Effect of sewage sludge application on heavy metals contamination in soil and carrot

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Abstract. One of the many environmental problems in the modern world is the disposal of production and consumption waste, including sewage sludge. The aim of our research was to study the content and accumulation of heavy metals in soil and carrots when using increasing doses of sewage sludge as fertilizer and its effect on the yield of products. Sewage sludge with a moisture content of 44.5% was introduced into gray forest soils. After fertilizing the soil, agrochemical analyzes of soil samples from the plots of the experimental plot for the content of heavy metals were carried out. We also studied the content of heavy metals in carrot biomass and its yield. It was found that the content of heavy metals in various variants of experiments with the use of sewage sludge increased. It was found that the dynamics of migration of heavy metals into the biomass of carrots correlates with an increase in their concentration in the soil and affects the yield of carrots.

1. Introduction

Intensive development of industrial enterprises and numerous environmental disasters cause pollution of environmental objects and food products with ecotoxics dangerous to human and animal health, which include heavy metals [1, 2]. The anthropogenic input of heavy metals into the environment significantly exceeds the natural one. Studying the sources of heavy metals in the soil, the main natural resource of mankind, is important, as it allows avoiding these risks [3, 4].

Heavy metal contamination has a direct impact on the fertility of agricultural soils, the behavior of these toxicants is due to the specificity of their basic biochemical properties, and their removal from the soil is very difficult [5].

In the modern world, sewage treatment plants accumulate a huge amount of sewage sludge (SS), and the issue of their disposal remains relevant today. Thus, in Russia, according to Rosstat data for 2017, more than 1.3 million tons of dry matter sediment was formed, and these huge volumes of precipitation must be disposed of without violating many environmental and sanitary-epidemiological requirements.

Sewage sludge is stored on the territories of treatment facilities, which turns them into a source of environmental pollution, so the question arises about their disposal. The main methods of utilization of sewage sludge include incineration, burial, composting, and use as a complex organic-mineral fertilizer of agricultural crops on low-fertile soils [6].

As a rule, sediments dewatered and treated by various methods, including composting or aging for several years in natural conditions, contain a significant amount of macro - and microelements, organic substances, but along with this, the main limiting factor for the use of SS in agricultural production is the ingress of heavy metal salts together with them into the soil. The use of such fertilizers provides a
number of advantages, for example, increased productivity, but in the end we face the problem of pollutants that accumulate in the soil after regular use of waste and pose an environmental risk [7].

The conducted studies on agricultural utilization of SS indicate that a differentiated approach to their use as fertilizer is required, since different batches of sewage sludge are individual in their chemical composition [8, 9].

Many researchers note a high and increasing need for soil fertilization due to a significant anthropogenic load [10, 11]. Analysis of these literature sources has shown that in a number of countries, including Russia, there is a positive experience of using SS as a fertilizer in agriculture [12, 13]. On this basis, we made an assumption about the possibility of using the SS of treatment facilities as an organo-mineral fertilizer on gray forest soil in the cultivation of carrots. To confirm this hypothesis, a number of studies were conducted, the results of which are presented below.

Analysis of numerous experiments has shown that the use of fertilizers in science-based technological modes does not pose a danger to nature, but violation of the norms and technological requirements for the use of fertilizers leads to unfavorable environmental consequences. One of these consequences is the abnormal use of SS – a source of heavy metals entering the soil, ground water, and plants. Therefore, the use of sewage sludge is environmentally safe with systematic monitoring and comprehensive assessment of possible negative consequences [14].

The purpose of our research was to study the content and accumulation of heavy metals in the soil and carrots under conditions of using increasing doses of sewage sludge as a fertilizer and its effect on the yield of products.

2. Materials and methods

The practical part of the work was carried out in the village Anatkas-Margi of the Cheboksary district of the Chuvash Republic on typically gray forest heavy loam soils.

The subject of research was sewage sludge of Novocheboksarsk stored at the sludge banks for more than ten years, gray forest loam soils, tops and carrot root crops. We chose carrots as a vegetable crop, since its root crops were necessary in further research for feeding laboratory animals. The content of zinc, copper, lead, cadmium, mercury and arsenic was determined in the subjects of research.

