Heavy metals accumulation in vegetable crop grown on typical chernozem soils

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Abstract. The article presents agrochemical techniques that reduce the accumulation of heavy metals in vegetable crops, such as potatoes and table beets, when they are cultivated on typical chernozem soils with a heavy loam granulometric composition. The data obtained allowed to conclude that the use of lime, as well as the simultaneous use of lime and manure, reduce the penetration of cadmium in potato tubers by 22 and 18%, respectively. In addition, the use of organic in its pure form reduces the penetration of this element by 8%. The studied cultures absorbed copper, lead and zinc in amounts not exceeding the threshold limit value (TLV), also in plots artificially contaminated with these metals. Heavy metals are more intensely absorbed by the aerial part of potato. During the experiments, it was found that the use of lime, organics, as well as their simultaneous application contributed to a decrease in the studied elements penetration into table beet plants. The increase in the dose of mineral fertilizers doubled positive effect of lower penetration of copper and lead into plants, although the difference was within the experimental error. A double dose of mineral fertilizer did not have any positive effect on the penetration of cadmium and zinc.

1. Introduction
Protection of cultivated lands from chemical pollution is one of the priority social and economic tasks. Currently, there is a real threat of soil pollution with heavy metals.

Heavy metals can enter the soil in two main ways. The first is manifested under the influence of natural factors, such as the effect of various types of weathering, erosion processes, volcanic activity. The second way of heavy metals entry the soil is technogenic processes, such as mining, fuel combustion, integrated influence of the agricultural sector.

A certain amount of technogenic waste in the form of the thinnest aerosols travels with the movement of air masses over great distances and leads to global pollution.

The second part penetrates into water ponds without runoff, where these metals accumulate and become the reason of secondary pollution. In other words, hazardous pollution forms as a result of the manifestation of physical and chemical processes taking place directly in the environment. One of the features of heavy metals is that their maximum amount accumulates in the upper horizons of the soil and then they migrate very slowly in the processes of leaching, plant uptake, manifestations of erosion processes [1, 2].

Heavy metals are characterized by increased ability to go into various chemical, physical and chemical, as well as biological reactions. Most of them have a mixed valence and are involved in oxidation-reduction process. This group of metals and their compounds, like many other chemical
compounds, have the ability to move and redistribute in living environments. The movement of heavy metals compounds mostly happens in the form of organo-mineral complexes. Part of the organic compounds with which metals interact is the products of microbiological activity.

A soil cover contaminated with heavy metals may become unsuitable for agricultural purposes for a long time [3]. The movement of these elements within agricultural ecosystems is determined by a number of factors. Whereof the precedence belongs to soil conditions and biological characteristics of plant organisms [4]. In turn, this dictates the necessity for more detailed studies in the soil - fertilizer - plant system.

In this regard, the study and development of techniques that reduce the penetration of heavy metals into plants is one of the key tasks in the production of crop products.

2. Methodology

The purpose and objectives of studies. The aim of our research was to study methods for reducing the penetration of heavy metals into tubers and tops of potatoes, and roots and tops of table beets.

For this purpose, the following tasks were set:

- to study the effect of lime, manure, simultaneous use of lime and manure, as well as double dose of mineral fertilizers on the penetration of cadmium, copper, lead and zinc into tubers and tops of potatoes, and roots and tops of table beets.

Materials, conditions and methods. The studies were carried out on typical chernozem soils with a heavy loam granulometric composition under the conditions of Central Black Earth Region.

The experiment was repeated four times, according to the following scheme:

- Control (without fertilizers and additional introduction of heavy metals (HM));
- N180P180K180;
- N180P180K180 + HM;
- N180P180K180 + lime (4 t/ha) + HM;
- N180P180K180 + manure (50 t/ha) + HM;
- N180P180K180 + lime (4 t/ha) + manure (50 t/ha) + HM;
- N360P360K360 + HM.

Nutritional characteristics of the experimental plot: the humus content is 5.8%, pH\textsubscript{KCl} is 5.6, mobile phosphorus – 312 mg/kg, exchange potassium – 174 mg/kg, easy hydrolysable nitrogen – 175 mg/kg. Cultivated land of the plot – 4.5 m\textsuperscript{2}. Nitrophoska was used for the experiment.

