after the application of lime and manure did not have a positive effect, and in the second and third years of cultivation, the accumulation
of copper decreased under the influence of manure and lime in the main production of red beet and beans. In the link of vegetable crop rotation, beans accumulate the maximum amount of copper and cadmium as the main and by-products.

The value of the coefficient of biological absorption in the cultivation of vegetable crops on soils contaminated with heavy metals depends not only on the application of lime, manure, mineral fertilizers, but also on the physiological characteristics of the crops themselves. The most intensive accumulation of heavy metals is beans. According to the intensity of accumulation of cadmium and copper, the studied plants can be distributed as follows: beans> potatoes> red beet.

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