A mixed sample of sewage sludge was taken in the third decade of April, sewage sludge from the sludge sites was taken by the method of point samples: the site was divided into 4 equal parts, and then samples were taken from the center of each square in layers for the entire thickness of the precipitation layer (point samples from depths of 0-5 cm, 5-20 cm, 20-40 cm, 40-60 cm). The mass of each point sample is not less than 200 g each. The point samples were thoroughly mixed, and one combined mixed sample weighing 1 kg was taken by quartering.

When studying the migration of heavy metals in the chain: soil - plants five variants of plots with an area of 2.5 m² in 5 replicates have been laid; when laying the experiment, a protective strip of 5 m in width was left, bordering the entire test plot. A headland within 0.5 m was left between neighboring plots, and 2.0 m between layers. Sewage sludge of natural humidity in the following options and doses were applied by five-fold replications to the prepared test plots with an area of 2.5 m²: option 1 – control (without SS); option 2 – SS application in the amount of 30 t/ha; option 3 – SS application – 60 t/ha; option 4 – SS application – 120 t/ha; option 5 – SS application – 240 t/ha. After SS application, the soil of plots of all options was turned over to a depth of 20 cm.

After leveling the surface by harrowing before planting carrots in the second decade of May, soil samples were taken. A mixed soil sample was taken from experimental plots according to the interstate standard [15] for this purpose, point soil samples weighing about 500 g were taken from a depth of 0-20 cm by the envelope method on each plot; then point samples from all plots were mixed, and one average sample weighing 1 kg was taken, which was Packed in a container for sending to the laboratory.

Next, carrots of the Losinoostrovskaya-13 variety were sown on experimental plots. For sowing, seeds of the same reproduction were selected. Sowing was carried out in 5 rows, the distance between rows was 25 cm, from the edges – 10 cm, one row of plants was selected as side dividing protective
strips. For sowing, seeds of a known origin of the same reproduction were selected, based on the sowing density of 5 kg/ha, seeding depth 1.5-2.0 cm, followed by packing.

During the vegetation period of carrot plants, in order to mellow soil and destruct weeds, four inter-row treatments were carried out to a depth of 5-7 cm. Weeds in the rows were weeded out manually twice with simultaneous thinning.

The carrot crop from the experimental plots was harvested manually on September 10 in one day. Samples of carrots and tops were taken from plots using the envelope method, while carrot plants were selected from five points of the plot with 5 bushes at each selection point. The total mass of root crops and tops in each plot was one average mixed sample. 5 mixed samples weighing about 2 kg of carrots and 1.5 kg of tops were taken from each variant.

All laboratory tests were conducted in the budgetary institution of the Chuvash Republic "Chuvash Republican veterinary laboratory" of the state veterinary service of the Chuvash Republic.

All experimental samples were analyzed for the content of zinc, copper, lead, and cadmium using the atomic absorption method on the Kvant-Z. ETA-1 spectrometer in accordance with the interstate standard [16]. Sample preparation was carried out in an analytical autoclave of ANKON-AT-24, the method is based on complete mineralization of the sample with a mixture of nitric acid and hydrogen peroxide in a hermetically sealed volume of the analytical autoclave under the influence of high temperature and pressure. The spectrometer uses the method of electrothermal atomic absorption spectrometry. The analyzed sample is vaporized in a graphite furnace tube furnace heated by electric current. The free atoms of the element being detected absorb resonant radiation, with the maximum absorption occurring on the analytical resonant spectral line, which is usually used for atomic absorption measurements. Atomic absorption is uniquely determined by the concentration of the element to be determined in the analyzed solution. The unknown concentration of the element is determined by the calibration function.

The mercury analysis was performed on the "Julia" analyzer according to the normative document [17] the Method is based on wet acid salting of the sample with subsequent reduction of mercury to a metallic form and quantitative determination by the method of flame-free atomic absorption on a mercury analyzer of the "Julia-2" type.