Mineral, organic and lime fertilizers were applied simultaneously to the soil surface and backfilled by manual digging. Heavy metals in doses: CuSO\textsubscript{4} (176.8 g/m\textsuperscript{2}), CdSO\textsubscript{4} (10.3 g/m\textsuperscript{2}), ZnSO\textsubscript{4} (395.6 g/m\textsuperscript{2}), Pb(CH\textsubscript{3}COO)\textsubscript{2} \times Pb(OH)\textsubscript{2} (82.0 g/m\textsuperscript{2}), each was introduced separately after mixing their salts with the soil, so that there was no direct contact between them. Then the plot's soil was dug up. The introduction of water-soluble salts of cadmium, copper, zinc and lead into the soil led to an increase in the content of their total forms at average: cadmium in 13-17, copper 2-2.4, zinc 1.4-1.8 and lead 1.6-3.4 times against the APC level and amounted to: 13.5-17.7, 122-156, 158-193 and 106-146 mg/kg, respectively.

Nutritional characteristics of the soil were determined by the following methods: pH\textsubscript{KCl} - by potentiometric method; humus – according to Tyurin; easy hydrolysable nitrogen – according to Kornfild; phosphorus – according to Chirikov; potassium – according to Chirikov.

The measurement of heavy metals content was carried out according to the Guidelines developed by the Central Research Institute of Agrochemical Services (1993).

3. Results and discussion

One of the main quality indicators of agricultural products is the content of toxic elements. Accumulation of heavy metals in products is especially dangerous for humans and animals. Therefore,
decreasing of toxic elements penetration into crop products is one of the main tasks when cultivating crops on soils contaminated with heavy metals.

The penetration of pollutant elements into potato tubers is presented in table 1.

**Table 1.** The content of heavy metals in potato tubers three-year average, mg/kg.

| Variants                        | Cd   | Cu   | Pb   | Zn   |
|---------------------------------|------|------|------|------|
| Control                         | 0.037| 0.423| 0.287| 5.583|
| N_{180}P_{180}K_{180}           | 0.037| 0.373| 0.297| 5.020|
| N_{180}P_{180}K_{180} + HM      | 0.073| 0.537| 0.380| 7.287|
| N_{180}P_{180}K_{180} + HM + lime| 0.057| 0.597| 0.367| 7.007|
| N_{180}P_{180}K_{180} + HM + manure| 0.067| 0.580| 0.383| 7.807|
| N_{180}P_{180}K_{180} + HM + manure + lime | 0.060| 0.523| 0.350| 6.820|
| N_{360}P_{360}K_{360}+ HM       | 0.083| 0.643| 0.427| 8.153|
| Threshold limit value           | 0.030| 5.000| 0.500| 10.000|

At the control plot and in the N_{180}P_{180}K_{180} variant, the cadmium content was 0.037 mg/kg, which is 0.007 mg/kg higher than the TLV. In the variants N_{180}P_{180}K_{180} + HM and N_{360}P_{360}K_{360}+ HM it was 0.073 and 0.083 mg/kg, respectively, which is 2.4 and 2.8 times higher than the TLV.

The introduction of lime, the simultaneous introduction of lime and manure, as well as the introduction of manure reduced the penetration of cadmium by 0.016, 0.013 and 0.006 mg/kg, respectively, compared with the variant N_{180}P_{180}K_{180} + HM. A double dose of mineral fertilizers did not have any positive effect on the reduction of cadmium content in potato tubers. The maximum decrease in the cadmium penetration into potato tubers was observed in the variant with the introduction of lime, as well as in the variant with the simultaneous introduction of lime and manure.

Thus, the introduction of lime reduces the penetration of cadmium by 22%, the simultaneous introduction of lime and manure – by 18%, and the introduction of manure – by only 8%.

The penetration of copper into potato tubers is negligible even in variants contaminated with this element. Its content is from 0.537 mg/kg in the variant N_{180}P_{180}K_{180} + HM to 0.643 in the variant N_{360}P_{360}K_{360}+ HM, which is 8-9 times lower than the TLV.

The lead content in potato tubers three-year average in all cases contaminated with heavy elements also does not exceed the TLV and ranges from 0.380 mg/kg to 0.427 mg/kg. However, it should be noted that the introduction of lime and the simultaneous introduction of lime and manure reduce the lead accumulation in potato tubers by 0.013 and 0.03 mg/kg, respectively.

