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Heavy metals in the "soil-plant" system when using sewage sludge

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Abstract. This article presents the results of studies of the content of chemical elements in the "soil-plant" system when various doses of sewage sludge are introduced into the soil. The degree of soil contamination with heavy metals was assessed, chemical concentration coefficients were calculated, the soils were classified by permissible pollution, with the possibility of use for any agricultural crops, and theoretical calculations of the maximum possible one-time dose of sewage sludge to the soil according to the limiting indicator of the concentration of heavy metals were given. The concentration of heavy metals in the carrot and table beet biomass has been studied. It was found that the use of sewage sludge as fertilizer affected the content of dry matter, ash and chemical elements in carrot, the dynamics of migration of heavy metals into plant biomass correlates with an increase in their concentration in the soil, and the accumulation of chemical elements in the photosynthetic part is more intense.

1 Introduction

In the modern world, the disposal of production and consumption waste, including sewage sludge, is one of the urgent environmental problems. Storage of sewage sludge in the territories of treatment facilities leads to the fact that it turns into a source of environmental pollution. To date, there are several methods of sewage sludge disposal, one of which is their use on low-fertile soils as a complex organo-mineral fertilizer for agricultural crops [1-3].

The degraded lands of Russia need unconventional land reclamation to solve unfavorable agrochemical, water-physical properties of the soil and problems of humus content replenishing [4]. Recently, the issue of urban sewage sludge use to increase soil fertility is particularly relevant, since the use of traditional organic and mineral fertilizers in agriculture has sharply decreased [5-6].

In the Chuvash Republic, the soil background is mainly represented by the type of gray forest soils that occupy more than 60% of agricultural land.

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In the region, more than 80% of arable land is subject to degradation processes, mainly caused by water erosion. All this leads to the annual removal of mineral and organic substances from the arable soil layer, worsening its biological, agrochemical, and physical properties. To create a deficit-free balance of humus in arable lands, it is necessary to introduce 10-12 tons/ha of organic matter into the soil, and therefore there is a need to use all types of organic fertilizers, including sewage sludge [7, 8].

In terms of fertilizing efficiency, sewage sludge is not inferior to traditional organic and mineral fertilizers, nevertheless, there are a number of restrictions related to sanitary and hygienic standards, including a high content of heavy metals. Heavy metal pollution 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 at the same time their removal from the soil is very difficult [9].

The conducted studies on agricultural utilization of sewage sludge indicate that a differentiated approach to their use as fertilizer is required, since different batches of sewage sludge are individual in their chemical composition [10-15]. With systematic control and comprehensive assessment of possible negative consequences, the use of sewage sludge can be environmentally safe [16].

2 Materials and Methods

The work was carried out in the Chuvash Republic on typically gray forest heavy clay-loamy soils, the agrochemical characteristics of which are typical for the soils of the Chuvash Republic [17-19].

The objects of research were sewage sludge, gray forest heavy clay-loamy soils, carrot and table beet biomass. The content of zinc, copper, lead, cadmium, mercury, arsenic, ash, calcium, magnesium, phosphorus, and potassium were determined in research objects.

Sewage sludge (SS) from sludge beds was collected in accordance with federal environmental regulations 12.1:2:2.2:2.3:3.2-03: "Methodological recommendations for sampling soils, grounds, bottom sediments, silts, sewage sludge, industrial wastewater sludge, production and consumption waste" by the method of spot sampling the mass of each of which at least 200 g. A combined sample weighing 1000 g was made by quartering method.

To study the accumulation of chemical elements in the "soil – plant" system, five variants of plots with an area of 2.5 m² in 5 repetitions were laid in accordance with the pre-declared requirements. Sewage sludge of natural moisture was introduced in fivefold repetition in four experimental versions with the introduction of certain doses: option – control (without SS); option 1 – at a dose of 30 t/ha; option 2 – 60 t/ha; option 3 – 120 t/ha, and option 4 - 240 t/ha. After the SS introduction, all pre-sowing activities were carried out on plots of all variants.