The method of wet mineralization is based on the complete destruction of organic substances of the product sample when heated with sulfuric and nitric concentrated acids with the addition of perchloric acid or hydrogen peroxide or when heated only with hydrogen peroxide and is intended for all types of raw materials and products, except butter and animal fats. Determination of arsenic was performed with the colorimetric method using photoelectric photometer KFK-3. The principle of operation of the photometer is based on comparing the radiation flux passed through the "blank sample" (the solvent or control solution in relation to which the measurement is made) and the radiation flux passed through the test solution. The colorimetric method for determining arsenic is based on measuring the color intensity of a solution of a complex compound of arsenic with silver diethyldithiocarbamate in chloroform.

The results of chemical analyses were used to calculate the concentration coefficients (Cs) of heavy metals and the total indicator of soil contamination (Zc), and based on the mathematical calculations made, an assessment of the degree of danger of soil contamination with a complex of heavy metals was given.

3. Research results

The producer of sewage sludge in the Chuvash Republic is the State Unitary Enterprise of the Chuvash Republic “Biological Treatment Plants”. This enterprise was put into operation in 1967 and treats municipal sewage of Cheboksary and Novocheboksarsk. The design capacity of the enterprise is 322000 m³ of sewage per day. In SS samples with a moisture content of 44.5%, the content of cadmium, lead, mercury, copper, zinc and arsenic was determined; the data obtained are shown in table 1.

The analysis of obtained data indicates that the total content of heavy metals in SS did not exceed the permissible rates according to sanitary rules and regulations 2.1.7. 573-96 “Hygienic requirements to wastewater and sewage sludge use for land irrigation and fertilization”.

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### Table 1. Total content of heavy metals in SS, mg/kg.

| Heavy metals | Rate (in dry matter) | Research results |
|--------------|----------------------|------------------|
|              |                      | In natural substance | On a dry basis |
| Zinc         | not < 4000.0         | 487.2±70.0        | 877.8          |
| Copper       | not < 1500.0         | 358.2±68.0        | 645.4          |
| Lead         | not < 1000.0         | 10.45±3.1         | 18.8           |
| Cadmium      | not < 30.0           | 2.57±0.5          | 4.6            |
| Mercury      | not < 15.0           | 0.1±0.01          | 0.18           |
| Arsenic      | not < 20.0           | < 0.01            | -              |

The content of heavy metals in soil samples of the arable soil layer of different variants of the experiment was compared with each other. In the soils of plots of the control option (without the use of SS), the total zinc content was 52.8 ± 0.4; copper – 18.7 ± 0.4; lead – 4.88 ± 0.07; cadmium 0.57 ± 0.04; mercury – 0.03 ± 0.01 mg/kg, arsenic – less than 0.01 mg/kg.

Chemical tests of soil samples showed that the total zinc content in the soil as a result of SS usage increased in all cases and increased, respectively, with the dose of SS from 63.7 ± 0.4 to 121.4 ± 0.4 mg/kg, which is 1.2-2.3 times higher than the control option indicator. At the same time, the approximately allowable concentration (APC) for soils with heavy loam size composition is not more than 220 mg/kg. The results of studies of the total copper content in the arable layer indicated that it also increased in the test plots soil by 1.6-3.6 times, and naturally increased with an increase in the SS dose from 29.3 ± 0.4 to 67.2 ± 0.5 mg/kg, with APC of not more than 132 mg/kg.

An analysis of lead concentration in the soil indicated that in all options its content, compared with the control indicator, increased in options with the SS application. So, in the option of 30 t/ha, the lead content increased by 21.1% and then in other options it naturally increased with an increase in the dose of sludge, and was maximum in the option of 240 t/ha (by 74.0%). The mass content of total lead in a tilth top soil of the test options with SS application increased from 5.91 ± 0.05 in the control option to 8.49 ± 0.31 mg/kg when 240 mg/kg (APC – 32-130 mg/kg) of SS was applied.