The zinc content on contaminated soils in potato tubers ranged from 7.287 mg/kg to 8.153 mg/kg, which is lower than the TLV by 2.713 mg/kg – 1.847 mg/kg. A trend was observed for the zinc penetration decreasing to potato tubers in versions with the introduction of lime and the simultaneous introduction of lime and manure by 0.280 and 0.467 mg/kg, respectively.

We studied the penetration of heavy metals into the tops of potatoes.

Data on the accumulation of toxic elements in the tops of potatoes are presented in table 2.

**Table 2.** The content of heavy metals in potato tops three-year average, mg/kg.

| Variants                        | Cd   | Cu   | Pb   | Zn   |
|---------------------------------|------|------|------|------|
| Control                         | 0.087| 0.85 | 0.556| 3.796|
| N_{180}P_{180}K_{180}           | 0.097| 1.08 | 0.573| 4.400|
| N_{180}P_{180}K_{180} + HM      | 0.20 | 2.1  | 1.037| 10.930|
| N_{180}P_{180}K_{180} + HM + lime| 0.15 | 1.68 | 0.663| 6.970|
| N_{180}P_{180}K_{180} + HM + manure| 0.16 | 1.59 | 0.843| 7.453|
| N_{180}P_{180}K_{180} + HM + manure + lime | 0.17 | 1.61 | 0.770| 7.890|
| N_{360}P_{360}K_{360}+ HM       | 0.21 | 2.08 | 0.977| 10.987|
Data analysis shows that the maximum accumulation of toxic elements occurs in the tops of potatoes. In the control variant, the cadmium content three-year average amounted to 0.087 mg/kg, which is 2.35 times more than in tubers; in the variant \(N_{180}P_{180}K_{180} + \text{TM}\), the cadmium content was 0.2 mg/kg, the introduction of lime, manure and the simultaneous introduction of lime and manure reduce the penetration of this element by 0.05 mg/kg, 0.04 and 0.03 mg/kg, respectively.

The introduction of a double dose of mineral fertilizers did not have any positive effect on reducing the cadmium accumulation in the tops of potatoes. The copper content in potato tops was 0.85 mg/kg at the control plot, the introduction of mineral fertilizers contributed to the copper accumulation, resulting in a content of 1.08 mg/kg. In the variant \(N_{180}P_{180}K_{180} + \text{HM}\), the copper content was 2.1 mg/kg. The introduction of lime, manure and the simultaneous introduction of lime and manure reduced the penetration of copper into the tops of potatoes by 0.42 mg/kg, 0.51 mg/kg and 0.49 mg/kg, respectively. A double dose of mineral fertilizers did not reduce the penetration of a pollutant element into the tops of potatoes.

At the control plot, the lead content in potato tops was 0.556 mg/kg, in the variant \(N_{180}P_{180}K_{180} + \text{HM}\) – 1.037 mg/kg, which is 2.72 times higher than in potato tubers. The introduction of lime, manure and the simultaneous introduction of lime and manure reduced the accumulation of this element by tops by 0.374 mg/kg, 0.194 mg/kg and 0.267 mg/kg, respectively. A double dose of mineral fertilizers also reduced the accumulation of this element into the tops, but only slightly.

At the control plot the zinc content in the tops of potatoes was 3.796 mg/kg, and in the variant with the introduction of mineral fertilizers – 4.400 mg/kg.

At plots contaminated with heavy metals zinc content was 10.93 mg/kg (variant \(N_{180}P_{180}K_{180} + \text{HM}\)). The introduction of lime, manure and the simultaneous introduction of lime and manure reduced the content of this element in tops by 3.96, 3.477 and 3.04 mg/kg, respectively. A double dose of mineral fertilizers did not have any positive effect on the decrease in the penetration of this element.

Our studies show that the accumulation of heavy metals occurs more intensively in potato tops compared to tubers. The maximum accumulation of heavy metals by the main and by-products is in the variants \(N_{180}P_{180}K_{180} + \text{HM}\) and \(N_{360}P_{360}K_{360} + \text{HM}\).

The introduction of lime and the simultaneous introduction of lime and manure reduces the penetration of toxic elements in crop products. The introduction of manure only slightly reduces the cadmium content. However, it has a positive effect on the decrease in copper, zinc and lead accumulation only in the tops.