In the second decade of May, soil samples were taken before planting vegetables. The soil sample was taken from experimental plots according to the interstate standard 17.4.4.02-84 "Nature protection. Soils. Methods of sampling and preparation of samples for chemical, bacteriological, helminthological analysis", for this purpose, at each plot from a depth of 0-20 cm, spot samples of soils weighing about 500 g were taken by the envelope method, an average sample was formed and sent for laboratory studies.

Next, carrot seeds of the Losinoostrovskaya-13 variety and table beet of the Bordo variety were sown on the prepared plots. Sowing was carried out with seeds of the same reproduction, considering all the requirements. All the necessary agrotechnical measures have been carried out during plant growing season.

Samples of root crops and tops were taken from plots manually in the first decade of September in one day according to methodological guidelines 2051-79 "Unified rules for sampling agricultural products, food and environmental objects for the determination of trace amounts of pesticides."

The analysis of experimental samples for the content of zinc, copper, lead, and cadmium was carried out by the atomic absorption method, mercury – by flame-free atomic absorption, arsenic– by the colorimetric method on the photoelectric photometer KFK-3. The analysis of soil samples for ash content and macronutrients was carried out by conventional methods.

The results of chemical analyses were used to calculate the concentration coefficients (Kc) of heavy metals and the total soil pollution index (Zc).

3 Results and Discussion

In the Chuvash Republic (ChR), sewage sludge is produced at the State Unitary Enterprise of the ChR "Biological Treatment Facilities".

The sewage sludge used in the experiments was stored for several years on the silt site, and overgrown with weeds. The SS that had stored for 5 years was a dark gray earthy mass having a crumbly lumpy and finely lumpy structure, with individual lumpy particles up to 6-7 cm in size. The SS moisture was 44.5%, the content of organic matter in the dry matter was 38.5%, total nitrogen – 1.34%, phosphorus – 0.55%, calcium – 5.14%, magnesium – 1.27%, potassium – 0.08%. In the SS a relatively low content of the chemical element potassium, which is very important for the growth and development of plants. The mass fraction of heavy metals in the dry matter of the SS was: zinc – 0.0878%, copper – 0.0645%, lead – 0.0018%, cadmium – 0.00046%, mercury – 0.000018%, arsenic – less than 0.00001%.

The theoretical calculation of the possible permissible maximum dose of the SS introduction into the soil is based on the fact that the total content of heavy metals (in the soil and SS) should not exceed the MPC, i.e. the inequality should be observed: $F + D \leq MPC$, where F is the background content of HM in the soil, mg/kg; D is an additional dose of HM, introduced with SS, mg/kg; MPC – the maximum permissible concentration of HM in the soil, mg/ kg. The mass of the arable soil layer is conventionally assumed to be 3000 t/ha [7]. The SS application rate (Dosv) is calculated according to the following formula:

$$\text{Dosv (t/ha)} = \frac{(\text{MPC mg/kg} - \text{F mg/kg}) \times 3000 \text{ t/ha}}{\text{C(mg/kg)}} \quad (1)$$

where C is the concentration of the element being determined in the SS, mg/kg.

The calculation results are shown in Table 1.

Table 1. Theoretical calculations of the maximum possible single dose of SS into the soil according to the limiting indicator of the HM concentration.

Initial data	Zn	Cu	Pb	Cd	Hg	As
HM content in SS, mg/kg	487	358	10.45	2.57	0.1	0.01
Background content in soil, mg/kg	45	30	72	0.21	0.03	1.4
MPC of HM in soil, mg/kg	300	100	100	5	5	50
Single dose of SS, t/ha	1571	587	8038	5591	149100	14580000

According to Table 1 it can be seen that the maximum possible single introduction of SS into the soil before reaching the MPC limits copper, and amounts to 587 t/ha.

In samples of sewage sludge, the gross content of HM did not exceed the permissible norms of SanPiN 2.1.7. 573-96 "Hygienic requirements for the use of wastewater and its sediments for irrigation and fertilizing".

The content of chemical elements in soil samples of the arable soil layer of different variants of the experiment were compared with each other. Analysis of the dynamics of the accumulation of chemical elements in gray forest heavy clay-loamy soil with a single application of sewage sludge with a moisture content of 44.5% as fertilizer at doses of 30, 60, 120, and 240 t/ha revealed their natural increase, but no exceedances of the approximately permissible concentrations were revealed.