In the soil of test plots, the cadmium concentration also increased with an increase in sludge dose, and amounted to 0.61 ± 0.05 – 0.78 ± 0.03 mg/kg, which is 1.1-1.4 times higher than the control indicator, with an approximate permissible concentration of not more than 2 mg/kg. The mercury content in the control option was 0.03 ± 0.004 mg/kg, and in the test options – 0.05 ± 0.006 – 0.1 ± 0.01 mg/kg, with an APC of 5 mg/kg. The arsenic element in the soil of all test options was detected in a very low concentration (less than 0.01 mg/kg).

Thus, the study of the dynamics of the accumulation of heavy metals in gray forest heavy loamy soil with a single application of sewage sludge with a moisture content of 44.5% in doses of 30, 60, 120 and 240 t/ha revealed a natural increase, while exceeding the approximate permissible concentrations was not detected.

To assess the degree of soil contamination with heavy metals, we calculated the concentration coefficients of chemicals (K<sub>c</sub>), which are determined by the ratio of the analyte actual content in mg/kg of soil to the element content in contaminated soil (background value), as well as the total contamination index (Z<sub>c</sub>), determined according to the formula:

\[
Z_c = (K_{c1} + K_{c2} + ... + K_{cn}) - (n - 1)
\]

where \(K_{c1}, K_{c2}, K_{cn}\) – heavy metal concentration factors; \(n\) – amount of chemical elements – heavy metals.

An assessment of the soil chemical contamination degree based on the total contamination index (Z<sub>c</sub>) is characterized by the following categories: pure, permissible contamination degree (Z<sub>c</sub> < 16), moderately hazardous (16-32), hazardous (32-128) and extremely hazardous (more than 128). 

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Since the arsenic content in the soil was in low concentration and when performing calculations to determine the coefficient (Ks), these indicators were insignificant, data in the table are not presented.

The calculated data on the total heavy metal contamination of soils in test plots are shown in Table 2.

**Table 2.** SS impact on the heavy metals (Kc) technogenic concentration and the total soil contamination indicator (Zc) coefficients.

| Research options        | Element concentration coefficients | Zc  |
|-------------------------|-----------------------------------|-----|
|                         | Zn       | Cu    | Pb    | Cd    | Hd    |
| Control                 | 0.88     | 1.04  | 0.31  | 2.85  | 0.20  | 0.28 |
| Soil + SS 30 t/ha       | 1.06     | 1.63  | 0.37  | 3.05  | 0.33  | 1.44 |
| Soil + SS 60 t/ha       | 1.38     | 2.26  | 0.42  | 3.40  | 0.47  | 2.93 |
| Soil + SS 120 t/ha      | 1.61     | 2.68  | 0.46  | 3.65  | 0.60  | 4.00 |
| Soil + SS 240 t/ha      | 2.02     | 3.73  | 0.53  | 3.90  | 0.67  | 5.85 |

The data analysis in table 2 indicates that the highest total indicator of soil contamination with heavy metals “Zc” was observed when using SS at a dose of 240 t/ha, which showed an average value of 5.85. According to the “Zc” level, the soils are classified as of permissible contamination, with the possibility of use for any crops.

In addition to technogenic contamination of the soil cover, their biogeneous accumulation has a significant effect on the content of heavy metals due to the removal of carrot plants biomass.

Carrots crop from the test plots was got on September 10 manually in one day. The research of carrot biomass in the test options indicates that the concentration of heavy metals in the tops is much higher than in the root crop as the Table 3.