The penetration of heavy metals into the table beet roots depending on the chemicals used are presented in table 3.

| Variants                  | Cd   | Cu   | Pb   | Zn   |
|---------------------------|------|------|------|------|
| Control                   | 0.015| 0.221| 0.263| 6.91 |
| \(N_{180}P_{180}K_{180}\) | 0.024| 0.262| 0.311| 6.93 |
| \(N_{180}P_{180}K_{180} + \text{HM}\) | 0.036| 0.358| 0.565| 8.53 |
| \(N_{180}P_{180}K_{180} + \text{HM} + \text{lime}\) | 0.025| 0.258| 0.324| 7.54 |
| \(N_{180}P_{180}K_{180} + \text{HM} + \text{manure}\) | 0.033| 0.304| 0.495| 8.50 |
| \(N_{180}P_{180}K_{180} + \text{HM} + \text{manure} + \text{lime}\) | 0.031| 0.336| 0.358| 8.41 |
| \(N_{360}P_{360}K_{360} + \text{HM}\) | 0.036| 0.339| 0.688| 9.58 |
| Threshold limit value      | 0.03 | 5.0  | 0.5  | 10.0 |

At the control variant, the cadmium content in root crops was 0.015 mg/kg two-year average, the introduction of mineral fertilizers influenced the accumulation of this element. Its content amounted to 0.024 mg/kg, which is 0.009 mg/kg higher than in the control plot. In soils contaminated with heavy metals (in the variant \(N_{180}P_{180}K_{180} + \text{HM}\)), the cadmium content was 0.036 mg/kg, which is higher compared to the variant \(N_{180}P_{180}K_{180}\) by 0.012 mg/kg or 1.2 times higher than the TLV. The
Introduction of lime and the simultaneous introduction of lime and manure reduced the penetration of the pollutant element by 0.011 and 0.005 mg/kg or by 31.0% and 14%, respectively. The introduction of manure also reduced the penetration of cadmium into the table beet roots but not significantly, by only 0.003 mg/kg. The introduction of a double dose of mineral fertilizers did not have a positive effect on reducing the cadmium penetration into crop products. Its content in root crops was at the level of the variant N₁₈₀P₁₈₀K₁₈₀ + HM.

The copper penetration into the roots of table beet even on plots contaminated with heavy metals is insignificant and amounted to 0.358 mg/kg in the variant N₁₈₀P₁₈₀K₁₈₀ + HM, which is 14 times lower than the TLV.

The introduction of lime reduces the penetration of copper into root crops by 0.100 mg/kg, the introduction of manure – by 0.054 mg/kg, the simultaneous introduction of lime and manure – by 0.022 mg/kg. The introduction of a double dose of mineral fertilizers also had a positive effect on reducing the copper penetration into root crops.

At the control variant, the lead content was 0.263 mg/kg, the introduction of mineral fertilizers increased the accumulation of this element up to 0.311 mg/kg. At the plots contaminated with toxic elements, the lead content in root crops increased and amounted to 0.565 mg/kg in the variant N₁₈₀P₁₈₀K₁₈₀ + HM, which is 0.065 mg/kg higher than the TLV. The introduction of lime and the simultaneous introduction of lime and manure reduced the content of lead by 0.241 mg/kg and 0.207 mg/kg, respectively, compared with the variant N₁₈₀P₁₈₀K₁₈₀ + HM. The lead content in the variant N₁₈₀P₁₈₀K₁₈₀ + manure was 0.495 mg/kg, which is lower than the TLV by 0.005 mg/kg and 0.07 mg/kg compared to the variant N₁₈₀P₁₈₀K₁₈₀ + HM. A double dose of mineral fertilizers contributed to the accumulation of lead in the roots of table beet up to 0.688 mg/kg, which is higher than the TLV by 0.188 mg/kg.

At the control plot, the zinc content was 6.91 mg/kg, the introduction of mineral fertilizers slightly increased the penetration of this element. At the plots contaminated with heavy metals, the zinc content was 8.53 mg/kg (in the variant N₁₈₀P₁₈₀K₁₈₀ + HM), which is lower than the TLV by 1.47 mg/kg. The introduction of lime, the simultaneous introduction of lime and manure also reduced the penetration of zinc into root crops. The introduction of manure also had a positive effect on reducing the content of this element in root crops, but only slightly. In the variant N₃₆₀P₃₆₀K₃₆₀ + HM, the zinc content in root crops was 9.58 mg/kg, which is 1.05 mg/kg higher than in the variant N₁₈₀P₁₈₀K₁₈₀ + HM.