To assess the degree of soil contamination with heavy metals (HM), chemical concentration coefficients (K_c) were calculated, which are determined by the ratio of the actual content of the substance being determined in mg/kg of soil to the element content in uncontaminated soil (background value), as well as the total pollution index (Zc), determined by the formula:

$$Zc = (Kc_1 + Kc_2 + ... + ...Kc_n) - (n - 1) \quad (2)$$

where Kc_1, Kc_2, Kc_n are the concentration coefficients of heavy metals; n is the number of chemical elements – heavy metals.

The assessment of chemical contamination degree of the soil by total pollution indicator (Zc) is determined by the following categories: pure, permissible degree of contamination (Zc< 16), moderately dangerous (16-32), dangerous (32-128), and extremely dangerous (more than 128).

The obtained calculated data of the HM concentration coefficients and the total indicator of heavy metal contamination of the soils of the experimental plots are shown in Figure 1.

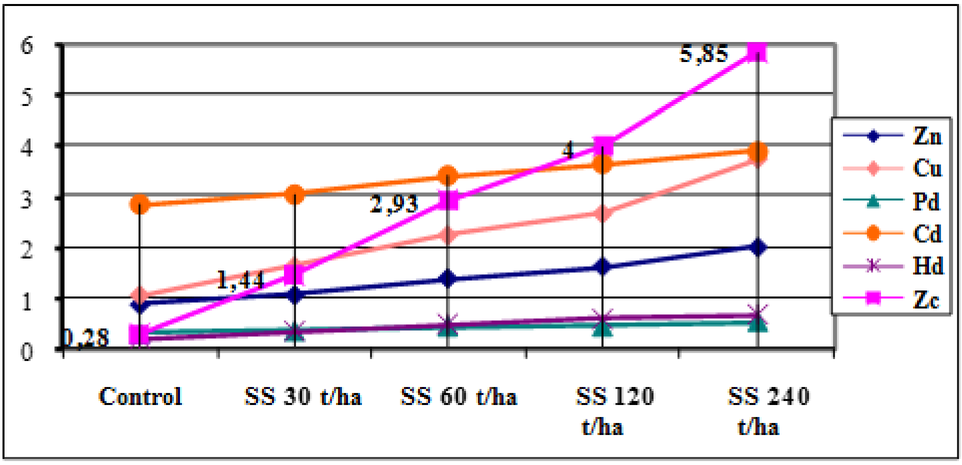

Fig. 1. The coefficients of HM concentration and the total indicator of contamination with heavy metals of the soil.

Since the arsenic content in the soil was in a negligible concentration and when performing calculations to determine the coefficient (Kc), the indicators were insignificant, the data are not reflected in the figure.

Analysis of the figure data indicates that the highest total indicator of soil contamination with heavy metals "Zc" was observed when using SS at the maximum dose, which showed an average value of 5.85. According to the "Zc" level, the soils are classified as permissible pollution, with the possibility of use for any agricultural crops.

In addition to technogenic pollution of the soil cover, their biogenic accumulation has a significant effect on the content of heavy metals in it, due to the removal of plant biomass with the harvest.

When studying the content of arsenic and mercury in plant biomass, the indicators of the analytical device were below its sensitivity.

A carrot sample with a maximum zinc content of 6.75±0.05 mg/kg was established when using sewage sludge as a fertilizer in the fourth experimental version, which was 1.61 times higher in comparison with the control sample. The results of the analysis of copper content in the prototypes were 1.28-2.99 mg/kg, which is maximum 2.41 times higher than the control variant. The analysis of the lead content indicated that the highest concentration of 0.149±0.01 mg/kg was at the maximum use of SS and, compared with the control sample, exceeded 1.55 times. The maximum cadmium content in carrots was 0.013±0.001, which exceeded the control indicator by 1.3 times.