**Table 3.** The content of heavy metals in carrot root crops and leaves, mg/kg.

| Option                        | Heavy metals |          |          |          |
|-------------------------------|--------------|----------|----------|----------|
|                               | zinc         | copper   | lead     | cadmium  |
| Control (gray forest soils)   | 6.52±0.03*   | 1.49±0.02| 0.098±0.01| 0.007±0.001|
|                               | 4.18±0.03**  | 1.24±0.01| 0.096±0.05| 0.010±0.001|
| Soil + SS 30 t/ha             | 9.75±0.05    | 1.54±0.01| 0.153±0.03| 0.010±0.001|
|                               | 5.31±0.05    | 1.28±0.01| 0.099±0.010| 0.010±0.001|
|                               | 9.90±0.10    | 1.76±0.01| 0.225±0.05| 0.012±0.001|
| Soil + SS 60 t/ha             | 5.75±0.05    | 1.41±0.01| 0.105±0.05| 0.011±0.001|
|                               | 11.40±0.10   | 1.86±0.01| 0.241±0.001| 0.014±0.001|
|                               | 6.40±0.10    | 2.27±0.01| 0.131±0.05| 0.012±0.001|
| Soil + SS 120 t/ha            | 14.45±0.05   | 2.48±0.02| 0.245±0.005| 0.017±0.001|
|                               | 6.75±0.05    | 2.99±0.01| 0.149±0.001| 0.013±0.001|
| MPL                           | 100.0        | 50.0     | 5.0      | 0.3      |

* Numerator – content in leaves.
** Denominator – content in root crops.

The content of mercury and arsenic in the carrot biomass was below the sensitivity of analytical instrumentation. The concentration of zinc in the carrot root crops using various doses of SS as a fertilizer varied in the range of 5.31-6.75 mg/kg with a maximum permissible concentration (MCL) of 100 mg/kg, which is 1.27-1.61 times higher than in the control. The copper concentration ranged within 1.24-2.99 mg/kg with a MCL of 50.0 mg/kg, which is 1.03-2.41 times higher than the control. The lead content when using SS was in the range of 0.099-0.149 mg/kg with a MCL of 5.0 mg/kg, which is also 1.03-1.55 times higher than the control. The cadmium concentration in the carrot root crops was
in the range of 0.01-0.013 mg/kg with a MCL of 0.3 mg/kg, which is 1.3 times higher than the control indicator.

In the carrot tops, the zinc concentration ranged from 9.75-14.45 mg/kg; these indicators in comparison with the control are 1.50-2.22 times higher. The copper content was in the range of 1.54-2.48 mg/kg, which is 1.03-1.66 times higher than the control. The lead concentration in the carrot tops varied within 0.153-0.245 mg/kg, which exceeded the control indices by 1.56-2.5 times. The cadmium content in the tops was 0.01-0.017 mg/kg, which was 2.43 times higher than the control.

The lower content of heavy metals in root crops and the higher content in leaves is explained by the fact that organic ligands increase the level of bioavailability, that is, they translate them into a more mobile form. Thus, in plant organisms, heavy metals (trace elements) are mainly involved in redox reactions occurring in mitochondria and chloroplasts, heavy metals (trace elements) from root crops mainly migrate to the leaves.

Thus, it was found that the content of heavy metals in the carrot biomass compared with the control increased significantly with increasing dose of SS as a fertilizer. We also conducted a comparative analysis of SS effect on carrot cropping capacity. The data obtained indicate that with a single use of sewage sludge as a fertilizer in doses of 30 and 60 t/ha, the yield of carrots compared to the control variant – 401.6±3.3 c/ha, increased and amounted to 450.0±5.8 (P<0.05) and 499.6±4.8 (P<0.05) c/ha, which is higher than the control indicator by 12.1 and 24.4 %, respectively. When using SS at doses of 120 and 240 t/ha, the yield was 378.7±5.2 (P<0.05) and 340.1±5.4 (P<0.05) c/ha, which is lower by 5.7% and 15.3% (P<0.05) compared to the control indicator. Based on the studies performed, it can be concluded that SS at doses of 30 and 60 t/ha is effective for growing carrots, but the use of higher doses requires further research.

4. Conclusion

Based on the data obtained, it can be argued that with a single application of sewage sludge with a humidity of 44.5% in the amount of 30, 60, 120 and 240 t/ha, the gross content of heavy metals naturally increased, but did not exceed the approximate permissible concentrations.

Migration of heavy metals from the soil to carrots indicates that with an increase in the gross content in the soil, their concentration in the carrot biomass increases, and a large concentration is observed in the leaves.

The results of scientific research have shown that a single application of SS in doses of 30 or 60 t/ha as a fertilizer led to an increase in carrot yield on gray forest heavy loamy soils.

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