The content of heavy metals in the tops of table beets are presented in Table 4.

| Variants               | Cd     | Cu     | Pb     | Zn   |
|------------------------|--------|--------|--------|------|
| Control                | 0.024  | 0.136  | 0.886  | 5.91 |
| N₁₈₀P₁₈₀K₁₈₀           | 0.025  | 0.135  | 0.874  | 6.01 |
| N₁₈₀P₁₈₀K₁₈₀ + HM     | 0.064  | 0.174  | 1.02   | 13.30|
| N₁₈₀P₁₈₀K₁₈₀ + HM + lime | 0.052  | 0.162  | 0.973  | 8.93 |
| N₁₈₀P₁₈₀K₁₈₀ + HM + manure | 0.060  | 0.166  | 1.010  | 8.83 |
| N₁₈₀P₁₈₀K₁₈₀ + HM + manure + lime | 0.056  | 0.155  | 0.956  | 9.00 |
| N₃₆₀P₃₆₀K₃₆₀ + HM      | 0.065  | 0.157  | 0.991  | 13.35|

Two-year average, the cadmium content at the control was 0.024 mg/kg, in the variant N₁₈₀P₁₈₀K₁₈₀ – 0.025 mg/kg. In the variant N₁₈₀P₁₈₀K₁₈₀ + HM, the cadmium content in the tops was 0.064 mg/kg, which is 0.028 mg/kg higher than in root crops. The introduction of lime and the simultaneous introduction of lime and manure reduced the penetration of this element by 0.012 and 0.008 mg/kg, respectively. The introduction of manure also had a positive effect on reducing the cadmium content, but only slightly. The introduction of a double dose of mineral fertilizers did not have a positive effect.
on reducing the cadmium accumulation. At the control plot, the copper content in the tops was 0.136 mg/kg, the introduction of mineral fertilizers did not contribute to the accumulation of this element, and its content was 0.135 mg/kg. In the variant N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} + HM, the copper content in the tops was 0.174 mg/kg, which is 0.184 mg/kg lower than in root crops. The introduction of lime, the simultaneous introduction of lime and manure, the introduction of manure and a double dose of mineral fertilizers reduce the penetration of this element by 0.012; 0.019; 0.008 and 0.017 mg/kg, respectively.

At the control plot, the lead content in the tops of table beets was 0.886 mg/kg, in the variant N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} – 0.874 mg/kg, which is higher than in root crops by 0.623 and 0.563 mg/kg, respectively.

In the variant N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} + HM, the lead content was 1.02 mg/kg, which is 1.8 times higher than in root crops. The introduction of lime, manure, the simultaneous introduction of lime and manure and a double dose of mineral fertilizers reduces the penetration of a pollutant element into the tops of table beets, but only slightly.

At the control plot, the zinc content in the tops was 5.91 mg/kg, the introduction of mineral fertilizers slightly increased the content of this element.

In the variant N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} + HM, the zinc content increased and amounted to 13.30 mg/kg. The introduction of lime, manure and the simultaneous introduction of lime and manure reduced the penetration of this element by 4.37; 4.47 and 4.30 mg/kg, respectively.

The introduction of a double dose of mineral fertilizers did not have a positive effect on reducing the zinc penetration.

4. Conclusion
Our studies show that the accumulation of cadmium and lead occurs more intensively in the tops of table beets compared with root crops. The accumulation of copper occurs more intensively in the roots of table beets, and the accumulation of zinc at the control variants occurs equal in root crops and tops, in the variants N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} + HM and N\textsubscript{360}P\textsubscript{360}K\textsubscript{360} + HM, the accumulation of this element is redistributed and its content in the tops is higher by 4.77 mg/kg and 3.77 mg/kg, respectively, than in root crops. In contaminated areas with the introduction of lime, manure and the simultaneous introduction of lime and manure, the zinc content in root crops and tops is almost the same.

The maximum accumulation of heavy metals by the main and by-products is in the variant N\textsubscript{180}P\textsubscript{180}K\textsubscript{180} + HM.

Consequently, the introduction of lime, manure and the simultaneous introduction of lime and manure reduce the penetration of cadmium, copper, lead and zinc into root crops and tops of table beets. A double dose of mineral fertilizers reduces the penetration of copper and lead, but only slightly, as well as it does not have a positive effect on reducing the accumulation of cadmium and zinc.

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