The maximum zinc content in carrot leaves at a dose of 14.45±0.05 mg/kg was determined in the fourth experimental version, which is 2.22 times higher compared to the control sample. The copper concentration of 2.48±0.02 mg/kg was the maximum, which in comparison with the control variant exceeded by 1.66 times. The concentration of lead in the experimental variants was in the range of 0.153-0.245 mg/kg, which, in comparison with the control variant, was 2.5 times higher as much as possible. The cadmium content in the experimental samples was also higher than the control sample and exceeded it maximum by 2.43 times.

The maximum zinc content in beet roots of the fourth variant was 9.3±0.05 mg/kg, which was 2.11 times higher in comparison with the control variant. The copper content in the experimental beet samples was 1.14-1.74 mg/kg, which exceeded the control version maximum by 1.57 times. The lead concentration of 0.175±0.05 mg/kg was the maximum in the fourth variant, the excess of the control variant was 1.9 times. The cadmium concentration of 0.013 mg/kg was also maximum in the fourth variant, the excess of the control variant was 1.3 times.

In beet leaves, the maximum zinc content was determined at a dose of 18.4±0.10 mg/kg, which was 1.22 times higher than in the control variant. The concentration of copper was 3.51±0.01 mg/kg, which was 2.15 times higher than in the control variant. The lead content was in the range of 0.160-0.231 mg/kg, which exceeded the control variant by 2.1 times. The cadmium content in the experimental samples was also higher than the control sample and exceeded it maximum by 1.8 times.

The study of the carrot and table beet biomass of experimental variants indicates that the concentration of chemical elements in the leaves is higher than in root crops. Due to the fact that organic ligands increase the level of bioavailability and there is a transition to a more mobile form, there is a greater accumulation of HM in the leaf part.

The analysis of the data obtained indicates that the content of heavy metals in the biomass of root crops compared with the control indicators increased unreliably with an increase in the introduced dose of SS, but no excess of the normative indicators was revealed.

Organoleptic quality indicators of carrot root crops were also analyzed and it was revealed that in variants with high SS doses of 120 and 240 t/ha, in comparison with the control variant, carrot pulp was more coarse and tasteless.

The study of the chemical composition of carrot root crops showed that the use of SS as a fertilizer also affected the content of dry matter, ash, and chemical elements in the products (Table 2).

Table 2. The chemical composition of carrot roots.

No.	Options	Moisture, %	Root crops contained in dry matter, %				
			Ash	Ca	Mg	P	K
1	Control	87.4	0.52	0.03	0.01	0.03	0.23
2	SS 30 t/ha	88.1	0.57	0.03	0.01	0.03	0.24
3	SS 60 t/ha	87.9	0.57	0.03	0.01	0.03	0.23

4	SS 120 t/ha	88.2	0.60	0.04	0.02	0.04	0.22
5	SS 240 t/ha	88.5	0.75	0.05	0.03	0.05	0.21

The chemical analysis data presented in Table 2 show that the dry matter content decreases slightly with an increase in the dose of SS, but the ash content increases from 0.52% in the control variant to 0.75% in the variant using 240 t/ha of SS. In root crops, with an increase in the dose of SS, the content of calcium, magnesium, and phosphorus steadily increases, potassium – decreases. An increase in the ratio of calcium and magnesium to potassium indicates a deterioration in both the table qualities and the storage duration of carrot roots. It is potassium that is responsible for the accumulation of sugars in root crops and provides cell turgor.

The phosphorus content in carrots in variants using SS has increased, which increases its feed value in meat farming.

4 Conclusions

Analysis of the data obtained indicates that with a single application of sewage sludge with a moisture content of 44.5% in the amount of 30, 60, 120, and 240 t/ha to the soil as a fertilizer, the gross content of heavy metals in the soil-plant system naturally increased, but no exceedances of the approximate permissible concentrations were established.

Migration of heavy metals in the soil-plant system is characterized by an increase in their gross content in soil and plant biomass, a large concentration is observed in leaves.

It was revealed that the use of salt as a fertilizer affected the content of dry matter, ash, chemical elements in the products and with an increase in the dose of salt, the content of calcium, magnesium and phosphorus steadily increases, and potassium decreases, which indicates a deterioration in both the table qualities and the duration of storage of carrot root crops.

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